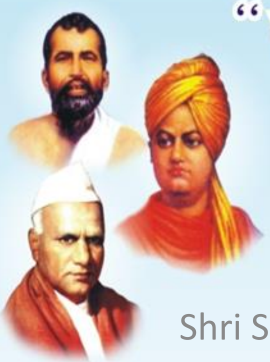
“ ज्ञान, विज्ञान आणि सुसंस्कार यासाठी शिक्षण प्रसार ”
शिक्षण महर्षी डॉ.बापूजी साळुंखे



Shri Swami Vivekanand Shikshan Sanstha, Kolhapur’s

Ramkrishna Paramhansa Mahavidyalaya, Osmanabad

NAAC Reaccredited ‘**B+**’ Grade
UGC Status: College with Potential for Excellence
DBT-Star College by Govt. of India

Research Papers

2022

Index

Sr. No.	Name of the author/s	Title of paper	View Document
1	Mr. Balaji Karhade	Women in Selected Dalite Literature	View Document
2	Dr .Vidhya Deshmukh	Impact of Acide Attack - In India	View Document
3	Dr. Sambhaji Dhumal	A facile synthesis of quinoxalines by using So42-/ ZrO2- TiO2 as an efficient and recyclable heterogeneous catalyst	View Document
4	Dr. B. V. More	A New Species of Genus Eimeria (apicomplexa:eucoccidiorida) From Sheep	View Document
5	Dr. K. M. Kshirsagar	Faniswarnath Renu Ke Upanyaso Ki Prasangkata	View Document
6	Dr. Sambhaji Dhumal	DTP/SiO2 Assisted synthesis of New Benzimidazole- Thiazole Conjugates Targeting Antitubercular and antioxident Activities	View Document
7	Mr. M. U. Ugile	Mahila Sabalikaran :Svarup ani uddishtey	View Document
8	Dr. Sambhaji Dhumal	Meglumine Cataysed Green Synthesis of Ethyl-6-amino-5-cyano-2-methyl-4 phenyl-4-H-pyran-3- carboxylate Derivatives	View Document
9	Dr. V. M. Sarnaike	Chatrapati Shivaji Maharajancha Dharmik Drashtikon:- chikitsak Mandani	View Document
10	Dr. V. M. Sarnaike	Britishkalin Tantrashikshan; Vishesh Sandharbh Kolhapur Sansthan	View Document

Index

Index

Index

15

ISSN 2278-8158
AN INTERNATIONAL MULTIDISCIPLINARY
HALF YEARLY RESEARCH JOURNAL

ROYAL

Volume - X Issue - II December - May - 2021-22

English Part - I

Peer Reviewed Refereed
and UGC Listed Journal
Journal No. 47037

ज्ञान-विज्ञान विमुक्तये

IMPACT FACTOR / INDEXING
2019 - 5.756
www.sjifactor.com

❖ EDITOR ❖
Assit. Prof. Vinay Shankarrao Hatole
M.Sc (Math's), M.B.A. (Mkt), M.B.A (H.R),
M.Drama (Acting), M.Drama (Prod & Dirt), M.Ed.

❖ PUBLISHED BY ❖

Ajanta Prakashan
Aurangabad. (M.S.)

CONTENTS OF ENGLISH PART - I

4. Women in Selected Dalit Literature

Mr. Balaji Hanmanlu Karhade
Asst. Professor & Head, Department of English Ramkrishna Paramhansa
Mahavidyalaya, Osmanabad.

Abstract

Literature is the mirror of the society. It depicts the society in oral and written records in different forms. Writers use literature as a medium to express their views about society, the world they see around with its all follies and shortcomings. Literature presents both real and imaginary worlds. Indian Literature can be divided into 'mainstream' literature and 'Dalit' literature. Dalit writings/literature is a literature of Dalits, group of the marginalised which includes the inferior castes and classes and women as well, who have penned down their thoughts and feelings. On the other hand, the mainstream literature tries to take one in different world the imaginary world forgetting this world. The present paper makes an attempt to examine the representation of the enslaved, exploited life of Dalit women in translated Autobiographies by writers, namely, Sharankumar Limbale's 'Akkarmashi', and Baby Kable's 'Jin Amucha'.

The word Dalit means 'oppressed' or 'broken' which has been used in in 1930s as a Hindi and Marathi translation of 'depressed castes'. It was first used by Jyotiba Phule and B.R. Ambedkar in the early decades of the twentieth century and has been used since the First Conference of the Maharashtra Dalit Sahitya Sangha in the state of Maharashtra, India in 1958. Known by different names of Achut, Panchamas, Atishudras, Avarnas and untouchables they constitute a huge percentage of the population of India. These women, who comprise about 16% of India's female population, face a "triple burden" of gender bias, caste discrimination and economic deprivation.

"The Dalit female belongs to the most oppressed group in the world; she is a victim of the cultures, structures and institutions of oppression, both externally and internally. This manifests in perpetual violence against Dalit women" Dr. Suraj Yengde, author of Caste Matters. (1)

Women in general are always marginalized by patriarchy, so Dalit women are more marginalized than Dalit men; they are facing humiliation due to upper caste people as well as due to their own men folk. Slowly but surely the scenario is changing: Dalit women trying to break their shackles and resist to oppression they face. These women were inspired by B.R.Amedkar and JotibaPhule Movement.According to Ambedkar in one of his speeches,

> I am conscious of the fact that if women are conscientized the untouchable community will progress. I believe that women should organize and this will play a major role in bringing an end to social evils ... The progress of the Dalit community should be measured in terms of the progress made by its women folk. Every woman should stand by her husband, not as his slave but as his contemporary, as his friend. (Dr. B.R. Ambedkar, speech to the Dalit Mahila Federation in 1942)

Dalit Literature is an attempt to articulate unheard, unspoken voices. Dalit Literature forms an important and distinct part of the Indian literature. It started with writings in Marathi language and soon appeared in other different regional languages like Hindi, Kannada, Telugu and Tamil in different genres like fictions, drama, poems short stories, autobiographical and biographical nature. English language promised writers of regional Indian literature, worldwide readership and fame. Due to this reason works written in various Indian regional languages were translated into English. In the case Dalit writers, they were marginalized in their pursuit of knowledge so they did not have access to English language or preferred their own regional languages over English language to write about their agony. So their works were translated into English language.

Autobiography can be defined as the story of one's own self. Indian Dalit author chose this genre to voice their concerns and agonized tales. They wanted to tell their stories of pain and marginalization. Sharankumar Limbale once said,

> "For me and for other Dalit writers writing is a form of rebellion. Our protest is both on the streets and on paper. My words are my weapons". (2)

The Outcaste

Sharankumar Limbale wrote 'Akkarmashi' at the age of 25 which was translated as 'The Outcaste' in 2008 by Santosh Bhoomkar. 'Akkarmashi' or 'The Outcaste' is an autobiography in Marathi of a half-caste growing up in the mahar community and the anguish he suffers due to the lack of belongingness. Limbale's 'Akkarmashi' where he acknowledges his mother while tracing his history.

> "My history is my mother's life, at the most my grandmother's." (Limbale ix)

While describing the horrors of caste Sharan narrates how the plight of the women is multiplied by internal and external intrigues. Two women Santamai and his mother Masomi play a very important role in his life. Sharan was brought up by Santamai and it was always love-hate relationship with his mother. Santamani was more a mother to him than a grandmother. She did all sorts of work like sweeping, the village streets, collecting dung and making round cakes of dung, selling them dry. When Sharan used to cry out of starvation for Bhakari his Santamai would beg around the village and got him something to eat. The liquor business in their home was very tormenting for him. Limbale's mother sold liquor for money but her customers would also start flirting with her.

"Many a time I saw them holding my mother's hand while she served them drinks. I was helpless, the very nature of this liquor business was such" (Limbale 29).

Dalit women were always taken granted and upper caste men preserved absolute chastity of their women.

Sharan's mother and her husband Ithal Kamble had led a happy life even in their poverty. Ithal Kamble worked as a bonded labour to the landlord Hanmanta Limbale. Because of this rich man his mother was forced to divorce her husband and separate from her suckling baby and four year old son Dharma. Masamai had no family and started doing all sorts of work to fill her tummy. Ithal Kamble remarried as a man it was permitted but Masamai was never remarried but had many children. She was given a rented house at Akkalakot and she took as a kind of revenge to live openly with the same man who had exiled her from her family. To be born beautiful among Dalits is a curse. Masamai was beautiful and she suffered for it she was divorced by her husband, after which Hanmanta enjoyed her and then deserted her.

The Man from the upper caste exploited Dalits women as he wished. Dalits were renounced in the society but their wives were accepted to appease sexually. Masami had ten children, two from her husband, one from Patil Nimbale and the rest by another Patil Yeshwantrao Sidramappa. So many children were born one after the other from one womb but from different fathers. Sharan is very furious when he thinks about his mother's life. He hates her way of life,

> "Mortgaging herself to one owner after another and being used as commodity? Her lot has been nothing but the tyranny of sex".(Limbale 59)

The first meeting of Sharan with his father was also disturbing. His mother was in full rage as Kaka had brought his father Hanmanta not to meet his son but to sleep with his mother. The agony of a Mahar woman is ruthless because of her body. That night Sharan had seen his mother's pain but was unable to understand anything. The two men wanted to share her body as though it's a commodity. Sharan's mother was strong enough to deny this and sent them away by threatening to burn himself.

> "That night she hugged me as she slept and cried a lot. Her sobbing was like the explosion of a Volcano". (Limbale 61)

The Dalit women are sexually abused by their own men folk. Limbale narrates the story of Dhanavva whose husband had died and she was made pregnant by her own father who said,

> "I have sown the seed from which she has grown as a plant. Why shouldn't I eat the fruits of this plant?" (Limbale 67)

Masami who was a deserted wife and divorced by Ithal Kamble was brought to her in his last days. When all the treatment was unsuccessful on him they had thought as he had wronged and dishonoured Masami he had to be absolved by her. Masami had taken vow to save her ex-husband and did her best to save him. For all her plights he was responsible but strangely she had accepted her duties of wife at his end.

"Violence against women and girls is a problem of pandemic proportions. At least one out of every three women around the world has been beaten, coerced into sex, or otherwise abused in her lifetime with the abuser usually someone known to her." (3)

'The Prisons We Broke'

'Jeena Amucha' is an autobiography by Baby Kamble which is translated as 'The Prisons We Broke' in 1986. The work was translated by Maya Pandit. The author represents her community, critiques the Hindu caste system. It is one of the first Dalit women autobiographies which talks about position of women in patriarchy and as well as in Indian caste system. She talks about the life in her village, called Veergaon, as a woman of the Maharwada community. Maharwadas suffered from ignorance and starvation, they never saw a prosperous side of life. They were considered as dirt by upper caste Hindus and they in turn reflected upper caste as pious as God. Baby Kamble wrote in autobiography in order to speak out her misery and show resistance towards age long traditions of suppression.

The title "Jina Amucha' literally means 'Our Existence', which is reflective of the existence of the Dalits, often reduced to absence by the upper castes and powerful people. Their existence comes into action only when they break the prisons around themselves. The prison is of ignorance, lack of knowledge, suffering, caste, class and gender. Baby Kamble brings into focus the Ambedkar movement and Dalits' response towards it. Showing the different rituals they perform and the ignorance behind, the writer gives a different outlook to the story, which makes it different from an autobiographical mode of writing. It is an autobiography not of a particular person; it is an expression of the whole downtrodden society.

The writer deals with the Dalit community and the history of their pain and oppression. The work is to fill the people of her community with a sense of pride as she states in her foreword. It gives a different view to the society and women. It deals with a very detailed description of the women folk toiling throughout the day and striving through their miserable situation. The light that appears as Ambedkar enters their lives and the gradual movement into the arena of knowledge from that of ignorance and darkness is what the latter focuses on. Women play a very vital role in the development of the family and the society as did the writer's aaji (grandmother). She was the lady who as per Ambedkar's speech stopped the practice of eating dead animals in the village. They came to know the value of education. It was the only means by which they could change their social, cultural and thought processes. She wrote about the otherness of Dalit women within their own community and she extols the role played by fellow women in following in the footsteps of Dr Babasaheb Ambedkar to dream of equality with upper-caste Hindus in the social order.

Dalit women are referred as 'thrice Dalit'(Grey 127) due to their triple oppression – being female, a Dalit and a poor. In narratives written by Dalit writer, Dalit women have restlessly tried to find out the meaning in the meaningless existence of life. The awareness of the self and their rebel against the various difficulties they had to face in the society is the centre to these narratives. The Caste system endowed by Manusmrithi declared Dalits as 'the other' in the society. Though the Dalits take birth like every other human being but they are treated differently, as the 'Other' by the high-caste people.

Works Cited

1. Grey, M. 'Dalit Woman and Struggle for Justice in a World of Globle Capitalism' Feminist Theology September, 2005 14(1) 127-149
2. Limbale, Sharankumar. (2008) The Outcaste – Akkarmashi. Trans. by Santosh Bhoomkar, New Delhi: OUP
3. Kamble, B. (2008). The Prisons We Broke. New Delhi Orient Longman.

Webliography

1. https://www.bbc.com/news/world-asia-india-54418513
2. https://www.smore.com/mt8a0-about-the-author
3. https://www.who.int/pmnch/media/news/2011/day_violenceagainstwomen/en/

28

(12)

ISSN 2278-8158

AN INTERNATIONAL MULTIDISCIPLINARY
HALF YEARLY RESEARCH JOURNAL

ROYAL

Volume - X Issue - II December - May - 2021-22

English Part - I

**Peer Reviewed Refereed
and UGC Listed Journal
Journal No. 47037**

ज्ञान-विज्ञान विमुक्तये

**IMPACT FACTOR / INDEXING
2019 - 5.756
www.sjifactor.com**

❖ EDITOR ❖

Assit. Prof. Vinay Shankarrao Hatole
M.Sc (Math's), M.B.A. (Mkt), M.B.A (H.R),
M.Drama (Acting), M.Drama (Prod & Dirt), M.Ed.

❖ PUBLISHED BY ❖

Ajanta Prakashan
Aurangabad. (M.S.)

13. Impact of Acid Attack - In India

Dr. Smita D. Kolhe
Assistant Professor, Dr. Bapuji Salunkhe Law Collge Mahavidyalaya Osmanabad.
Dr. Vidya J. Deshmukh
Professor & Head Ramkrushna Paramhans Osmanabad.

Abstract

"Acid attack woman are not victims, they are survivors. They change their faces not their dreams, they destroy their profile not their imperishable soul."

Acid attack on women is increasing day by day, basically on the girls in the age of 11-35 years. An acid attack involves the premeditated throwing of acid on a victim, usually on her upper part of the body. The easy availability of inexpensive acid makes the perpetrators to use it as an ideal weapon against the women. Illegal sale and purchase of acid are considered as non - bailable offence still it is readily accessible in all most the grocery and hardware stores in urban and rural areas. As per the study, it can be concluded that 78% of the acid attack incident is for refusal to marry, rejection of love or for any personal causes. Increasing acid attack towards women brought a gendered aspect in this heinous crime. India has the highest number of acid attacks in the world, but the worst conviction rates. It is high time now something stringent needs to be done to curb this evil in our society. Otherwise it will be too late, and innocent creatures on this earth will continue to suffer for no fault of theirs. This paper wants to highlight the impact of the acid attack on this innocent womens and the problems and hindrance suffered by the victims. This paper ends with suggesting measures for solving such a heinous crime.

Introduction

Now – a – days the concept of crime has been dazzled everywhere. Social Scientist all over the world are focussing on violence against women in developing and developed countries. Use of acid to commit a crime is not something which is new for us but it is just the way of doing crime has been reformed. Previously people use acid for household purpose but now the use of acid has revolutionized his way and used for destroying the life of people. Acid attack is a worldwide problem affecting all irrespective of age, caste and religion. The victims of acid violence are overwhelmingly women and children, and attackers often target the upper part of the body in order to maim, disfigure and blind. Perpetrators aim is not to kill the victim but to leave her in a pathetic condition. The accumulation of victims or sufferers are due to the ineffective laws or the lack of implementation of proper laws which makes the people think of the after effects if they commit such crimes. There are many reasons behind this dreadful crimes which extend from rejection of marriage proposals to dowry issues.

What is acid attack ?

Acid attack or vitriolage is defined as the act of throwing acid onto the body of a person "with the intention of injuring or disfiguring [them] out of jealousy or revenge". According to national commission of India acid attack can be viewed to mean "any act of throwing acid or using acid in any form on the victim with the intention of or with knowledge that such person is likely to cause to the other person permanent or partial damage or deformity or disfiguration to any part of the body of such person."

In acid attacks the use of sulphuric acid, nitric acid and hydrochloric acid is common.

Acid Violence - A Worldwide Tragedy

Violence against women and girls is the most widespread form of systematic abuse worldwide, affecting one third of all women in their lifetime. A literature review show the global nature of the problem of acid based violence and reinforces that it is not confined to particular regions, religions or cultures. It also highlights that the cause and characteristics of burn injuries vary widely across the globe, with significant age and gender differences of victims among countries.

It is difficult to gauge the true scale and prevalence of the issue for a number of reasons. Most developing countries to not have a comprehensive national system for recording and monitoring burn injuries. All too often it's a crime that goes unreported and unpunished. In International law, states have a due diligence obligation to prevent such violence from occurring, to protect victims, to punish perpetrators, and to provide compensation to those who have suffered from it.

Impact of Acid Attack

Acid attack is possibly one of the nastiest infliction committed on human beings which results in complete debilitation, loss of prospects and income, and even social requisitioning. The effects of this are not temporary, but are permanent lasting throughout a person's life. Consequently, the victim is faced with physical challenges, which require in depth intervention from psychologists and counselors at each stage of physical recovery. The victims are often left with no legal recourse, limited access to medical or psychological assistance and have no means to support themselves.

Physical

Physical impact is horrifying, dismaying and too awful for words. As majority of acid attacks are aimed at the face. Severity of the damage depends on the concentration of the acid and the period of time before the acid is thoroughly washed off with water of neutralizing agent. The acid can rapidly eat away skin, and in some cases even the underlying bone. Eyelids and lips may be completely destroyed, the nose and ears severely damaged. It becomes very difficult to eat and speak even. Acid attack victims also face the possibility of septicemia, renal failure, skin depigmentation and even death.

Psychological

Acid assault survivors face many mental health issues upon recovery. It has gigantic and gargantuan psychological effect on her leading to lack of personality, trepidation, frustration, lack of confidence, tremor, disordered eating, nightmares, insomnia, despair, negative feelings about themselves, lack of self - assurance, feeling of worthlessness and feeling of abandonment which might lead to suicidal tendencies. According to the Rosenberg Scale, the women reported lowered self- esteem and increased self-consciousness, both in general and in the social sphere. Obviously, physical and psychological impact as aforesaid would require long-term treatment-medically as well as intercession from the counselor to deal with the psychological challenges and repercussions.

Social

Many social implications exist for acid survivors, especially women. The appearance of the person becomes so dreadful and frightful that victims become socially outcast, either by the society or by self. Greater number of acid attack victims is forced to give up their education, occupation, and carry out normal activities of life due to their physical appearance of physical disabilities rendering them dependent on either their spouse or family for everyday activities, such as eating and running errands. These dependencies are increased by the fact that many acid survivors are not able to find suitable work due to impaired vision and physical handicapped. There is always a sense of trepidation, scorning and scoffing of the people around them, not to forget the disgusting looks of the society at large. All these things build so much of inferiority complex in the victims that they themselves shun away from the society.

Financial

This heinous crime also puts an acid victim in a financial crunch. The treatment of acid attack victim involves assorted number of surgeries, skin grafting, medication, etc. Since single surgery does not suffice leading to multiple surgeries, it makes a person out- of - pocket fiscally. Apart from this, acid attack leads to a number of physical disabilities,and those people who are already employed, they face a number of challenges in their employment and are unable to cope up with their job. For those people who are jobless, people are hesitant to hire them, though they might show full empathy with them.

Legislation in India

Before 2013, acid attack was not regarded as a separate crime by the Indian Penal code. Sections 326 A and 326 B were introduced into the Indian Penal code by way of criminal Law (Amendment Act). 2013 providing punishment for acid attack and attempted acid attack. The offence is registered under Indian Penal code Section 320, 322, 325, 326 and 307. In the case of Laxmi Versus UOI, the Supreme Court passed an order to regulate the sale of acid in shops. In this case compensation was given to the victim of an acid attack for the first time.

According to section 326 A of Indian Penal code, "Whoever causes permanent or partial damage or maims or disfigures or disables, any part or parts of the body of a person or causes grievous hurt by throwing acid on or by administering acid to that person, or by using any other means with the intention of causing or with the knowledge that he is likely to cause such injury or hurt, shall be punished with imprisonment of either description for a term which shall not be less than ten years but which may extend to imprisonment for life, and with fine.

The prevention of Acid Attacks and Rehabilitation of Acid Attack Victims Bill, 2017 has been enacted to provide for the prevention of acid attacks by restricting the sale, supply and use of acid or other steps and rehabilitation of women victims of acid attacks and related matter. No person shall be allowed, according to this bill to sell or supply acid to any person without documenting his identity, the quantity of acid and the reason for which the acid is to be used. With the issuance of government licences, the purchase of acid can only be performed by people over the age of 18 years.

Compensation to the Victims of acid attacks is also provided by the government under various schemes namely PMNRF, Central Government Victim compensation Fund scheme (CVCF),etc.

Suggestions

Many countries posses a high level of violence against women. Violence is rooted in gender – based discrimination. So the best way to stop acid attack is to preventing it first by addressing what is the root cause for it. Education is crucial for ending all kinds of violence against women. Prevention should start early in life, by educating and working with young boys and girls promoting respectful relationships and gender equality.

The central and state government role is not limited to providing monetary compensation to the victim. Their work also includes helping victims restore in society.

Research also helps to gain an understanding of the cause and effects of acid attacks. Quality research enables to establish consensus for change, especially helps in persuading policymakers to change policies, laws.

Every Government hospital, specially the tertiary ones, must have a separate public rehabilitative center for patients who experienced vitriolage. These centers must work under the departments of plastic and reconstructive surgery.

Hospitals dealing with acid burn patients must work with NGO's for providing social support. Formation of support groups should be encouraged where victims of vitriolage meet to share and discuss the trauma they experienced.

Victims of acid attack need to be trained for suitable jobs through which they can support themselves, but unfortunately no importance has been given to this and the victim is left to fend for themselves.

India has acknowledged the cancer of acid attacks by framing suitable laws. But clearly these laws need better implementation so as to put survivors on the road to rehabilitation. Also, acid attack case in the country has to be tried speedily and justice should be given on priority.

Conclusion

Though these acid attacks are getting attention but much more needs to be done to prevent this dreadful crime. It has long lasting consequences on the life of the Victim who faces perpetual torture, permanent damage and other problems for the rest of her life. Even if they are willing to pursue a normal life, there is no guarantee that society itself will treat them as normal human beings given appearance and disabilities after an attack. They may not be able to work or be able to find a job, and thus perpetually struggle to survive. Unregulated sale of acid is the major reason in the increasing number of these crimes. So, it is incumbent on the government to take rigorous measures and give harsher punishments to these disgusting criminals.

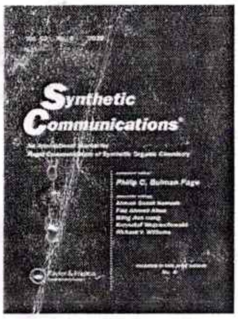
We, as a member of society should understand the plight of the victims of acid attack. We should treat them as our equals.

They deserve respect and dignity like any other human beings. Apart from society, law should ensure that justice is served and the victims get adequate compensation.

References

1. A case study of community based responses to rural women buttering. Van hightower NR, Gorton J Violence against women 2002 : 845 – 872 (Google Scholar)
2. National Commission of India, July 2009
3. Acid Violence as on www.acidviolence. Org/index. Php/acid- violence.
4. Dissanaike and Rahimi 2009 rpidemiology of burn injuries : highlighting altural and sociodemographic aspects. International review of psychiatry, 2(6) , 505-511 https://doi.org/10.3109/09540260903340865.
5. www.wikipedia.com.

6. ASTI – A worldwide problem. www.asti.org.UK.
7. The Indian renal code, Ratanlal and Dhirajlal.
8. Acid Offences Prevention Act. Posted : 2002
9. Law commission of India report -226 (2009). Proposal for inclusion of acid attacks as specific offences in Indian penal code and a law for compensation for victims of crime.
10. Amlanika Bora and Harshita Priyadarshi, the concept of victimology Through the Lens of acid attack victims: A Judicial Paradigm, 6 Int J. Sci. Res., 1458, 1461 (2017).
11. S. Senthalir, Acid Is Not the Answer to Anything, 48 Econ. Politic. Week, 35,35 (2013).
12. Vageshwari Deswal, Acid Attacks, A study of the underlying clauses of acid attacks against women in India and the nature of state. Response : Study conducted by Delhi University in collaboration with National Commission for Women, 2013, at 16.
13. Justice J.S.Verma, Report of the committee on Amendments to criminal law 147, para 5 (January 2013).
14. Patel M.A. desire to disfigure: Acid attack in India Int J Criminal Social theory 2014;7:1-11
15. National crime records bureau. Ministry of Home Affairs. Crime in India 2015 statistics chapter(1) : (22)
16. Taylor, L M (2000). Saving Face: Acid attack laws after the unconvention on the elimination of all forms of discrimination against women. Ga. J. Int'l and Comp.L. ;29 , 395.
17. www. Indiankanoon. Org/doc/73735.
18. www.google.com.



Taylor & Francis
Taylor & Francis Group

Synthetic Communications
An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

A facile synthesis of quinoxalines by using $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and recyclable heterogeneous catalyst

Sushil V. Shelke, Sambhaji T. Dhumal, Akshay Y. Karale, Tejshri R. Deshmukh & Meghshyam K. Patil

To cite this article: Sushil V. Shelke, Sambhaji T. Dhumal, Akshay Y. Karale, Tejshri R. Deshmukh & Meghshyam K. Patil (2022) A facile synthesis of quinoxalines by using $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and recyclable heterogeneous catalyst, Synthetic Communications, 52:4, 597-607, DOI: 10.1080/00397911.2022.2039711

To link to this article: https://doi.org/10.1080/00397911.2022.2039711

SYNTHETIC COMMUNICATIONS®
2022, VOL. 52, NO. 4, 597–607
https://doi.org/10.1080/00397911.2022.2039711

Taylor & Francis
Taylor & Francis Group

A facile synthesis of quinoxalines by using SO_4^{2-}/ZrO_2-TiO_2 as an efficient and recyclable heterogeneous catalyst

Sushil V. Shelke[a], Sambhaji T. Dhumal[b], Akshay Y. Karale[a],
Tejshri R. Deshmukh[c], and Meghshyam K. Patil[a]

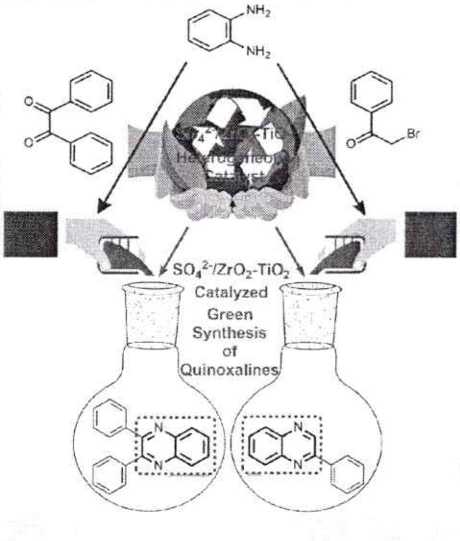
[a]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad, India; [b]Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad, India; [c]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India

ABSTRACT
Quinoxaline derivatives have been synthesized in good to excellent yields by the cyclocondensation reaction of *o*-pheneylenediamine with substituted phenacyl bromides/benzil in the presence of SO_4^{2-}/ZrO_2-TiO_2 as an efficient and heterogeneous catalyst. The catalyst can be recovered up to five catalytic cycles without significant loss in catalytic activity. The reported SO_4^{2-}/ZrO_2-TiO_2 catalyst has been thoroughly characterized by using infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and powder X-ray diffraction (XRD). Here, we have used ethanol as a green solvent in this cyclocondensation. This new method has several advantages, such as excellent yields, short reaction time, nontoxic, and easily recoverable catalyst.

ARTICLE HISTORY
Received 29 November 2021

KEYWORDS
SO_4^{2-}/ZrO_2-TiO_2; quinoxalines; recyclable; heterogeneous catalyst; cyclocondensation

GRAPHICAL ABSTRACT



CONTACT Meghshyam K. Patil meghshyam_patil@yahoo.com Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad 413501, India.

Supplemental data for this article can be accessed on the publisher's website.

Introduction

Quinoxalines are one of the important classes of nitrogen-containing heterocycles.[1] They are rarely occurred in nature and mostly synthesized by using various synthetic approaches.[2] In a quest to develop sustainable and greener synthetic strategies for quinoxalines, most of the researchers have been developing different greener synthetic approaches that involve recyclable catalysts, mild reactants, and reaction conditions.[3] Over the last few years, quinoxalines have grabbed more attention by researchers as they display a broad range of pharmaceutical as well as biological applications.[4] Various derivatives of quinoxalines have revealed a wide variety of bioactivities, such as antitubercular,[5] anti-inflammatory, antioxidant,[6] antifungal, anticancer, anti-HIV,[7] and antiprotozoan,[8] etc. Most of the clinically used drugs also possess quinoxalinyl moiety in their structural scaffold as an active pharmacophoric unit. Some of them are summarized in Figure 1.

In recent years, focusing on several environmental issues and considering the pharmacological importance of quinoxaline scaffolds there are numerous synthetic methods have been reported. Some of them are the condensation of *o*-phenylenediamine with 1,2-dicarbonyl compounds,[9] oxidation trapping of α-hydroxy ketones,[10] and 1,2-diazenylbutens.[11] Following are the various synthetic protocols involved for the synthesis of quinoxalines, such as heteropoly acid,[12] cellulose sulfuric acid,[13] hypervalent iodine (III) in PEG-400,[14] polyaniline-sulfate salt,[15] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,[16] PVPPOTf,[17] and $Ga(ClO_4)_3$.[18]

Among the aforementioned protocols, condensation of *o*-phenylenediamine with phenacyl bromides in the solid phase is highly preferred. This method has involved the use of a catalyst-free approach[19] as well as by using transition metal catalysts[20] and various heterogeneous catalysts like $HClO_4$-SiO_2,[21] silica-supported dodecatungstophosphoric acid,[1] TMSCl,[22] β-cyclodextrin,[23] silica-supported phosphomolybdic acid,[24] miceller SDS,[25] T3PDMSO or T3P,[26] *N*-Bromosuccinimide,[27] and ionic liquid.[28]

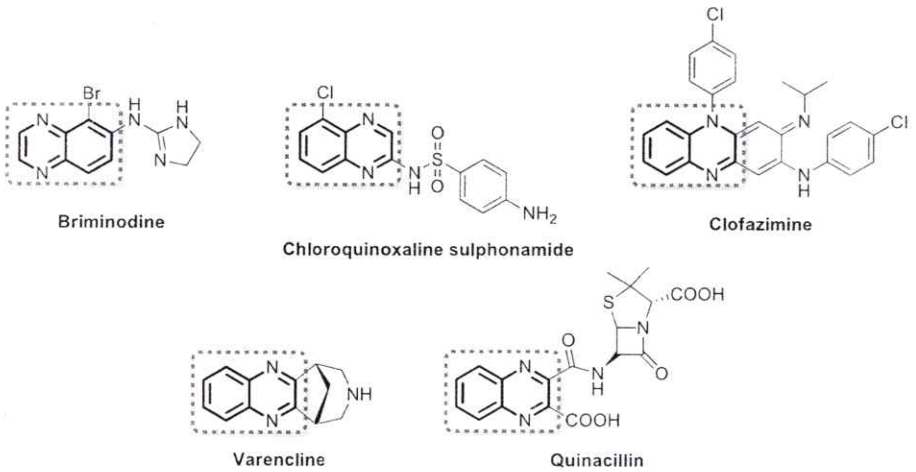


Figure 1. Some clinically used drugs bearing quinoxalinyl moiety.

Among the reported synthetic protocols, there are many synthetic approaches that having some limitations or lacunas, such as the use of $HClO_4$-SiO_2 catalyst is hazardous in nature than its potential application, the reaction catalyzed by TMSCl required higher temperature with low yield, the β-cyclodextrin, and miceller SDS catalyzed reactions were required longer time. Considering these lacunas/limitations with reported synthetic methods and used catalysts, still, there is a need for designing appropriate synthetic methods with the development of new catalysts having acidic strength and recyclability to be environmentally benign.

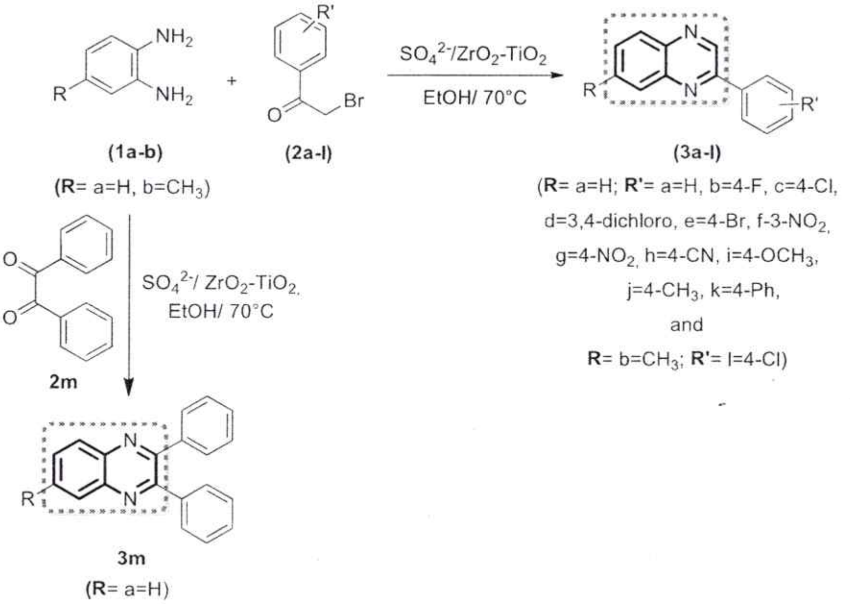
Results and discussion

The synthesis of quinoxalines was carried out by reacting substituted phenacyl bromides/benzil (**2a–m**) (0.001 mol) and *o*-pheneylenediamine (**1a–b**) (0.001 mol) in the presence of SO_4^{2-}/ZrO_2-TiO_2 as a catalyst. Further, the reaction mass was stirred at 70 °C for 50–80 min. afforded quinoxalines (**3a–m**) with excellent yields and high purity. This reaction is outlined in Scheme 1.

The structures of all the synthesized quinoxalines (**3a–m**) are shown in Figure 2.

The model reaction was carried out in presence of *o*-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as shown in Scheme 2.

The optimization of the reaction was performed by varying the reaction parameters, such as reaction time, solvent, and temperature. It was observed that the quinoxaline formation in ethanol solvent proceeds with an excellent yield at 70 °C for 50 min (Table 1, entry 3). Whereas, no reaction was observed in presence of water as a solvent (Table 1, entry 1).



Scheme 1. Synthesis of quinoxalines (**3a–m**) using $SO_4^{2-/}ZrO_2$-TiO_2 catalyst.

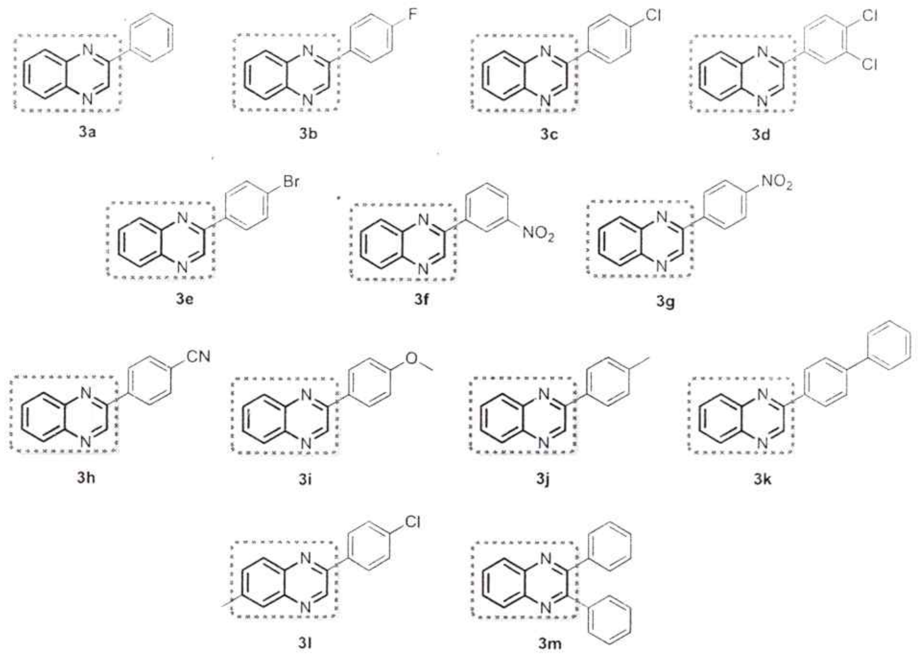
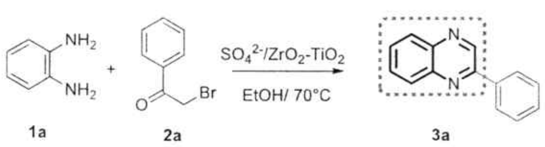


Figure 2. Structures of all the synthesized quinoxalines (**3a–m**).



Scheme 2. Model reaction for the optimization of solvent and catalyst.

Table 1. Screening of reaction condition with respect to solvent and catalyst loading **3a**.[a]

Sr. No.	Solvent	Catalyst	Yield[b] (%)
1	Water	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	NR
2	Methanol	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	82
3	Ethanol	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	94
4	Dichloromethane	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	65
5	Acetonitrile	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	75
6	Dimethylformamide	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	64
7	1,4-Dioxane	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	58
8	Dimethylformamide	$SO_4^{2-}/ZrO_2\text{-}TiO_2$	65
9	EtOH	No catalyst	03

NR: no reaction.

[a] Reaction conditions: Phenacyl bromide (0.001 mol), *o*-phenylenediamine (0.001 mol), 20 $SO_4^{2-}/ZrO_2\text{-}TiO_2$ in 10 ml EtOH, at 70 °C for 50 min.

[b] Isolated yields.

Characterization of $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst

XRD pattern of sulfated $TiO_2\text{-}ZrO_2$ solid acid catalyst is shown in Figure 3. The diffraction pattern confirms the presence of the anatase phase of TiO_2 (JCPDS-211272), and the tetragonal and monoclinic structure of ZrO_2 (JCPDS-897710 and JCPDS-371484).

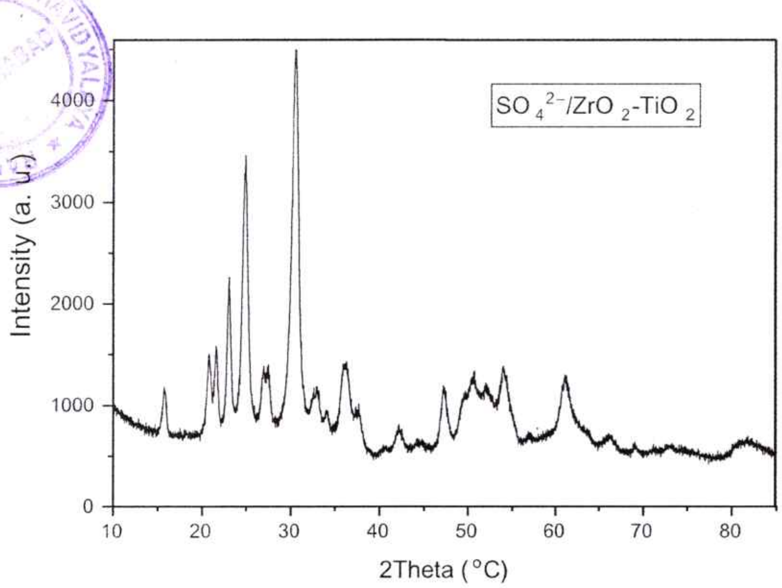


Figure 3. X-ray diffraction pattern of as prepared $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst.

In Figure 3, diffraction peaks are observed due to anatase TiO_2 at 24.83, 36.15, 37.67, 47.20, 53.98, 61.08, and 68.94°, which corresponds to the crystal planes (101), (103), (004), (200), (105), (204), and (116), respectively.[29] However, diffraction peaks are detected due to tetragonal ZrO_2 at the 27.47, 30.49, 32.91, 33.97, 50.57, 59.11, and 75.06° that corresponds to the reflections of crystal planes (−111), (101), (111), (110), (112), (211), and (220), respectively.[30,31]

Figure 4 shows the FT-IR spectra of sulfated $TiO_2\text{-}ZrO_2$ solid acid catalyst. The peaks at 1348, 1440 cm^{-1}, and in the region 1180–1050 cm^{-1}, can be attributed to the asymmetric and symmetric stretching frequency of the O=S=O and O-S-O groups.[32–34] The peaks at lower frequency in the range 500–1100 cm^{-1} are due to M-O stretching, which confirms the presence of metal oxides. Whereas, the peak observed at 1625 cm^{-1} was refers to the bending modes of the -OH groups of water molecules present in the sample.

Figure 5 shows the differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) of sulfated $TiO_2\text{-}ZrO_2$ uncalcinated sample. The TGA measurements agreed fairly well with those expected decompositions of uncalcinated sulfated metal oxide samples. The weight loss events below 600 °C were corresponds to the removal of adsorbed water and the dehydroxylation process. However, the major weight loss in the temperature range is about 600–800 °C, which refers to the decomposition of sulfate groups. Differential scanning calorimetry has shown the endothermic peaks that correspond to the removal of adsorbed water, dihydroxylation process, and decomposition of sulfate groups.

We have also investigated the recyclability of $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst for the model reaction of *o*-phenylenediamine (**1**) and phenacyl bromide (**2a**) in ethanol solvent at 70 °C for 50 min. and observed results were incorporated in Figure 6.

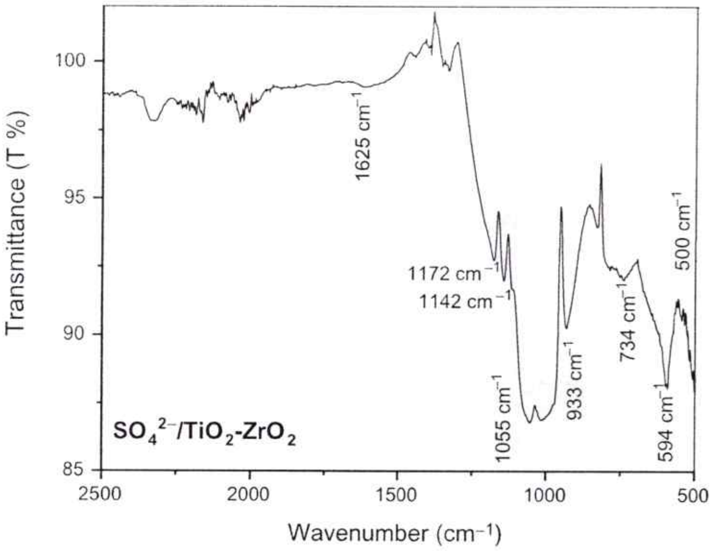


Figure 4. FT-IR spectra of as prepared SO_4^{2-}/TiO_2-ZrO_2 catalyst.

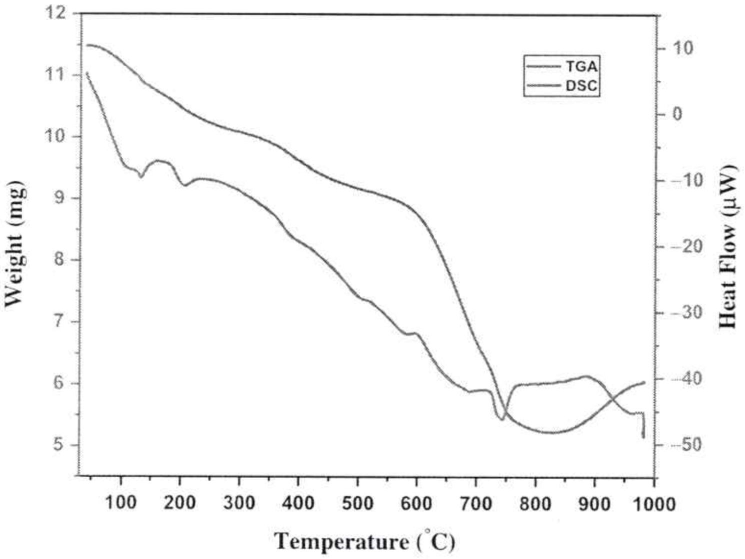


Figure 5. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) pattern of uncalcinated sulfated TiO_2-ZrO_2 sample.

The plausible mechanism for the quinaxolines synthesis was depicted in Scheme 3, which involves the protonation of the carbonyl group of phenacyl bromide over SO_4^{2-}/ZrO_2-TiO_2 catalyst (**A**). Later on, it reacts with *o*-pheneylenediamine that involves dehydration and dehalogenation simultaneously resulting in the formation of cyclic product **B**, which is readily oxidized in air to form desired product **C**.

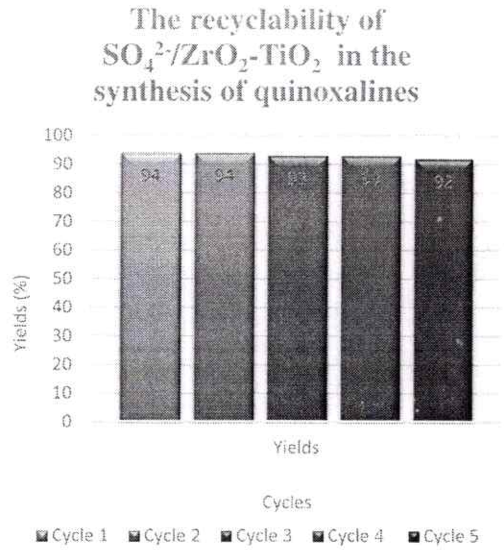


Figure 6. The recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the synthesis of quinoxalines.

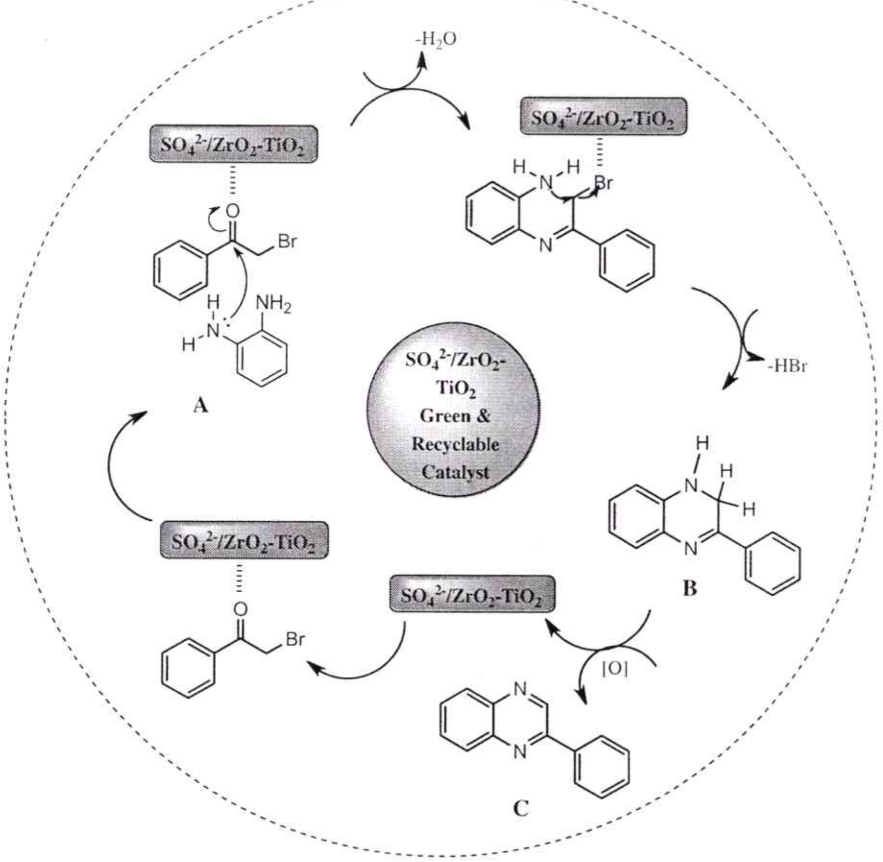
Conclusion

In conclusion, we have developed a mild, efficient, and environmentally benign synthetic protocol for the synthesis of quinoxalines (**3a–m**) from substituted phenacyl bromides/benzil and *o*-pheneylenediamines using SO_4^{2-}/ZrO_2-TiO_2 catalyst. The key feature of the current protocol involves simple reaction conditions, no side reaction with the formation of the desired product in high yield. The present method is an alternative to the conventional processes for the synthesis of quinoxalines. The catalyst could be recovered several times without loss of catalytic activity, which makes the process cost-effective.

Experimental

General procedure for the preparation of SO_4^{2-}/ZrO_2-TiO_2 catalyst

SO_4^{2-}/TiO_2-ZrO_2 solid acid catalyst has been synthesized by sol-gel synthetic method followed by impregnation method. Initially the solution of 50 mL ethyl alcohol, 2 mL conc. HCl and 0.5 mL acetic acid were stirred for 30 min. To this solution, titanium isopropoxide (3.16 mL) and zirconium propoxide (3.35 mL) were added dropwise with constant stirring for 1 h. The solution has been treated at 50 °C for a gel formation and the ethanol has been evaporated. The formed gel has been dried in an oven to form a powder. The formed powder has been used for sulfate impregnation. Here, we have used the 15 mL 0.5 M H_2SO_4 per gram of powder. After this, the formed powder has been added to the H_2SO_4 solution. The water has been evaporated by heating on the sand bath. The formed sulfonated powder has been calcined at 650 °C for 4 h.



Scheme 3. Plausible mechanism for the synthesis of quinoxaline derivatives.

General experimental procedure for synthesis of quinoxalines

Phenacyl bromides/benzil (**2a–m**) (0.001 mol) and $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst (50 mg) were dissolved in EtOH (3 mL) at room temperature for 10 min. Then *o*-phenylenediamine (**1a–b**) (0.001 mol) was added slowly to the reaction mass. The resultant mixture was heated for a stipulated time. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was recovered by simple filtration. The crude product was purified by crystallization using ethanol to afford the pure quinoxalines (**3a–m**). The melting points of the desired products were found to be in good agreement with those reported in the literature.[35–41]

2-(Phenyl)quinoxaline (3a)

The compound (**3a**) was obtained by $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyzed reaction in between o-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as bright yellow solid; yield 94%; mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48–7.77 (m, 5H, Ar-H), 8.06–8.14 (m, 4H, Ar-H), 9.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 126.42, 128.15, 129.43, 131.32, 135.22, 141.62, 142.15, 143.12, 150.34; HRMS (ESI$^+$) calcd. for $C_{14}H_{10}N_2$ $(M + H)^+$: 207.0923; found 207.0926.

2,3-Diphenylquinoxaline (3m)

The compound (**3m**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-pheneylenediamine (**1a**) and benzil (**2m**) as white solid; yield 91%; mp 123–125 °C; 7.32–7.54 (m, 5H, Ar-H), 7.74–7.80 (m, 2H, Ar-H), 8.18–8.20 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 128.28, 128.81, 129.21, 129.83, 129.97, 139.06, 141.23, 153.48; HRMS (ESI$^+$) calcd. for $C_{20}H_{14}N_2$ $(M + H)^+$: 283.1235; found 283.1238.

Disclosure statement

The authors declare no conflict of interest.

ORCID

Sambhaji T. Dhumal http://orcid.org/0000-0003-3018-6179
Tejshri R. Deshmukh http://orcid.org/0000-0002-1818-0316

References

[1] Hebade, M. J.; Deshmukh, T. R.; Dhumal, S. T. Silica Supported Dodecatungstophosphoric Acid (DTP/SiO_2): an Efficient and Recyclable Heterogeneous Catalyst for Rapid Synthesis of Quinoxalines. *Synth. Commun.* **2021**, *51*, 2510–2520. DOI: 10.1080/00397911.2021.1939060.

[2] Dietrich, B.; Diederichsen, U. Synthesis of Cyclopeptidic Analogues of Triostin a with Quinoxalines or Nucleobases as Chromophores. *Eur. J. Org. Chem.* **2005**, *2005*, 147–153. DOI: 10.1002/ejoc.200400548.

[3] Nageswar, Y. V. D.; Reddy, H. V.; Ramesh, K.; Murthy, S. N. ChemInform Abstract: Recent Developments in the Synthesis of Quinoxaline Derivatives by Green Synthetic Approaches. *Org. Prep. Proc. Int.* **2013**, *45*, 1–27. DOI: 10.1080/00304948.2013.743419.

[4] Pereira, J. A.; Pessoa, A. M.; Cordeiro, M. N. D. S.; Fernandes, R.; Prudencio, C.; Noronha, J. P.; Vieira, M. Quinoxaline, Its Derivatives and Applications: A State of the Art Review. *Eur. J. Med. Chem.* **2015**, *97*, 664–672. DOI: 10.1016/j.ejmech.2014.06.058.

[5] Seitz, L. E.; Suling, W. J.; Reynolds, R. C. J. Synthesis and Antimycobacterial Activity of Pyrazine and Quinoxaline Derivatives. *J. Med. Chem.* **2002**, *45*, 5604–5606. DOI: 10.1021/jm020310n.

[6] Cheng, G.; Sa, W.; Cao, C.; Guo, L.; Hao, H.; Liu, Z.; Wang, X.; Yuan, Z. Quinoxaline 1,4-di-N-Oxides: Biological Activities and Mechanisms of Actions. *Front. Pharmacol.* **2016**, *7*, 64. DOI: 10.3389/fphar.2016.00064.

[7] Loriga, M.; Piras, S.; Sanna, P.; Paglietti, G. Quinoxaline Chemistry, Part 7, 2-[Aminobenzoates]- and 2-[Aminobenzoylglutamate]-Quinoxalines as Classical Antifolate Agents. Synthesis and Evaluation of *In Vitro* Anticancer, Anti-HIV and Antifungal Activity. *Farmaco* **1997**, *52*, 157–166.

[8] Hui, X.; Desrivot, J.; Bories, C.; Loiseau, P. M.; Franck, X.; Hocquemiller, R.; Figadere, B. Synthesis and Antiprotozoal Activity of Some New Synthetic Substituted Quinoxalines. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 815–820. DOI: 10.1016/j.bmcl.2005.11.025.

[9] More, S. V.; Sastry, M. N. V.; Yao, C. F. Cerium (IV) Ammonium Nitrate (CAN) as a Catalyst in Tap Water: A Simple, Proficient and Green Approach for the Synthesis of Quinoxalines. *Green Chem* **2006**, *8*, 91–95. DOI: 10.1039/B510677J.

[10] Robinson, R. S.; Taylor, R. J. K. Quinoxaline Synthesis from α-Hydroxy Ketones via a Tandem Oxidation Process Using Catalysed Aerobic Oxidation. *Synlett* **2005**, *2005*, 1003–1005. DOI: 10.1055/s-2005-864830.

[11] Aparicio, D.; Attanasi, O. A.; Filippone, P.; Ignacio, R.; Lillini, S.; Mantellini, F.; Palacios, F.; de Los Santos, J. M. Straightforward Access to Pyrazines, Piperazinones, and Quinoxalines by Reactions of 1,2-Diaza-1,3-Butadienes with 1,2-Diamines under Solution, Solvent-Free, or Solid-Phase Conditions. *J. Org. Chem.* **2006**, *71*, 5897–5905. DOI: 10.1021/jo060450v.

[12] Huang, T. K.; Shi, L.; Wang, R.; Guo, X. Z.; Lu, X. X. Keggin Type Heteropolyacids-Catalyzed Synthesis of Quinoxaline Derivatives in Water. *Chinese Chem. Lett.* **2009**, *20*, 161–164. DOI: 10.1016/j.cclet.2008.10.048.

[13] Shaabani, A.; Rezayan, A. H.; Behnam, M.; Heidary, M. Green Chemistry Approaches for the Synthesis of Quinoxaline Derivatives: Comparison of Ethanol and Water in the Presence of the Reusable Catalyst Cellulose Sulfuric Acid. *C. R. Chim.* **2009**, *12*, 1249–1252. DOI: 10.1016/j.crci.2009.01.006.

[14] Lin, P. Y.; Hou, R. S.; Wang, H. M.; Kang, L. J.; Chen, L. C. Hypervalent Iodine(III) Sulfonate Mediated Synthesis of Quinoxalines in Liquid PEG-400. *J. Chinese Chem. Soc.* **2009**, *56*, 683–687. DOI: 10.1002/jccs.200900102.

[15] Srinivas, C.; Kumar, C. N. S. S. P.; Rao, V. J.; Palaniappan, S. Efficient, Convenient and Reusable Polyaniline-Sulfate Salt Catalyst for the Synthesis of Quinoxaline Derivatives. *J. Mol. Catal. A Chem.* **2007**, *265*, 227–230. DOI: 10.1016/j.molcata.2006.10.018.

[16] Hasaninejad, A.; Zare, A.; Mohammadizadeh, M. R.; Karami, Z. Synthesis of Quinoxaline Derivatives *via* Condensation of Aryl-1,2-Diamines with 1,2-Diketones Using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as an Efficient, Mild and Reusable Catalyst. *JICS.* **2009**, *6*, 153–158. DOI: 10.1007/BF03246514.

[17] Khaksar, S.; Tajbakhsh, M.; Gholami, M.; Rostamnezhad, F. A Highly Efficient Procedure for the Synthesis of Quinoxaline Derivatives Using Polyvinylpolypyrrolidone Supported Triflic Acid Catalyst (PVPP·OTf). *Chinese Chem. Lett.* **2014**, *25*, 1287–1290. DOI: 10.1016/j.cclet.2014.04.008.

[18] Pan, F.; Chen, T. M.; Cao, J. J.; Zou, J. P.; Zhang, W. $Ga(ClO_4)_3$-Catalyzed Synthesis of Quinoxalines by Cycloaddition of α-Hydroxyketones and *o*-Phenylenediamines. *Tetrahedron Lett.* **2012**, *53*, 2508–2510. DOI: 10.1016/j.tetlet.2012.02.113.

[19] Kumar, K.; Mudshinge, S. R.; Goyal, S.; Gangar, M.; Nair, V. A. A Catalyst Free, One Pot Approach for the Synthesis of Quinoxaline Derivatives via Oxidative Cyclisation of 1,2-Diamines and Phenacyl Bromides. *Tetrahedron Lett.* **2015**, *56*, 1266–1271. DOI: 10.1016/j.tetlet.2015.01.138.

[20] Bhunia, S.; Ghosh, P.; Patra, S. R. Gold Catalyzed Oxidative Alkyne Functionalization by N–O/S–O/C–O Bond Oxidants. *Adv. Synth. Catal.* **2020**, *362*, 3664–3708. DOI: 10.1002/adsc.202000274.

[21] Das, B.; Venkateswarlu, K.; Suneel, K.; Majhi, A. An Efficient and Convenient Protocol for the Synthesis of Quinoxalines and Dihydropyrazines via Cyclization-Oxidation Processes Using $HClO_4\cdot SiO_2$ as a Heterogeneous Recyclable Catalyst. *Tetrahedron Lett.* **2007**, *48*, 5371–5374. DOI: 10.1016/j.tetlet.2007.06.036.

[22] Wan, J. P.; Gan, S. F.; Wu, J. M.; Pan, Y. Water Mediated Chemoselective Synthesis of 1,2-Disubstituted Benzimidazoles Using *o*-Phenylenediamine and the Extended Synthesis of Quinoxalines. *Green Chem.* **2009**, *11*, 1633–1637. DOI: 10.1039/b914286j.

[23] Madhav, B.; Murthy, S. N.; Reddy, V. P.; Rao, K. R.; Nageswar, Y. V. D. Biomimetic Synthesis of Quinoxalines in Water. *Tetrahedron Lett.* **2009**, *50*, 6025–6028. DOI: 10.1016/j.tetlet.2009.08.033.

[24] Tejeswararao, D. Synthesis of Quinoxaline Using Silica Supported Phosphomolybdic Acid as Reusable Heterogeneous Catalyst. *Asian J. Chem.* **2016**, *28*, 2353–2356. DOI: 10.14233/ajchem.2016.19533.

[25] Ghosh, P.; Mandal, A. Sodium Dodecyl Sulfate in Water: Greener Approach for the Synthesis of Quinoxaline Derivatives. *Green. Chem. Lett. Rev.* **2013**, *6*, 45–54. DOI: 10.1080/17518253.2012.703245.

[26] Harsha, K. B.; Rangappa, K. S. One-Step Approach for the Synthesis of Functionalized Quinoxalines Mediated by T3P-DMSO or T3P via a Tandem Oxidation-Condensation or Condensation Reaction. *RSC Adv.* **2016**, *6*, 57154–57162. DOI: 10.1039/C6RA03078E.

[27] Pardeshi, S. D.; Sathe, P. A.; Vadagaonkar, K. S.; Chaskar, A. C. One-Pot Protocol for the Synthesis of Imidazoles and Quinoxalines Using N-Bromosuccinimide. *Adv. Synth. Catal.* **2017**, *359*, 4217–4226. DOI: 10.1002/adsc.201700900.

[28] Meshram, H. M.; Ramesh, P.; Kumar, G. S.; Reddy, B. C. One-Pot Synthesis of Quinoxaline-2-Carboxylate Derivatives Using Ionic Liquid as Reusable Reaction Media. *Tetrahedron Lett.* **2010**, *51*, 4313–4316. DOI: 10.1016/j.tetlet.2010.05.099.

[29] Barkul, R. P.; Sutar, R. S.; Patil, M. K.; Delekar, S. D. Photocatalytic Degradation of Organic Pollutants by Using Nanocrystalline Boron-Doped TiO_2 Catalysts. *ChemistrySelect* **2021**, *6*, 3360–3369. DOI: 10.1002/slct.202003910.

[30] Sutar, R. S.; Barkul, R. P.; Patil, M. K. Visible Light Assisted Photocatalytic Degradation of Methylene Blue Dye and Mixture of Dyes Using ZrO_2-TiO_2 Nanocomposites. *Cnano* **2021**, *17*, 120–129. DOI: 10.2174/1573413716999200605154956.

[31] Manoharan, D.; Loganathan, A.; Kurapati, V.; Nesamony, V. J. Unique Sharp Photoluminescence of Size-Controlled Sonochemically Synthesized Zirconia Nanoparticles. *Ultrason. Sonochem.* **2015**, *23*, 174–184. DOI: 10.1016/j.ultsonch.2014.10.004.

[32] Li, X.; Nagaoka, K.; Lercher, J. A. Labile Sulfates as Key Components in Active Sulfated Zirconia for *n*-Butane Isomerization at Low Temperatures. *J. Catal.* **2004**, *227*, 130–137. DOI: 10.1016/j.jcat.2004.07.003.

[33] Ghafuri, H.; Rashidizadeh, A.; Ghorbani, B.; Talebi, M. Nano Magnetic Sulfated Zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$): an Efficient Solid Acid Catalyst for the Green Synthesis of α-Aminonitriles and Imines. *New J. Chem.* **2015**, *39*, 4821–4829. DOI: 10.1039/C5NJ00314H.

[34] Nasseri, M. A.; Alavi, S. A.; Kazemnejadi, M.; Allahresani, A. The $CuFe_2O_4@SiO_2@ZrO_2/SO_4^{2-}/Cu$ Nanoparticles: An Efficient Magnetically Recyclable Multifunctional Lewis/Brønsted Acid Nanocatalyst for the Ligand- and Pd-Free Sonogashira Cross-Coupling Reaction in Water. *RSC Adv.* **2019**, *9*, 20749–20759. DOI: 10.1039/C9RA03406D.

[35] Harsha, K. B.; Rangappa, S.; Preetham, H. D.; Swaroop, T. R.; Gilandoust, M.; Rakesh, K. S.; Rangappa, K. S. An Easy and Efficient Method for the Synthesis of Quinoxalines Using Recyclable and Heterogeneous Nanomagnetic-Supported Acid Catalyst under Solvent-Free Contdition. *ChemistrySelect* **2018**, *3*, 5228–5232. DOI: 10.1002/slct.201800053.

[36] Lian, M.; Li, Q.; Zhu, Y.; Yin, G.; Wu, A. Logic Design and Synthesis of Quinoxalines via the Integration of Iodination/Oxidation/Cyclization Sequences from Ketones and 1,2-Diamines. *Tetrahedron* **2012**, *68*, 9598–9605. DOI: 10.1016/j.tet.2012.09.056.

[37] Jadhav, S. A.; Sarkate, A. P.; Shioorkar, M. G.; Shinde, D. B. Expeditious One Pot Multicomponent Microwave Assisted Green Synthesis of Substituted 2-Phenyl Quinoxaline and 7-Bromo-3-(4-Ethylphenyl)Pyrido[2,3-*b*]Pyrazine in Water-PEG and Water-Ethanol. *Synth. Commun.* **2017**, *47*, 1661–1667. DOI: 10.1080/00397911.2017.1337153.

[38] Nagarapu, L.; Palem, J. D.; Reddy, A. R. K.; Bantu, R. A Facile and Efficient Synthesis of Quinoxalines from Phenacyl Bromides and Ortho Phenylenediamine Promoted by Zirconium Tungstate. *Org. Chem. Curr. Res.* **2014**, *S4*, 1–5. DOI: 10.4172/2161-0401.S4-4001.

[39] Tanwar, B.; Purohit, P.; Raju, B. N.; Kumar, D.; Kommi, D. N.; Chakraborti, A. K. An "All-Water" Strategy for Regiocontrolled Synthesis of 2-Aryl Quinoxalines. *RSC Adv.* **2015**, *5*, 11873–11883. DOI: 10.1039/C4RA16568C.

[40] Khalafy, J.; Habashi, B. P.; Marjani, A. P.; Moghadam, P. N. The Synthesis of 2 Arylquinoxaline Derivatives. *Curr. Chem. Lett.* **2012**, *1*, 139–146. DOI: 10.5267/j.ccl.2012.5.002.

[41] Yang, J.; Zhu, H.; Huang, Y.; Huang, W.; Wang, W. Design and Synthesis of Extended Quinoxaline Derivatives and Their Charge Transport Properties. *RSC Adv.* **2016**, *6*, 100067–100071. DOI: 10.1039/C6RA22677A.

International Journal of Zoology and Applied Biosciences
Volume 7, Issue 2, pp: 6-9, 2022
https://doi.org/10.55126/ijzab.2022

ISSN: 2455-9571

http://www.ijzab.com

Research Article

A NEW SPECIES OF GENUS *EIMERIA* (APICOMPLEXA : EUCOCCIDIORIDA) FROM SHEEP

[1]B.V. More and [2]Y.M.Bhosale

[1]Department of Zoology, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad (M.S.) India
[2]Department of Zoology, Nanasaheb Yashwantrao Narayanrao Chavan ASC College
Chalisgaon, Dist. Jalgaon M.S. India

Article History: Received 30th January 2022; Accepted 28th February 2022; Published 07th March 2022

ABSTRACT

The present communication deals with the description of a new species of genus *Eimeria*. This new species *Eimeria beedatus* is different from all known species of the genus in shape, length and width of the oocyst, sporocysts and sporozoites. Oocysts were collected from Beed District for the period of two years (June 2007 to may 2009). During the investigation total 2462 samples of sheep were collected, of which 594 were found to be positive for Eimerian oocysts. Sporulation time of species was also recorded.

Keywords: Coccidiosis, *Eimeria* Species, Apicomplexa, Sporozoite, Sporocyst.

INTRODUCTION

Coccidia is one of the common intestinal disease found in Sheep Goats, chicken, Horse, and Pig etc. It causes coccidiosis in theses organism. coccidia is one of the major group of protozoa have been progressively increasing as an intestinal paras[illegible]s, causing extensive pathological damage and mortality in Sheep and Goats, which is results in to great economic losses of sheep and Goat owners. Studies on coccidia are one of the great biological, medical and veterinary importances. There are several species of coccidia are found worldwide in the recent time. Up to this time more than two hundred species of seventeen genra are well described in different publications. The necessity of basic taxonomic study of Eimeria is almost necessary to understand the pathogenesity, mortality and economic losses.

MATERIAL AND METHODS

The material for the study of coccidia of goats and sheep was obtained from various slaughter houses as well as from different fields in and around Beed (M.S.). Different parts of the intestine of slaughtered goats were examined and processed within 4-5 hours after collection. The faecal contents were diluted with distilled water and sieved to remove the large faecal debris. After repeated washing the oocysts were concentrated by centrifugation at 3000 rpm for 10 minutes. The oocysts were then spread out in shallow petri dishes and covered with 2.5% solution of potassium dichromate for sporulation.

RESULTS AND DISCUSSION

During the study ten species of *Eimeria* are found in sheep, eight species are redscribed and two are new species. *Eimeria crandallis* was the most frequent, being found in 108 out of 594 positive samples (18.18%) or 4.38% of the total samples. *Eimeriaparva* was the second common species found in 90 out of 594 positive samples, representing 15.15% of the positive samples and 3.65% of the total samples examined. *Eimeriawey bridgensis* was the third species found in 82 out of 594 positive samples, representing 13.80% of the positive samples and 3.33% of the total samples examined. *Eimerianinakohlyakimovae* was the fourth found in 75out of 594 positive samples, representing 12.62% of the positive samples and 3.04% of the total samples examined. *Eimeria intricata* was the fifth found in 61out of 594 positive samples, representing 10.26% of the positive samples and 2.47% of the total

---

*Corresponding Author: Dr. B.V. More, Department of Zoology, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad. (M.S.) India. Email: drbabasahebmore@gmail.com

samples examined. *Eimeria ahsata* was the sixth species found in 55 out of 594 positive samples, representing 9.25% of the positive samples and 2.23% of the total samples examined. *Eimeria ovina* was the seventh species found in 41 out of 594 positive samples, representing 6.90% of the positive samples and 1.66% of the total samples examined. *Eimeria ajantai* was the eighth species found in 34 out of 594 positive samples, representing 5.72% of the positive samples and 1.38% of the total samples examined. Two new species are recorded, *Eimeria balloonii* and *Eimeria beedatus. Eimeria balloonii(n.sp.)* was the new species found in 26 out of 594 positive samples, representing 4.37% of the positive samples and 1.05% of the total samples examined. *Eimeria beedatus (n.sp.)* was the new species found in 22 out of 3.70% of the positives samples and 0.89% of the total samples examined. The species was found only in sheep. The oocysts are egg shaped with micropyle but without micropylar cap. The oocyst wall is double layered and about 2.1µm thick. The outer layer is yellowish in colour and about 1.1µm thick. The inner layer is 1.0µm thick and brownish in colour. The micropyle measures 2µm wide. The unsporulatedoocyst shows spherical sporoblast near the micropylar region of the oocyst, it measures about 12 to 14µm in diameter. The polar granule and oocystic residuum are absent. The four subspherical to ovoid sporocysts without stieda body are observed. The sporocystic residuum is in the form of compact granular mass in between two sporozoites. The sporozoites are roughly rounded in shape with a refractile globule.

Table 1. The dimensions of the sporulated oocysts of *Eimeria beedatus* from sheep are as follows (All measurements are in microns).

Particulars	Oocyst from sheep
Length of the oocyst	20.2 -26.4 (23.41)
Width of the oocyst	10.4 -18.3 (16.10)
Length width ratio of the oocyst	1.4 -1.4 (1.45)
Length of the sporocyst	5.2 -6.4 (7.36)
Width of the sporocyst	5.2 -6.4 (7.36)
Length width ratio of the sporocyst	1.0 -1.0 (1.0)

Sporulation time: The sporulation time of the oocysts was 84 hours. Prevalence: The species was found in 0.89% of the 2462 sheep examined from Beed district.

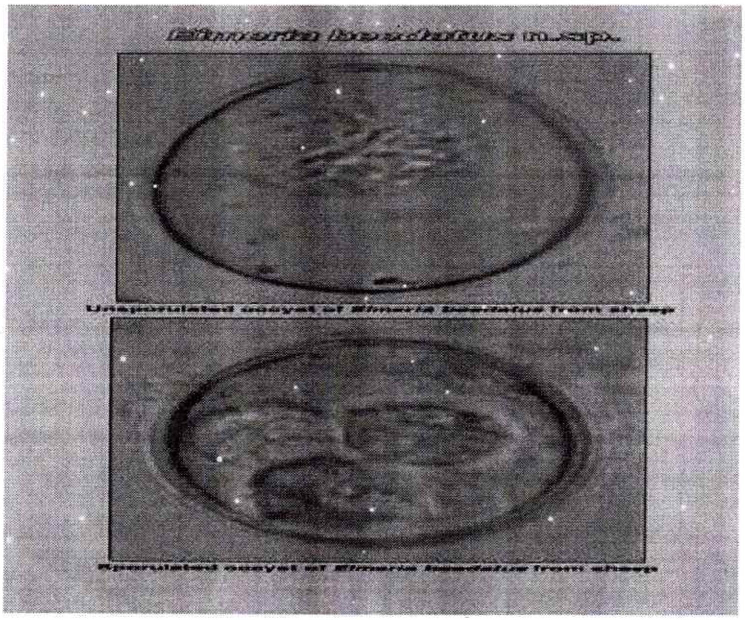


Figure 1. The frequency distribution of the lengths and widths of the oocysts of *Eimeriabeedatus* from sheep shown.

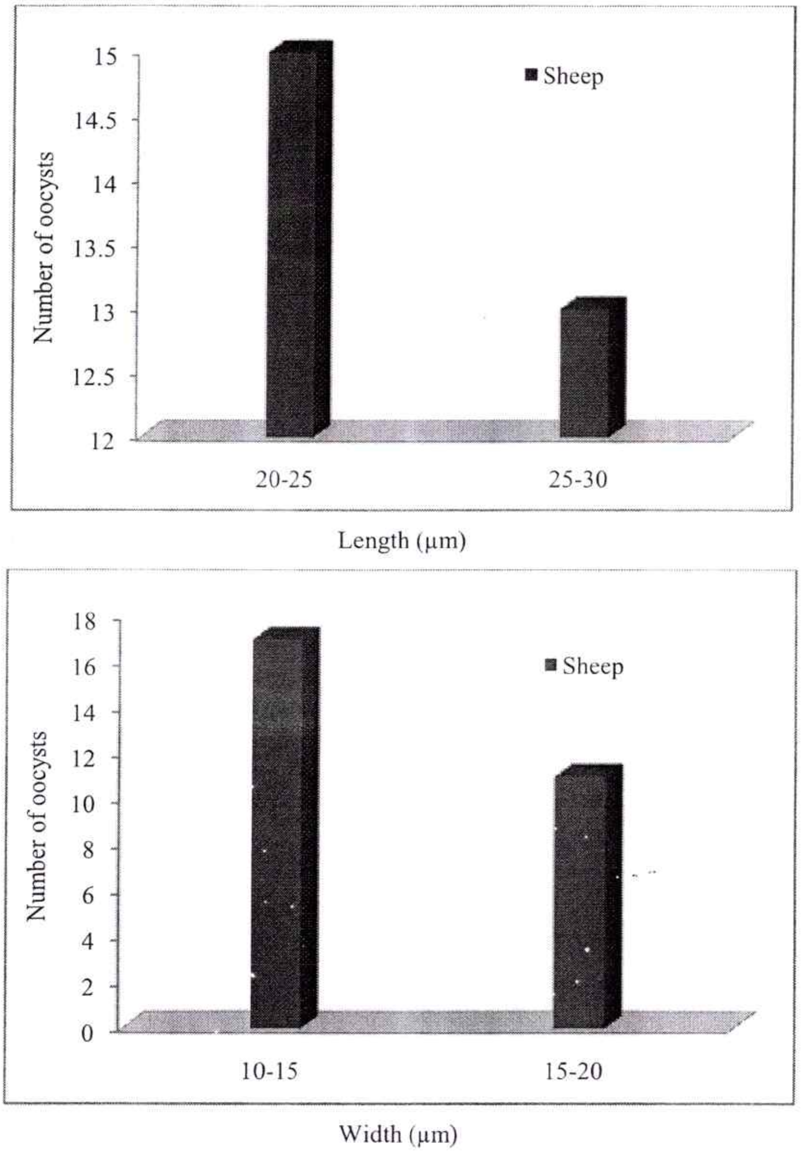


Figure 2. Showing the frequency distribution of the lengths and widths of oocysts of *Eimeria beedatus* from sheep.

Table 1. Comparative chart showing an account of old and new species of the genus *Eimeria* Schneider 1875.

Species character	*E. faurei* (Moussu and Marotel, 1902 Martin, 1909)	*E. compactum* (Bawazir 1980)	*E. ninakohlyakimovae* (Yakim off and Rastegaieff,1930)	n.sp.
Shape of oocyst	Ovoid or egg shaped (Single layer)	Ellipsoidal or ovoidal	Subspherical	Egg shaped
Measurement of oocyst in µm.	18.0 -31.0 x 14.5- 21.0	31.62 -39.78 x 22.44 x 27.54	17.0 -23.0 x 12.0 -19.5	20.2 -26.4 x 14.2 - 18.3
Micropyle and micropylar cap	Micropyle but without micropylar cap, (2µm. wide)	Prominent micropyle but without micropylar cap ,(4-8 µm wide)	Micropyle but without micropylar cap, (1µm. wide)	Micropyle present but without micropylar cap (2µm wide)
Polar granule	Absent	Absent	Present	Absent
Oocystic residuum	Absent	Absent	Absent	Absent

Shape of sporocyst	Ovoid to pyriform	Elongate, ovoid	Ovoid	Spherical to ovoid
Measurement of sporocyst in µm.	8.0 -15.0 x 6.0 -9.0 (in sheep)	14.28 -19.38 x 7.14 - 10.2	5.0 -12.0 x 3.0 -8.0	5.2 -6.4 x 5.2 -6.4
Stieda body	Absent but in few cases very small	Conspicuous	Small stieda body present	Absent
Sporocystic residuum	Absent	Present in the form of a dark and compact granule on one side of the sporocyst	Present	Compact granular mass in between two sporozoites
Shape of sporozoites	Elongate	Lie head to tail and arranged more or less longitudinally in the sporocysts	Elongate lying wise in the sporocyst	Roughly round in shape
Refractile globule	Each sporozoites has two refractile globules one at each end	One or two refractile globule are present	A conspicuous refractile globule present	One refractile globule present
Host	Sheep / goat	Sheep	Sheep / goat	Sheep

When this species is studied by the present author it is observed that it is with a micropyle but without micropylar cap so it is compared with the species which are only with micropyles. *Eimeria faurei* (Mossu and Marotel, 1902, Martin 1909), *Eimerianinakohlyakimovae* (Yakimoff and Rastegaiff,1930), *Eimeria compactum* (Bawazir, 1980) and *Eimeria balloonii* (from sheep)and *Eimeria straightatus* (from goat). The shape of the present species matches with *E. faurei;* remaining species are somewhat different in shapes than the present one. Oocysts of present species are smallest in size when compared with all above species except *E.ninakohlyakimovae* in sheep which is smaller than the present oocyst. Size of the micropyle similar to *E. faurei*, *E.balloonii* but smaller than *E.compactum*, *E.straightatus* and larger than *E.ninakohlyakimovae*. Oocystic residuum is absent in all above species including the present one. Shape of sporocysts of the present species is different than the previous species. (Sub spherical to ovoid, without stieda body).Stieda body is absent in *E.ninakohlyakimovae* (in goat) same feature is found in present species, in remaining species stieda body is present. Sporocystic residuum is present in *E.compactum*, *E.ninakohlyakimovae*, *E.straightatus* and *E.balloonii*except *E. faurei*. Shape of the sporozoites in all the previous species is elongate tapering while in the present species they are roughly rounded. When the species is compared with all the previous species it is seen that some distinguishing features are found in the present species. (Comparative chart is given in Table -1). The ovoid sporocysts are smaller than all the previous species. Main distinguishing feature is its rounded sporozoite which is not seen in previous species. Ovoid to subspherical sporocysts and rounded sporozoites are very typical, not found in the previous species. Because of these distinct features the species is considered new to science and designated as *Eimeriabeedatus*. Host-*Ovisaries,* Habitat- Oocyst found in intestinal content Locality- Beed, (M.S).

ACKNOWLEDGEMENT

The Authors are grateful to the head Department of Zoology Dr. B.A.M. University, Aurangabad (M.S.) for providing the library and laboratory facilities.

REFERENCES

Bawazir, S. S. (1980). Studies on the coccidia of some mammals. Ph.D. Thesis, Marathwada University Library, Aurangabad. 1-211, 273-285, 413-421.

Martin, A. (1909). Les coccidioses des animaux domestiques. Rev. Vet. Toulouse, 66, 273-285.

Moussu, G., & Marotel, G. (1902). La coccidiose du mouton et son parasite. Arch. Parasit, 6, 82-98.

Yakimoff, W. L. and Rastegaiff, F. F. (1930). Zur frage uber coccidian der ziegen. Archive in Protistenk, 70,185-191.

INTERNATIONAL INTERDISCIPLINARY RESEARCH JOURNAL (AIIRJ)

Monthly e-Journal

VOL-IX ISSUE-III MAR 2022

Address
- Devgiri Nagar, Ambajogai Road, Latur.
- Tq. Latur, Dis. Latur 413512 (MS.)
- (+91) 9922455749, (+91) 8999250451

Email
- aiirjpramod@gmail.com
- aayushijournal@gmail.com

Website
- www.aiirjournal.com

CHIEF EDITOR – PRAMOD PRAKASHRAO TANDALE

फणीश्वरनाथ रेणु के उपन्यासों की प्रासंगिकता

- डॉ. केशव क्षिरसागर
हिंदी विभाग,
रामकृष्ण परमहंस महाविद्यालय,
उस्मानाबाद.

फणीश्वरनाथ रेणु जी उन उपन्यासकारों में से हैं जिन्होंने जनयुग को, जन रूचि को, अपनी चेतना का आधार बनाया I उनकी पहली रचना 'मैला आँचल' इस दृष्टि से एक प्रौढ़ कृति है I उसमें पारंपरिक कथा — सृष्टि का कोई तत्त्व नहीं मिलता, वह आँचलिक यथार्थवादी रचना हैं जिसने 'रेणुजी' को साहित्याकाश में दैदीप्यमान बना दिया I १९५४ में प्रकाशित 'मैला आँचल' से औपन्यासिक विचारधारा को एक नया मोड़ मिल गया, आँचलिक उपन्यासों का प्रचलन आरंभ हुआ I

आँचलिकता में कथा — सृष्टि की परंपरा का स्वरूप नहीं रह सकता क्योंकि आँचलिक उपन्यास अंचल विशेष की संस्कृति, उसके खान — पान, रीति — रिवाज, धर्म — विश्वास, भौगोलिक स्थिति आदि सभी तानों — बानों से कथानक का सुरम्य — सुगन्धित जीवन का चित्र प्रस्तुत करता है जिसमें उस धरती की सौंधी सुगंध होती है वह विशिष्ट एवं अत्यंत यथार्थ कथानक होता है I 'मैला आँचल' में केवल आँचलिक जन — जीवन का चित्रण ही नहीं बल्कि उसमें तत्कालीन राष्ट्रिय, अंतर्राष्ट्रीय अतिविधियों का भी पर्याप्त मात्रा में चित्रण मिलता है I रेणु जी के आँचलिक उपन्यासों की सबसे बड़ी विशेषता यह है कि वे अतिशय सीमित क्षेत्र की घटना भाषा और बोलचाल से सम्बद्ध होते हुए भी एक विलक्षण सांकेतिकता के द्वारा संपूर्ण राष्ट्रिय जीवन को ध्वनित और व्यंजित करते हैं I उन्होंने अपने उपन्यासों में क्षेत्र विशेष के जीवन की बारीक़ से बारीक़, विविधता का प्रदर्शन और चित्रण दवारा संपूर्ण सामयिक राष्ट्रिय जीवन — चेतना को अभिव्यक्त किया है I उनके उपन्यासों में स्थानिकता के आकर्षण के साथ — साथ गतिशील राष्ट्रिय चेतना की सम्पूर्णता का आकर्षण भी हैं I रूप, रस, गंध, स्पर्श के तो रेणुजी चितेरे कलाकार हैं I

"मैला आँचल" में स्वातंत्र्योत्तर भारत के नवोन्मेषित 'पूर्णियां' के मेरीगंज गाँव की कथा है, उनकी मैली जिंदगी और पिछड़ेपन की कहानी इसका मेरुदंड हैं जो सोते से अंगड़ाई लेकर जाग रहें हैं I जिसके आलोड़न — विलोड़न से मेरीगंज का पिछडा धूल भरा ''मैला आँचल' अपनी हर अच्छाई — बुराई, आशा — आकांक्षा, सुख — दुःख, हँसी — ख़ुशी, तीज — त्यौहार, आर्थिक — वैषम्य, नये — पुराने मूल्यों की टकराहट आदि के साथ अपनी समग्रता में उभरकर आया है, जिसमें एक काल विशेष का सजीव चित्र मूर्त्त हो उठा हैं I डॉक्टर प्रशांत के साथ मोटर में बैठी ममता देखती है — "विशाल मैदान, वन्ध्या धरती, यही है वह मशहूर मैदान नेपाल से शुरू होकर गंगा किनारे तक, वीरान धूमिल अंचल I"१ इसी धूमिल क्षेत्र के एक गाँव मेरीगंज के दागदार जीवन का यथा तथ्य, करुणा की आर्द्रता का संवेदनशील चित्रण रेणु जी ने किया है I उपन्यास की भूमिका में वे स्वयं लिखते हैं — "यह है मैला आँचल एक आँचलिक उपन्यास I कथानक है पूर्णिया, पूर्णिया बिहार राज्य का एक जिला है, इसके एक ओर नेपाल, दूसरी ओर पाकिस्तान और पश्चिम बंगाल I विभिन्न सीमा रेखाओं से इसकी बनावट मुकम्मल हो जाती है, जब हम दखिन में संथाल परगना और पश्चिम में मिथिला की सीमा रेखा खींच देते हैं I मैंने इसके एक हिस्से के एक ही गाँव को पिछड़े गाँव का प्रतिक मानकर उपन्यास का कथा क्षेत्र बनाया है I इसमें फूल भी हैं, शूल भी हैं, धूल भी हैं, गुलाल भी, कीचड़ भी, चंदन भी, सुंदरता भी है, कुरूपता भी I"२ रेणु जिस

फोटोग्राफिक शैली से छोटे – छोटे स्नैपशॉट लेते गए हैं, उससे धूल भरा मैला आँचल जीवंत हो उठा है I रेणु जी को इस अंचल के ग्रामवासियों के प्रत्येक गतिलेश से निसर्ग सिद्ध सहानुभूति हैं I

रेणु जी का दूसरा उपन्यास 'परती परिकथा' उसी परंपरा की दूसरी कड़ी है जिसका आरंभ मैला आँचल से हुआ था I 'परती परिकथा' उस धूसर वीरान धरती की कथा है, जिसका प्रतिपाद्य है परानपुर I परती परिकथा अपने शीर्षक से ही अपनी कथावस्तु का संकेत देती है I इस इलाके के लोग परानपुर को सारे अंचल का प्राण कहते हैं I यही परानपुर ग्राम 'परती परिकथा' का मुख्य प्रतिपाद्य है I इसमें पूर्णिया जिले के दूसरे ग्राम परानपुर को अपेक्षाकृत उन्नत गाँव ले प्रतीक रूपं में चित्रित किया गया है I

'परती परिकथा' स्वतंत्रता प्राप्ति के बाद विकास और निर्माण की कथा है I इसमें स्वतंत्रता के पश्चात् जमींदारी – उन्मूलन और भूमि के पुनर्विभाजन की पृष्ठभूमि पर परानपुर के ग्राम्य जीवन की कथा का सुंदर चित्रण किया गया है, उसमें युगीन समस्याओं का मार्मिक चित्रण किया गया है I रेणु जी लिखते हैं – "हिन्दुस्थान में संभवत: सबसे पहले पूर्णिया जिले पर ही लैण्ड सर्वे ऑपरेशन किया गया I जिले के जमींदारों और राजाओं की जमींदारियों का विनाश आवश्य हुआ है किन्तु हिन्दुस्थान के सबसे बड़े किसान यहीं बसते हैं I"[३]

परती परिकथा का दूसरा पहलु है, विज्ञान के माध्यम से ग्रामीणों के जीवन में आमूल परिवर्तन की कल्पना करना I जितेंद्र मिश्र द्वारा वन्ध्या जमीन पर गुलाब की खेती, रोमांटिक कल्पना होते हुए भी ग्रामीणों की दमित लालसा की अभिव्यक्ति है I पानी की समस्या को सुन्नरी नैका और दंता राकस की कथा के माध्यम से प्रस्तुत किया गया है I द्वितीय परिवर्तन में कोसी योजना का विधिवत वर्णन है I योजना विकास के प्रति जो उल्लास स्वतंत्रता के प्रथम दशक में रहा है वहीं इस उपन्यास में भी अभिव्यक्त हुआ है I इस प्रकार रेणु जी ने यह स्पष्ट किया है कि भूमि भारतीय ग्रामीणों के जीवन का केंद्र है, जिसके द्वारा उनकी सामाजिक, राजनीतिक, आर्थिक समस्याएँ निर्मित व् विघटित होती रहती है I

'परती परिकथा' देश के नवनिर्माण में जनता की स्वावलंबी चेतना का उपन्यास है I बावनदास महात्मा गांधी जी का प्रतिरूप है देश के उन काँग्रेसी नेताओं का जो पद का लोभ नहीं करते, गाँधीजी का अनुकरण करते रहें तथा अपने सिधान्तों के लिए जिए और मरे I बावनदास दुलारचंद कापरा द्वारा गाड़ी न हटाने पर अपना बलिदान कर देता है, यह आदर्श विशुद्ध गाँधीवादी हैं I आज के राजनीतिक दलों की स्खलित स्थिति का चित्रण भी 'परती परिकथा' में मिलता है I गाँव में मुख्यत: तीन राजनैतिक दल हैं समाजवादी, काँग्रेस, कम्युनिस्ट इन दलों के नेता महामूर्ख हैं I कुबेर सिंह के माध्यम से रेणु जी ने नगर – राजनीति की शुन्यता और अव्यवस्था पर भी प्रकाश डाला हैं I इस प्रकार 'परती परिकथा' उपन्यास में चित्रित स्थितियाँ आज भी जैसी की वैसी लागु होती हैं I

'जुलूस' नामक अपने तीसरे उपन्यास में रेणु जी ने समसामयिक गतिविधियों का सुंदर चित्रण किया है I रेणु जी कहतें है कि यह भारतीय जीवन एक अर्थ हीन 'जुलूस' हैं I 'जुलूस' की भूमिका में वे लिखते है – "पिछले कुछ वर्षों से मैं एक अद्भुत भ्रम में पड़ा हूँ दिन – रात, सोते – बैठते, सोते – बैठते, खाते – पीते मुझे लगता है एक विशाल जुलूस के साथ चल रहा हूँ अविराम I"[४] 'जुलूस' उपन्यास १९४७ के विभाजन के परिणाम स्वरूप विस्थापित हुए जिला मैमन सिंह के गाँव जुमापुर के हिन्दुओं की संघर्ष गाथा हैं I जिन्हें बिहार के पूर्णिया जिले में बसाया जाता है, इसे विस्थापित बंगाली नौबिन नगर भी कहते हैं I तो पड़ोसी गोडियर गाँव के बिहारी लोग इसे 'पाकिस्तानी टोला' कहते हैं I जिस तरह यशपाल जी ने 'झूठा सच' में विशाल कैनवास पर वतन और देश की समस्या को अभिव्यक्त किया है उसी तरह रेणु जी ने बहुत ही सीमित और छोटे फलक पर उसकी सशक्त मर्मस्पर्शी झाँकी प्रस्तुत की है I जुलूस में युग – बोध और समसामयिकता के दर्शन होते हैं, तत्कालीन राजनीति का सुंदर वर्णन जुलूस की पहचान बन गया है – "एक झूठ को दूसरे झूठ से, दूसरे झूठ को तीसरे झूठ से और तीसरे को चौथे से ढँकते – ढँकते मूल झूठ की जड़ मजबूत हो जाती हैं I"[५]

'दीर्घतपा' रेणु जी का चौथा आँचलिक उपन्यास हैं I इस उपन्यास में तपी हुई नारी की कथा हैं, जो देश की आजादी के नाम पर कुछ सह गई और बांके

की कायरता का फल बहुत दिनों तक भोगती रही I इसमें बांकीपुर के 'विमेन्स वेलफेअर बोर्ड' नामक समाज सेवी संस्था का वर्णन हुआ है I सांकेतिक रूप में रेणु जी ने यही बताने की कोशिश की है कि देश में इस प्रकार के विमेन्स वेलफेअर संस्थाओं को किस प्रकार स्वार्थ – सिद्धि के लिए बड़े लोंगों, पूँजीपतियों, मंत्रियों की कामुकता के लिए चकला घर बना दिया जाता है I अंजु – मंजू जैसी लड़कियों से कम वासना की तुष्टि की जाती है I मिसेज आनंद जैसी महिला कार्यकर्ता की आज देश में कमी नहीं हैं जो ऐसी संस्थाओं की सम्माननीय सचिव हैं जो संस्थाओं में आनेवाली दवा और दूध के स्टॉक बड़ी सफाई से गायब कर देती है और पच्चीस हजार रुपये का फायदा कर लेती हैं I रेणु जी ने इसके माध्यम से यह बताने की कोशिश की है कि किस स्तर तक आदमी गिर सकता है, स्वार्थपरता, भ्रष्टाचार घूसखोरी किस हद तक सभी स्तरों पर काम कर रही है I स्त्री – पुरूषों की कामुकता ने समाज में अनैतिकता का वातावरण प्रस्तुत कर दिया है I

'कितने चौराहे' रेणु जी का पाँचवा उपन्यास हैं, जो मातृभूमि की स्वतंत्रता के लिए संघर्ष करनेवाले जीवित राष्ट्र की प्राणवती गाथा प्रस्तुत करता है I गाँधीजी का सत्य, सेव एवं अहिंसा पर आधारित नीति और भगतसिंह जैसे देशभक्त क्रांतिकारियों क संघर्ष से १९६५ के पाकिस्तानी आक्रमण तक, यह राष्ट्र एक के बाद एक कितनें चौराहों को पार करता गया इस वास्तविकता का यथार्थ चित्रण इस उपन्यास का प्रमुख विषय रहा हैं I कुछ स्वार्थी तत्त्व हिन्दुस्थान – पाकिस्तान के नाम पर लुट – खसोट चाहते रहे हैं किन्तु नवनिर्मित राष्ट्र ज्वलंत समस्याओं का सामना करता हुआ राह में आई हुई बाधाओं का सामना करता हुआ आगे ही बढ़ता हुआ कितने ही चौराहों को पार कर अपने मुख्य गंतव्य की ओर आगे ही बढ़ता जा रहा है I

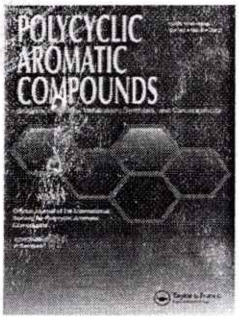
गाँव में भी नवयुग की चेतना का प्रभाव पड़ता है गाँधीजी की गिरफ्तारी ने युवकों को उत्तेजित कर दिया है I वे सब मिलकर कहते हैं हम लोग हड़ताल करेंगे, स्ट्राइक, स्कुल नहीं जायेंगे I बाजार बंद रहेगा, हम लोग खाना नहीं खाएँगे I इसमें सन १९३३ – ३४ के राजनीतिक भारत का चित्रण हैं I

'पल्टू बाबु रोड' रेणु जी का अंतिम उपन्यास हैं, जो देश के विभाजन की त्रासदी को अत्यंत मार्मिकता से स्पष्ट करता है I इसका एक पात्र घंटा कहता है – "साइकोएनालिसस के लिए घर ही सर्वोत्तम लेबोरेटरी है I"६ इसमें पल्टू बाबु के रूप में रेणु जी ने आज के राजनीतिज्ञों तथा उनकी कुटिल बुद्धि को रूपायित किया है I बहुपार्टी व्यवस्था के कारण समाज का स्वरूप दिनों दिन गिरता ही चला गया I औदयोंगीकरण के कारण आज मनुष्य जीवन की जो प्रधान – वृत्ति है प्रेम उसका भी व्यवसायीकरण हो गया है I न उम्र की, न पारिवारिक संबंध की और न नैतिकता की सीमा रह गई है I

रेणु जी के सभी उपन्यासों की कथानक – सृष्टि में जिस कौशल का परिचय मिलाता है वह भी बहुत सरल, सहज और स्पष्ट है I जो अत्यंत यथार्थवादी, चेतना का निरूपण करनेवाला है जिसमें मनुष्य का जीवन और उसका परिवेश अपनी समस्त जटिलताओं एवं संपूर्ण विसंगतियों के साथ उजागर होता जाता है I उन्होंने जो कुछ देखा, भोगा और महसूस किया है उसकी प्रमाणिक अभिव्यक्ति अपनें उपन्यासों के माध्यम से समाज के सामने रखने की कोशिश रेणु जी ने की है, जो अत्यंत सराहनीय और आज भी उतनी ही प्रासंगिक हैं जितनी उस समय थी यही इसकी सबसे बड़ी विशेषता एवं उपलब्धि हैं I

संदर्भ : -

१) आलोचना : अक्टूबर, १९५७, १५
२) मैला आँचल – प्रथम संस्करण १९५४ भूमिका
३) परती परिकथा – पृ. क्र. २३ - २४
४) जुलूस : भूमिका
५) जुलूस : पृ. क्र. ११७
६) पल्टू बाबु रोड – पृ. क्र. १७



Polycyclic Aromatic Compounds

Taylor & Francis
Taylor & Francis Group

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gpol20

DTP/SiO$_2$ Assisted Synthesis of New Benzimidazole-Thiazole Conjugates Targeting Antitubercular and Antioxidant Activities

Madhav J. Hebade, Sambhaji T. Dhumal, Sonali S. Kamble, Tejshri R. Deshmukh, Vijay M. Khedkar, Shrikant V. Hese, Rajesh N. Gacche & Bhaskar S. Dawane

To cite this article: Madhav J. Hebade, Sambhaji T. Dhumal, Sonali S. Kamble, Tejshri R. Deshmukh, Vijay M. Khedkar, Shrikant V. Hese, Rajesh N. Gacche & Bhaskar S. Dawane (2022): DTP/SiO$_2$ Assisted Synthesis of New Benzimidazole-Thiazole Conjugates Targeting Antitubercular and Antioxidant Activities, Polycyclic Aromatic Compounds, DOI: 10.1080/10406638.2022.2056210

To link to this article: https://doi.org/10.1080/10406638.2022.2056210

POLYCYCLIC AROMATIC COMPOUNDS
https://doi.org/10.1080/10406638.2022.2056210

Taylor & Francis
Taylor & Francis Group

DTP/SiO_2 Assisted Synthesis of New Benzimidazole-Thiazole Conjugates Targeting Antitubercular and Antioxidant Activities

Madhav J. Hebade[a], Sambhaji T. Dhumal[b], Sonali S. Kamble[c], Tejshri R. Deshmukh[d], Vijay M. Khedkar[e], Shrikant V. Hese[f], Rajesh N. Gacche[g], and Bhaskar S. Dawane[h]

[a]Department of Chemistry, Badrinarayan Barwale Mahavidyalaya, Jalna, Maharashtra, India; [b]Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad, Maharashtra, India; [c]Department of Biochemistry, Gramin Science (Vocational) College, Nanded, Maharashtra, India; [d]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India; [e]Department of Pharmaceutical Chemistry, School of Pharmacy, Vishwakarma University, Pune, Maharashtra, India; [f]Department of Chemistry, D. D. Bhoyar College of Arts and Science Mouda, Nagpur, India; [g]Department of Biotechnology, Savitribai Phule Pune University, Pune, Maharashtra, India; [h]School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, India

ABSTRACT

A series of new substituted benzimidazole-thiazoles (**9a–l**) have been designed and synthesized using 2-aminothiazole as a starting material by using molecular hybridization approach. The newly synthesized compounds were characterized by ^1H NMR, ^{13}C NMR and HRMS analyses. The compounds (**9a–l**) were evaluated for their *in vitro* antitubercular activity against *Mtb* (MTCC 300) strain. Among the screened compounds **9a**, **9b**, **9c** and **9d** have displayed promising antitubercular activity with MIC 7.55, 4.60, 15.39 and 28.38 μg/mL, respectively. All the compounds were further evaluated for their DPPH radical scavenging activity. The compounds **9a**, **9b** and **9d** were exhibited excellent radical scavenging activity. In addition to this, single crystal structure of compound **9a** was also studied. Furthermore, the high potency of these molecules was supported by ADME properties prediction as well as molecular docking study to gain an insight into the binding mode and affinity toward mycobacterial InhA.

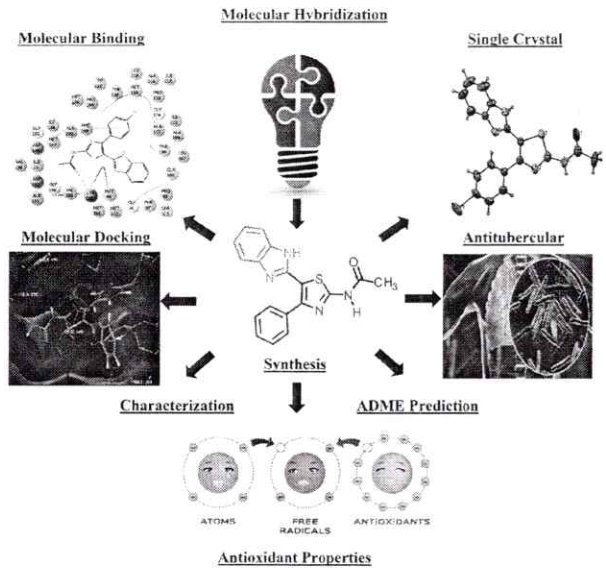
ARTICLE HISTORY
Received 29 November 2021
Accepted 14 March 2022

KEYWORDS
Dodecaphosphotungestic acid; benzimidazole-thiazole conjugates; single crystal structure; antitubercular activity; antioxidant activity; molecular docking study

---

CONTACT Madhav J. Hebade mjhebade@gmail.com Department of Chemistry, Badrinarayan Barwale Mahavidyalaya, Jalna, MS 431213, India.

Supplemental data for this article can be accesse online at http://dx.doi.org/10.1080/10406638.2022.2056210



Introduction

Tuberculosis (TB) is triggered by pathogen *Mycobacterium tuberculosis* (*Mtb*). It is awfully contagious disease accountable for high fatalities worldwide, along with the spread of HIV infection causing unsmiling threat to mankind. As per the World Health Organization (WHO) report in 2018, tuberculosis still remains one of the most intimidating health problems that estimated 10 million people fell ill with TB worldwide.[1] The prevailing first line and second line multicomponent mode of treatments for tuberculosis are practiced but now they are facing solemn threats. The offered mentioned existing pattern requires longer period for treatment. Therefore, the pathogenic strains responsible for tuberculosis are found to be acquiring noncompliance to the drugs[2] as well as new forms of tuberculosis like multidrug resistant tuberculosis (MDR TB) and extensively drug resistant tuberculosis (XDR TB) becoming a challenge for medicinal chemists.[3] Along with this, the population of patients having HIV and TB as co-infections is increasing. Considering the solemnity of above threats now more attention is found to be paid on the search of appropriate drugs for treating both the diseases simultaneously and efficiently.[4] Thus, chemists are paying more attention to synthesize new chemical entities with hope to obtain better antitubercular activity with less toxicity and treatment duration.[5]

The oxidative provocation is the prime source of tissue inflammation in tuberculosis. During the tuberculosis infection, the poor nutritional consumption of micronutrients, the free radicals are disrupted from activated macrophages and antituberculosis drugs. If these free radicals were not neutralized by the antioxidants then it can leads toward the pulmonary inflammation.[6] These antioxidants utilize their effects by hunting or avoiding the production of reactive oxygen species (ROS)[7] that helps to shield the growth of free radicals and reduce the growth of pulmonary inflammation.

In search of potent antitubercular agents, various new nitrogen and sulfur containing bioactive heterocyclic scaffolds such as thiazoles and benzimidazoles have been synthesized. Among them, thiazole and its derivatives are gaining immense importance in medicinal chemistry due to their therapeutic activities like antitubercular,[8] anticancer,[9] antibacterial,[10] anti-inflammatory,[11]

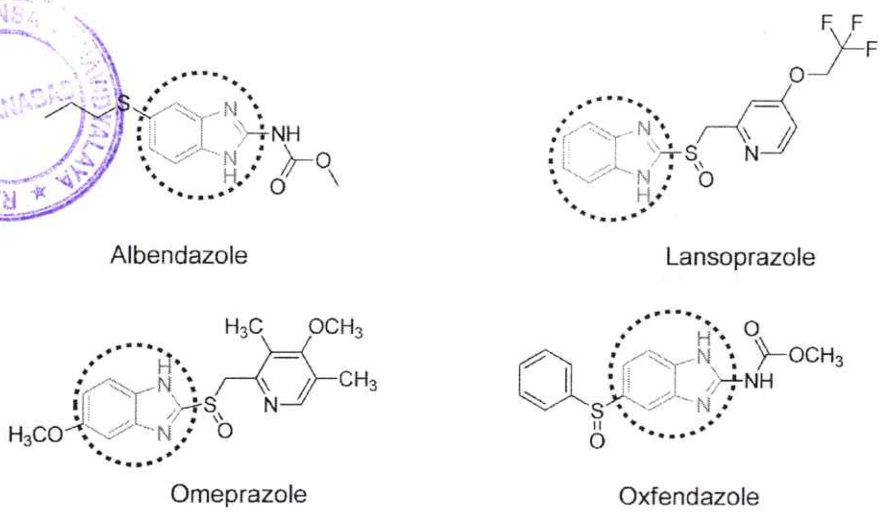
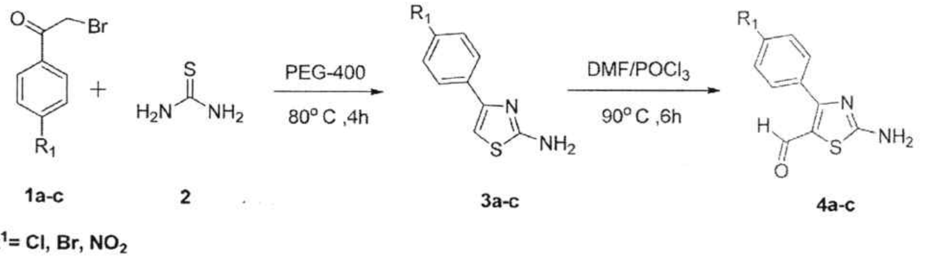


Figure 1. Some bioactive molecules containing benzimidazole-thiazole conjugates.



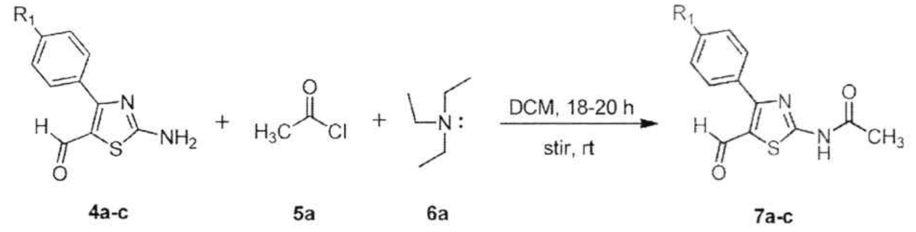
Scheme 1. Synthesis of 2-Amino-4-(substitutedphenyl)thiazole-5-carbaldehydes (4a–c).

antioxidant[12] and antifungal.[13] Thiazole moiety is an important pharmacophore in many medicaments used against several tropical infectious diseases. Thiazole ring is the key constituent of nizatidine, thiamin, penicillin, fanetizole, meloxicam and ritonavir.[14]

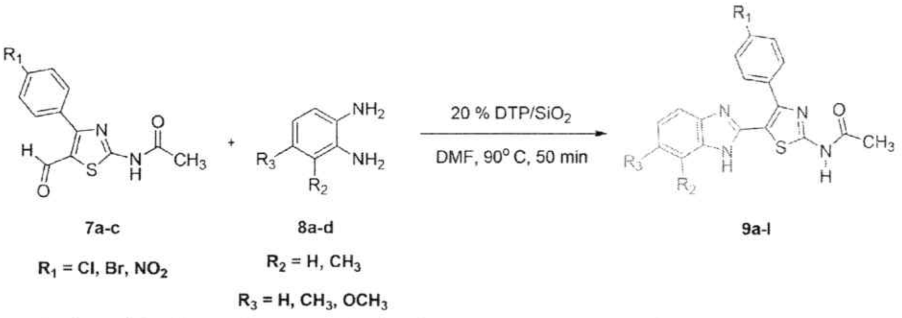
Benzimidazole and its derivatives are paying much relevance due their heroic importance in the field of medicinal chemistry research and their foremost biological applications.[15] The structural resemblance of benzimidazoles with some naturally occurring moieties such as purines helps to it bind with enzymes or receptors of living entities easily.[16] Many ratified drugs contain a benzimidazole skeleton, for example, albendazole, lansoprazole, omeprazole and oxfendazole (Figure 1).

Literature survey also reveals that benzimidazole and its derivatives are acts as versatile scaffold, which is observed in various pharmaceutical agents and displays broad spectrum of biological activities such as antiviral,[17] antifungal,[18] antitumor,[19] antihypertensive,[20] anti-inflammatory[21] and antimicrobial.[22]

Motivated from our previous work[23–30] and considering aforementioned therapeutic potential of thiazoles and imidazole here, we deliberate to synthesize some new benzimidazole entities, which having biodynamic cores within one molecular architectural frame with anticipation to get the new leads with enhanced antitubercular activity. Considering above facts in mind and urgency to treat various tubercular infections herein, we have planned to synthesize new *N*-(5-(1*H*-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamides



Scheme 2. Synthesis of 4-(-4-Substitutedphenyl-)-5-formylthiazol-2-yl)actamides (**7a–c**).



Scheme 3. Synthesis of (5-Substituted-benzo[d]imidazol-2-yl)-4-(4-substitutedphenyl)thiazol-2-yl)acetamides (**9a–l**).

(**9a–l**) by using multistep synthetic route and evaluated them for their *in vitro* antitubercular as well as antioxidant properties.

Results and discussion

Chemistry

As we have planned and synthesized new analogues in which thiazole motif is amalgamated to the benzimidazole system. The synthetic strategies adopted for the synthesis of target *N*-(5-(1H-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamides (**9a–l**) by succeeding multistep approach, starting from 4-(4-bromophenyl)thiazol-2-amines (**3a–c**). The synthesis of 2-aminothiazole-5-carbaldehydes (**4a–c**, Scheme 1), were carried *via* the Vilsmeier-Haack formylation reaction by following previously reported procedure. 2-Amino thiazole-5-carbaldehydes (**4a–c**) were acylated with acetyl chloride to obtain the key intermediates, *N*-(4-(4-bromophenyl)-5-formylthiazol-2-yl)acetamides (**7a–c**, Scheme 2). Finally, the cyclocondensation of *N*-(4-(4-bromophenyl)-5-formylthiazol-2-yl)acetamides (**7a–c**) with substituted orthophenylenediamines (**8a-d**) was carried in presence of DTP/SiO_2 in dimethyl formamide as a solvent at 90 °C for 50 min. to obtain the titled compounds, *N*-(5-(1*H*-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamides (**9a–l**, Scheme 3) with better to excellent yields.

All the newly synthesized compounds have been thoroughly characterized using ^1H NMR, ^{13}C NMR and HRMS spectral analysis. The ^1H NMR spectrum of compound **9a** display peaks, as a singlet at δ 2.21 ppm, due to the -CH_3 and multiplet in the region at δ 7.20- δ 7.59 ppm for eight aromatic protons, respectively. The two-sharp singlets are assigned at δ 12.42 and δ 12.56 ppm correspondence to the amido-H and imidazolyl-H, respectively. Characteristics carbon signals are observed at δ 22.84, δ 158.20 and δ 169.59 ppm in ^{13}C NMR spectrum of **9a** owing to the signals of carbons of CH_3, $C=N$ and $C=O$ of the imidazolyl ring carbons, respectively, confirming the

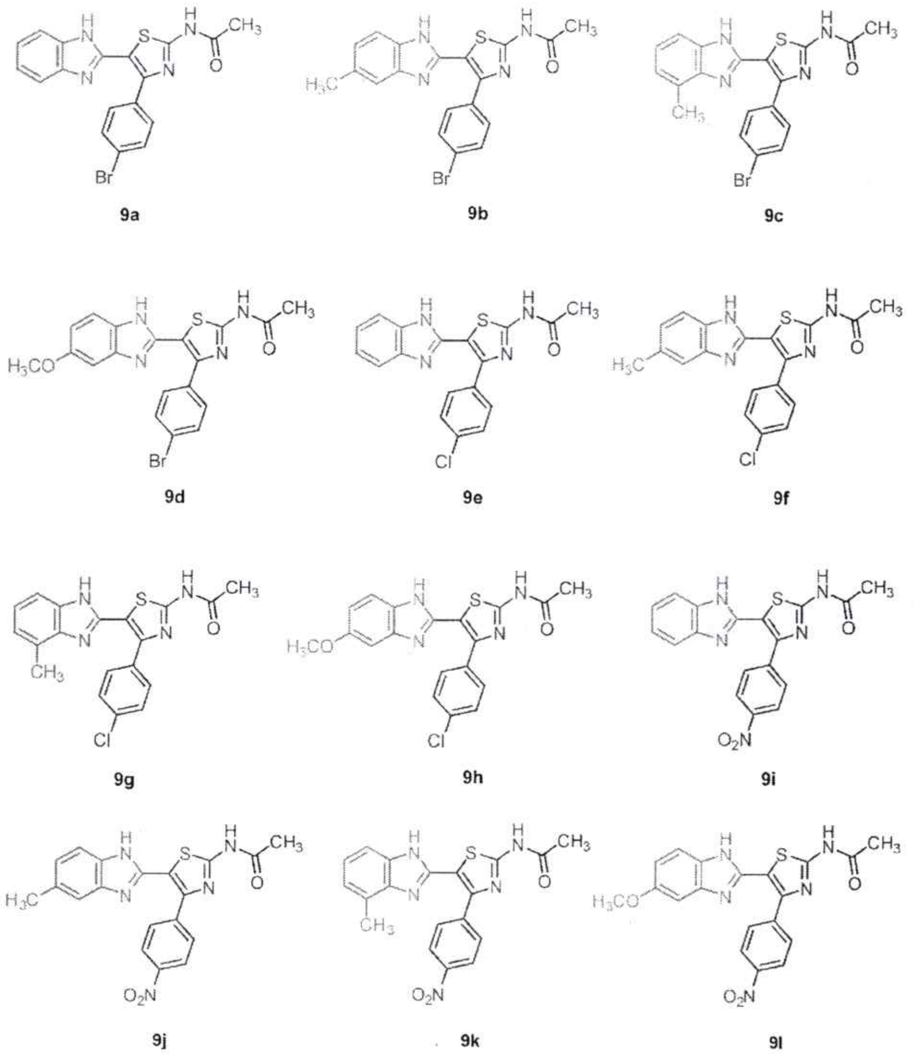


Figure 2. Structures of all the newly synthesized compounds (**9a–l**).

Table 1. Screening of the solvent for synthesis of compound **9a**.[a]

Entries	Solvent	Time (Min)	Yields %
1	DMF	50	94
2	PEG-400	120	49
3	MeOH	90	45
4	DMSO	75	78
5	1,4-Dioxane	65	87
6	CHCl3	90	65
7	EtOH	110	48
8	THF	80	72
9	Toluene	90	80
10	CH3CN	85	82
11	DCM	110	76

[a] **Reaction conditions:** Aldehyde (**7a**) (0.001 mol), *o*-phenylenediamine (**8a**) (0.001 mol), DTP/SiO$_2$ (20 mol%), solvent (10 mL), at 80 °C, [b] Isolated yields.

Table 2. Optimization of amount of DTP/SiO_2 as a catalyst required for the cyclocondensation.[a]

Entry	Catalyst concentration	Compound (yield%[b])
1	10% DTP/SiO_2	75
2	15% DTP/SiO_2	85
3	20% DTP/SiO_2	94
4	25% DTP/SiO_2	94
5	30% DTP/SiO_2	94
6	35% DTP/SiO_2	93
7	40% DTP/SiO_2	93

[a]**Reaction conditions:** Aldehyde **(7a)** (0.001 mol), *o*-phenylenediamine **(8a)** (0.001 mol), DTP/SiO_2 solvent DMF (10 mL), at 80 °C,
[b]Isolated yields.

Table 3. The recyclability of DTP/SiO_2 catalyst.

Entry	Run	(Yields %[b])
1	Fresh	94
2	Run-1	94
3	Run-2	94
4	Run-3	94
5	Run-4	93
6	Run-5	92

[a]**Reaction conditions:** Aldehyde **(7a)** (0.001 mol), *o*-phenylenediamine **(8a)** (0.001 mol), DTP/SiO_2 solvent DMF (10 mL), at 80 °C,
[b]Isolated yields.

formation of an imidazolyl ring in **9a**. The HRMS spectrum further strengthen the structure assigned to **9a** as *N*-(5-(1*H*-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamideas it displays $[M+H]^+$ ion peak at m/z 413.0052 for the molecular formula $C_{18}H_{13}N_4OS$. The structure of the compound **9a** also confirmed by single crystal structure. The structures of all the newly synthesized compounds **(9a–l)** are summarized in Figure 2, whereas, the experimental procedures and spectral details are given in supporting information.

Considering the potential of benzimidazole and its derivatives in medicinal and pharmaceutical chemistry various protocols have been reported for the synthesis of benzimidazoles such as the reaction of orthophenylene diamine with acids, acid anhydride, acid chloride, ester, aldehyde, ketone, amide, and nitrile using the catalysts like Zn (OTF_2),[31] CAN,[32] $Na_3AlF_{6,}$[33] BF_3-etharate,[34] $K_4[Fe(CN)_6]$,[35] $NaHSO_{3,}$[36] $In(OTF)_{3,37}$ Au-$CeO_{2,}$[38] $ZnCl_2$-$SiO_{2,}$[39] $LaCl_{3,}$[40] Montmorillonite K-10,[41] Amberlite IR-120,[42] SDS Micelles,[43] CuI/L-Proline,[44] AcOH/$O_{2,}$[45] TMSCl,[46] Dowex 50-W,[47] $Cu(NO_3).3H_2O$,[48] $SbCl_3/Al_2O_{3,}$[49] NH_4OAc,[50] $Na_2S_2O_5$,[51] silica boron sulfonic acid (SBSA).[52] Some of these methods suffer from one or more disadvantages such as environmental damage, the use of strong acids, high temperatures, and use of toxic metal catalysts and hazardous reagents that is in conflict with green chemistry. Therefore, a research for novel reagent and the development of new protocol are still of practical importance in synthetic chemistry. Keeping the above observations in mind and motivated from our previous work here, first time DTP/SiO_2 backed strategy for the cyclocondensation of *o*-phenylenediamines with new aldehydes have been reported for obtaining high yields of benzimidazole scaffolds **(9a–l)**.

In the present work, freshly prepared aldehydes **(7a–c)** have been cyclocondensed with *o*-phenylenediamine using DTP/SiO_2 as reusable catalyst. Attempts were made to accomplish precise reaction conditions for the cyclocondensation. In search of specific reaction conditions, the model reaction has been carried out by varying amount of DTP/SiO_2 catalyst and solvents. Firstly, we accomplished cyclocondensation of a newly synthesized aldehyde **(7a)** with *o*-phenylenediamine **(8a)** as a model reaction in the presence of DTP/SiO_2 to obtain **9a**. This model reaction was performed under identical condition in different solvents. The screening results of the model reaction run in different solvents at 80 °C in the presence of DTP/SiO_2 are noted in Table 1, entry 1–11. Among the screened solvents, DMF was found to be the utmost solvent to afford product **9a**.

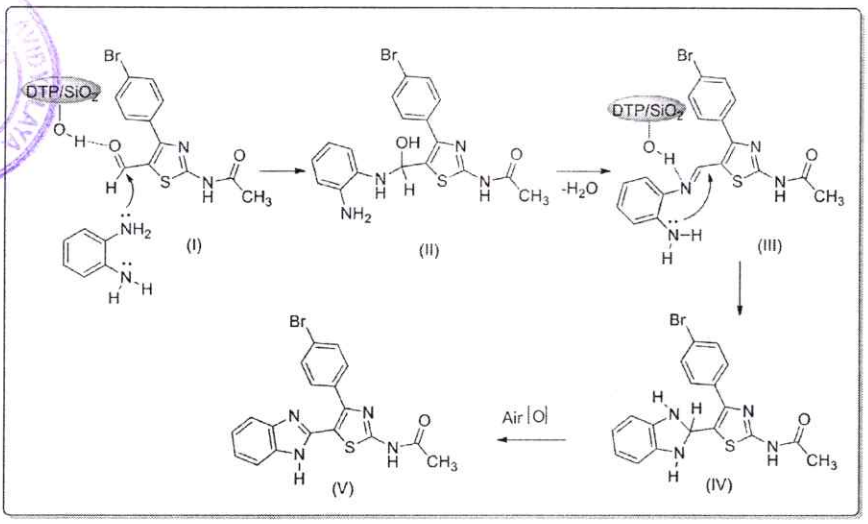


Figure 3. Plausible mechanism for the synthesis of (5-substituted-benzo[d]imidazol-2-yl)-4-(4-substitutedphenyl)thiazol-2-yl)acetamide.

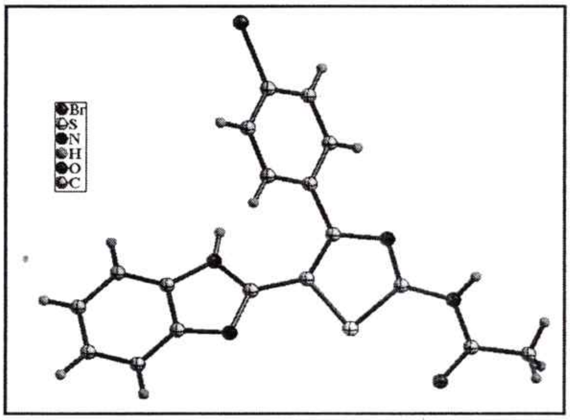


Figure 4. Molecular structure of *N*-(5-(1*H*-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl) acetamides (**9a**).

To optimize the amount of DTP/SiO$_2$ catalyst, required to carry the model cycloacondensation, we attempted the cyclocondensation in DMF by varying amounts of DTP/SiO$_2$ from 10 mole % to 40 mole % using aldehyde **(7a)** (0.001 mol) and *o*-phenylenediamine (**8a**) (0.001 mol). It was observed that high yield of 5-(1*H*-benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamide (**9a**) was obtained, when the model reaction was performed in the presence of 20 mole% catalyst using 0.001 mol initial concentration of each of the reactant (Table 2, entry 3). The cyclocondensation was found to be completed within 50 min. and 94% yield of imidazole was obtained (**9a**). Therefore, 20 mole% of DTP/SiO$_2$ catalyst was selected as the optimal quantity for the reaction. To investigate the role of the DTP/SiO$_2$ the cyclocondensation was performed under identical conditions in the absence of DTP/SiO$_2$ and observed that reaction did not proceed even when constantly heated for more than 20 h. This observation clearly shows that DTP/SiO$_2$ has played key role in accelerating the rate of reaction.

Table 4. Selected hydrogen bonding geometry (A°) for compound **9a**.

D–H···A	D···H	H···A	D···A	D-H···A	Symmetry code
N4–H4N···N7	0.8600	1.9900	2.814(4)	161.00	2-x,-1/2 + y,1/2-z 1 + x,y,z
N5–H5N···O4	0.8600	1.9900	2.835(5)	166.00	———————
N8–H8N···N3	0.8600	2.1200	2.896(4)	151.00	
N11–H11N···N15	0.8600	1.9800	2.808(5)	160.00	1-x,1/2 + y,1/2-z −1 + x,y,z
N13–H13N···O1	0.8600	2.0400	2.877(5)	165.00	–
N16–H16N···N12	0.8600	2.1200	2.947(4)	160.00	

Table 5. Crystal data and structure refinement parameters for compound **9a**.

Crystal Parameters	Data
Empirical formula	$C_{72}H_{52}N_{16}O_4S_4Br_4$
Formula mass	1653.17
CCDC number	2025483
Crystal system	Monoclinic
Space group	*P2₁/c* (No.14)
a /Å	21.545 (5)
b /Å	15.461 (5)
c /Å	23.909 (5)
α (°)	90
β (°)	97.887 (5)
γ(°)	90
V(Å^3)	7981 (4)
Crystal Size (mm)	0.24 × 0.28 × 0.36
Z	4
ρ(g cm^{-3})	1.370
μ(mm^{-1})	2.177
F(000)	3328
T(K)	298
λ(Mo Kα)(Å)	0.71073
Θmin(°)	2.3
Θmax(°)	28.4
Total data	165517
Unique data	19951
Rint	0.086
Data[I > 2σ(I)]	9538
^{a}R1	0.0712
^{b}wR2	0.1901
S	1.03

$^{a}R1 = \sum = Fo = - = Fc = /\sum = Fo =, \ ^{b}wR_2 = [\ \sum w(Fo_2\text{-}Fc_2)2/\sum w(Fo_2)_2]1/2$

In accordance with the environmental concern as well as need of green and sustainable development of heterogeneous recyclable catalyst, we have established efficiency of the DTP/SiO$_2$ catalyst in cyclocondensation reactions. Here, we have investigated the recyclability and reusability of catalyst for the synthesis of imidazoles (**9a–l**) from aldehyde (**7a**) and *o*-phenylenediamine (**8a**) under standard reaction condition. The results are shown in Table 3. The DTP/SiO$_2$ catalyst can be used to next run without loss of significant activity. This cyclocondensation proceeded very smoothly and afforded the desired products (**9a–l**) with excellent yield. (Table 3, entries 2–6).

The plausible mechanism for synthesis of (5-Substituted-benzo[d]imidazol-2-yl)-4-(4-substitutedphenyl)thiazol-2-yl)acetamide is shown in Figure 3.

In this present study, the single crystal structure of compound **9a** was also determined to support the structural confirmation (Figure 4).

Compound **9a** crystallizes in *Monoclinic* crystal system with centrosymmetric ***P2₁/c*** space group. The experimental details on X-ray crystallography in supplementary file. The single crystal X-ray diffraction reveals that the entire molecule is non-planar with a bromo-benzene in anti-planar arrangement. The assymetric unit consist of four molecular units of compound **9a** which are

Table 6. Antitubercular and antioxidant activities of benzimidazole-thiazole conjugates (**9a–l**).

Sr. No.	Comp. Code	Anti-TB activity MIC (μg/mL)	Antioxidant activity DPPH (%)	OH (%)	SOR (%)	Glide Score	Glide energy (Kcal/mol)
1	**9a**	7.55	75.25	65.32	69.91	−8.428	−47.124
2	**9b**	4.60	80.28	72.28	70.39	−8.734	−48.938
3	**9c**	15.39	68.63	72.95	65.65	−8.111	−42.559
4	**9d**	28.35	80.36	76.57	73.92	−8.015	−40.362
5	**9e**	59.65	70.24	65.37	71.68	−7.841	−37.707
6	**9f**	72.36	72.21	70.61	60.89	−7.444	−35.509
7	**9g**	104.32	69.37	72.36	60.24	−7.434	−34.078
8	**9h**	129.25	73.58	65.02	72.10	−7.202	−31.144
9	**9i**	150.28	69.28	50.66	48.37	−7.019	−28.803
10	**9j**	175.69	63.24	67.78	61.29	−6.965	−26.647
11	**9k**	188.32	60.38	68.20	62.24	−6.805	−25.948
12	**9l**	205.50	62.30	66.25	68.8	−6.794	−24.286
Ascorbic Acid		NA	85.42	84.12	75.38	NA	NA
INH		62.5	NA	NA	NA	NA	NA
RIF		0.97	NA	NA	NA	NA	NA

stabilized by inter and intra-molecular hydrogen bonding as shown in Table 4. The crystal parameters of compound **9a** are summarized in Table 5.

Biological screening

In vitro antitubercular activity

After the synthesis and characterization, all the newly synthesized imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamide hybrids (**9a–l**) were evaluated for their *in vitro* antitubercular activity against *Mycobacterium tuberculosis* (MTCC 300) strain, by using Microplate Alamar Blue assay in terms of minimum inhibitory concentration (MIC) values. The MIC values in μg/mL of compounds (**9a–l**) along with the standard drugs like Isoniazid and Rifampicin are presented in Table 6. The activity results in terms of MIC are found in the range of 4.60–205.50 μg/mL. Results proves that among the twelve compounds, four compounds **9a** (MIC-7.55), **9b** (MIC-4.60), **9c** (MIC-15.39) and **9d** (MIC-28.35) μg/mL were found to possess potent antitubercular activity compared with standard drugs, Isoniazid and Rifampicin. Other compounds, **9e** (MIC-59.65) and **9f** (MIC-72.36) have shown moderate antitubercular activity, whereas the remaining compounds **9 g**, **9 h**, **9i**, **9j**, **9k** and **9 l** have displayed average activity against *Mtb*.

Antioxidant activity

The new synthesized molecular scaffolds (**9a–l**) were also evaluated for their antioxidant activity. DPPH radical scavenging activity[53] is the mostly used technique for screening antioxidant activities of the generous biotic as well as synthetic antioxidants. In DPPH assay the compound **9a** with $\mathbf{R_1}$ bromo and $\mathbf{R_2}$, $\mathbf{R_3}$, and $\mathbf{R_4}$ are hydrogen group (75.25%), **9b** (80.28%), and **9d** (80.36%) with $\mathbf{R_1}$ is bromo and $\mathbf{R_3}$, $\mathbf{R_4}$ are methyl group and the compounds **9e** (70.24%), **4f** (72.21%) and **9 h** (73.58%) in which $\mathbf{R_1}$ is chloro, $\mathbf{R_2}$ is hydrogen and $\mathbf{R_3}$, $\mathbf{R_4}$ is methyl groups exhibits the excellent radical scavenging activity when it compared with the Ascorbic acid as a standard. Whereas the remaining compounds displayed the moderate radical scavenging activity. The results are shown in Table 6.

The overall range of DPPH radical activity was found to be (80.36–60.38%). The OH radicals are utmost frenzied reactive between the interactive oxygen species and that spatter each type of molecule obtained in living system. Physiologically momentous biomolecules such as sugar,

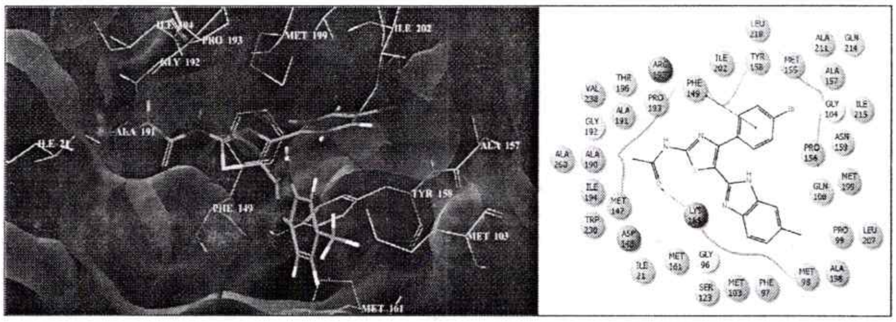


Figure 5. Binding mode of **9b** into the active site of mycobacterial enoyl ACP reductase (InhA).

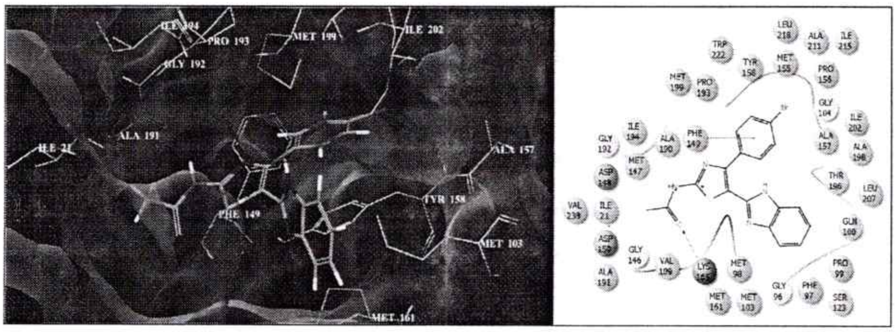


Figure 6. Binding mode of **9a** into the active site of mycobacterial enoyl ACP reductase (InhA).

amino acids, phospholipids, DNA bases, organic acids may undertake reaction with OH radicals and may amend normal physiological function of cells.[54] Among these synthesized compounds, the cautious OH radical scavenging activities was shown by compounds **9b** (72.28%), **9c** (72.95%), **9d** (76.57%), **9f** (70.61%) and **9 g** (72.36%). Whereas, the rest of compounds shows average scavenging in the range of 68.20–50.66%. Summary of SOR scavenging activities stipulates the compound **9b** (70.39%), **9d** (73.92%), **9e** (71.68%) and **9 h** (72.10%) demonstrated moderate SOR scavenging activity as compared to the standard used ascorbic acid (75.38%), while other compounds showed monotonous SOR scavenging activity (69.91–48.37%).

Computational study

Molecular docking

Molecular docking has become an important common component of the drug discovery process to model the interaction between a small molecule and a target protein at the atomic level, which allows to understand the behavior of small molecules in the active site of target protein as well as to elucidate fundamental biochemical processes. Thus, with an objective to rationalize the antitubercular activity demonstrated by the benzimidazole-thiazole conjugates (**9a–l**), molecular docking study was performed against mycobacterial target enoyl ACP-reductase (InhA) (pdb code: 4TZK) using the standard protocol implemented in the GLIDE (Grid-Based Ligand Docking with Energetics) module of the Schrödinger molecular modeling software.[55]

InhA or enoyl acyl carrier protein reductase of *Mycobacterium tuberculosis* (mtInhA) is one of the key enzymes involved in the type II fatty acid biosynthesis pathway of *Mtb*. Inhibition of

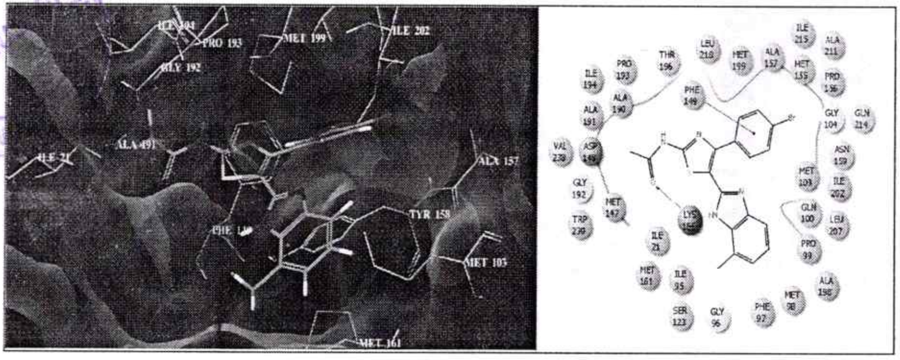


Figure 7. Binding mode of **9c** into the active site of mycobacterial enoyl ACP reductase (InhA).

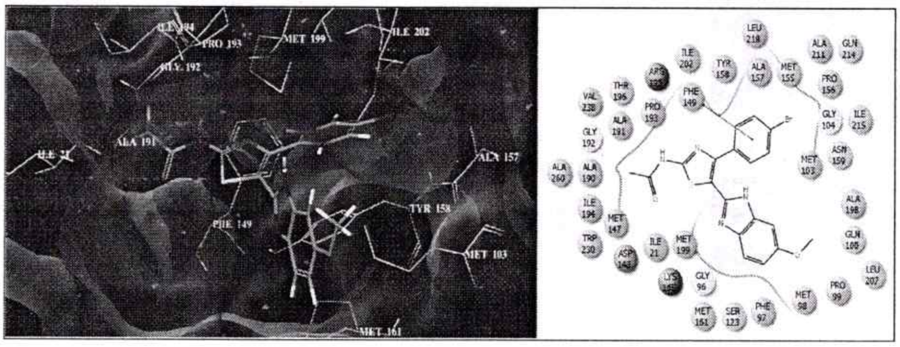


Figure 8. Binding mode of **9d** into the active site of mycobacterial enoyl ACP reductase (InhA).

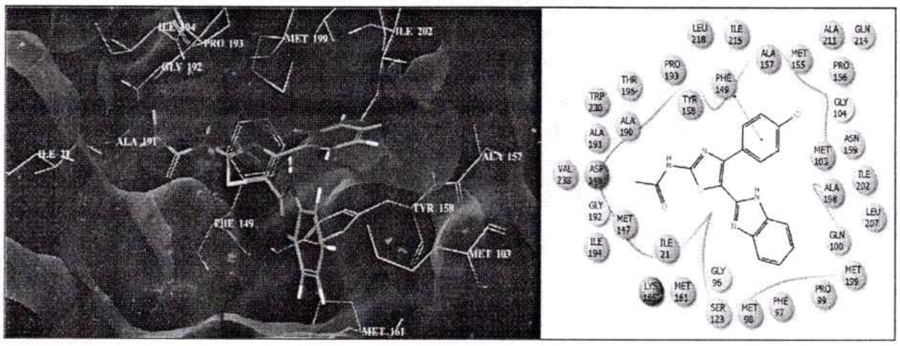


Figure 9. Binding mode of **9e** into the active site of mycobacterial enoyl ACP reductase (InhA).

InhA would disrupt the integrity of mycobacterial cell wall by inhibiting the biosynthesis of mycolic acids, a long chain fatty acids containing component of the cell envelope, which qualifies InhA as an attractive target in antitubercular drug discovery.[56] Molecular docking study showed that benzimidazole-thiazole conjugates (**9a–l**) could well fit into the active site of InhA through a close network of bonded and non-bonded interactions. Their binding affinity was found to be in agreement with their observed antitubercular activity wherein the most active molecules (**9a, 9b, 9c** and **9d**) showed relatively higher affinity over the rest of the molecules in the series wherein the affinity declined with the decrease in potency (Figure 5–9). At the right side of all docking

Table 7. Pharmacokinetic parameters for *in silico* ADME prediction.

Entry	% ABS[a]	TPSA[b] (A2)	n-ROTB[c]	MV[d]	MW[e]	miLog[f]	n-ON[g]	n-OH NH[h]	Lipinski violations[i]	Drug likeness model score
Rule	–	–	–	–	<500	≤ 5	<10	<5	≤ 1	–
9a	84.62	70.67	3	304.07	413.30	4.42	5	2	0	0.05
9b	84.62	70.67	3	320.63	427.33	4.85	5	2	0	0.44
9c	84.62	70.67	3	320.63	427.33	4.82	5	2	0	0.18
9d	81.43	79.91	4	329.62	443.33	4.46	6	2	0	0.32
9e	84.62	70.67	3	299.72	368.85	4.29	5	2	0	−0.13
9f	84.62	70.67	3	316.28	382.88	4.72	5	2	0	−0.16
9g	84.62	70.67	3	316.28	382.88	4.69	5	2	0	0.17
9h	81.43	79.91	4	325.26	398.88	4.33	6	2	0	0.50
9i	68.81	116.50	4	309.52	379.40	3.57	8	2	0	0.13
9j	68.81	116.50	4	326.08	393.43	4.00	8	2	0	0.81
9k	68.81	116.50	4	326.08	393.43	3.97	8	2	0	−0.44
9l	65.62	125.73	5	335.06	409.43	3.61	9	2	0	−0.49

[a]Percentage Absorption; [b]Topographical polar surface area; [c]Number of rotatable bonds; [d]Molecular volume; [e]Molecular Weight; [f]Lipophilicity; [g]No. of hydrogen bond acceptors; [h]No. of hydrogen bond acceptors; [i]Number of violations.

figures, the presence of green and pink lines indicates π-π stacking and hydrogen bonding interactions, respectively.

In order to gain a detailed insight into the binding affinity, a per-residue interaction analysis was carried out to identify the most significantly interacting residues of the active site and the type of thermodynamic interaction governing the binding affinity. This is elaborated in the next section for the most active analogue **9b**. The best docked conformation of **9b** (Figure 5) could show that the molecule binds to the active site of InhA with a significantly higher binding affinity (Glide score: −8.734, Glide energy: −48.938 kcal/mole) at co-ordinates close to the co-crystallized ligand. The enhanced binding affinity of **9b** is attributed to a network of significant van der Waals interactions observed with the 4-(4-Bromophenyl)-thiazolyl acetamide component of the molecule through Met147(-1.979 kcal/mol), Phe149(-4.383 kcal/mol), Met155(-1.916 kcal/mol), Ala157(-1.244 kcal/mol), Tyr158(-6.649 kcal/mol), Lys165(-1.274 kcal/mol), Ala191(-1.319 kcal/mol), Pro193(-1.81 kcal/mol), Ile194(-2.323 kcal/mol), Ile202(-1.614 kcal/mol), Ile215(-2.54 kcal/mol) and Leu218(-1.266 kcal/mol) residues lining the active site. These interactions were well balanced by van der Waals interactions observed through 6-methyl-1H-benzo[d]imidazol-2-yl section of **9b** through Ile21(-1.227 kcal/mol), Ile95(-1.281 kcal/mol), Gly96(-2.902 kcal/mol), Phe97(-2.176 kcal/mol), Met98(-2.111 kcal/mol), Met103(-4.159 kcal/mol), Asp148(-1.683 kcal/mol), Met161(-2.657 kcal/mol) and Met199(-4.449 kcal/mol) residues.

Furthermore, the compound **9b** also exhibited significant favorable electrostatic interactions with through Lys118 (-1.254 kcal/mol), Asp150 (-1.257 kcal/mol), Lys165(-3.855 kcal/mol), Gly192(-1.151 kcal/mol), Met199(-1.72 kcal/mol), Glu219(-1.464 kcal/mol), Asp234(-1.006 kcal/mol) and Asp261(-1.761 kcal/mol) residues. Along with these non-bonded interactions, compound **9b** was also seen to be engaged in a close hydrogen bonding interaction through Lys165 (2.109 Å) with the acetamide group while the Phe149(2.574 Å) residue exhibited a pi-pi (π-π) stacking interaction with the phenyl group. These types of interactions serve as "anchor" to orient the ligand into the 3D space of active site and further facilitate the steric and electrostatic interactions. Thus, the per-residue interaction analysis suggest that benzimidazole-thiazole conjugates possess the pharmacophore essential to exhibit promising binding affinity toward the Mycobacterial InhA qualifying them as leads for structure-based lead optimizations.

ADME properties prediction

In support to the biological assay, we have carried out computational studies for all the newly synthesized compounds (**9a–l**). Computational study plays key role in drug designing. This includes oral bioavailability, ADME property prediction, Lipinski violations and drug likeness property. This study was carried out by determining various pharmacokinetic parameter such as percentage of absorption (% ABS), topological polar surface area (TPSA), number of rotatable bonds (n-ROTB), molecular volume (MV), molecular weight (MW), logarithm of partition coefficient (mi LogP) and number of hydrogen bond acceptors (n-ON) as shown in Table 7.

To predict the oral bioavailability of any drug, we have to calculate percentage of absorption (% ABS). It is calculated by using the formula % ABS = 109-(0.345 × TPSA).[57] ADME stands for Absorption, Distribution, Metabolism and Excretion. Prediction of ADME properties followed by calculation of Lipinski violations. All orally active drugs must obeys the Lipinski's rule of five.[58] After this, we have calculated the drug likeness model score, which is used to know drug like properties of any compound. All the results of computational studies were determined by using Molinspiration online property calculation toolkit[59] and MolSoft software.[60] The obtained results were also summarized in Table 7.

According to obtained results, most of the property profiles were found within the acceptable range. The % ABS for all the compounds were ranging from 65.62 to 84.62%, which is supposed to be good absorption. There are zero Lipinski violations for all the compounds, it means that all compound obeys. Lipinski's rule of five. Most of the compounds displayed positive drug likeness score that signs drug like properties of the compounds.

Experimental methods

Chemistry

All the chemicals used were purchased from Alfa Aesar and Spectrochem and used without further purification. Melting points of all the synthesized compounds were recorded in an open capillary tube and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu FT-IR spectrometer ATR technique. ^{1}H NMR spectra were recorded on a Bruker DRX-400 MHz NMR spectrometer, and the ^{13}C NMR spectra were recorded on a Bruker DRX-100 MHz NMR in DMSO-d_6 using tetramethylsilane (TMS) as an internal standard, and the chemical shifts recorded in δ ppm. High-resolution mass spectra (HRMS) were recorded on an Agilent 6520 (QTOF) ESI-HRMS instrument and LC-MS spectrometer. The purity of each of the compounds was checked by thin layer chromatography (TLC) using silica gel (60F254), and visualization was accomplished by iodine/ultraviolet light.

General procedure for the preparation of 2-Amino-4-(4-bromophenyl/chlorophenyl/nitrophenyl) thiazole-5-carbaldehyde (4a–c)

The Vilsmeire-Haack reagent was prepared by adding phosphorus oxychloride (3 mL) to dimethyl formamide (20 mL) at 0 °C with stirring. Then, compound 4-(4-Bromophenyl) thiazol-2-amine (0.01 mol) was added to the reagent and stirred at 0 °C for 30 min. The mixture was further stirred at room temperature for 2 h and then at 60 °C for an additional 2 h. The reaction mixture was then poured onto sodium carbonate solution and stirred at 90 °C for 2 h. After cooling, the mixture was diluted with water and extracted with ethyl acetate and dried over anhydrous sodium sulfate and the residue obtained after removal of the solvent was crystallized from ethanol. Similar procedure was adopted for the synthesis of compound **4b** and **4c**.

General method of synthesis of amides (7a–c)

A mixture of 4-(4-Bromo/chlorophenyl)-thiazol-2-amine (0.0020 mol) and 1.2 molar equivalent of triethylamine (TEA) dissolved in dichloromethane and stirred at 5 °C for 15 min. To this reaction mixture acetyl chloride (0.0020 mol) were added dropwise by using pressure equalizing dropping funnel. The resultant reaction mass was stirred at room temperature for 18–20 h. After complete conversion, the solvent was removed in vacuum, poured on crushed ice and neutralized with saturated $NaHCO_3$ solution. The precipitated solids were recrystallized from ethanol.

General procedure for the preparation of DTP/SiO_2

DTP impregnate SiO_2 (20% DTP/SiO_2) catalyst was prepared by an incipient wetness technique[28] as follows; 2 g of dry dodecatungstophosphoric acid (DTP) was weighed accurately. This was then dissolved in 10 mL of methanol. The solution was added in small portion of 1 mL each time to the silica with constant stirring with a glass rod properly. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, silica was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 20 min resulted in a free-flowing powder. The performed catalyst was dried at 120 °C for removal of water and other volatiles and subsequently calcined at 285 °C for 3 h.

General method of synthesis of 5-(1H-Benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamide (9a–l)

A mixture of (4-(4-bromophenyl)-5-formylthiazol-2-yl)acetamide (**7a–c**) (0.001 mole), substituted orthophenylenediamine (0.001 mole) and DTP/SiO_2 (20 mol %) in DMF were charged in a 100 mL round-bottom flask equipped with a mechanical stirrer and a condenser. The reaction mixture was heated at 90 °C for 50 min. The progress of the reaction was monitored by Thin layer chromatography. The completion of the reaction was confirmed by the TLC using Pet ether: ethyl acetate (8:4) as the solvent. After completion of reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and catalyst was recovered by filtration. The filtrate was washed with aqueous $NaHCO_3$ and then with water followed by separation of aqueous layer and organic layer. The organic layer is dried over anhydrous Na_2SO_4 and concentrate in vacuum to obtain the crude product (**4a–l**). The crude product was purified by crystallization using ethanol to afford the pure product.

5-(1h-Benzo[d]imidazol-2-yl)-4-(4-bromophenyl)thiazol-2-yl)acetamide (9a)

Yield 94%; yellow crystalline; mp 200–202 °C. FT-IR: 3647 (-NH, benzimidazole), 3174 (-NH, amido), 3046 (-CH, aromatic), 2739 (-CH, Aliphatic), 1669 (C = O, Amido), 1544 (N-H amido), ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, CH_3-C = O), 7.37–7.57 (m, 8H, Ar-H), 12.36 (s, 1H, amido N-H), 12.49 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 22.69, 112.25, 116.51, 119.39, 122.50, 122.57, 123.45, 131.21, 132.10, 134.12, 135.47, 144.20, 147.00, 158.51, 169.87; HRMS (ESI)$^+$ m/z calc. for $C_{18}H_{13}BrN_4OS$: $(M+H)^+$ 413.0072 and found 413.0052.

4-(4-Bromophenyl)-5-(6-methyl-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamide (9b)

Yield 90%; Red Amorphous; mp 173–175 °C. FT-IR: 3363 (-NH, benzimidazole), 3158 (-NH, amido), 3048 (-CH, aromatic), 1673 (C = O, Amido), 1543 (N-H bend, amido), ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, CH_3-C = O), 2.36 (s, 3H, Ar-CH3), 6.96–7.56 (m, 8H, Ar-H), 12.22 (s, 1H, H-N-C = O or amidic), 12.47 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.85, 22.97, 111.78, 118.83, 124.74, 129.01, 130.73, 133.60, 133.64, 140.92, 142.31, 144.23, 146.52, 169.70; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}BrN_4OS$ $(M+H)^+$ 427.0228; found 427.0208.

N-(4-(4-chlorophenyl)-5-(7-methyl-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamide (9 C)

Yield 89%; off red Amorphous; mp 265–267 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 3H, CH$_3$-C = O), 2.42 (s, 3H, Ar-CH$_3$), 7.10–8.25 (m, 7H, Ar-H), 12.40 (s, 1H, H-N-C = O or amidic), 12.52 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.14, 22.68, 112.65, 117.58, 120.35, 124.47, 126.61, 127.58, 128.34, 130.21, 135.26, 137.12, 138.77, 144.35, 155.12, 164.20, 168.25; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}ClN_4OS$, $(M+H)^+$ 427.0228; found 427.0231.

N-(4-(4-bromophenyl)-5-(6-methoxy-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamides (9d)

Yield 90%; Red Amorphous; mp 173–175 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.19 (s, 3H, CH$_3$-C = O), 2.21 (s, 3H, Ar-CH$_3$), 6.91–7.66 (m, 7H, Ar-H), 12.20 (s, 1H, H-N-C = O or amidic), 12.46 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 22.61, 56.97, 105.27, 112.68, 118.49, 120.58, 127.53, 129.59, 131.01, 132.13, 134.76, 137.28, 140.92, 142.57, 154.28, 156.24, 160.21, 168.02; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}BrN_4O_2S$ $(M+H)^+$ 443.0177; found 443.0159.

5-(1h-Benzo[d]imidazol-2-yl)-4-(4-chlorophenyl)thiazol-2-yl)acetamide (9e)

Yield 94%; yellow Amorphous; mp 204–206 °C. 3386 (-NH, benzimidazole), 3183 (-NH, amido), 3046 (-CH, aromatic), 2739 (-CH, Aliphatic), 1673 (C = O, Amido), 1545 (N-H bend, amido), ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.18 (s, 3H, CH$_3$-C = O), 7.16–7.61 (m, 8H, Ar-H), 12.39 (s, 1H, H-N-C = O or amidic), 12.53 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 22.84, 111.95, 116.19, 119.10, 122.21, 123.16, 128.90, 130.64, 133.54, 135.18, 143.91, 144.72, 146.67, 158.20, 169.59; HRMS (ESI, m/z): calcd (m/z); for $C_{18}H_{13}ClN_4OS$ $(M+H)^+$ 369.0577; found 369.0556.

4-(4-Chlorophenyl)-5-(6-methyl-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamide (9f)

Yield 88%; Red Amorphous; mp 190–192 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, CH$_3$-C = O), 2.36 (s, 3H, Ar-CH$_3$), 7.59–6.96 (m, 8H, Ar-H), 12.26 (s, 1H, H-N-C = O or amidic), 12.50 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.68, 22.82, 111.62, 116.36, 118.67, 122.19, 123.76, 130.85, 131.76, 133.84, 135.41, 142.07, 144.08, 146.43, 158.05, 169.54; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}ClN_4OS$ $(M+H)^+$ 383.0733; found 383.0716.

N-(4-(4-chlorophenyl)-5-(7-methyl-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamide (9 g)

Yield 90%; Light Red; mp 181–183 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, CH$_3$-C = O), 2.39 (s, 3H, Ar-CH$_3$), 6.78–7.46 (m, 7H, Ar-H), 12.10 (s, 1H, H-N-C = O or amidic), 12.38 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.48, 22.32, 114.31, 118.21, 120.07, 121.78, 126.83, 127.74, 129.51, 132.35, 136.60, 139.24, 140.02, 142.31, 155.23, 162.25, 169.79; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}ClN_4OS$ $(M+H)^+$ 383.0733; found 383.0734.

N-(4-(4-chlorophenyl)-5-(6-methoxy-1H-benzo[d]imidazol-2-yl)thiazol-2-yl)acetamide (9 h)

Yield 90%; Light Red; mp 181–183 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH$_3$-C = O), 3.39 (s, 3H, O-CH$_3$), 6.60–7.41 (m, 7H, Ar-H), 12.14 (s, 1H, H-N-C = O or amidic), 12.36 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 22.32, 56.08, 101.22, 111.31, 116.21, 119.07, 121.78, 128.21, 129.44, 132.51, 134.88, 135.69, 139.24, 142.72, 152.31, 156.53, 161.45, 169.30; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}ClN_4O_2S$ $(M+H)^+$ 399.0682; found 399.0693.

N-(5-(1H-benzo[d]imidazol-2-yl)-4-(4-nitrophenyl)thiazol-2-yl)acetamide (9i)

Yield 90%; Red amorphous; mp 272–274 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.16 (s, 3H, CH_3-C = O), 7.14–8.22 (m, 8H, Ar-H), 12.52 (s, 1H, H-N-C = O or amidic); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 23.18, 118.52, 122.90, 124.17, 130.25, 141.33, 144.69, 145.68, 147.47, 159.13, 170.11; HRMS (ESI, m/z): calcd (m/z); for $C_{18}H_{13}N_5O_3S$ 380.0817 $(M + H)^+$ found 380.0797.

N-(5-(6-methyl-1H-benzo[d]imidazol-2-yl)-4-(4-nitrophenyl)thiazol-2-yl)acetamide (9j)

Yield 87%; Off red amorphous; mp 278–280 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.22 (s, 3H, CH_3-C = O), 2.41 (s, 3H, Ar-CH_3), 7.02–8.26 (m, 7H, Ar-H), 12.45 (s, 1H, H-N-C = O or amidic), 12.53 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.64, 22.86, 118.62, 118.67, 122.19, 124.02, 127.81, 130.02, 135.80, 141.07, 145.33, 147.30, 156.65, 158.42, 162.09, 169.77; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}N_5O_3S$, 394.0974 $(M + H)^+$ found 394.0954.

N-(5-(7-methyl-1H-benzo[d]imidazol-2-yl)-4-(4-nitrophenyl)thiazol-2-yl)acetamide (9k)

Yield 89%; Red amorphous; mp 265–267 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.20 (s, 3H, CH_3-C = O), 2.39 (s, 3H, Ar-CH_3), 7.12–8.28 (m, 7H, Ar-H), 12.43 (s, 1H, H-N-C = O or amidic), 12.49 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 21.84, 22.58, 116.52, 123.47, 126.42, 128.02, 138.21, 138.42, 139.80, 141.80, 144.53, 147.90, 157.42, 161.20, 169.75; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}N_5O_3S$ $(M + H)^+$ 394.0974 found 394.0978.

N-(5-(6-methoxy-1H-benzo[d]imidazol-2-yl)-4-(4-nitrophenyl)thiazol-2-yl)acetamide (9 l)

Yield 89%; Red amorphous; mp 247–249 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.25 (s, 3H, CH_3-C = O), 3.89 (s, 3H, O-CH_3), 2.29 (s, 3H, Ar-CH_3), 7.02–8.11 (m, 7H, Ar-H), 12.33 (s, 1H, H-N-C = O or amidic), 12.09 (1H, -NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm; 23.04, 57.22, 104.64, 113.58, 117.36, 119.87, 126.46, 128.72, 136.41, 139.42, 140.33, 142.56, 148.83, 154.90, 157.85, 162.45, 169.69; HRMS (ESI, m/z): calcd (m/z); for $C_{19}H_{15}N_5O_4S$ $(M + H)^+$ 410.0923; found 410.0928.

Biology

Evaluation of anti-antitubercular activity

The Mycobacterium strain *Mtb* (MTCC 300) was obtained from Microbial Type Culture and Gene Bank, Institute of Microbial Technology, Chandigarh (PB), India, and was sub cultured and sustained onto Lowenstein Jensen media as illustrated previously.[61] The sensitivity of test *Mtb* (MTCC 300) strain toward the synthesized compounds (**9a–l**) was exhibited by agar diffusion technique[62] Stock solutions (0.1, 0.5, and 1.0 mg/mL) of the individual compounds were all prepared in dimethyl sulfoxide (DMSO). A sterile cork borer of 7-mm diameter was used to bore holes into the inoculum-seeded solidified Middle brook 7H9 agar. A 30-μL volume of individual compounds was loaded into the labeled well in the prepared media plate using sterile pipette. The test was executed in three similar experiments. The plates were put up in refrigerator for pre-diffusion of the sample and incubated at 37 °C for 48 h. Growth of test organisms was observed after the incubation of 48 h, and the diameter of inhibition of zone was measured. The antimycobacterial activity of Rifampicin (a standard antitubercular drug) was also demonstrated at the same time.

Resazurinmicrotiter assay (REMA) plate method for determination of MIC

Susceptibility of multidrug resistant *Mtb* (MTCC 300) was estimated against synthesized compounds by the colorimetric method Resazurin microtiter assay (REMA). The REMA plate assay was carried out in an identical fashion as depicted earlier[63–65] with slight variations. Prior to the experiment a stock solution of resazurin sodium salt powder (Hi media, India) was prepared at 0.02% (wt/vol) in distilled water, sterilized by filtration, and stored at 4 °C for up to 1 week. The inoculum was prepared from fresh Middle brook 7H9 broth supplemented with 0.1% casitone, and 0.5% glycerol and supplemented with oleic acid, albumin, dextrose, and catalase, adjusted spectrophotometrically to a no. 1 McFarland tube standard (2 × 108 cfu/mL), and further diluted 1:10 in 7H9-S broth for the test. Concisely, all perimeter wells of 96-well microtiter plate (Becton Dickinson, Falcon) were filled with the sterile deionized freeze cold water to reduce evaporation of medium in the left-over wells during incubation. Remaining wells are filled with 100 μL Middle brook 7H9 broth. And serial two-fold dilutions of each drug were prepared directly in the plate. 100 μL of inoculums was added to each well. The plate was sealed with a plastic tape and incubated at 37 °C. After 7 days of incubation, 30 μL of resazurin solution was added to each well, and the plate was re-incubated overnight. The bacterial growth results in the reduction of resazurin which indicates the change in color from blue to pink. The change in the color from blue to pink indicates the growth of bacteria. The MIC was calculated as the lowest drug concentration which prevents color change from blue to pink.[66–67]

Antioxidant activity

The involvement of ROS and the free radical-mediated oxidative damage of cell membranes, DNA, and proteins in degenerative process related to aging, cancer, inflammation atherosclerosis, is a cause of concern. Therefore, there is increasing interest in the protective and preventative functions of foods and their constituents against oxidative damage caused by ROS and free radicals.[68] In the present study, we investigated the antioxidant properties of benzimidazole derivatives using DPPH,[69] OH[70] and SOR (superoxide anion) radical scavenging activity[71] with respect to the standard AA and using a spectrometric assay.

DPPH radical scavenging activity

A concentration of 0.5–1 mM of the individual benzimidazole derivatives were added to 10^{-4} M ethanol solution of DPPH. After 30 min of incubation period at room temperature, the absorbance was measured against a blank at 517 nm. AA was used as positive control.

OH, radical scavenging activity

OH, radicals were generated by using the ferric ion (Fe^{3+})/AA reaction system. The detection of OH radicals was carried out by measuring the amount of formaldehyde generated from the oxidation of dimethyl sulfoxide. The reaction cocktail contained 0.1 mM EDTA, 167 mM Fe^{3+}, 33 mM DMSO in phosphate buffer of 50 mM (pH 7.4), 0.05–0.1 mL individual substituted benzimidazole derivative (0.5–1 mM) solution. AA (150 mL, 10 mM in phosphate buffer) was added finally to initiate the reaction. Trichloroacetic acid (17% w/v) was used to terminate the reaction. The contents were observed spectrophotometrically at 412 nm for the detection of formaldehyde. AA (1 mM) was used as a reference compound for comparative study.

Superoxide anion radical (SOR) scavenging activity

The superoxide anions were generated using PMS/NADH system. The superoxide anions were subsequently made to reduce NBT, which yields a chromogenic product having $k_{\max}$ at 560 nm. The concentration dependent (0.5–1 mM) radical scavenging activities were performed separately. The reaction mixture contained NBT (300 mM), NADH (936 mM), PMS (120 mM), and individual concentrations of substituted benzimidazole (0.5–1 mM) in Tris-HCl buffer (100 mM, pH 7.4). The reaction was initiated by adding PMS to the mixture. After 5 min time of incubation at room temperature, the mixtures were read at 560 nm using Thermo make Automatic Ex-Microplate Reader (M 51118170).

The percent activity of DPPH, OH, SOR radical scavenging and cytotoxicity activity was calculated using following equation.

$$\text{Activity } (\%) = 1 - T/C \times 100$$

Where, T is the absorbance of the test sample and C is the absorbance of the control sample.

Conclusions

Here, we conclude that the pivotal aspect of the contemporary effort was the development of new bioactive skeletons based on benzimidazole clubbed thiazole molding structure with the anticipation of generating new bioactive entities that could be worthwhile as potent antitubercular and antioxidant agents. Among the synthesized compounds **9a**, **9b**, **9c** and **9d** have exhibited significant activity against the growth of *M. tuberculosis* with MIC of 7.55, 4.60, 15.39 and 28.35 μg/mL, respectively. The structure activity relationship reveals that various substituents on the benzimidazole rings affect significantly the anti-TB activity of these compounds. Furthermore, molecular docking study showed that these compounds occupied an energetically favorable position in the active site cavity of InhA engaging in a network of favorable bonded and non-bonded interactions with the amino acid residues located inside the active site. Compounds **9b**, **9d**, **9e** and **9 h** have also displayed very congenial (DPPH) radical scavenging activity which adds to the utility of these molecules. These results indicate the importance of molecular hybridization and the development of benzimidazole-thiazole based lead candidates as potential anti-tubercular agents. The antitubercular activity can further be enhanced by slight alterations in the ring substituents and/or extensive additional functionalization, which validates further investigation. We believe that the observed consequences could offer to global efforts toward the discovery of new lead compounds with improved antitubercular activity.

Acknowledgments

One of the Authors MJH acknowledge UGC, New Delhi for FDP under FDP Program award F. No.31-21/14 (WRO PUNE). Authors also acknowledge Schrödinger Inc. for providing Small-Molecule Drug Discovery Suite to carry out the molecular docking.

Disclosure statement

Authors declare no conflict of interest.

ORCID

Madhav J. Hebade http://orcid.org/0000-0003-0008-8834
Sambhaji T. Dhumal http://orcid.org/0000-0003-3018-6179
Sonali S. Kamble http://orcid.org/0000-0002-1408-065X

Tejshri R. Deshmukh http://orcid.org/0000-0002-1818-0316
Vijay M. Khedkar http://orcid.org/0000-0001-9982-7785
Shrikant V. Hese http://orcid.org/0000-0002-5274-1148
Rajesh N. Gacche http://orcid.org/0000-0002-6300-1436
Bhaskar S. Dawane http://orcid.org/0000-0003-2359-9012

References

1. World Health Organization. 2018. “Global Tuberculosis Report 2018.” WHO United Nations. https://www.who.int/tb/global-report-2019.
2. Beena, D. S. Rawat, “Antituberculosis Drug Research: A Critical Overview,” *Medicinal Research Reviews* 33 (2013): 693–764. doi:10.1002/med.21262.
3. T. R. Deshmukh, S. P. Khare, V. S. Krishna, D. Sriram, J. N. Sangshetti, V. M. Khedkar, and B. B. Shingate, “Synthesis, Bioevaluation and Molecular Docking Study of New Piperazine and Amide Linked Dimeric 1,2,3-Triazoles,” *Synthetic Communications* 50, no. 2 (2020): 271–88. doi:10.1080/00397911.2019.1695275.
4. T. R. Deshmukh, V. S. Krishna, D. Sriram, J. N. Sangshetti, and B. B. Shingate, “Synthesis and Bioevaluation of α,α’-Bis(1H-1,2,3-Triazol-5-Ylmethylene) Ketones,” *Chemical Papers* 74, no. 3 (2020): 809–20. doi:10.1007/s11696-019-00908-5.
5. M. Yan, and S. Ma, “Recent Advances in the Research of Heterocyclic Compounds as Antitubercular Agents,” *Chemmedchem* 7, no. 12 (2012): 2063–75. doi:10.1002/cmdc.201200339.
6. R. Vidhya, K. Rathnakumar, V. Balu, and K. V. Pugalendi, “Oxidative Stress, Antioxidant Status and Lipid Profile in Pulmonary Tuberculosis Patients before and after anti-Tubercular Therapy,” *The Indian Journal of Tuberculosis* 66, no. 3 (2019): 375–81. doi:10.1016/j.ijtb.2018.11.002.
7. T. R. Deshmukh, S. P. Khare, V. S. Krishna, D. Sriram, J. N. Sangshetti, O. Bhusnure, V. M. Khedkar, and B. B. Shingate, “Design and Synthesis of New Aryloxy-Linked Dimeric 1,2,3-Triazoles *via* Click Chemistry Approach: Biological Evaluation and Molecular Docking Study,” *Journal of Heterocyclic Chemistry* 56, no. 8 (2019): 2144–62. doi:10.1002/jhet.3608.
8. S. T. Dhumal, A. R. Deshmukh, M. R. Bhosle, V. M. Khedkar, L. U. Nawale, D. Sarkar, and R. A. Mane, “Synthesis and Antitubercular Activity of New 1,3,4-Oxadiazoles Bearing Pyridyl and Thiazolyl Scaffolds,” *Bioorganic & Medicinal Chemistry Letters* 26, no. 15 (2016): 3646–51. doi:10.1016/j.bmcl.2016.05.093.
9. S. T. Dhumal, A. R. Deshmukh, K. R. Kharat, B. R. Sathe, S. S. Chavan, and R. A. Mane, “Copper Fluorapatite Assisted Synthesis of New 1,2,3-Triazoles Bearing Benzothiazolyl Moiety and Their Antibacterial and Anticancer Activities,” *New Journal of Chemistry* 43, no. 20 (2019): 7663–73. doi:10.1039/C9NJ00377K.
10. M. B. Bhalerao, S. T. Dhumal, A. R. Deshmukh, L. U. Nawale, V. M. Khedkar, D. Sarkar, and R. A. Mane, “New Bithiazolyl Hydrazones: Novel Synthesis, Characterization and Antitubercular Evaluation,” *Bioorganic & Medicinal Chemistry Letters* 27, no. 2 (2017): 288–94. doi:10.1016/j.bmcl.2016.11.056.
11. Chetna Kharbanda, Mohammad Sarwar Alam, Hinna Hamid, Kalim Javed, Sameena Bano, Abhijeet Dhulap, Yakub Ali, Syed Nazreen, and Saqlain Haider, “Synthesis and Evaluation of Pyrazolines Bearing Benzothiazole as anti-Inflammatory Agents,” *Bioorganic & Medicinal Chemistry* 22, no. 21 (2014): 5804–12. doi:10.1016/j.bmc.2014.09.028.
12. A. S. M. Hosan, “Synthesis, Modelling and Molecular Docking of New 5-Arylazo-2-Chloroacetamido Thiazole Derivatives as Antioxidant Agent,” *Journal of Molecular Structure* 1206 (2020): 127712–6.
13. Sally I. Eissa, Amel M. Farrag, Samir Y. Abbas, Mohamed F. El Shehry, Ahmed Ragab, Eman A. Fayed, and Yousry A. Ammar, “Novel Structural Hybrids of Quinoline and Thiazole Moieties: Synthesis and Evaluation of Antibacterial and Antifungal Activities with Molecular Modeling Studies,” *Bioorganic Chemistry* 110 (2021): 104803. doi:10.1016/j.bioorg.2021.104803.
14. Alla Zablotskaya, Izolda Segal, Athina Geronikaki, Tatiana Eremkina, Sergey Belyakov, Marina Petrova, Irina Shestakova, Liga Zvejniece, and Vizma Nikolajeva, “Synthesis, Physicochemical Characterization, Cytotoxicity, Antimicrobial, anti-Inflammatory and Psychotropic Activity of New *N*-[1,3-(Benzo)Thiazol-2-yl]-ω-[3,4-Dihydroisoquinolin-2(1*H*)-yl]Alkanamides,” *European Journal of Medicinal Chemistry* 70 (2013): 846–56. doi:10.1016/j.ejmech.2013.10.008.
15. Y. Bansal, and O. Silakari, “The Therapeutic Journey of Benzimidazoles: A Review,” *Bioorganic & Medicinal Chemistry* 20, no. 21 (2012): 6208–36. doi:10.1016/j.bmc.2012.09.013.
16. Pankaj Sharma, Dinesh Thummuri, T. Srinivasa Reddy, Kishna Ram Senwar, V. G. M. Naidu, Gannoju Srinivasulu, Suresh K. Bharghava, and Nagula Shankaraiah, “New (E)-1-Alkyl-1H-Benzo[d]Imidazol-2-yl)Methylene)Indolin-2-Ones: Synthesis, *in Vitro* Cytotoxicity Evaluation and Apoptosis Inducing Studies,” *European Journal of Medicinal Chemistry* 122 (2016): 584–600. doi:10.1016/j.ejmech.2016.07.019.

17. T. M. A. Eldebss, A. M. Farag, M. M. Abdulla, and R. K. Arafa, "Novel Benzo[d]Imidazole-Based Heterocycles as Broad Spectrum anti-Viral Agents: Design, Synthesis and Exploration of Molecular Basis of Action," *Mini Reviews in Medicinal Chemistry* 16, no. 1 (2016): 67–83. doi:10.2174/138955751601151029115533.
18. A. Mobinikhaledi, N. Foroughifar, M. Kalhor, and M. Mirabolfathy, "Synthesis and Antifungal Activity of Novel 2-Benzimidazolylimino-5-Arylidene-4-Thiazolidinones," *Journal of Heterocyclic Chemistry* 47 (2009): 77–80. doi:10.1002/jhet.264.
19. H. M. Refaat, "Synthesis and Anticancer Activity of Some Novel 2-Substituted Benzimidazole Derivatives," *European Journal of Medicinal Chemistry* 45, no. 7 (2010): 2949–56. doi:10.1016/j.ejmech.2010.03.022.
20. P. Naik, P. Murumkar, R. Giridhar, and M. R. Yadav, "Angiotensin II Receptor Type 1 (AT$_1$) Selective Nonpeptidic Antagonists: A Perspective," *Bioorganic & Medicinal Chemistry* 18, no. 24 (2010): 8418–56. doi:10.1016/j.bmc.2010.10.043.
21. M. Mader, A. de Dios, C. Shih, R. Bonjouklian, T. Li, W. White, B. L. de Uralde, C. Sanchez-Martinez, M. de Prado, C. Jaramillo, et al, "Imidazolyl Benzimidazoles and Imidazo[4,5-b]Pyridines as Potent p38alpha MAP Kinase Inhibitors with Excellent *in Vivo* Antiinflammatory Properties," *Bioorganic & Medicinal Chemistry Letters* 18, no. 1 (2008): 179–83. doi:10.1016/j.bmcl.2007.10.106.
22. D. Seenaiah, P. R. Reddy, G. M. Reddy, A. Padmaja, V. Padmavathi, and N. S. Krishna, "Synthesis, Antimicrobial and Cytotoxic Activities of Pyrimidinyl Benzoxazole, Benzothiazole and Benzimidazole," *European Journal of Medicinal Chemistry* 77 (2014): 1–7. doi:10.1016/j.ejmech.2014.02.050.
23. P. P. Mogle, R. J. Meshram, S. V. Hese, R. D. Kamble, S. S. Kamble, R. N. Gacche, and B. S. Dawane, "Synthesis and Molecular Docking Studies of a New Series of Bipyrazol-yl-Thiazol-Ylidene-Hydrazinecarbothioamide Derivatives as Potential Antitubercular Agents," *MedChemComm* 7, no. 7 (2016): 1405–20. doi:10.1039/C6MD00085A.
24. A. N. Ambhore, S. S. Kamble, S. N. Kadam, R. D. Kamble, M. J. Hebade, S. V. Hese, M. V. Gaikwad, R. J. Meshram, R. N. Gacche, and B. S. Dawane, "Design, Synthesis and *in Silico* Study of Pyridine Based 1,3,4-Oxadiazole Embedded Hydrazinecarbothioamide Derivatives as Potent anti-Tubercular Agent," *Computational Biology and Chemistry* 80 (2019): 54–65. doi:10.1016/j.compbiolchem.2019.03.002.
25. M. J. Hebade, R. D. Kamble, S. V. Hese, P. P. Mogle, A. N. Ambhore, S. N. Kadam, and B. S. Dawane, "A Rapid, Mild, and Efficient Method for C-5 Iodination/Thiocyanation of 2-Aminothiazoles," *Phosphorus, Sulfur, and Silicon and the Related Elements* 191, no. 8 (2016): 1155–9. doi:10.1080/10426507.2016.1149851.
26. S. N. Kadam, A. N. Ambhore, M. J. Hebade, R. D. Kamble, S. V. Hese, M. V. Gaikwad, P. D. Gavhane, and B. S. Dawane, "Metal-Free One-Pot Chemoselective Thiocyanation of Imidazothiazoles and 2-Aminothiazoles with in Situ Generated N-Thiocyanatosuccinimide," *Synlett* 29, no. 14 (2018): 1902–8. doi:10.1055/s-0037-1609553.
27. Shrikant V. Hese, Rohan J. Meshram, Rahul D. Kamble, Pratima P. Mogle, Kapil K. Patil, Sonali S. Kamble, Rajesh N. Gacche, and Bhaskar S. Dawane, "Antidiabetic and Allied Biochemical Roles of New Chromeno-Pyrano Pyrimidine Compounds: synthesis, *in Vitro* and *in Silico* Analysis," *Medicinal Chemistry Research* 26, no. 4 (2017): 805–18. doi:10.1007/s00044-017-1794-0.
28. M. J. Hebade, T. R. Deshmukh, and S. T. Dhumal, "Silica Supported Dodecatungstophosphoric Acid (DTP/SiO$_2$): an Efficient and Recyclable Heterogeneous Catalyst for Rapid Synthesis of Quinoxalines," *Synthetic Communications* 51, no. 16 (2021): 2510–20. doi:10.1080/00397911.2021.1939060.
29. S. T. Dhumal, A. R. Deshmukh, L. D. Khillare, M. Arkile, D. Sarkar, and R. A. Mane, "Synthesis and Antitubercular Activity of New Thiazolidinones with Pyrazinyl and Thiazolyl Scaffolds," *Journal of Heterocyclic Chemistry* 54, no. 1 (2017): 125–30. doi:10.1002/jhet.2552.
30. A. R. Deshmukh, S. T. Dhumal, L. U. Nawale, V. M. Khedkar, D. Sarkar, and R. A. Mane, "Dicationic Liquid Mediated Synthesis of Tetrazoloquinolinyl Methoxy Phenyl 4-Thiazolidinones and Their Antibacterial and Antitubercular Evaluation," *Synthetic Communications* 49, no. 4 (2019): 587–601. doi:10.1080/00397911.2018.1564928.
31. R. Srinivasulu, K. R. Kumar, and P. V. V. Satyanarayana, "Facile and Efficient Method for Synthesis of Benzimidazole Derivatives Catalyzed by Zinc Triflate," *Green and Sustainable Chemistry* 4, no. 1 (2014): 33–7. doi:10.4236/gsc.2014.41006.
32. M. Kidwai, A. Jahan, and D. Bhatnagar, "Polyethylene Glycol: A Recyclable Solvent System for the Synthesis of Benzimidazole Derivatives Using CAN as Catalyst," *Journal of Chemical Sciences* 122, no. 4 (2010): 607–12. doi:10.1007/s12039-010-0095-7.
33. Liene Grigorjeva, Edvards Liepinsh, Solofoniaina Razafimahefa, Aleh Yahorau, Sviatlana Yahorava, Philippe Rasoanaivo, Aigars Jirgensons, and Jarl E. S. Wikberg, "Semisynthesis of Libiguin a and Its Analogues by Trans-Lactonization of Phragmalin," *The Journal of Organic Chemistry* 79, no. 9 (2014): 4148–53. doi:10.1021/jo500318w.
34. R. R. Nagawade, and D. B. Shinde, "BF$_3$OEt$_2$ Promoted Solvent-Free Synthesis of Benzimidazole Derivatives," *Russian Journal of Organic Chemistry* 42, no. 3 (2006): 453–6. doi:10.1134/S1070428006030201.

35. K. A. Shaikh, and V. A. Patil, "An Efficient Solvent-Free Synthesis of Imidazolines and Benzimidazoles Using $K_4[Fe(CN)_6]$ Catalysis," *Organic Communications* 5 (2012): 12–7.
36. J. Zhu, Z. Zhang, C. Miao, W. Liu, and W. Sun, "Synthesis of Benzimidazoles from o-Phenylenediamines and DMF Derivatives in the Presence of PhSiH3," *Tetrahedron* 73, no. 25 (2017): 3458–62. doi:10.1016/j.tet.2017.05.018.
37. R. Trivedi, S. K. De, and R. A. Gibbs, "A Convenient One-Pot Synthesis of 2-Substituted Benzimidazoles," *Journal of Molecular Catalysis A: Chemical* 245, no. 1–2 (2006): 8–11. doi:10.1016/j.molcata.2005.09.025.
38. V. R. Ruiz, A. Corma, and M. J. Sabater, "New Route for the Synthesis of Benzimidazoles by a One-Pot Multistep Process with Mono and Bifunctional Solid Catalysts," *Tetrahedron* 66, no. 3 (2010): 730–5. doi:10.1016/j.tet.2009.11.048.
39. T. Mahajan, K. Dhimant, G. Kapse, and M. Hugar, "$ZnCl_2$-SiO_2 Catalyzed Solvent Free Synthesis of Benzimidazole Derivatives under Microwave Irradiation," *Journal of Applied Chemistry* 2 (2013): 50–4.
40. Y. Venkateswarlu, S. R. Kumar, and P. Leelavathi, "Facile and Efficient One-Pot Synthesis of Benzimidazoles Using Lanthanum Chloride," *Organic and Medicinal Chemistry Letters* 3, no. 1 (2013): 7. doi:10.1186/2191-2858-3-7.
41. Z. Gan, Q. Tian, S. Shang, W. Luo, Z. Dai, H. Wang, D. Li, X. Wang, and J. Yuan, "Imidazolium Chloride-Catalyzed Synthesis of Benzimidazoles and 2-Substituted Benzimidazoles from o-Phenylenediamines and DMF Derivatives," *Tetrahedron* 74, no. 52 (2018): 7450–7456. doi:10.1016/j.tet.2018.11.014.
42. S. D. Sharma, and D. Konwar, "Practical, Ecofriendly, and Chemoselective Method for the Synthesis of 2-Aryl-1-Arylmethyl-1*H*-Benzimidazoles Using Amberlite IR-120 as a Reusable Heterogeneous Catalyst in Aqueous Media," *Synthetic Communications* 39, no. 6 (2009): 980–991. doi:10.1080/00397910802448440.
43. K. Bahrami, M. M. Khodaei, and A. Nejati, "Synthesis of 1,2-Disubstituted Benzimidazoles, 2-Substituted Benzimidazoles and 2-Substituted Benzothiazoles in SDS Micelles," *Green Chemistry* 12, no. 7 (2010): 1237–1241. doi:10.1039/c000047g.
44. B. Zou, Q. Yuan, and D. Ma, "Synthesis of 1,2-Disubstituted Benzimidazoles by a Cu-Catalyzed Cascade Aryl Amination/Condensation Process," *Angewandte Chemie (International ed. in English)* 46, no. 15 (2007): 2598–2601. doi:10.1002/anie.200700071.
45. D. Azarifar, M. Pirhayati, B. Maleki, M. Sanginabadi, and R. T. Yami, "Acetic Acid-Promoted Condensation of o-Phenylenediamine with Aldehydes into 2-Aryl-1-(Arylmethyl)-1H-Benzimidazoles under Microwave Irradiation," *Journal of the Serbian Chemical Society* 75, no. 9 (2010): 1181–1189. doi:10.2298/JSC090901096A.
46. J. Wan, S. Gan, J. Wu, and Y. Pan, "Water Mediated Chemoselective Synthesis of 1,2-Disubstituted Benzimidazoles Using o-Phenylenediamine and the Extended Synthesis of Quinoxalines," *Green Chemistry* 11, no. 10 (2009): 1633–1637. doi:10.1039/b914286j.
47. C. Mukhopadhyay, A. Datta, R. J. Butcher, B. K. Paul, N. Guchhait, and R. Singha, "Water Mediated Expeditious and Highly Selective Synthesis of 2-Aryl-1-Arylmethyl-1H-Benzimidazoles by Dowex 50W: fluorescence Properties of Some Representative Compounds," *Arkivoc* 2009, no. 13 (2009): 1–22. doi:10.3998/ark.5550190.0010.d01.
48. G. A. N. K. Durgareddy, R. Ravikumar, S. Ravi, and S. R. Adapa, "A Cu $(NO_3)_2 3H_2O$ Catalysed Facile Synthesis of Substituted 4(3H)-Quinazolinones and Benzimidazoles," *Journal of Chemical Sciences* 125, no. 1 (2013): 175–182. doi:10.1007/s12039-012-0343-0.
49. A. Kumar, and K. K. Kapoor, "Antimony Chloride Immobilized on Neutral Alumina: An Efficient Catalyst for the Solvent-Free Selective Synthesis of 1,2-Disubstituted Benzimidazoles," *Journal of Chemical and Pharmaceutical Research* 3 (2011): 369–374.
50. H. Sharghi, O. Asemani, and R. Khalifeh, "New One-Pot Procedure for the Synthesis of 2-Substituted Benzimidazoles," *Synthetic Communications* 38, no. 7 (2008): 1128–1136. doi:10.1080/00397910701863657.
51. S. I. Alaqeel, "Synthetic Approaches to Benzimidazoles from *o*-Phenylenediamine: A Literature Review," *Journal of Saudi Chemical Society* 21, no. 2 (2017): 229–237. doi:10.1016/j.jscs.2016.08.001.
52. S. Sajjadifar, S. A. Mirshokraie, N. Javaherneshan, and O. Louie, "SBSA as a New and Efficient Catalyst for the One-Pot Green Synthesis of Benzimidazole Derivatives at Room Temperature," *American Journal of Organic Chemistry* 2, no. 2 (2012): 1–6. doi:10.5923/j.ajoc.20120202.01.
53. M. Burits, and F. Bucar, "Antioxidant Activity of Nigella Sativa Essential Oil," *Phytotherapy Research* 14, no. 5 (2000): 323–328. doi:10.1002/1099-1573(200008)14:5<323::AID-PTR621>3.0.CO;2-Q.
54. S. B. Nimse, and D. Pal, "Free Radicals, Natural Antioxidants, and Their Reaction Mechanisms," *RSC Advances* 5, no. 35 (2015): 27986–28006. doi:10.1039/C4RA13315C.
55. R. A. Friesner, R. B. Murphy, M. P. Repasky, L. L. Frye, J. R. Greenwood, T. A. Halgren, P. C. Sanschagrin, and D. T. Mainz, "Extra Precision Glide: docking and Scoring Incorporating a Model of Hydrophobic

Enclosure for Protein-Ligand Complexes," *Journal of Medicinal Chemistry* 49, no. 21 (2006): 6177–6196. doi:10.1021/jm051256o.

56. X. He, A. Alianc, R. Paul, and O. de Montellano, "Inhibition of the Mycobacterium tuberculosis Enoyl Acyl Carrier Protein Reductase InhA by Arylamides," *Bioorganic & Medicinal Chemistry* 15, no. 21 (2007): 6649–6658. doi:10.1016/j.bmc.2007.08.013.
57. T. R. Deshmukh, V. M. Khedkar, R. G. Jadhav, A. P. Sarkate, J. N. Sangshetti, S. V. Tiwari, and B. B. Shingate, "A Copper-Catalyzed Synthesis of Aryloxy-Tethered Symmetrical 1,2,3 Triazoles as Potential Antifungal Agents Targeting 14 a-Demethylase," *New Journal of Chemistry* 45, no. 29 (2021): 13104–13118. doi:10.1039/D1NJ01759D.
58. L. Z. Benet, C. M. Hosey, O. Ursu, and T. I. Oprea, "BDDCS, the Rule of 5 and Drugability," *Advanced Drug Delivery Reviews* 101 (2016): 89–98. doi:10.1016/j.addr.2016.05.007.
59. "Molinspiration Chemoinformatics Brastislava, Slovak Republic." http://wwwmolinspirationcom/cgi-bin/properties2014
60. "Drug-Likeness and Molecular Property Prediction." http://wwwmolsoftcom/mprop
61. V. Chaturvedi, N. Dwivedi, P. R. Tripathi, and S. Sinha, "Evaluation of Mycobacterium smegmatis as a Possible Surrogate Screen for Selecting Molecules Active against Multi-Drug Resistant Mycobacterium tuberculosis," *The Journal of General and Applied Microbiology* 53, no. 6 (2007): 333–337. doi:10.2323/jgam.53.333.
62. R. D. Kamble, S. V. Hese, R. J. Meshram, J. R. Kote, R. N. Gacche, and B. S. Dawane, "Green Synthesis and *in Silico* Investigation of Dihydro-2H-Benzo [1,3]Oxazine Derivatives as Inhibitors of Mycobacterium tuberculosis," *Medicinal Chemistry Research* 24, no. 3 (2015): 1077–1088. doi:10.1007/s00044-014-1165-z.
63. V. Katawera, M. Siedner, and Y. Boum Ii, "Evaluation of the Modified Colorimetric Resazurin Microtiter Plate-Based Antibacterial Assay for Rapid and Reliable Tuberculosis Drug Susceptibility Testing," *BMC Microbiology* 14, no. 1 (2014): 1–4. doi:10.1186/s12866-014-0259-6.
64. K. Mlisana, P. Jaglal, and M. Pillay, "Resazurin Microtitre Plate Assay and Sensititre MycoTB for Detection of Mycobacterium tuberculosis Resistance in a High Tuberculosis Resistance Setting," *African Journal of Laboratory Medicine* 8, no. 1 (2019): 1–9. doi:10.4102/ajlm.v8i1.840.
65. R. A. Khalifa, M. S. Nasser, A. A. Gomaa, N. M. Osman, and H. M. Salem, "Resazurin Microtiter Assay Plate Method for Detection of Susceptibility of Multidrug Resistant Mycobacterium tuberculosis to Second-Line anti-Tuberculous Drugs," *Egyptian Journal of Chest Diseases and Tuberculosis* 62, no. 2 (2013): 241–247. doi:10.1016/j.ejcdt.2013.05.008.
66. S. B. Rajput, R. B. Shinde, M. M. Routh, and S. M. Karuppayil, "Anti-Candida Properties of Asaronaldehyde of Acorus Gramineus Rhizome and Three Structural Isomers," *Chinese Medicine* 8, no. 1 (2013): 18–8. doi:10.1186/1749-8546-8-18.
67. A. Ahmad, A. Khan, N. Manzoor, and L. A. Khan, "Evolution of Ergosterol Biosynthesis Inhibitors as Fungicidal against Candida," *Microbial Pathogenesis* 48, no. 1 (2010): 35–41. doi:10.1016/j.micpath.2009.10.001.
68. I. Gulcin, "Antioxidant Properties of Resveratrol: A Structure Activity Insight," *Innovative Food Science and Emerging Technologies* 11 (2010): 210–218.
69. M. P. de Torre, R. Y. Cavero, M. I. Calvo, and J. L. Vizmanos, "A Simple and a Reliable Method to Quantify Antioxidant Activity *in Vivo*," *Antioxidants* 8, no. 5 (2019): 142. doi:10.3390/antiox8050142.
70. M. M. Rahman, M. B. Islam, M. Biswas, and A. K. Alam, "*In Vitro* Antioxidant and Free Radical Scavenging Activity of Different Parts of Tabebuia Pallida Growing in Bangladesh," *BMC Research Notes* 8, no. 1 (2015): 1–9. doi:10.1186/s13104-015-1618-6.
71. K. Lalhminghlui, and G. C. Jagetia, "Evaluation of the Free-Radical Scavenging and Antioxidant Activities of Chilauni, Schima Wallichii Korth *in Vitro*," *Future Science OA* 4, no. 2 (2018): FSO272. doi:10.4155/fsoa-2017-0086.

Impact Factor – 8.575 **ISSN – 2278-9308**

B.Aadhar

Peer-Reviewed & Referred Indexed

Multidisciplinary International Research Journal

March-2022

ISSUE No- (CCCXLIV) 344- C

WOMEN IN INDIA AND ABROAD

Prof. Virag.S.Gawande
Chief Editor
Director
Aadhar Social Research &, Development Training Institute, Amravati.

Dr.Daisy Rani Chutia
Editor
Assistant professor ,
Department of Education . Marangi College Golaghat Assam

Dr. Baliram Pawar
Editor
Head, Department of Sociology
Mahatma Phule College Kingaon , Latur Maharashtra .413523

Aadhar International Publication

For Details Visit To : www.aadharsocial.com

B.Aadhar' International Peer-Reviewed Indexed Research Journal
Impact Factor -(SJIF) -8.575,Issue NO, 344 (CCCXLIV) C
ISSN : 2278-9308
March, 2022

Editorial Board

Chief Editor -
Prof.Virag S.Gawande,
Director,
Aadhar Social Research &,
Development Training Institute, Amravati. **[M.S.] INDIA**

Executive-Editors -

- **Dr.Dinesh W.Nichit** - Principal, Sant Gadge Maharaj Art's Comm,Sci Collage, **Walgaon.Dist. Amravati.**
- **Dr.Sanjay J. Kothari** - Head, Deptt. of Economics, G.S.Tompe Arts Comm,Sci Collage Chandur Bazar Dist. Amravati

Advisory Board -

- **Dr. Dhnyaneshwar Yawale** - Principal, Sarswati Kala Mahavidyalaya , Dahihanda, Tq-Akola.
- **Prof.Dr. Shabab Rizvi** ,Pillai's College of Arts, Comm. & Sci., New Panvel, Navi Mumbai
- **Dr. Udaysinh R. Manepatil** ,Smt. A. R. Patil Kanya Mahavidyalaya, Ichalkaranji,
- **Dr. Sou. Parvati Bhagwan Patil** , Principal, C.S. Shindure College Hupri, Dist Kolhapur
- **Dr.Usha Sinha** , Principal ,G.D.M. Mahavidyalay,Patna Magadh University.Bodhgay Bihar

Review Committee -

- **Dr. D. R. Panzade,** Assistant Pro. Yeshwantrao Chavan College, Sillod. Dist. Aurangabad (MS)
- **Dr.Suhas R.Patil** ,Principal ,Government College Of Education, Bhandara, Maharashtra
- Dr. **Kundan Ajabrao Alone** ,Ramkrushna Mahavidyalaya, Darapur Tal-Daryapur, Dist-Amravati.
- **DR. Gajanan P. Wader** Principal , Pillai College of Arts, Commerce & Science, Panvel
- **Dr. Bhagyashree A. Deshpande**, Professor Dr. P. D. College of Law, Amravati]
- **Dr. Sandip B. Kale,** Head, Dept. of Pol. Sci., Yeshwant Mahavidyalaya, Seloo, Dist. Wardha.
- **Dr. Hrushikesh Dalai** , Asstt. Professor K.K. Sanskrit University, Ramtek

Our Editors have reviewed paper with experts' committee, and they have checked the papers on their level best to stop furtive literature. Except it, the respective authors of the papers are responsible for originality of the papers and intensive thoughts in the papers.

- **Executive Editor**

Published by -
Prof.Virag Gawande
Aadhar Publication ,Aadhar Social Research & Development Training Institute, New Hanuman Nagar,
In Front Of Pathyapustak Mandal, Behind V.M.V. College,Amravati
(M.S) India Pin- 444604 **Email :** aadharpublication@gmail.com
Website : www.aadharsocial.com **Mobile :** 9595560278 /

B.Aadhar' International Peer-Reviewed Indexed Research Journal
Impact Factor -(SJIF) –8.575,Issue NO, 344 (CCCXLIV) C
ISSN : 2278-9308
March, 2022

INDEX

B.Aadhar' International Peer-Reviewed Indexed Research Journal
Impact Factor -(SJIF) –8.575,Issue NO, 344 (CCCXLIV) C
ISSN : 2278-9308
March, 2022

महिला सबलीकरण : स्वरूप व उद्‌दिष्टये

प्रा. उगीले माधव उत्तमराव
समाजशास्त्र विभाग रामकृष्ण परमहंस महाविद्यालय,उस्मानाबाद ,मो.९४२३७२१३९०
email : ugilemahadev@gmail.com

प्रस्तावना:—

महिला सबलीकरण ही स्त्री अधिकाराचा पुरस्कार करणारी, स्त्रीयांना पुरूषाच्या बरोबरीने विकासाची संधी उपलब्ध करून देणारी आणि स्त्री पुरूष समानतेवर आधारीत नवीन व्यवस्था निर्मितीचे उद्‌दिष्ट ठेवणारी एक प्रक्रिया—चळवळ आहे. महिला सबलीकरणामुळे आधुनिक काळात महिलामध्ये अनेक महत्वपूर्ण बदल पहावयास मिळतात. आज प्रत्येक क्षेत्रात स्त्री पुरूषाच्या बरोबरीने खांद्याला खांदा लावून काम करत आहे. आज महिला या पारंपारिक रूढीवादी जोखडातून बाहेर पडत आहेत. आजची स्त्री केवळ गृहिणीपुरतीच मर्यादीत राहीली नाही तर अधिकारी, जबाबदार आणि कार्यप्रवण महिला म्हणून कार्यरत असलेली दिसते. महिला सबलीकरणाचा प्रभाव हा शहरी भागातील सुशिक्षीत महिलांवर त्यातही मध्यमवर्गीय महिलांवर जास्त पडत आहे. शहरी भागात शिक्षण, नोकरी, उद्योग याच्या माध्यमातून महिलांना व्यक्तीमत्व विकासासाठी आणि अधिकाराची जाणीव करून देण्यासाठी नवनवीन दिशा दाखवल्या जात आहेत. त्यामुळे महिला सबलीकरणास चालना व गती मिळत आहे.

भारतात पुरूषप्रधान संस्कृती असल्यामुळे स्त्रीयांना दुय्यम स्थान दिले जाते. स्त्री व पुरूषामध्ये नेहमी फरक केला जातो. महिलांना दुय्यम स्थान दिले जाते. महिलाकडे कायम अबला म्हणून पाहण्यात आले. तिचे क्षेत्र चुल आणि मूल इथपर्यंतच सिमित ठेवण्यात आले. महिला कौटुंबिक अत्याचाराच्या बळी ठरत गेल्या. महिलांना मुख्य प्रवाहाचा घटक मानले जात नव्हते. महिलांना विकास प्रक्रियेत सहभागी करून घेतल्याशिवाय देशाचा विकास होवू शकत नाही. स्त्रीया पुरूषाच्या तुलनेत कुठेच कमी नाहीत. गुणवत्ता व नियोजनामध्ये स्त्रीया पुरूषाबरोबर आहेत. हे सत्य उमजल्यामुळे आज महिला सबलीकरणासाठी सर्व स्तरातून प्रयत्न होताना दिसत आहेत. महिला सबलीकरण म्हणजे महिलांना पुरूषाप्रमाणेच कोणताही भेदभाव न करता प्रगतीची, विकासाची समान संधी सर्व क्षेत्रात व सर्व अंगाने मिळणे ती मिळत नसेल तर संधी देणारी नवी व्यवस्था निर्माण करणे होय. महिलामध्ये आत्मविश्वास व सहास निर्माण करणे हा महिला सबलीकरणाचा मुख्य उद्‌देश आहे. तसेच विकासाच्या प्रत्येक क्षेत्रात सत्ता संधी व अधिकार देणे हे महिलांच्या सबलीकरणाचा हेतू आहे.

संशोधनाची उद्‌दिष्टे:—

१. महिला सबलीकरण ही संकल्पना स्पष्ट करणे.
२. महिला सबलीकरणाचे स्वरूप जाणून घेणे.
३. महिला सबलीकरणाची उद्‌दिष्ट्ये अभ्यासणे.
४. महिला सबलीकरणाचे पैलू जाणुन घेणे.
५. महिला सबलीकरणाचे महत्त्व जाणून घेणे.

संशोधन पध्दती:—

प्रस्तुत शोधनिबंधासाठी दुय्यम साधनाचा वापर करण्यात आला असून त्यामध्ये प्रकाशीत संदर्भग्रंथ, मासिके, वृत्तपत्र, अहवाल, इंटरनेट इत्यादीचा उपयोग करण्यात आला आहे.

महिला सबलीकरण संकल्पना:—

भारतीय स्त्रीयांना पिढ्यान—पिढ्या पुरूषाकडून होणाऱ्या शोषणाला बळी पडावे लागले आहे. त्यामुळे त्यांचा शारीरिक, मानसिक, बौध्दिक व आर्थिक विकास खुंटल्याने त्या शक्तीहीन बनल्या परंतु देशाचा सर्वांगीण विकास साधण्याच्या दृष्टीने त्या शक्तीशाली बनविण्याचा विचार सुरू झाला आणि तेथूनच महिला सबलीकरणाची संकल्पना पुढे आली.सबलीकरण ही बहुआयामी संकल्पना आहे. सबलीकरण ही दुर्बलता नष्ट करणारी संकल्पना आहे. ??महिलांना सामाजिक, आर्थिक, राजकीय, कौटुंबिक, मानसिक व प्रशासकीय क्षेत्रात योग्य प्रमाणात सहभागी करून घेणे म्हणजे महिला सबलीकरण होय.?? स्त्रीयांच्या अंगी निर्णय घेण्याचो, नियंत्रण करण्याची, संघटन करण्याची क्षमता, मतप्रदर्शन करणे, कृतीशील कार्यक्रम घडवून आणणे, लोकसंपर्क, आर्थिक व्यवहार, तिची आवड पूर्ण होणे याला महिला सबलीकरण असे म्हणतात. स्त्री—पुरूष समानतेवर आधारीत व्यवस्थेची निर्मीती स्त्रीयांना सामाजिक आणि आर्थिक न्याय मिळवून देणे. स्त्रीयावरील अन्याय, अत्याचार दूर करणे, स्त्रीयांचे खच्चीकरण थांबविणे, स्त्रीयांना रोजगाराभिमुख बनविणे. राजकीय निर्णय प्रक्रियेत महिलांचा सहभाग वाढविणे स्त्रीयांचा मानसिक आणि बौध्दीक विकास घडवून आणणे. स्त्रीयांना उपेक्षित ठेवणाऱ्या शक्तीचे मतपरिवर्तन घडवून आणणे इत्यादी महिला सबलीकरणाची वैशिष्ट्ये आहेत.

साक्षरता, आर्थिक स्वावलंबन, राजकीय निर्णय प्रक्रियेमध्ये सहभाग, दबावतंत्र, प्रशिक्षण, जनजागृती, महिला सबलीकरणासाठीचे कायदे, प्रसारमाध्यमे, आरक्षण इत्यादी ही महिला सबलीकरणाची साधने आहेत.

महिला सबलीकरणाचे स्वरूप :—

महिला सबलीकरणाची संकल्पना ही स्त्रीयांसाठी सकारात्मक दृष्टीकोन निर्माण करणारी संकल्पना आहे. महिला सबलीकरण ही स्त्रीयांना शक्ती देऊन त्याद्वारे त्यांचे इतरांवर श्रेष्ठत्व निर्माण करणे होय. स्त्री सबलीकरण हे स्त्रीयांना सबल करणारे असेल. स्त्री सबलीकरणाची सुरूवात ही स्त्रीने तिच्या सामाजिक, मानसिक, सांस्कृतिक, आर्थिक आणि राजकीय शक्ती ओळखून त्याबद्दल जागरूक राहणे. जेव्हा स्त्री ही जेव्हा स्वत:च्या सकारात्ममक व्यक्तीमत्वाबद्दल व प्रतिमेबद्दल, सकारात्मक अधिकार व कर्तव्याबद्दल जागरूक होईल तेव्हाच महिलांचे खऱ्या अर्थाने सबलीकरण होईल असे म्हणता येईल. महिला सबलीकरण ही एक सक्रिय बहुआयामी प्रक्रिया आहे जी स्त्रीयांना स्वअस्तित्वाच्या शक्तीची जाणीव करून देते. महिला सबलीकरणाचा खरा अर्थ असा की, स्त्रीयांच्या जीवनातील प्रत्येक क्षेत्राला हाताळण्याचे सामर्थ्य तिच्यात निर्माण करणे होय. केवळ त्यांना क्षमतेची जाणीव करून न देता त्या सोबतच त्यांना संधी सुविधा व बाहय आणि आंतरिक वातावरण निर्माण करून देणे. सत्तावंचित संधिवंचित महिलांना कोणताही भेदभावाशिवाय प्रगती करण्याची संधी देणे म्हणजे महिला सबलीकरण होय.

महिला सबलीकरणाचे उद्दिष्टे:—

१. स्त्री—पुरूष समानता :—

समाजात लिंगभेदावर आधारीत व्यवस्था आढळते ही व्यवस्था नष्ट करून स्त्री—पुरूष समानता असणारी व्यवस्था निर्माण करणे. समाजात स्त्रीयाकडे पाहण्याचा जो दुय्यम दृष्टीकोन आहे तो बदलून स्त्री—पुरूष समानतेचा दृष्टीकोन लोकामध्ये निर्माण झाला पाहिजे. स्त्रीयांना दुय्यम लेखून स्त्रीचे जे शोषण केले जाते ते थांबले पाहीजे. स्त्रीयांना उपेक्षित ठेवून राष्ट्राचा विकास होऊ शकत नाही. त्यामुळे देशाच्या विकासाच्या प्रवाहात स्त्रीयांना समान संधी समान दर्जा सत्तेत महत्त्वाचा वाटा मिळाला पाहीजेत. स्त्री शोषण मुक्त समाजव्यवस्था निर्माण होण्यासाठी स्त्री—पुरूष समानता समाज व्यवस्थेत निर्माण करणे हे महिला सक्षमीकरणाचे उद्दिष्ट आहे.

२. आर्थिक स्वावलंबन :—

स्त्रीयांनी स्वत:च्या पायावर उभ राहण्यासाठी आर्थिकदृष्ट्या स्वावलंबी बनल्या पाहिजेत. स्त्रीया आर्थिकदृष्टया स्वावलंबी झाल्या की कुटुंब व राष्ट्र विकसित होईल. राष्ट्राच्या विकास प्रक्रियेत स्त्रीयांचा सहभाग वाढेल म्हणूनच आर्थिक स्वावलंबन हे महिला सबलीकरणाचे उद्दिष्ट आहे.

३. समान संधी :—

संविधानाने स्त्रीयांना पुरूषाच्या बरोबरीने सर्व क्षेत्रात समान संधी उपलब्ध करून दिली आहे. परंतु समाजात मात्र स्त्रीयांना सर्व क्षेत्रात पुरूषाच्या बरोबरीने समान संधी उपलब्ध होत नाही. महिला सबलीकरणाच्या माध्यमातून सर्व क्षेत्रात पुरूषाच्या बरोबरीने स्त्रीयांना समान संधी मिळवून देण्याचे कार्य करण्यात येते. महिलांना समान संधी प्राप्त करून देणे हे महिला सबलीकरणाचे उद्दिष्ट आहे.

४. सामाजिक व राजकीय न्याय :—

स्त्रीयांना सामाजिक व राजकीय अधिकारापासून दूर ठेवण्यात आले आहे याचा परिणाम म्हणजे महिलांच्या विकासावर मर्यादा आलेल्या आहेत. या मर्यादेचे बंधन दूर करून महिलांना या व्यवस्थेत अंतर्भुत करून घेणे व समाजाच्या विकासासाठी स्त्रीयांचा विकास करणे गरजेचे आहे.

महिला सबलीकरणाचे पैलू :—

१. शैक्षणिक सबलीकरण
२. आर्थिक सबलीकरण
३. आरोग्यविषयक सबलीकरण
४. कौटुंबिक आणि सामाजिक निर्णय प्रक्रियेत सहभाग
५. मानसिक सबलीकरण
६. भावनिक सबलीकरण
७. राजकीय सबलीकरण
८. सामाजिक सबलीकरण

असे महिला सबलीकरणाचे अनेक पैलू आहेत. महिला सबलीकरणात सर्वात महत्त्वाची बाब म्हणजे तिला माणूस म्हणून जगण्याची संधी देऊन तिला तिचे व्यक्तीमत्व विकसित करण्यास कुटुंब आणि समाजातून प्रोत्साहन मिळावे.

महिला सबलीकरणाचे महत्त्व:—

१. हक्काची जाणीव होण्यासाठी
२. महिलांवरील अन्यायाला वाचा फोडण्यासाठी
३. निर्णय घेण्यास सक्षम बनवण्यासाठी
४. महिलांचे जीवनमान उंचावण्यासाठी
५. स्त्री—पुरूष समानता निर्माण करण्यासाठी

निष्कर्ष:—

महिला सबलीकरणामुळे महिलांचा कौटुंबिक व सामाजिक दर्जा उंचावत आहे. आज महिला विविध क्षेत्रात आपले कर्तृत्व सिध्द करून प्रतिष्ठा प्राप्त करत आहेत. महिला सबलीकरणामुळे महिला आर्थिकदृष्ट्या स्वावलंबी बनल्यामुळे त्याच्यामध्ये आत्मविश्वास निर्माण होत आहे. महिला नियोजन व निर्णय प्रक्रियेत जाणीवपूर्वक सहभाग घेत आहेत. आज महिला पुरूषाच्या बरोबरीने काम करून सन्मानाने जगत आहेत. महिला सबलीकरणामुळे महिलामध्ये स्वअस्तित्वाची जाणीव निर्माण झाली आहे. स्त्रीयांना पुरूषाच्या बरोबरीने स्थान प्राप्त करून देण्याची संधी प्राप्त झाली

Journal of Applied Organometallic Chemistry

2022, Volume 2, Issue 1

Original Article: Meglumine Catalysed Green Synthesis of Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate Derivatives

Ganesh Baburao Pund[a] | **Sambhaji Tukaram Dhumal**[b] | **Madhav Janardan Hebade**[c] | **Mazahar Farooqui**[d] | **Bhagwansing Shivsing Dobhal**[c,*]

[a]*Department of Chemistry, Dr. Rafiq Zakariya College for Women, Aurangabad (MS) India- 431001.*
[b]*Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad (MS) India- 431501.*
[c]*Department of Chemistry, Badrinarayan Barwale Mahavidyalaya, Jalna (MS) India- 431213.*
[d]*Department of Chemistry, Maulana Azad College of Arts Science and Commerce, Aurangabad, (MS) India- 431001.*

Use your device to scan and read the article online

Citation G. B. Pund, S.T. Dhumal, M.J. Hebade, M. Farooqui, B.S. Dobhal*.**Meglumine Catalysed Green Synthesis of Ethyl-6-Amino-5-Cyano-2-Methyl-4-Phenyl-4*H*-Pyran-3-Carboxylate Derivatives.** *J. Appl. Organomet. Chem.*, **2022**, *2*(1), 15-23.

https://doi.org/10.22034/jaoc.2022.324493.1046

Article info:
Received: **14-02-2022**
Accepted: **03-02-2022**
Available Online: **05-03-2022**
ID: **JAOC-2201-1046**
Checked for Plagiarism: **Yes**
Peer Reviewers Approved by:
Dr.SUNIL V. GAIKWAD
Editor who Approved Publication:
Professor Dr. AbdelkaderZarrouk

Keywords:
Meglumine; recyclable;Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylates; reusable; cyclocondensation

ABSTRACT

An efficient and simple one-pot synthetic protocol has been developed for the first time to synthesize the series of Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylates. This was achieved by the cyclocondensation of aromatic aldehydes, malononitrile, and ethylacetoacetate in the presence of the catalytic amount of Maglumine as a readily available, reusable,and biodegradable catalyst. This technique is very promising asit provides mild reaction conditions, an environmentally benign greener approach, easy workup process, high yield, less reaction time, low cost, and recycled up to five catalytic cycles without substantial loss of catalytic activity or product yield.

Introduction

One of the most important challenges in organic synthesis is to design easy synthetic pathways for commonly used organic molecules using easily available reagents. Single-step, one-pot, and three-component condensation reactions are now widely used for the synthesis of various heterocyclic compounds in synthetic organic chemistry.As compared to multistep techniques, one-pot protocols are more efficientasitoffers higher yield in shorter reaction time with easy workup processes.

4*H*-pyranare oxygen-containing heterocyclic moiety, with several biological properties including antibacterial,[1],[2] anticancer,[3]antiviral,[4]antitumor,[5]antifungal, antioxidant[6], [7], and antimicrobial activities[8]as well as shows anti-corrosion properties[9].Asillustrated in **Figure 1**, the

---

**Corresponding Author:* *Bhagwansing Shivsing Dobhal (drbsdobhal@gmail.com)* pyran scaffold acts as asignificant structural motif in various bioactive compounds such as beta-lapachone,alpha-lapachone,zanamivir,laninamivir. Correspondingly, derivatives of 4*H*-pyrans have been found as highly bioactive compounds because of their biodegradable abilities. They are alsofound in cosmetics, dyes, pigments,and agrochemicals[10].Consequently,the organic community has been encouraged to discover an excellent method for the synthesis of 4*H*-pyran.

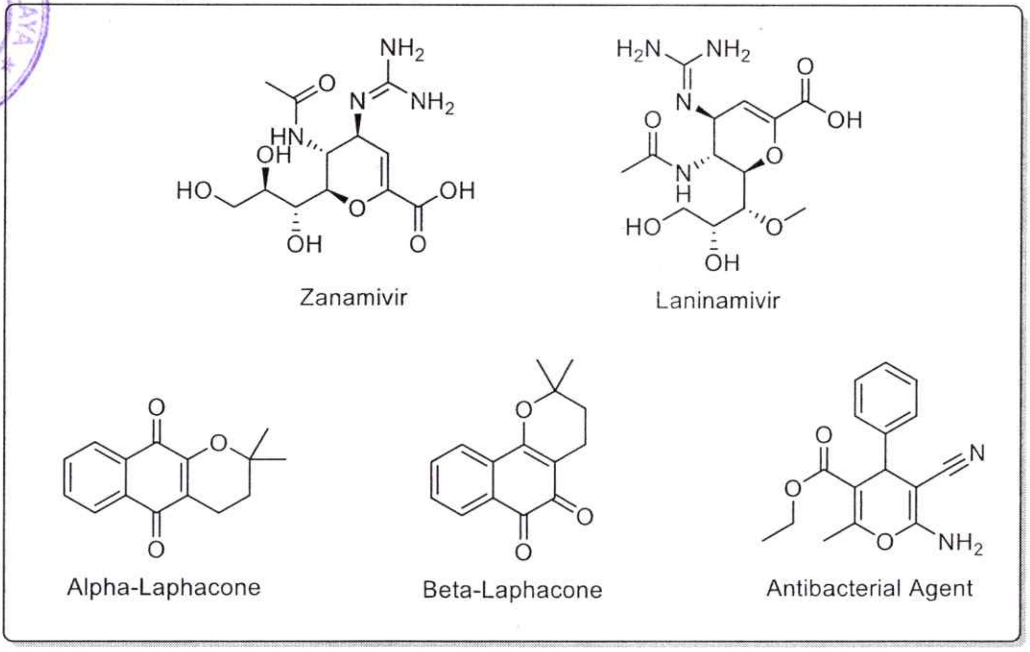


Figure 1. Some pharmacologically active derivatives of pyran

A review of the literature indicates that 4*H*-pyran could be synthesized by several different protocols, which includethe two-step approachas well as the one-pot three-component system.Mostly, 4*H*-pyrans are synthesized by a one-pot cyclocondensationreaction in betweenan aromatic aldehyde, malononitrile, and ethylacetoacetatein presence of a basic catalyst.This synthetic approachwas involved in presence of various catalysts such as $BaFe_{12}O_{19}$@IM,[11]PPh_3,[12]Potassium fluoride,[13]Mg/La mixed oxide,[14] tetramethylguanidine-[bmim][BF_4],[15]potassium phthalimide,[16]molecular sieve-supported zinc,[17]$BNFe_3O_4$,[18]Silica Supported V_2O_5,[19]thiourea dioxide[20]and Baker's yeast.[21]However, these above-mentioned protocols have one or more disadvantages, and the majority of therequired heating conditions and provide moderate yields even after a considerable reaction time. This clearly indicates that there is still scope for improvement in terms of developing an effective and environmentally friendly protocol for the synthesis of 4*H*-pyrans.

Hence, we have planned to synthesize Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylateby using Meglumine as a catalyst.The presence of hydroxyl groupsand an amino groupfrom the Meglumine tends to activate the nucleophilicas well as electrophilic centers, which helps inhydrogen bonding and electron donation.Meglumine shows fantastic propertiessuch as low toxicity, biodegradability, physiological inertness, reusability, low cost, and non-corrosion nature.Because of the above findings andour ongoing efforts [22-25] to developenvironment-friendly synthetic methods for various reactions, herein,we present Meglumine as a biodegradable catalyst for one-pot synthesis of ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylatebyreactingaromatic aldehydes,malononitrile,andethylacetoacetatein Ethanol:Water at room temperature.

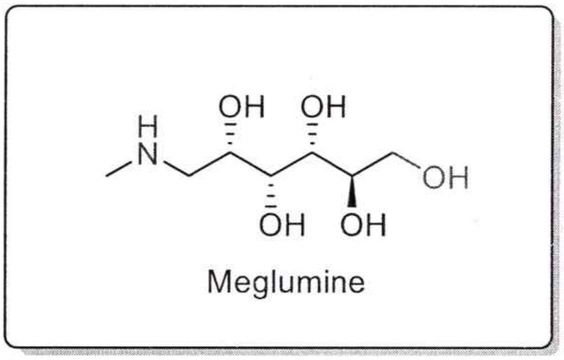
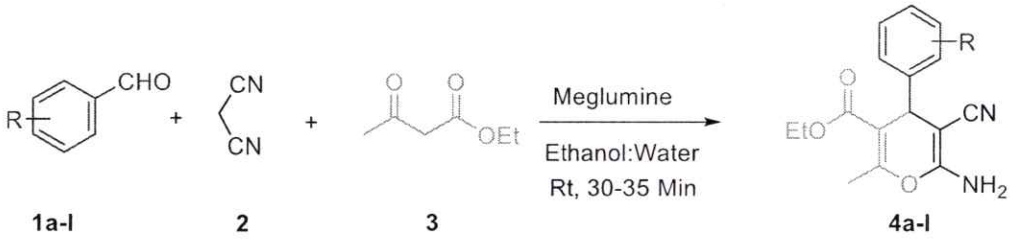


Figure 2. Structure of Meglumine Catalyst

Results and Discussion

The synthesis of Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylatederivativeswas achieved by reacting substituted aromatic benzaldehydes**(1a-l)** with malononitrile**(2)** and ethylacetoacetate**(3)**in ethanol:water in the presence of Meglumine as a catalyst. The product was obtained after stirring the reaction mixture for30-35 minutes at room temperature. Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylatederivatives**(4a-l)** were obtainedwith high purity and better toexcellent yields, as shown in **Scheme 1.**



R= a=H, b=2-Cl, c=4-Cl, d=4-Br,
e=2-Br, f=2-NO_2, g=3-NO_2,
h=4-NO_2, i=4-CH_3, j=4-OCH_3,
k=4-CN, l=4-OH.

Scheme 1. Synthesis of 4*H*-pyran using Meglumine catalyst

The structures of all the newly synthesized Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylates(**4a-l**) are depicted in **Figure 3.**

Optimization of the reaction parameters was performed bymodel reaction of benzaldehyde**(1a)**, malononitrile **(2)**, and ethylacetoacetate **(3)** as shown below.

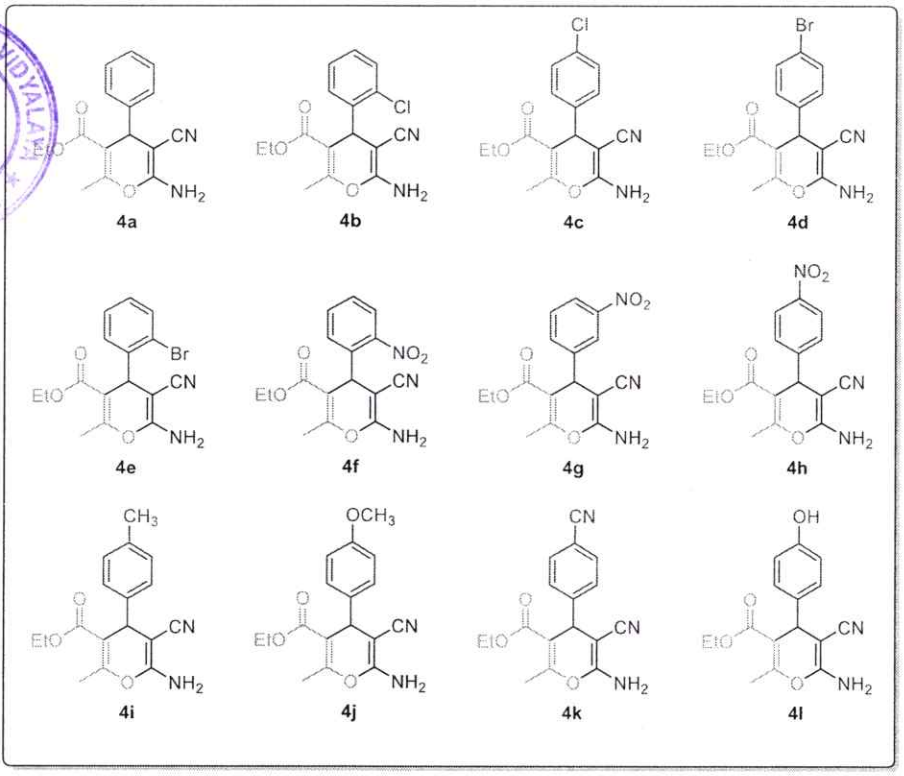
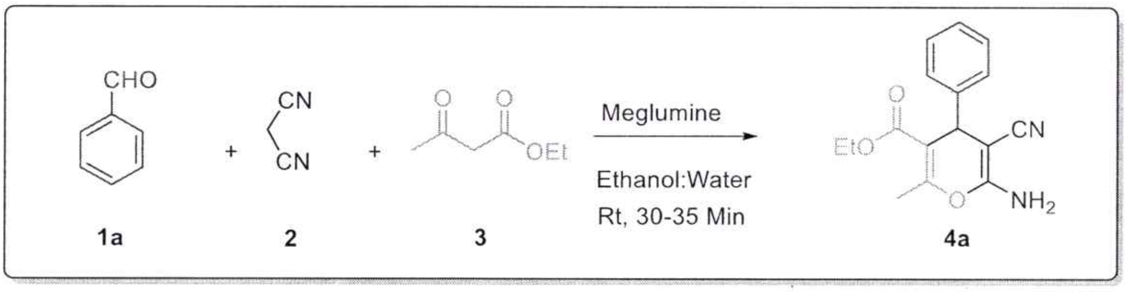


Figure 3. Structures of the synthesized Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate derivatives (**4a-l**)



Scheme 2. Model reaction for Synthesis of 4*H*-pyran

Firstly, we have considered solvent parameters and observed reactions in different solvents like water, methanol, PEG-400, and ethanol as protic solvents as well as DCM, DMF, and acetonitrile as aprotic solvents. We observed that the solvent has an important role in the progress of the reaction. The reaction with ethanol:water gave the corresponding product in good yields, whereas the findings with other solvents such as DCM, DMF, and acetonitrile, yielded the product **4a** in fewer quantities, neither PEG-400 nor water were particularly given good results.Further,it has beendecided the impressive and ideal solvent for this conversion was aqueous ethanol (water:ethanol, 9:1, v/v).

Table 1. Screening of reaction conditions with respect to solvent and catalyst loading **4a**[a]

Entry	Solvent	Catalyst(mol%)	Yield[b](%)
1	Water	10% Meglumine	N R
2	Methanol	10% Meglumine	74
3	Ethanol	10% Meglumine	79
4	PEG-400	10% Meglumine	58
5	DCM	10% Meglumine	26
6	DMF	10% Meglumine	29
7	Acetonitrile	10% Meglumine	31
8	Ethanol:Water(1:1)	10% Meglumine	79
9	Ethanol:Water(9:1)	5% Meglumine	90
10	Ethanol:Water(9:1)	10% Meglumine	96
11	Ethanol:Water(9:1)	15% Meglumine	93
12	Ethanol:Water(9:1)	No catalyst	09

[a]**Reactionconditions:**Benzaldehyde (1mmol), Malononitrile (1mmol), Ethylacetoacetate(1mmol), 10mol% Meglumine in 5 mL ethanol:water, at room temperature for 30-35 min.[b]Isolated yields, NR: No Reaction

However, in the model reaction, the influence of catalyst loading was also investigated. The results revealed that a catalyst concentration of 10mol% was a great choice for this process. Increasing the catalyst concentration 10 to 15mol% resulted in a low effect on yield and not be further increased.When the reaction was conducted with reducing amounts of catalyst, the yield of **4a** could not be further increased.Under optimized conditions when the standard reaction was performed in absence of Megluminethere was less conversion of reactants to products after stirring at room temperature(**Table 1**, entry 12). This result motivates us to investigate the methods for synthesis of Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylates from substituted benzaldehydes,malononitrile, and ethylacetoacetate using a 10mol%Meglumine catalyst and ethanol:water as a solvent in an optimized reaction condition.

The recyclability of the meglumine catalyst was further examined for the standard reaction of benzaldehyde (**1a**), malononitrile (**2**), and ethylacetoacetate(**3**) in ethanol:water solvent at room temperature for 30-35 minutes. The results are shown in **Figure 4**.

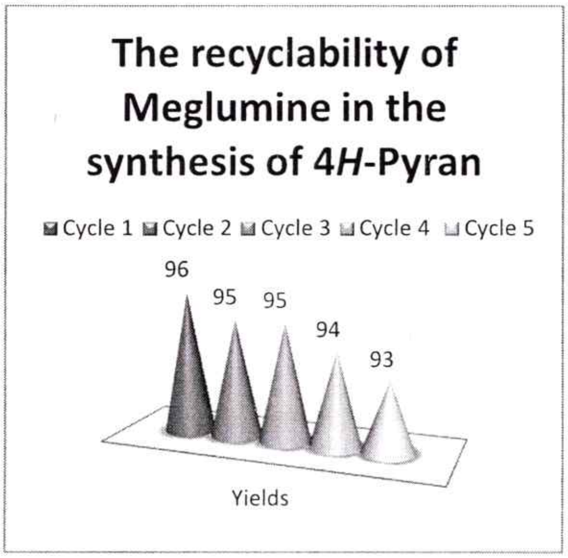
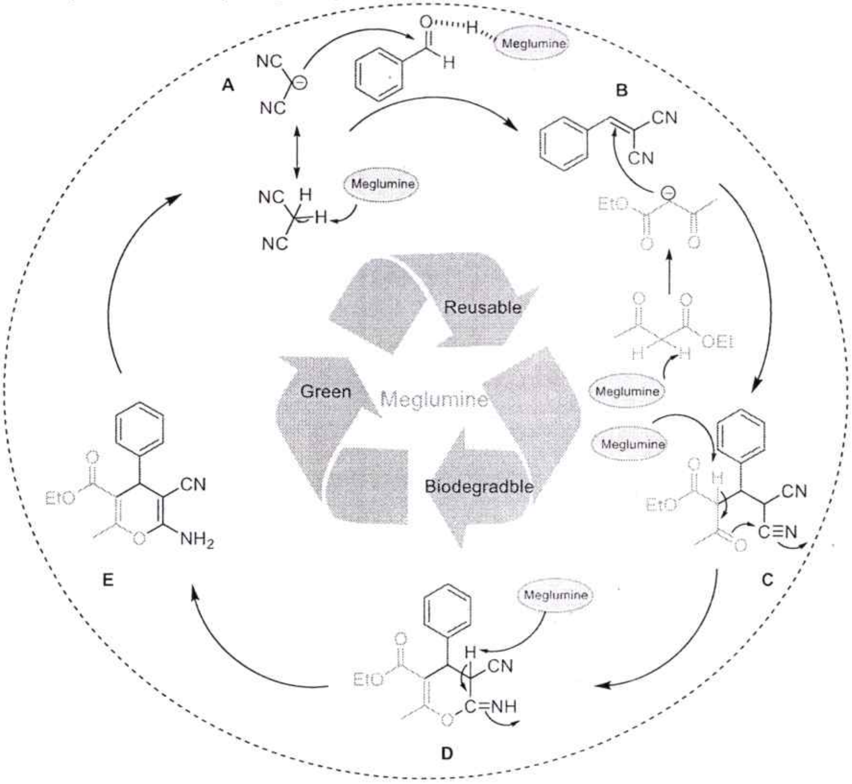


Figure 4. The recyclability of Meglumine[a] in the synthesis of 4*H*-pyran

After the completion of the reaction, the catalyst was recovered andthe filtrate was dried. The recovered catalyst was reused after drying for the next run. The catalyst was reused for four runs, and the target compounds were formed in yields (96% to 94%) in their corresponding reaction periods in each and every reaction.

The plausible mechanism for the synthesis of Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate(**4a**)as shown in **Scheme 3**, involves the proton abstraction of the active methylene group of malononitrile by the Meglumineindicated as **A**, later it reacts with benzaldehyde involves the dehydration resulting in the formation of **B**, which on the attack of active methylene group of ethylacetoacetateto form **C**, after that abstraction of hydrogen by Meglumine from **C** and **D** to form desired product **E**.



Scheme 3. Plausible mechanism for the synthesis of Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylatederivative(**4a**)

Conclusion

Finally, by utilizing Meglumine as a green and recyclable catalyst, we designed a mild, rapid, and environmentally sustainable synthesis process for Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate **(4a-l)** from aromatic benzaldehyde, malononitrile, and ethylacetoacetate.Simple reaction conditions, no side reactions, and high yield product formation are all essential features of the technique. For the synthesis of Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate, the current technique is an alternative to traditional methods. The catalyst was retrieved several times without losing catalytic activity, resulting in a cost-effective method.

Experimental

General experimental procedure for the synthesis of ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate

In a dry and clean 50mL round bottom flask, a mixture of substituted benzaldehyde (1 mmol), malononitrile (1mmol), and ethylacetoacetate(1mmol) was stirred in 5 mL ethanol:water as a solvent along with Meglumine(10 mole%) as a catalyst at room temperature for 30-35 min. The progress of the reaction was monitored by thin-layer chromatography. After the completion of the reaction, the reaction mixture was poured oncrushed ice, which was then filtered. The crude product was crystallized using ethanol to yield pure 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate.The melting points of the products are in good agreement with those described in the literature[26-32].

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (4a)

The compound **(4a)** was synthesized with Megluminecatalyzed reaction in betweenbenzaldehyde**(1a)**,malononitrile**(2)**andethylacetoacetate**(3)** aswhite solid; yield 96%; Mp 190-192°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm):1.00-1.03 (t, 3H, CH_3-CH_2-), 2.31 (s, 3H, CH_3), 3.92-3.99 (m, 2H, CH_2-CH_3), 4.37 (s, 1H, pyran-H), 4.40 (s, 2H, NH_2), 7.12-7.24 (m, 5H, Ar-H).;^{13}C NMR (75 MHz, $CDCl_3$)δ (ppm) :12.86, 17.37, 37.74, 59.65, 76.00, 106.98, 117.80, 126.17, 126.49, 127.56, 142.73, 155.76, 156.39, 164.84.; LCMS (ESI$^+$) calcd. for $C_{16}H_{16}N_2O_3(M+H)^+$: 285.12; found 285.14.

Ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4c)

The compound **(4c)** was synthesized with Megluminecatalyzed reaction in between4-chlorobenzaldehyde**(1c)**,malononitrile**(2)**andethylacetoacetate**(3)** as light yellow solid; yield 94%; mp 138-139°C;^{1}H-NMR (300 MHz, $CDCl_3$)δ (ppm) :1.03-1.05(t, 3H,CH_3-CH_2-), 2.30 (s, 3H,CH_3), 3.96-4.00 (q, 2H,CH_2-CH_3), 4.36 (s, 1H,pyran-H), 4.49 (s, 2H,NH_2), 7.06-7.08 (d, 2H, Ar-H), 7.19-7.20 (d, 2H, Ar-H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) :12.77, 17.30, 37.16, 59.62, 75.88, 106.46, 117.52, 127.59, 127.76, 131.80, 141.24, 155.90, 156.37, 164.49.; LCMS (ESI$^+$) calcd. for $C_{16}H_{15}ClN_2O_3(M+H)^+$: 319.08; found 319.09.

Ethyl 6-amino-5-cyano-2-methyl-4-(2-nitrophenyl)-4H-pyran-3-carboxylate (4f)

The compound **(4f)** was synthesized with Meglumine catalyzed reaction in between2-nitrobenzaldehyde**(1f)**, malononitrile**(2)**andethylacetoacetate**(3)** as yellowish solid; yield 94%;Mp 178-179°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm) :0.88-0.91 (t, 3H, CH_3-CH_2-), 2.31 (s, 3H,CH_3), 3.85-3.87 (q, 2H, CH_2-CH_3), 4.56 (s, 2H, NH_2), 5.16 (s, 1H, pyran-H), 7.17–7.72 (m, 4H, Ar-H).; ^{13}C NMR (75 MHz, $CDCl_3$)δ (ppm):12.51, 17.30, 31.83, 59.79, 75.61, 106.15, 117.00, 122.91, 126.76, 129.46, 132.08, 137.95, 147.95, 156.91, 157.09, 163.89;LCMS (ESI$^+$) calcd. for $C_{16}H_{15}N_3O_5(M+H)^+$: 330.31; found 330.35.

Supporting Information

Full experimental detail, LCMS, ^{1}H, and ^{13}C NMR spectra. This material can be found via the "Supplementary Content" section of this article's webpage.

Acknowledgments

The author G.B.P. is very much thankful to the Council for Scientific and Industrial Research (CSIR), New Delhi, for theaward senior research fellowship. File No. 08/613(0005)/2018-EMR-I

Conflict of Interest

The authors declare no conflict of interest.

Orcid:

Ganesh Baburao Pund
https://orcid.org/0000-0003-1560-6171
Sambhaji Tukaram Dhumal
https://orcid.org/0000-0003-3018-6179
Madhav Janardan Hebade
https://orcid.org/0000-0003-0008-8834
Mazahar Farooqui

https://orcid.org/0000-0003-2236-6639
Bhagwansing Shivsing Dobhal
https://orcid.org/0000-0002-9469-3869

References

[1]R.R. Kumar, S. Perumal, P. Senthilkumar, P. Yogeeswari, D. Sriram, *Bioorganic Med. Chem. Lett.*,**2007**, *17*,6459–6462. [Crossref], [Google Scholar], [Publisher]

[2]D. Kumar, V.B. Reddy, S. Sharad, U. Dube, S. Kapur, *Eur. J. Med. Chem*., **2009**, *44*, 3805–3809. [Crossref], [Google Scholar], [Publisher]

[3]W. Kemnitzer, J. Drewe, S. Jiang, H. Zhang, C. Crogan-Grundy, D. Labreque, M. Bubenick, G. Attardo, R. Denis, S. Lamothe, H. Gourdeau, B. Tseng, S. Kasibhatla, S.X. Cai, *J. Med. Chem*.,**2008**, *51*,417–423. [Crossref], [Google Scholar], [Publisher]

[4]P.G. Wyatt,B.A. Coomber, D.N. Evans, T.I. Jack, H.E. Fultone, A.J. Wonacott, P. Colman, J. Varghese, *Bioorganic Med. Chem. Lett*.,**2001**,*11*, 669–673. [Crossref], [Google Scholar], [Publisher]

[5]M. Kidwai, S. Saxena, M.K.R. Khan, S.S. Thukral, *Bioorganic Med. Chem. Lett*.,**2005**, *15*,4295–4298.[Crossref], [Google Scholar], [Publisher]

[6]L. Moafi, S. Ahadi, A. Bazgir, *Tetrahedron Lett*.,**2010**, *51*,6270–6274.[Crossref], [Google Scholar], [Publisher]

[7]M.G. Dekamin, M. Eslami, A. Maleki, *Tetrahedron*,**2013**, *69*,1074–1085.[Crossref], [Google Scholar], [Publisher]

[8]C.B. Sangani, D.C. Mungra, M.P. Patel, R.G. Patel, *Chinese Chem. Lett*.,**2012**,*23*, 57–60. [Crossref], [Google Scholar], [Publisher]

[9]A. El Hattak, S. Izzaouihda, Z. Rouifi, F. Benhiba, S. Tabti, A. Djedouani, N. Komiha, H. Abou El Makarim, R. Touzani, H. Oudda, I. Warad, A. Zarrouk, *Chem. Data Collect*.,**2021**, *32*, 100655.[Crossref], [Google Scholar], [Publisher]

[10] E. Abdel, A. Hafez, M.H.Elnagdi,*Heterocycles*,**1987**,*26*,903–907.[Crossref], [Google Scholar], [Publisher]

[11] S. Amirnejat, A. Nosrati, R. Peymanfar, S. Javanshir, *Res. Chem. Intermed*.,**2020**, *46*, 3683–3701.[Crossref], [Google Scholar], [Publisher]

[12] S.S. Ramadoss, H. Kiyani, H. Mansoor,*Iran. J. Chem. Chem. Eng*.,2017, 36,19–26.[Crossref], [Google Scholar], [Publisher]

[13] B. Maleki, S. Sheikh, *Org. Prep. Proced. Int*.,**2015**, *47*, 368–378. [Crossref], [Google Scholar], [Publisher]

[14] N. Seshu Babu, N. Pasha, K.T. Venkateswara Rao, P.S. Sai Prasad, N. Lingaiah, *Tetrahedron Lett*.,**2008**, *49*, 2730–2733. [Crossref], [Google Scholar], [Publisher]

[15] Y. Peng, G. Song, F. Huang, *Monatshefte fur Chemie*,**2005**, *136*,727–731.[Crossref], [Google Scholar], [Publisher]

[16] H. Kiyani, F. Ghorbani, *J. Saudi Chem. Soc*.,**2014**, *18*, 689–701.[Crossref], [Google Scholar], [Publisher]

[17] A. Magyar, Z. Hell,*Green Process. Synth*.,**2018**, *7*,316–322.[Crossref], [Google Scholar], [Publisher]

[18] A. Molla, S. Hussain, *RSC Adv*., **2016**, *6*,5491–5502.[Crossref], [Google Scholar], [Publisher]

[19] E.A. Mostafa, T.K. Khatab, *Org. Chem. An Indian J. Res*.,**2018**, *14*, 2–7. [Crossref], [Google Scholar], [Publisher]

[20] S.S. Mansoor, K. Logaiya, K. Aswin, P.N. Sudhan,*J. Taibah Univ. Sci*.,**2015**, *9*,213–226. [Crossref], [Google Scholar], [Publisher]

[21] U.R. Pratap, D.V. Jawale, P.D. Netankar, R.A.Mane, *Tetrahedron Lett*., **2011**,*52*, 5817–5819.[Crossref], [Google Scholar], [Publisher]

[22] M.J. Hebade, R.D. Kamble, S.V. Hese, P.P. Mogle, A.N. Ambhore, S.N. Kadam, B.S. Dawane, *Phosphorus, Sulfur Silicon Relat. Elem*.,**2016**, *191*, 1155–1159.[Crossref], [Google Scholar], [Publisher]

[23] S.N. Kadam, A.N. Ambhore, M.J. Hebade, R.D. Kamble, S.V. Hese, M.V. Gaikwad, P.D. Gavhane, B.S. Dawane, *Synlett*,**2018**, *29*, 1902–1908.[Crossref], [Google Scholar], [Publisher]

[24] S.T. Dhumal, A. Deshmukh, K.R. Kharat, B.R. Sathe, R.A.Mane,*New J. Chem*., **2019**, 1–27. [Crossref], [Google Scholar], [Publisher]

[25] M.J. Hebade, T.R. Deshmukh, S.T. Dhumal, *Synth. Commun*.,**2021**, *51*, 2510–2520. [Crossref], [Google Scholar], [Publisher]

[26] P.B. Hiremath, K. Kantharaju, *ChemistrySelect*, **2020**, *5*, 1896–1906. [Crossref], [Google Scholar], [Publisher]

[27] M. Kamalzare, M. Bayat, A. Maleki, *R. Soc. Open Sci.*,**2020**, *7*,200385.[Crossref], [Google Scholar], [Publisher]

[28] A. Sanchez, F. Hernandez, P.C. Cruz, Y. Alcaraz, J. Tamariz, F. Delgado, M.A. Vazquez, *J. Mex. Chem. Soc.*, **2012**, *56*, 121–127. [Crossref], [Google Scholar], [Publisher]

[29] A.M. Zonouz, D. Moghani, *Commun. Catal.*,**2018**, *1*,13–20. [Crossref], [Google Scholar], [Publisher]

[30] B. Chowhan, M. Gupta, N. Sharma, *ChemistrySelect*,**2019**, *4*, 12689–12700. [Crossref], [Google Scholar], [Publisher]

[31] A. Moshtaghi Zonouz, D. Moghani, S. Okhravi, *Curr. Chem. Lett.*,**2014**, *3*, 71–74. [Crossref], [Google Scholar], [Publisher]

[32] R. Smits, S. Belyakov, A. Plotniece, G. Duburs, *Synth. Commun.*,**2013**, *43*, 465–475. [Crossref], [Google Scholar], [Publisher]

साहित्य, कला आणि लोकसंस्कृतीला वाहिलेले त्रैमासिक

तिफण

वर्ष १३ वे, अंक - पहिला; एप्रिल-मे-जून २०२२

UGC Care Listed Journal
ISSN 2231 - 573X

● संपादक ●

डॉ. शिवाजी हुसे

पत्ता : संपादक, तिफण, 'शिवार', श्रीराम कॉलनी,
हिवरखेडा रोड, कन्नड, जि. औरंगाबाद - ४३११०३
मो. ९९०४००३९९८

UGC Care Listed Journal ISSN 2231 - 573X

साहित्य, कला आणि लोकसंस्कृतीला वाहिलेले त्रैमासिक

तिफण

MAH MAR 34737/13/1/2009-TC

वर्ष १३ वे, अंक - पहिला; एप्रिल-मे-जून २०२२

कुळवाडीभूषण छत्रपती शिवाजी महाराज विशेषांक

[भाग-३]

● संपादक ●

डॉ. शिवाजी हुसे

● अतिथी संपादक ●

डॉ. सर्जेराव जिगे डॉ. यशवंत सोनुने

मूल्य : २५० रुपये

पत्ता : संपादक, तिफण, 'शिवार', श्रीराम कॉलनी, हिवरखेडा रोड,
कन्नड, जि. औरंगाबाद – ४३११०३, मो. ९९०४००३९९८

छत्रपती शिवाजी महाराजांचा धार्मिक दृष्टिकोन : चिकित्सक मांडणी

- प्रा. डॉ. विकास मोहन सरनाईक
इतिहास विभाग, रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद
ई-मेल : sarnaik.viki@gmail.com

छत्रपती शिवाजी महाराज (इ.स. १६३०-१६८०) यांची कारकीर्द मध्ययुगीन भारताच्या इतिहासातील एक वैशिष्ट्यपूर्ण कालखंड होता. मध्ययुगात, महाराष्ट्रातच नव्हे, तर जगभर विविध धर्मांचा प्रभाव असलेली धर्माधिष्ठित राज्ये निर्माण झालेली होती. या काळात धर्माने राज्यकर्त्यांवरच नव्हे, तर संपूर्ण समाजावर आपले प्रभावक्षेत्र निर्माण केले होते. परिणामी, तत्कालीन राजेही धर्माच्या प्रभावापासून अलिप्त राहिली नाहीत. या काळात बहुतांश राज्याच्या निर्मितीमागील मुख्य उद्देश धर्मरक्षण व धर्मविस्तार असा होता. परिणामी, तत्कालीन राज्याच्या उदयापासून ते राज्यविस्तारवादी धोरणापर्यंत सर्वत्र धर्माचा आधार घेणे क्रमप्राप्त होते, कळीचा मुद्दा म्हणजे धर्माच्या आधाराशिवाय राज्याला जनतेची अधिमान्यता मिळणे जवळपास अशक्य होते.

या सर्व पार्श्वभूमीवर मध्ययुगीन भारताचा विचार करता, दिल्लीचे सुलतान आणि त्यानंतर आलेले मुघल हे मध्ययुगीन भारतीय इतिहासातील प्रमुख राज्यकर्ते इस्लाम धर्मीय होते. इस्लाम धर्माचा उदय महंमद पैगंबर यांनी मध्य आशियात केला. पैगंबरांनंतर इस्लाम धर्माचे सर्व हक्क अधिकार खलिफाने स्वतःकडे केंद्रित केले. खलिफा धर्म व राजकारणाचा केंद्र बनला. तो इस्लाम धर्माचा प्रचार आणि प्रसारासाठी महत्त्वाकांक्षी सुलतानांना धर्माचा पाठिंबा देऊ लागला, विशिष्ट हक्क व अधिकार बहाल करू लागला. मध्ययुगीन भारतात आलेल्या मुस्लीम सत्ताधीशांनीही खलिफाच्या परवानगीने आणि निर्देशानुसारच राज्य सुरू केलं. मात्र भविष्यात राज्यकर्त्यांवरील खलिफाचे नियंत्रण कमजोर होत गेल्याने स्थानिक गरजेनुसार सत्ताधीश आपल्या धार्मिक व राजकीय धोरणात परिवर्तन करू लागले. या मुस्लीम सत्तेने भारतावर जवळपास सहाशे वर्षे राज्य केले. या काळात अपवाद सोडल्यास बहुतांश सत्ताधीशांनी हिंदू धर्माविषयी सामंजस्य व समन्वयाची भूमिका घेतली. ज्या इस्लामधर्मीय राज्यकर्त्यांनी हिंदूंचे मुस्लीम धर्मात धर्मांतर केले. मंदिरे फोडली व लुटली. यामागचा प्रमुख हेतू हिंदूंच्या मनामध्ये देवाविषयी श्रद्धा विशेषतः देव आपला तारणहार आणि रक्षणकर्ता असल्याची भावना होती, जर देवालाच फोडून काढले, तर हिंदू समाजाचे मानसिक खच्चीकरण होईल आणि दुसरे म्हणजे मंदिरातील प्रचंड संपत्तीची लूट करण्याचा होता. असे असले तरी प्रत्येक राज्यकर्त्याने धर्मांतर करणे आणि मंदिरे फोडणे हेच उद्दिष्ट ठेवले नाही. असे असते तर इस्लामधर्मीय सत्ताधीशांच्या ६०० वर्षांच्या काळानंतरचे भारताचे चित्र खूपच वेगळे दिसले असते. यावरून इतके स्पष्ट होते की, तत्कालीन सत्ताधीश जरी धर्माच्या प्रभावाखाली असले तरीही त्यांनी आपल्या प्रशासनात धर्म व राजकारण हे वेगवेगळे ठेवण्याचा प्रयत्न केला होता, त्यामध्ये ते निश्चितच यशस्वी झालेले दिसतात. उपरोक्त विवेचनाच्या प्रकाशात प्रस्तुत संशोधकाने छत्रपती शिवरायांच्या धार्मिक धोरणाची चिकित्सा करण्याचा प्रयत्न केलेला आहे.

शिवाजी महाराज धर्मनिरपेक्ष, धर्मसहिष्णू की निधर्मी? -

कोणताही समाज आपला वारसा व मुळे भूतकाळात शोधण्याचा प्रयत्न करत असतो. वर्तमान काळातील काही विशिष्ट व्यक्ती किंवा समूह स्वतःच्या स्वार्थासाठी, स्वतःची अशी तथाकथित मते किंवा विचार भूतकाळावर व वर्तमानकाळावर लादण्याचा प्रयत्न करत असतो. आपल्या मताच्या समर्थनार्थ त्या व्यक्ती व समूह आपल्या सोयीचे पुरावे/संदर्भ गोळा करतो अथवा वेळप्रसंगी तशी साधने तयारही करतो. याआधारे शिवरायांच्या धार्मिक धोरणाबाबत विचार करता, या धोरणाची मुळे शोधावी लागतील, ती आपल्याला १९ व्या शतकात सापडतात. ब्रिटिशांनी भारतावर सत्ता प्रस्थापित केल्यानंतर 'फोडा आणि राज्य करा' धोरणाचा

पुरस्कार केला. त्यानुसार हिंदू आणि मुस्लीम या दोन स्वतंत्र विचारांच्या व वेगळ्या इतिहास असलेल्या जमाती आहेत, असे इतिहास व राजकारणाच्या माध्यमातून पटवून देण्यास सुरुवात केली. या धोरणाला यश येऊन भारताची धर्माधारित फाळणी झाली. यानंतरही स्वतंत्र भारतात परंपरावादी, फुटिरतावादी व धर्माचा राजकारणाठी वापर करून सत्ता मिळवण्याचा प्रयत्न करणाऱ्या गटाकडून इतिहासातील शिवरायांच्या धार्मिक धोरणाची सोयीनुसार मांडणी केली. कोणत्याही कालखंडात परस्परांच्या विरोधात उभे राहणारे सत्ताकांक्षी, सत्ताधीश वा सत्तावंचित कोणत्या ना कोणत्या धर्माचे असतातच. त्यांच्यातील राजकीय महत्त्वाकांक्षेला, ध्येयवादाला दोन धर्मातील परस्परविरोधी संघर्ष मानणे चुकीचे ठरेल. तरीही याची पुनरावृत्ती जाणीवपूर्वक होतेय किंवा केली जातेय. त्यामुळे धर्मनिरपेक्षता, धर्मसहिष्णुता व निधर्मी या संकल्पना आधी थोडक्यात समजून घेणे व त्याद्वारे शिवाजी महाराजांच्या धार्मिक धोरणाची चिकित्सा करणे गरजेचे आहे.

१) **धर्मनिरपेक्षता** - "वैयक्तिक किंवा सामाजिक जीवनात उपस्थित होणारे प्रश्न सोडविताना त्यांच्याकडे धर्मनिरपेक्ष दृष्टीने, म्हणजेच मानवाच्या ऐहिक कल्याणाच्या दृष्टिकोनातून पाहावे मग हे प्रश्न नीती, शिक्षण, अर्थ, राजकीय व सामाजिक संस्था इ. जीवनाच्या कोणत्याही क्षेत्रातील असोत. या भूमिकेस धर्मनिरपेक्षता म्हणतात. मात्र धर्मनिरपेक्ष म्हणजे अपवित्र, धर्माबद्दल असहिष्णू असे नाही, धर्मनिरपेक्ष म्हणजे ऐहिक जीवनाची व्यवस्था लावताना धर्मकल्पना अप्रस्तुत होत त्यांच्याऐवजी शास्त्रीय ज्ञान, मानवी मूल्ये आणि विवेकनिष्ठ यांचे साहाय्य घेणे."[१]

२) **धर्मसहिष्णुता** - "आपल्या जीवनात अवतीभोवती निरनिराळ्या व्यक्ती वावरत असतात या सर्वांच्या जाती-पाती, धर्म, स्वभाव, वृत्ती, श्रद्धा, प्रथा अशा भेदावरून त्यातील कोणाची व्यक्तीचे मूल्यमापन न करणे यास धर्म सहिष्णुता म्हणता येईल."[२]

३) **निधर्मी राज्य** - "निधर्मी राज्य म्हणजे सर्वधर्मसमभाव व धर्मनिरपेक्ष स्वरूपाचे राज्य होय."[३]

उपरोक्त धर्मनिरपेक्षता, धर्मसहिष्णुता व निधर्मी या तिन्ही संकल्पना आधुनिक काळातील आहेत, हे आपण सर्वप्रथम मान्य केले पाहिजे, या तिन्ही संकल्पना आधुनिक काळातील शासन करण्यासाठी त्याच्या नियंत्रण व प्रगतीसाठी उपयुक्त असलेल्या दिसतात. ज्यामध्ये कोणत्याही विशिष्ट धर्माने दुसऱ्या विशिष्ट धर्मावर अतिक्रमण किंवा त्यांच्या मूलभूत हक्कांवर नियंत्रण आणू शकत नाही. हे सर्व [illegible] आहे.

असे असले तरीही मध्ययुगीन कालखंडातील सम्राट अकबर, छत्रपती शिवाजी महाराज यासारख्या राज्यकर्त्यांनी त्यांच्या काळाच्या मर्यादेत राहून धर्मनिरपेक्षता, धर्मसहिष्णुता व निधर्मी या धोरणाच्या बाबतीत आपल्या भूमिका घेतल्या. त्यांचा थोडक्यात परामर्श पुढीलप्रमाणे घेता येईल.

धर्मनिरपेक्षता, धर्मसहिष्णुता व निधर्मी राज्य शिवरायांची विचारधारणा -

छत्रपती शिवाजी महाराज ज्या पार्श्वभूमीतून उदयास आले, त्याचा अभ्यास केल्यास आपल्याला दिसून येते की त्यांचे पूर्वज मुस्लीम सत्तेचे सरदार होते. त्यांच्या आजोबा, वडिलांनी इस्लामी राज्यकर्त्यांची सेवा केली. तरीही मुस्लीम सत्ताधिशांनी त्यांचे धर्मांतर केले नव्हते, उलटपक्षी शिवरायांच्या पूर्वजांना त्यांनी मानसन्मान दिला. प्रत्यक्ष शिवरायांचे वडील शहाजीराजे व चुलते शरीफजी यांचे नावही अहमदनगरच्या शाहशरीफ या मुस्लीम फकिरापासून होते. परिणामी, शिवरायांनी स्थापन केलेल्या स्वराज्यातही त्यांनी राजकारण व धर्मकारण हे वेगळे ठेवण्याचा जाणीवपूर्वक प्रयत्न केल्याचा व हिंदू-मुस्लीम समन्वय साधल्याचा दिसून येतो. उदाहरणार्थ,

१) विजापूरचे प्रदेश जिंकल्यानंतर त्या प्रदेशातल्या मशिदी व दर्गे यांना असलेले धार्मिक अनुदान पुढेही चालू सुरू ठेवले. केळशीचे बाबा याकूत हे मुस्लीम संत होते, ज्यांना शिवराय खूप आदर्श व मान देत.

२) आपल्या शत्रूलाही मानसन्मान देणे, मृत्यूनंतर शत्रुत्व संपते असा विचार करून शिवरायांनी अफझलखानाच्या मृत्यूनंतर प्रतापगडाच्या पायथ्याशी त्याची कबर बांधली.

३) शिवरायांनी केवळ ब्राह्मण पंडित, ज्योतिषी, हिंदू साधू-संत यांनाच अनुदाने व पेन्शन दिली नाही, तर मुस्लीम बैरागी, साधू यांनाही स्वखर्चाने मठ बांधून दिले.

४) राज्याभिषेकाच्या वेळी रायगडावर जगदीश्वराचे मंदिर बांधले त्याचबरोबर आपल्या मुस्लीम बांधवांसाठी राजांनी स्वतःच्या महालासमोर मशीद बांधून घेतली.

५) सैन्य आणि प्रशासनात मुसलमानांना स्थान दिले. महाराजांनी काझी हैदर यांची मुख्य वकील म्हणून नियुक्ती केली. जो स्वराज्याच्या स्थापनेपासून एकमेव ब्राह्मणेतर वकील होता, जो मुस्लीम धर्माचा असूनही

त्याची पात्रता पाहून त्यास नियुक्त केले. इ.स.१६७०-७१ मध्ये औरंगजेबाचे सरदार बहादूरखान आणि दिलेरखानाबरोबर चर्चा करण्यासाठी स्वराज्याचा वकील म्हणून राजांनी त्याला पाठवलेला इतिहास आहे, तसेच अनेक मुस्लीम सैनिक होते जे शिवरायांशी अत्यंत प्रामाणिक होते. त्यामध्ये नौदल प्रमुख दौलतखान, शरीरसंरक्षक इब्राहिम बर्बर, शागिर्द मदारी मेहतर (मदारी मेहतरच्या मृत्यूनंतर त्यांची समाधी/कबर शिवरायांनी रायगडावर बांधून घेतली.) शिवरायांच्या कार्याची महती ऐकून विजापूरहून ७०० पठाण सेवेत रुजू झाले.[७]

६) औरंगजेब बादशहाचा दरबारी इतिहासकार भीमसेन सक्सेना आणि खाफीखान यांनीही शिवरायांच्या धार्मिक धोरणाची स्तुती केल्याचे दिसते, त्यांनी नमूद केले आहे की, 'शिवाजीचा आपल्या सैन्यांना सक्त आदेश होता की, मोहिमेवर असताना सैन्याने मशिदीस अथवा कुराणास इजा पोहोचवू नये, कुराणाची प्रत सापडल्यास ती पूज्य भावनेने आपल्या मुस्लिम सहकाऱ्याच्या स्वाधीन करावी.'[८]

७) औरंगजेब बादशहाने मुस्लिमेतरांना इ.स. १६७९ मध्ये जिझिया हा धार्मिक कर सुरु केला. शिवरायांनी या जिझियाला विरोध करून बादशहाला त्याच्या डोळ्यात झणझणीत अंजन घालणारे पत्र पाठवले. त्यामध्ये शिवराय जगत्गुरू सम्राट अकबराचा दाखला देतात, पुढे जाऊन ते ईश्वर आणि अल्ला एकच असून मंदिर आणि मशीद या दोन्ही ठिकाणी आपल्या ईश्वराचीच आराधना होते, त्यामुळे यामध्ये कोणतीही विभागणी अथवा दुजाभाव करू नये, असा उपदेशही करताना दिसतात.[९]

परंपरागत हिंदू धर्मातील अंधश्रद्धा, रूढी-परंपरा यांना फाटा दिला -

१. शिवाजी महाराजांनी सतीप्रथेला विरोध केला. विशेषत: शहाजीराज्यांच्या मृत्यूनंतर मातोश्री जिजाऊंना सती जाण्यापासून रोखले, शिवाय जबरदस्तीने सती देणे बंद केले.

२. सिंधूबंदी म्हणजे, समुद्राच्या खाऱ्या पाण्यावरून प्रवास करण्यावर निर्बंध होय. हिंदू धर्मीयांनी समुद्र प्रवास केल्यास धर्मबहिष्कृत करण्याची शिक्षा स्मृतिग्रंथामध्ये सांगितली आहे. त्यामुळे एकेकाळी समुद्रावर लीलया संचार करून सागरी व्यापारावर वर्चस्व ठेवणारे भारतीय यापासून वंचित झाले. परकीय व्यापार व संपर्क यामुळे जाणीवपूर्वक तोडला गेला; मात्र तत्कालीन राजकीय गरज व आरमाराचे महत्त्व ओळखून इ.स. १६५९ मध्ये छत्रपती शिवरायांनी शेकडो वर्षे चालत आलेला हा कायदा मोडून स्वतःचे आरमार उभे केले.[१०]

३. प्राचीन काळापासून अस्पृश्यता हा भारतीय समाजाला लाभलेला एक भयंकर शाप होता; मात्र शिवरायांनी स्वराज्य उभारणीत हेटकरी, रामोशी, न्हावी, महार, मांग, कोळी, भंडारी आदी अस्पृश्य जाती-जमातींना सामावून घेतले आणि हजारो वर्षांच्या या शापित परंपरेला छेद देण्याचे कालातीत काम केले.

४. अंधश्रद्धा, शकुन-अपशकुन या भारतीय समाज व धर्माला लागलेल्या जळू होत्या. यांना बाजूला सारून शिवरायांनी यावर मात केली. याचे उदाहरण म्हणजे त्यांनी काढलेल्या प्रत्येक युद्धमोहिमा या अमावास्येच्या तोंडावर होत्या. छत्रपती राजाराम महाराज पालथे जन्माला आले त्यावेळी हा अपशकून आहे असे बोलले जात असतानाच शिवराय म्हणाले की, मुघली साम्राज्य पालथे घालण्यासाठीच बाळराजांनी पालथा जन्म घेतलेला आहे.

५. बजाजी निंबाळकर, पिलाजी प्रभू, श्यामजी रावजी, नेताजी पालकर या जबरदस्तीने धर्मांतर केलेल्यांना पुन्हा हिंदू धर्मात घेतले.

६. ब्राह्मण हे पृथ्वीवरील देव आहेत, त्यांची हत्या करणे म्हणजे महापाप मानले जात होते; मात्र विजापूरचा सरदार अफझलखानाच्या मोहिमेवेळी झटापटीत खानाचा वकील कृष्णाजी भास्कर कुलकर्णी याला शिवरायांनी ठार केले. त्यावेळी तो ब्राह्मण आहे म्हणून महाराज गप्प बसले असते, तर त्यांना स्वतःचा जीव गमवावा लागला असता. अशी अनेक उदाहरणे देता येतील की, ज्यामधून शिवरायांनी विवेक आणि तर्कबुद्धीचा वापर केल्याचे दिसते. त्यांनी केव्हाही धर्माचा अतिरेक सहन केला नाही किंवा धर्मावर अंधविश्वास ठेवला नाही.

शेवटी मध्ययुगीन काळात, काळाच्या मर्यादेतही

शिवाजी महाराजांनी धर्म, जात आणि पंथ यांविषयी व्यापक व सर्वसमावेशक भूमिका स्वीकारून स्वराज्य स्थापन केले व ते रुजवले. स्वराज्यामध्ये प्रत्येक जात व धर्माला त्यांच्या-त्यांच्या म्हणून मर्यादा घालून देऊन त्यांना हक्क व अधिकार दिले. धर्मांधता आणि धर्मद्वेषपणामुळे कपाळमोक्ष होतो, राज्य साधत नाही हे महाराजांनी पुरते ओळखले होते, म्हणूनच त्यांनी आलमगीर बादशहा औरंगजेबाला सावधही केले होते; मात्र त्याचा काही उपयोग झाला नाही. शेवटी धर्मांधतेमुळे औरंगजेबाचा कपाळमोक्ष होऊन मुघल सत्तेचा ऱ्हास झाला.

आज २१ व्या शतकातही भारतात हिंदू आणि मुस्लीम धर्मातील बरेच राजकारणी औरंगजेबाचा वारसा चालवण्यासाठी तत्पर आहेत जे स्वतःबरोबरच देशाचा कपाळमोक्ष करण्यासाठी संधी शोधत आहेत; मात्र भारतीय राज्यघटनेने धर्मनिरपेक्ष राज्याचा पुरस्कार केल्यामुळे त्यांच्यावर अंकुश ठेवला आहे. तरी मात्र विध्वंसक प्रवृत्तीचे लोक शिवाजी महाराजांना मुस्लीम द्वेष्टे/ विरोधी, कट्टर हिंदुत्ववादी म्हणून उभे करून मुस्लीम धर्मीयांवर सूड उगवण्याचे नाहक राजकारण करताना दिसतात. यासाठी ते जहाल व भडक आणि बऱ्याचदा टोकाची मांडणी करतात. ही मांडणी समाजिक शांतता व सहजीवन भंग करणारी असते, जी भारतासारख्या धर्मनिरपेक्ष आणि सहिष्णू देशास घातक आहे.

वास्तविक परधर्म सहिष्णुता, धर्मस्वातंत्र्य, सुधारणेबद्दलची आवड आणि परस्पर सहकार्य आणि सामंजस्य इत्यादी गुणांच्या मदतीनेच आपणास धर्मनिरपेक्ष राष्ट्राची भक्कमता वाढवता येईल, यासाठी समाज, राज्यकर्ते आणि सरकार सर्वांचे वर्तन सहानुभूती, समत्वबुद्धी आणि न्याय या तत्त्वाप्रमाणे पाहिजे, स्वातंत्र्याच्या पूर्वसंध्येवर भारताने फाळणी पचवून आणि अनेक धर्मविग्रहाच्या विनाशकारी चळवळींना तोंड देत धर्मनिरपेक्षतेच्या मार्गावर वाटचाल चालू ठेवली आहे. यामध्ये अनेक अडथळे आले व येत राहतील. त्याला शरण न जाता, भारतातील विविध भाषा, धर्म, पंथ आणि संस्कृती या सर्वांचे जपणूक करणारे 'धर्मनिरपेक्षता' हे तत्त्व आपण स्वीकारले आहे, ते टिकवले पाहिजे. शिवाय आपले पूर्वसुरी बादशहा अकबर आणि छत्रपती शिवाजी महाराज यासारख्यांचे विचार व कार्याचाही आदर्श समोर ठेवला पाहिजे, तरच देशाचा विनाश आणि विघटन टळू शकते.

संदर्भ -

१. https://vishwakosh.marathi.gov.in/19225/

२. https://hi.wikipedia.org/wiki

३. https://www.weeklysadhana.in / view_article / nilam-gorhe-on-secularism-and-womens

४. Sen S.N., '*The Military System of Maratha*', Orient Longmans Pvt Ltd, Bombay, 1958, p.n. 18

५. Sarkar, Jadunath, '*Shivaji and His Times*', Orient Longman Ltd., Bombay, 1952, p.n. 30

६. Sardesai, G.S., '*New History of Maratha's*', Phoenix Publication, Bombay, 1948, p.n. 264-265

७. Mahajan T.T., '*Shivaji and his diplomats*', Commonwelth, New Delhi1991, p. 5-6.

८. कुलकर्णी अ. रा., खरे ग. ह. (संपा.), '*मराठ्यांचा इतिहास*' खंड पहिला, कॉन्टिनेंटल, पुणे, प्रथम आवृत्ती १९८४. पृ. ३६३-६४

८. Pagdi Setumadhvrao, '*Chhatrpati Shivaji*' Continental, Poona, 1947, p.n. 39

९. कुलकर्णी अ. रा., खरे ग. ह. (संपा.), उपरोक्त पृ. ३६३-६४

१०. शिखरे चंद्रशेखर, *प्रतिइतिहास (शिवइतिहासाचे सत्यस्वरूप)*', जिजाई प्रकाशन, २००५, पृ. ३९

◆ ◆ ◆ ◆ ◆

ISSN 2277 - 5730
AN INTERNATIONAL MULTIDISCIPLINARY
QUARTERLY RESEARCH JOURNAL

AJANTA

Volume - XI Issue - II April - June - 2022

MARATHI PART - II

Peer Reviewed Refereed
and UGC Listed Journal

Journal No. 40776

IMPACT FACTOR / INDEXING
2020 - 6.306
www.sjifactor.com

❖ EDITOR ❖
Asst. Prof. Vinay Shankarrao Hatole
M.Sc (Maths), M.B.A. (Mktg.), M.B.A. (H.R.),
M.Drama (Acting), M.Drama (Prod. & Dir.), M.Ed.

❖ PUBLISHED BY ❖

Ajanta Prakashan
Aurangabad. (M.S.)

EDITORIAL BOARD

Professor Kaiser Haq
Dept. of English. University of Dhaka,
Dhaka 1000, Bangladesh.

Dr. Ashaf Fetoh Eata
College of Art's and Science
Salman Bin Adbul Aziz University. KAS

Muhammad Mezbah-ul-Islam
Ph.D. (NEHU, India) Assot. Prof. Dept. of
Information Science and Library Management
University of Dhaka, Dhaka - 1000, Bangladesh.

Dr. S. Sampath
Prof. of Statistics University of Madras
Chennai 600005.

Dr. S. K. Omanwar
Professor and Head, Physics,
Sat Gadge Baba Amravati
University, Amravati.

Dr. Shekhar Gungurwar
Hindi Dept. Vasantrao Naik
Mahavidyalaya Vasarni, Nanded.

Dr. S. Karunanidhi
Professor & Head,
Dept. of Psychology,
University of Madras.

Dr. Walmik Sarwade
HOD Dept. of Commerce
Dr. Babasaheb Ambedkar Marathwada
University, Aurangabad.

Prof. P. T. Srinivasan
Professor and Head,
Dept. of Management Studies,
University of Madras, Chennai.

Roderick McCulloch
University of the Sunshine Coast,
Locked Bag 4, Maroochydore DC,
Queensland, 4558 Australia.

Dr. Nicholas Loannides
Senior Lecturer & Cisco Networking Academy Instructor.
Faculty of Computing, North Campus,
London Metropolitan University, 166-220 Holloway Road,
London, N7 8DB, UK.

Dr. Meenu Maheshwari
Assit. Prof. & Fomer Head Dept.
of Commerce & Management
University of Kota, Kota.

Dr. D. H. Malini Srinivasa Rao
M.B.A., Ph.D., FDP (IIMA)
Assit. Prof. Dept. of Management
Pondicherry University
Karaikal - 609605.

Dr. Rana Pratap Singh
Professor & Dean, School for Environmental
Sciences, Dr. Babasaheb Bhimrao Ambedkar
University Raebareily Road, Lucknow.

Memon Sohel Md Yusuf
Dept. of Commercee, Nizwa College
of Technology, Nizwa Oman.

Prof. Joyanta Borbora
Head Dept. of Sociology,
University, Dibrugarh.

Dr. Manoj Dixit
Professor and Head,
Department of Public Administration Director.
Institute of Tourism Studies,
Lucknow University, Lucknow.

Dr. P. Vitthal
School of Language and Literature
Marathi Dept. Swami Ramanand
Teerth Marathwada University, Nanded.

Rayat Shikshan Sanstha's,

CHHATRAPATI SHIVAJI COLLEGE, SATARA

(Autonomous)
Accredited at 'A+' Grade (CGPA: 3.51) by NAAC
RUSA Beneficiary College, ISO 9001:2015 Certified College
Department of History, Chhatrapati Shivaji College Satara &
Department of History, Shivaji University, Kolhapur
Jointly Organized
Two Days International Seminar under RUSA on
"Western Maharashtra in Transition (17th to 20th Century)"
21st and 22nd April, 2022

Certificate

This is to certify that Shri./Smt. Dr. Vikas Mohan Sarnaik of R.P. Mahavidyalaya, Osmanabad has actively participated and worked as a ~~Chairperson / Resource Person/Organizing Committee member~~ and paper presented entitled ब्रिटीशकालीन तंत्रशिक्षण: विशेष संदर्भ कोल्हापूर संस्थान (इ.स.१८८७ ते १९३२) in Two Days International Seminar on, "Western Maharashtra in Transition (17th to 20th Century)" under the aegis of RUSA jointly organized by the Department of History, Chhatrapati Shivaji College, Satara and Department of History, Shivaji University, Kolhapur on 21st and 22nd April, 2022.

Mr. M. S. Nikam **Coordinator** **International Seminar**	**Prof. (Dr.) D. B. Masal** **Head** **Department of History** **Chhatrapati Shivaji College, Satara**	**Dr. Avanish Patil** **Head** **Department of History,** **Shivaji University, Kolhapur**	**Dr. Vitthal Shivankar** **Principal** **Chhatrapati Shivaji College,** **Satara**

CONTENTS OF MARATHI PART - II

१९. ब्रिटीशकालीन तंत्रशिक्षण : विशेष संदर्भ कोल्हापूर संस्थान (इ.स. १८८७ ते १९२२)

डॉ. विकास मोहन सरनाईक
इतिहास विभाग, रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद.

गोषवारा

ब्रिटीशकालीन तंत्रशिक्षण: विशेष संदर्भ कोल्हापूर संस्थान (इ.स.१८८७ ते १९२२)

शिक्षण हे व्यक्ति, समाज व राष्ट्राच्या विकासाचे महत्त्वपूर्ण साधन आहे. छत्रपती शाहू महाराज इ.स. १९१७ मध्ये खामगाव परिषदेत जनतेला उद्देशून म्हणाले होते कि, "शिक्षणाने बहुजन समाजाचा उद्धार होणार हे शिक्षण आजच्या रोजगार हीन बेकारीसाठी, उद्योग व व्यवसाय निर्माण करण्यासाठी मिळाले तर व्यक्तिच्या स्वतःच्या प्रगतीबरोबरच देशाचीही प्रगती साध्य होईल. शाहूंनी या उदात्तहेतूने व्यक्तिबरोबरच राज्याच्या आर्थिक विकासासाठी कोल्हापूरात तांत्रिक व औद्योगिक शिक्षण सुरू केले. कारण छ. शाहू मानत होते की, "आपल्या संस्थानाची औद्योगिक विकास साध्य करायचा असेल तर आधुनिक काळातील बदलते तंत्रज्ञान आत्मसात करून आपल्या संस्थानातील हुशार व तरूण वर्गाला परदेशी पाठवावे किंवा परदेशातील तज्ज्ञ व्यक्तिंना शिक्षण देण्यासाठी आपल्या संस्थानात बोलविणे गरजेचे आहे.' या विचारातूनच छ. शाहूंनी इ.स. १८८७ मध्ये 'जयसिंगराव घाटगे टेक्निकल स्कूल' व इ.स. १९२० मध्ये 'राजाराम इंडस्ट्रियल स्कूल' सुरू केले. याचबरोबर वेळोवेळी आध्यादेश व हुकूमनामे काढून संस्थानातील तरूणांना परदेशी शिक्षणास पाठवण्याची व्यवस्था केली. छ. शाहू महाराजांच्या तांत्रिक व औद्योगिक शिक्षणाचा वारसा स्वातंत्र्योत्तरर काळामध्येही सुरू आहे. ज्यामुळे कोल्हापूरच्या आर्थिक व सामाजिक जडणघडणीमध्ये निश्चितच या शिक्षणाने मोलाचे योगदान दिले. त्यामुळे या काळातील तांत्रिक व औद्योगिक शिक्षणाचा अभ्यास करणे गरजेचे आहे.

स्वातंत्र्यपूर्व काळामध्ये कोल्हापूर हे ब्रिटीशांच्या साम्राज्यांतर्गत संस्थान होते. महाराष्ट्राच्या राजकारणात, अर्थकारणात व समाजकारणामध्ये कोल्हापूरचे महत्त्वपूर्ण योगदान आहे. इ.स. १८१८ मध्ये पेशवाईचा अंत होवून, मराठेशाहीवर इंग्रजांनी कब्जा मिळविला तरीही, एकेकाळी मराठ्यांची राजधानी असलेल्या कोल्हापूर संस्थानाचे अस्तित्व मात्र इ.स. १९४९ पर्यंत टिकून होते. १९ व्या शतकाच्या शेवटी कोल्हापूर संस्थानच्या गादीवर छ. शाहू महाराजांचा उदय झाला. ही घटना कोल्हापूरच्याच नव्हे तर संपूर्ण देशाच्या दृष्टीने महत्वपूर्ण होती. छ. शाहू महाराजांनी राजकीय, सामाजिक व आर्थिक विकासाबरोबरच शैक्षणिक व औद्योगिक क्षेत्रातही महत्त्वपूर्ण कार्य केले. उद्योगांच्या विकासासाठी तंत्रशिक्षणाचे महत्व ओळखून त्याची प्रत्यक्षात अंमलबजावणी करणारे देशातील पहिले संस्थानिक शाहू महाराज होते. या

दूरदृष्टी राजाने राबवलेल्या तंत्रशिक्षणाचा अभ्यास प्रस्तुत शोधनिबंधात करण्याचा प्रयत्न केला आहे. शिक्षणाचे महत्त्व सांगताना छ. शाहू महाराज इ.स.१९१७ मध्ये खामगाव परिषदेत म्हणाले होते कि, "शिक्षणाने बहुजन समाजाचा उद्धार होणार हे शिक्षण आजच्या रोजगारहीन बेकारीसाठी, उद्योग व व्यवसाय व्यवसाय निर्माण करण्यासाठी मिळाले तर व्यक्तिच्या स्वतःच्या प्रगतीबरोबरच देशाचीही प्रगती साध्य होईल."[१] छ. शाहूंच्या या विचारामध्ये शिक्षणाचे दोन वेगवेगळे उद्देश समाविष्ट आहेत. पहिला म्हणजे शिक्षणामुळे व्यक्तिला काय साध्य होते व दूसरा शिक्षणामुळे समाजाला आणि देशाला काय मिळते. त्यामुळे त्यामुळे शिक्षणाचा उद्देश केवळ ज्ञानलालसेसाठी नव्हे तर ज्ञानाबरोबरच व्यक्ति, समाज व देशाच्या आर्थिक आर्थिक गरजा भागवणारे असावे. या गरजा व्यावसायिक व तांत्रिक शिक्षणातून भागवण्याचा प्रयत्न केला जातो. त्यामुळे अशा महत्वपूर्ण शिक्षणासाठी शाहू महाराजांचे योगदान अभ्यासणे गरजेचे आहे.

तंत्रशिक्षणाबाबत छ. शाहूंचे विचार व प्रयत्न

भारतात, ब्रिटीशकालीन संस्थानिकांमध्ये तंत्रशिक्षणाचे महत्त्व ओळखून ते आपल्या संस्थानात सुरु करण्याचा पहिला मान शाहू महाराजांना जातो. त्यांनीच कोल्हापूरातील तंत्रशिक्षणाचा पाया पक्का केला. शाहू महाराज मानत होते की, "आपल्या संस्थानाची औद्योगिक प्रगति साध्य करावयाची असल्यास आधुनिक काळातील बदलते तंत्रज्ञान आत्मसात करणेसाठी आपल्या संस्थानातील हुशार व तरूण वर्गाला परदेशी पाठविणे, किंवा परदेशी तज्ज्ञांना तंत्रशिक्षण देण्यासाठी आपल्या संस्थानामध्ये बोलविणे गरजेचे आहे."[२] शाहू महारज केळव बोलके राज्यकर्ते नसून कर्ते होते, हे त्यांच्या कार्यातून सिद्ध होते, ते पुढीलप्रमाणे.

जयसिंगराव घाटगे टेक्निकल इन्स्टिट्यूट

छत्रपती शाहूंचे जनक पिता व कोल्हापूर संस्थानचे रिजंट जयसिंगराव उर्फ आबासाहेब घाटगे यांच्या स्मरणार्थ "जयसिंगराव घाटगे टेक्निकल इन्स्टिट्यूट" या नावाने शाहूंनी पहिली तंत्रशिक्षण संस्था इ.स. १८८७ मध्ये सुरू केली. प्रथमतः या संस्थेचा खर्च कागल जहागिरीमार्फत पाहिला जात होता. या संस्थेत कारपेंटरी, ब्रास ॲन्ड आयर्न वर्क, ड्राईंग, मेटल टर्निंग, ऑपरेटिव्ह सिंपल इंजिन, इलेक्ट्रिक कटिंग, वेल्डिंग इत्यादी सात प्रकारचे अभ्यासक्रम शिकविले जात होते. या संस्थेत विद्यार्थी क्षमता ४५ होती. या अभ्यासक्रमासाठी ४ थी पास ही पात्रता होती.[३] या संस्थेत तरूण विद्यार्थ्यांबरोबरच अकुशल कामगारांनाही प्रशिक्षणाची व्यवस्था होती. या संस्थेत शिकविल्या जाणाऱ्या सुतारकाम या पारंपारिक जातीनिहाय व्यवसायक्रमासाठी इ.स.१८८९ ते १९४६ या काळात ब्राह्मण-६७, मराठा-१४१, मुस्लिम-२० अशा वेगवेगळ्या जाती-धर्मातील तरूणांनी प्रवेश घेतला, ज्यामुळे तत्कालीन कठोर जातीव्यवस्थेत छेद देण्याचे कार्य या शिक्षणाने केले. तर इतर अभ्यासक्रमाचा लाभ १८८९ ते १९४५-४६ या काळात १६८५ इतक्या तरूणांनी घेतला. तंत्रशिक्षणावरती या काळात संस्थानातर्फे १,३९,३६२ रूपये इतकी रक्कम खर्च केली."[४] जयसिंगराव घाटगे टेक्निकल इन्स्टिट्यूटमध्ये शिकणाऱ्या विद्यार्थ्यांसाठी वेगवेगळ्या स्कॉलरशिपची व्यवस्था केली

होती. यामध्ये जयसिंगराव घाटगे स्कॉलरशिप, फर्ग्युसन स्कॉलरशिप व जयसिंगराव घाटगे टेक्निकल स्कूल स्कॉलरशिप अशा विविध होत्या. या स्कॉलरशिपसाठी आवश्यक पैसा 'इंम्पिरियल बँक ऑफ इंडिया' येथे जमा केला जात होता. १९२६-२७ मध्ये या संस्थेच्या खात्यावरती ४८,४०० रूपये इतकी रक्कम शिल्लक होती.[५] यसिंगराव घाटगे स्कूलला तरूणांचा वाढता प्रतिसाद व तांत्रिक शिक्षणाची गरज लक्षात घेवून १९२० मध्ये 'राजाराम इंडस्ट्रियल स्कूल' ही औद्योगिक शाळा सुरू केली. या शाळेच्या इमारतीसाठी ३०,००० रूपये खर्च केले. या इमारतीमध्ये ग्रामीण भागातील विद्यार्थ्यांना राहण्यासाठी वसतिगृहाची व्यवस्था करून यांचा खर्च संस्थानातर्फे देण्याची व्यवस्था केली.[६]

तंत्र व औद्योगिक शिक्षणासाठी छ. शाहूंचे आदेश व हूकूमनामे

संस्थानातील औद्योगिक प्रगतिसाठी तंत्रशिक्षणाचा प्रसार व्हावा. जास्ती-जास्त तरूणांना या शिक्षणाचा लाभ व्हावा व या शिक्षणासाठी लागणारा खर्च भरून काढावा यासाठी वेळोवेळी छ. शाहू यांनी आदेश व हूकूमनामे प्रसिद्ध केले. ०१/०२/१९०९ रोजी गणपत मार्तंड माने याने मेकॅनिकल इंजिनिअरिंगसाठी, पुण्यामध्ये सराव करण्यास स्कॉलरशिप मिळावी यासाठी अर्ज केला. त्यानुसार या तरूणास त्याचे शिक्षण पूर्ण होईपर्यंत महिना १० रूपये मिळावेत असा आदेश क्र. ११२० काढला.[७] तसेच शिक्षणाच्या आर्थिक तरतूदीसाठी १४/०८/१९१३ रोजी शिक्षणविषयक ठराव केला की, 'करवीर निवासिनीचा रथोत्सव पाहणेसाठी व श्री केदारलिंगवाडी रत्नागिरी या जत्रेसाठी विविध ठिकाणाहून लोक जमा होतात. यावेळी जयसिंगराव घाटगे टेक्निकल स्कूलमधील विद्यार्थ्यांनी बनवलेल्या वस्तु व शेती उपकरणे यांचे औद्योगिक प्रदर्शन भरवून हे पाहणेसाठी तिकीट आकारावे. त्या तिकिटातून मिळणारे उत्पन्न त्या शिक्षणसंस्थेसाठी व प्रदर्शनातील बक्षिसासाठी खर्च करावेत.[८] याचबरोबर जे तरूण परदेशी शिक्षणासाठी जात त्यांनाही आर्थिक मदत दिली जात १०/०५/१९१४ रोजी रामचंद्र धोंडो शेळके याला ॲग्रिकल्चर शिकणेसाठी अमेरिकेस जायचे होते त्यास बिनव्याजी १५०० रूपये देण्याचा ठराव क्र. ९९० केला.[९]

अशाप्रकारे शाहूंनी स्थापन केलेल्या जयसिंगराव घाटगे टेक्निकल स्कूल व राजाराम इंडस्ट्रियल स्कूल यामुळे अभियांत्रिकी व औद्योगिक शिक्षणाचा पाया कोल्हापूर संस्थानात घातला. शाहूंच्या या प्रयत्नामुळे पुरोगामी सामाजिक व आर्थिक परिवर्तन घडून येण्यास, विशेषत: कोल्हापूर जिल्ह्यातील आजच्या उद्यमनगराचा विकास घडून येण्यास चालना मिळाली.[१०] तर संस्थानातील तांत्रिक व औद्योगिक शिक्षणामुळे कोल्हापूरात पुढील काळात साखर कारखाने, ऑईल इंजिन्स, तेलाच्या गिरण्या, लोह-पोलादाचे कारखाने, ऑईल इंजिन व मोटारींना लागणारे सुट्टे भाग, ओतशाळा यासारख्या विविध उद्योगांना कुशल कामगारांचा पुरवठा होवून हे उद्योग भरभराटीस येण्यास मदत झाली.[११]

एकंदरीत कोल्हापूरातील उद्योग व व्यवसायांच्या विकासात या शिक्षण संस्थेचे मोलाचे योगदान आहेच, मात्र सर्वात मोठे योगदान सामाजिक विषमता कमी करण्याचे व चाकोरीबद्ध जातीनिहाय व्यासाय व उद्योगाला छेद देणारे आहे. कारण प्राचीन व मध्ययुगीन काळात व्यासाय व उद्योग जन्मजात होते, ते

बदलण्याची परवानगी कोणालाही न्हवती, कुंभारकाम, सुतारकाम, लोहारकाम, नाभिककाम, चर्मकार इत्यादी विविध व्यवसाय जातीनिहाय मानले जात होते. मात्र शाहूंनी सुतारकाम व लोहारकाम या पारंपारिक जातीनिहाय व्यवसायाच्या शिक्षणासाठी ब्राह्मण, मराठा व मुस्लिम या विविध जाती धर्मातील तरूणांना प्रवेश दिला. हे परिवर्तन म्हणजे तत्कालीन गरज व राजर्षी शाहूंच्या सामाजिक समतेच्या विचारांची परिणती होती.

संदर्भ

१. जाधव, अ.बा. (संपा.), 'राजर्षी शाहू महाराजांची भाषणे', कोल्हापूर, प्रथमावृत्ती, १९७१, पृ.७.
२. चौधरी, कि.का.(संपा.) 'महाराष्ट्र राज्य गॅझेटिअर', कोल्हापूर जिल्हा, दार्शनिक विभाग,
३. महाराष्ट्र राज्य मुंबई १९८९, पृ. ५८६.
४. Administration Report of Kolhapur State 1900-1901, P 42,44.
५. A.R.K.S. 1889-1990, P.58.
६. A.R.K.S. 1926-1927, P. 58.
७. Latthe, A. B., 'Memories of H. H. Rajarshi Shahu Chh. Maharaja of Kolhapur', (Part-I), Time Press Bombay, 1924, PP 149, 150.
८. मुडाबिद्रीकार, बी.एस.(संपा.), 'राजर्षी छ. शाहू महाराजांचे शैक्षणिक व सामाजिक हुकूमनामे, कार्यवाही व फलश्रुती',कोल्हापूर जिल्हा कारखाना, १९९४, पृ.१२.
९. कित्ता, पृ. १७.
१०. कित्ता, पृ. १९.
११. कित्ता, पृ. १०४.
१२. साळुंखे, पी.बी., 'राजर्षी शाहू गौरव ग्रंथ', महाराष्ट्र राज्य शिक्षण विभाग, सचिवालय, मुंबई, पृ. १९३.

International E-Conference on Life Sciences, Technology and Management
In Association with International Journal of Scientific Research in Science and Technology
Volume 9 | Issue 9 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)

Study of Web Mining, Algorithms of Web Mining and Applications of Web Mining

Sandhya Jagtap
Department of Computer Science, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad, Maharashtra, India

ABSTRACT

Without the internet, life would have been almost impossible. The web mining is application of data mining. Web Mining is the process of Data Mining techniques to automatically discover and extract information from Web documents and services. The data available on the web is so voluminous and heterogeneous that it becomes an essential factor to mine this available data to make it presentable, useful, and pertinent to a particular problem. Web mining deals with extracting these interesting patterns and developing useful abstracts from different sources. This paper tells how data on web are mined how ranks the web application. Also what types of algorithms are used for web mining? Applications of web mining.

Keywords: Web Mining, Types of web mining, HITS algorithms, PageRank algorithms, Applications

I. INTRODUCTION

Web is internet without internet we can't imagine our life. WWW is world wide web where heterogeneous data is resides. We access this information through internet sites. (Berners-Lee and Cailliau and Loutonen and Nielsen and Secret. 1994) WWW is connected to number of servers where web pages are linked. Whatever information we want is when you search is send by server on client side. Web is a collection of inter-related files on one or more Web servers. Web mining is part of data mining technology which mining large amounts of web data to improve service of internet. W3 provides information which user wants. But to identify the relevant piece of information web mining technics is used. Research in web mining tries to address this problem by applying techniques from data mining and machine learning to Web data and documents.

Web Mining: Web mining is actually an area of data mining related to the information available on internet. It is a concept of extracting informative data available on web pages over the internet (Kumar and singh 2016). Users use different search engines to fetch their required data from the internet, that informative and user needed data is discovered through mining technique called Web Mining.

II. TYPES OF WEB MINING

Web mining the application of data mining techniques to web-based data for the purpose of learning or extracting knowledge. (Cooley and Mobasher and Srivastava 1997)Web mining methodologies can generally be classified into one of three distinct categories as:-

1) Web Content Mining
2) Web Structure Mining
3) Web uses mining

1) **Web Content Mining:**-It is the process of extracting useful information from the contents of Web documents. The content may be data (text formatted information), audio, video, images or structured records. Content mining is the scanning and mining of text, pictures and graphs of a Web page to determine the related content to the search query. With the massive amount of information that is available on the World Wide Web, content mining provides the results lists to search engines in order of highest relevance to the keywords in the query.

Text mining is directed toward specific information provided by the customer search information in search engines (Johnson and Gupta2012). Main purpose of text mining is to extract previous information from content source.

Various algorithms are used for web content mining such as Decision Tree, Naïve Bayes, Neural Networks,

2) **Web Structure Mining:**- It is the application of discovering structure information from the web. The structure of the web graph consists of web pages as nodes, and hyperlinks as edges connecting related pages. Structure mining basically shows the structured summary of a particular website. It identifies relationship between web pages linked by information or direct link connection. To determine the connection between two commercial websites, Web structure mining can be very useful.

This allows a search engine to call web pages in which data resides which user wants. This process is completed by scanning the websites, retrieving the home page, then linking the information through reference links to bring the specific page containing the desired information.

Algorithms used for structured web mining HITS algorithm, PageRank algorithm, Distance Rank algorithm and so on.

3) **Web Uses mining:** - It is the application of discovering interesting usage patterns from large data sets. Depends on pattern understands what user want to search again and again on different sites.(Prabha and Suganya 2017) User access data on the web and collect data in form of logs. So, Web usage mining is also called log mining.

For web uses mining FP Growth algorithm, prefix spam, Apriori algorithm, and maxi-mal reference algorithms are used.

Different algorithms are used for web mining in different categorires.In this paper I discussed two of them i.e. HITS algorithm and page rank algorithm

III. ALGORITHMS OF STRUCTURAL WEB MINING

A) **HITS Algorithm:**-HITS stands for hyperlink induced topic search. It is used for web analysis. It is introduced by Jon Kleinberg (Shivakumar and Mylsami 2014) for ranking pages. There are two terms in HITS algorithm i.e Hubs & authorities.

Authorities: - The set of highly relevant web pages are called Roots .Roots are also called as Authorities.

Hub :- Pages that are not very relevant but point to pages in the Root are called Hubs.

An Authority is a page that many hubs link to whereas a Hub is a page that links to many authorities.

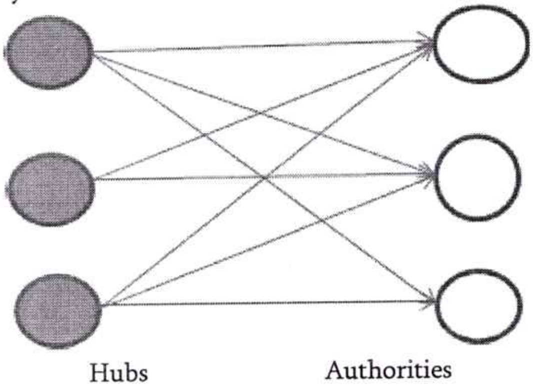


Fig 1. HITS (Hub & Authorities) (Sehgal. 2014)

Good authority is a page that is pointed by high hub weights and good hubs are pages that points to many authority pages with high weights which shown in Fig1.It is not easy to differentiate for some websites which is hub & authorities(sehgal.2014). HITS algorithms works in two way

1) if we use adjacency matrix given for linked web pages or as nodes in matrix
2) If we not used matrix

1) If we use adjacency matrix given for linked web pages or as nodes in matrix:- When adjacent matrix is given then we have to calculate Hub weighted graph (u) and Authority weighted graph(v) by using formula 1) Hub weighted graph (u) =A^*v 2) Authority weighted graph (v) =$A^{T*}u$

formBy using these formula we have to get score value of each pages or nodes. After that if ask for iteration (k) ,values calculated for hubs & authorities are calculated by using Normalize the scores by dividing each Hub score by square root of the sum of the squares of all Hub scores, and dividing each Authority score by square root of the sum of the squares of all Authority scores. (Optional)

Each row & column represents N1, N2, N3, N4 links. By take any example in adjacent matrix where N1,N 2,N3,N4 are web pages which connected write 1 not connected write 0.by taking example I calculate score of web pages in hub & authorities.

$$A = \begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad \text{and}$$

$$A^T = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 \end{bmatrix}$$

Transparency matrix obtains by interchanging row by column. After that assume u=1 i.e.

$v = A^T * u$

$$v = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 \end{bmatrix} * \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \\ 4 \\ 2 \end{bmatrix} Authority\ score\ of\ each\ page$$

u= A^* v

$$u = \begin{bmatrix} 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} * \begin{bmatrix} 1 \\ 2 \\ 4 \\ 2 \end{bmatrix} = \begin{bmatrix} 8 \\ 7 \\ 6 \\ 4 \end{bmatrix} Hub\ score\ of\ each\ page$$

Sequence of authorities web pages={ N3,{N1,N4},N1} & Sequence of hubs ={N1,N2,N3,N4}.

If iterations are given then we get values of each web pages which act as hubs & authorities so we apply normalization method on it as authorities score

1) N1= 1/ square root of($1^2+2^2+4^2+2^{2)}$ =1/5=0.5 And by calculating other values same as N2=0.4 ,N3=0.8 ,N4=0.4

Scores of hubs are 1) N1= 8/square root ($8^2+7^2+6^2+4^2$)=8/square root of 165=8/12.84 =9.96

2) N2=7/12.84=0.5451 3) N3=6/12.84=0.467 4) N4=4/12.84=0.311

Depends on score values that pages are send to user for related topics.

2) If we have not given adjacent matrix's HITS algorithms work as

1) Each node is assigned a Hub score = 1 and an Authority score = 1. 2) Let number of iterations be k. 3) Repeat for k

Hub update: Each node's Hub score = ∑ (Authority score of each node it points to).

Authority update: Each node's Authority score = ∑ (Hub score of each node pointing to it)

Normalize the scores by dividing each Hub score by square root of the sum of the squares of all Hub scores, and dividing each Authority score by square root of the sum of the squares of all Authority scores. (Optional)

B) **Page Rank algorithms:** Page Rank algorithm was developed by two famous authors L. Page and S. Brain(Shivakumar and Mylsami 2014)Both authors suggested that Google search engine works on page rank algorithms. This algorithm works on ranking the web pages which websites contain. If one web page linking to specific web pages indicates the importance of that web pages. This link is known as backlink. The backlink is produced from specific web page where that page is connected. then weightage of this link will be higher than those whose links are coming from non-important pages.

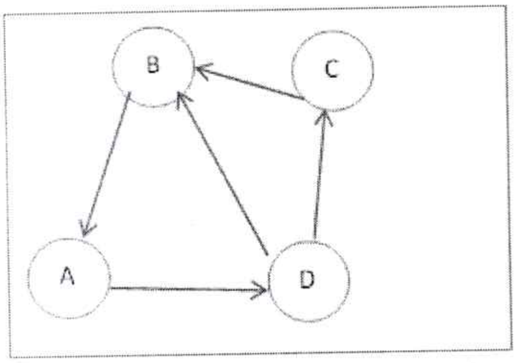


Fig 2 . Back Link structures of nodes (Shivakumar and Mylsami 2014)

Link from page A to page D is considered as a vote Shown in Fig. 2: Back link Structure. More the vote receives by the page more the importance of that specific page will be. If vote produced from a high weightage page then the importance of linking page will become higher.

Following is formula (Miguel and Zhiguo 2005) to find page rank of A

PR (A) = (1-d) $+d(\frac{PR(T1)}{C(T1)} + \cdots \frac{PR(Tn)}{C(Tn)})$

Where,

1) PR(A) is page rank of A
2) PR(Ti)=page rank of page (Ti is page rank of A)
3) C(Ti)=no of outlinks of i^th^ page
4) d = damping factor (value ranges from 0 to 1)

IV. APPLICATIONS OF WEB MINING

1) Web mining is used to discover how users navigate a website and the results can help in improving the site design and making it more visible on the web.
2) In digital world, popularity of use of digital images in social media is increased to improve digital image technology & convenient availability facilitated by internet. Images are not described so to find appropriated match of user want web mining is used.
3) Web mining is used for social network analysis. Social network is the study of social entities and their interactions and relationships The ideas from social network analysis are indeed instrumental to the success of Web search engines Social network analysis is useful for the Web because the Web is essentially a virtual society, and thus a virtual social network,

V. CONCLUSION

WWW is plaice where global information stored in the form of web pages. User can access it for any reason. Web mining technics discover & analysis these web pages to find certain patterens.Three types of mining are done i.e. content, structural, usages.

In content web mining we discover pattern on analysis the content in web pages. In structural web mining we analysis the relationships between the web pages by hyperlink also ranks the web pages. In usages web mining, we observe the users & web pages or websites relationship. For mining various algorithm are used for discovering pattern out of all algorithms in this paper two algorithms are discussed HITS & PageRank.

VI. REFERENCES

[1]. Anurag Kumar and Ravi Kumar Singh, "Web Mining Overview, Techniques, Tools and Applications: A Survey," International Research Journal of Engineering and Technology (IRJET), vol. 03, no. 12, pp. 1543-1547, December 2016

[2]. Berners-Lee, T., Cailliau, R., Loutonen, A., Nielsen, H., Secret, A.: The World- Wide Web. Communications of the ACM 37(8), 76–82 (1994)

[3]. Cooley R, Mobasher B. and Srivastava J., Web mining: Information and pattern discovery on the world wide web, 1997.

[4]. Faustina Johnson and Kumar Santosh Gupta, "Web Content Mining Techniques: A Survey," International Journal of Computer Applications (0975 – 888), vol. Volume 47– No.11, pp. 44-50, June 2012.

[5]. Miguel Gomes da Costa Júnior and Zhiguo Gong, "Web Structure Mining: An Introduction," International Conference on Information Acquisition, pp. 590-595, June 27 - July 3 2005.

[6]. Monica Sehgal, "Analysis of Link Algorithms for Web Mining," International Journal of Scientific and Research Publications, vol. 4, no. 5, May 2014.

[7]. Prabha.K and Suganya.T, "A Guesstimate on Web Usage Mining Algorithms and Techniques," International Journals of Advanced Research in Computer Science and Software Engineering, vol. 7, no. 6, pp. 518-521, June 2017

[8]. Parth Suthar and Prof. Bhavesh Oza, "A Survey of Web Usage Mining Techniques," (IJCSIT) International Journal of Computer Science and Information Technologies, vol. 6, pp. 5073-5076, 2015.

[9]. Shivakumar B.L. and Mylsami T., "SURVEY ON WEB STRUCTURE MINING," ARPN Journal of Engineering and Applied Sciences, vol. 9, pp. 1914-1923, October 2014.

Received: 26 May 2022 | Revised: 19 July 2022 | Accepted: 31 July 2022

DOI: 10.1002/jccs.202200248

JCCS JOURNAL OF THE CHINESE CHEMICAL SOCIETY

ARTICLE

Photocatalytic efficiency of sol–gel synthesized Mn-doped TiO_2 nanoparticles for degradation of brilliant green dye and mixture of dyes

Mangesh G. Bhosale[1,2] | **Radhakrishna S. Sutar**[1] | **Sandip B. Deshmukh**[2] | **Meghshyam K. Patil**[1]

[1]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus, Osmanabad, India

[2]Department of Chemistry, Ramkrishna Paramhans Mahavidyalaya, Osmanabad, India

Correspondence
Meghshyam K. Patil, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus Osmanabad-413501(M. S.), India.
Email: meghshyam_patil@yahoo.com

Abstract

The Mn-doped TiO_2 nanoparticle photocatalysts have been prepared by a simple sol–gel method. 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles have been prepared by using a stoichiometric amount of manganese acetate and titanium isopropoxide as precursors of Mn and Ti respectively. The physico-chemical characterization of the prepared samples has been studied by x-ray diffraction (XRD), Brunauer–Emmett–Teller surface area analysis, field emission scanning electron microscope, energy dispersive x-ray analysis, high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, Ultraviolet–visible spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). XRD study reveals the formation of pure anatase phase of TiO_2 and decrease in crystalline size of TiO_2 on increasing the Mn doping content. TGA reveals minimum weight loss in the high-temperature region of 500–1,000°C, showing the thermal stability of the catalyst. FTIR study shows highly bonding in metal atoms. These samples have been tested for photocatalytic degradation of brilliant green dye. 5 mol% Mn-doped TiO_2 is having nearly four times more photocatalytic activity than pure TiO_2. In addition, Mn-doped TiO_2 has shown excellent photodegradation of a mixture of three dyes namely, rhodamine B, brilliant green, and methylene blue.

KEYWORDS

kinetic study, Mn-doped TiO_2, nanoparticles, photocatalytic activity, sol–gel method

1 | INTRODUCTION

Various industries such as the manufacture of textile, paint, leather, pesticides, fertilizers, pharmaceuticals, and so on are primarily responsible for water pollution. By means of these industries, various organic pollutants have been dumped into the water bodies. The aquatic life and human life may be largely affected by these organic pollutants, which are exceptionally difficult to be degraded or eliminated by nature.[1–3] Numerous predictable methods such as biological methods, chemical precipitation, and membrane filtration are suggested for wastewater treatment, but these methods may not be greatly possible. However, chemical precipitation causes several disadvantages, large chemical feeding such as lime, oxidants, or H_2S and physicochemical monitors

such as pH are essential for the effluent, the excessive chemical usually causes a secondary pollution issue. Membrane filtration is an alternative physical method for wastewater treatment,[4] but its utility is affected by factors such as particle size, solubility, diffusivity, and charge.

In several countries, economic growth and industrial development go hand in hand, for example, textile industries play an important role in many countries such as China, Bangladesh, Vietnam, India, Sri Lanka, etc. These industries use different raw materials such as cotton, synthetic and woolen fibers, and several synthetic and natural dyes and chemicals. Approximately 10,000 different synthetic dyes are available in the global market. The worldwide annual production of these dyes is over 700,000 tons. Nearly 200,000 tons of synthetic dyes are lost into the environment because of the inefficient dyeing process used in textile industries. According to the World Bank estimation, the textile dyeing and finishing treatment is having about 17%–20% share of the total industrial wastewater generated.[4–6]

To tackle water pollution, among the number of processes, one of the most effective processes is the use of heterogeneous photocatalyst.[7–10] The most effective heterogeneous photocatalyst is titanium dioxide, because of its interesting properties such as nontoxicity, low cost, strong oxidizing power, chemical, and biological inertness, reusability, porosity, phase transformation, crystallinity, availability in nano-size and in different morphology and so on.[11–14] TiO_2 has a large band gap of ~3.20 eV, hence it functions effectively under ultraviolet (UV) light irradiation and limits its applications in direct sunlight or visible light. Another obstacle is the larger recombination rate of photo-generated electrons and holes, which further limits its efficiency.[15] One of the major challenges is to make an innovative photocatalyst, which can absorb light in the visible region rather than the UV region. In this direction, our focus is to prepare a TiO_2 catalyst, which on modification can absorb visible light rather than UV light, and minimize its band gap.

Enormous research has been carried out during the last few decades for developing TiO_2 catalyst to increase its activity in the visible region, for the achievement of higher absorbance of visible light by TiO_2. This includes several methods such as metal and non-metal ion doping and surface sensitization of TiO_2 coupling which helps in narrowing the band gap.[16–19] In literature, the number of transition metals such as V, Cr, Fe, Mg, Co, Zn, and Mo has been used as a dopant in TiO_2, which results in the enhanced photocatalytic activity of TiO_2.[20–24] Among these, Mn is one of the effective doping elements, which results in the red shift in absorption wavelength due to the contraction in the band gap via the formation of new energy levels in between the Ti 3d states of the conduction band and the O 2p states of the valence band.[25] Zhang et al. reported the synthesis of MnO_2-doped anatase TiO_2 nanoparticles, which showed higher photocatalytic activity than Degussa P25.[26] Li et al. synthesized visible light active Mn-TiO_2 photocatalyst with controlled size for degradation of Rhodamine B (RhB).[27] Further, Mn-TiO_2 has been reported for the degradation of NO and acetaldehyde under visible irradiation.[28–32] In view of these results, there is a scope to develop a new method for the synthesis of Mn-doped TiO_2.

In this study, we have synthesized Mn-doped TiO_2 catalysts by the low-temperature sol–gel method. Prepared materials have been characterized by several techniques such as x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, Field Emission Scanning Electron Microscope (FESEM), energy dispersive x-ray analysis (EDX), High-Resolution Transmission Electron Microscopy (HRTEM), x-ray photoelectron spectroscopy (XPS), UV–Visible spectroscopy, Photoluminescence (PL) spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). Further, photocatalytic activity has been evaluated for the degradation of brilliant green dye in an aqueous solution and for the degradation of a mixture of dyes in an aqueous solution. Effect of various parameters such as concentration of dye, pH of a solution, and catalyst loading on the degradation of brilliant green has been evaluated.

2 | MATERIAL AND METHOD

2.1 | Synthesis of Mn-doped TiO_2 nanoparticles by sol gel method

The Mn-doped TiO_2 nanoparticles were prepared by using sol–gel method. Firstly, 5 ml of titanium isopropoxide and 5 ml of glacial acetic acid were taken in a clean round bottom flask and stirred for 15 min. To this solution separately prepared solution Tween 80 (0.2 ml) in 10 ml of distilled water was added slowly with constant stirring for 2 hr. To this resultant solution, 80 ml of distilled water was added slowly with constant stirring for 2 hr. Further, the stoichiometric amount of manganese acetate was added to a reaction mixture and stirred for 4 hr. pH of this solution is adjusted to 10 by adding ammonia solution with constant stirring and further stirred for 3 hr at 60°C for removing excess ammonia. The reaction mixture was cooled to room temperature and the supernatant liquid has been removed by decantation. Further, 80 ml of distilled water was added and the mixture was stirred for 3 hr at 60°C. The mixture was

filtered, washed with ethanol and obtained precipitate has been dried at 110°C for 12 hr. The obtained powder was crushed and calcined at 400°C for 5 hr. Light brown powder of Mn-doped TiO_2 nanoparticles has been formed. By this procedure, 1, 3, and 5 mol% Mn-doped TiO_2 have been synthesized. The same procedure was adopted for the synthesis of bare TiO_2, without the addition of manganese acetate.

2.2 | Characterization

The XRD spectra of all prepared samples were recorded by using Regaku diffractometer with Cu Kα (1.5418 Å). The diffraction data were collected in the 2θ range of 10–90° at the scanning rate of 2°/min. The crystalline size has been calculated by the Scherer equation. BET surface area, pore volume, and pore diameter of the bare TiO_2 and 5 mol% Mn-doped TiO_2 have been studied by N_2 adsorption measurement at −196°C using NOVA touch 4LX, Quntachrome, USA. UV–Vis absorption spectrum of the prepared catalysts was recorded in the range of 200–800 nm by using ELICO double beam SL210 UV–visible spectrophotometer. Photoluminescence measurement of all the prepared catalysts has been studied with 330 nm excitation wavelength (at 3.76 eV excitation energy) using a JASCO spectrofluorometer. FTIR spectra of the nanoparticles were recorded on Thermo Scientific Nicolet iS10 in the range of 400–4,000 cm^{-1} in transmission mode. High-resolution transmission electron microscopy (HRTEM) images of the samples were recorded on a JEOL JEM 2100 Plus. The FESEM images with EDX were recorded using Carl Zeiss Supra 55 scanning electron microscope with a field emission electron gun, to know the morphology and elemental composition respectively. XPS measurements of the prepared sample have been recorded on a Shimadzu (ESCA 3400) spectrometer having Mg Kα (1,253.6 eV) radiation as the excitation source. The TGA data were recorded on Mettler Toledo TGA1 thermogravimetric analyzer; it shows the thermal stability of the prepared catalysts.

2.3 | Photocatalytic activity

Photocatalytic degradation of Brilliant green in an aqueous solution has been studied by employing Mn-doped TiO_2 catalysts. Further, degradation of a mixture of three dyes (including brilliant green, rhodamine B, and methylene blue) in an aqueous solution under direct sunlight has been studied by using the most active 5 mol% Mn-doped TiO_2. Also, the effect of various parameters (such as pH of the solution, the concentration of the brilliant green, and catalyst loading) have been examined on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 for degradation of brilliant green. The pH of the solution was adjusted by adding an appropriate quantity of 1 N NaOH and 1 N HCl solutions. In the photocatalytic study, all the experiments are studied thrice and observed with almost similar results. The corresponding error bar has been shown within the figures.

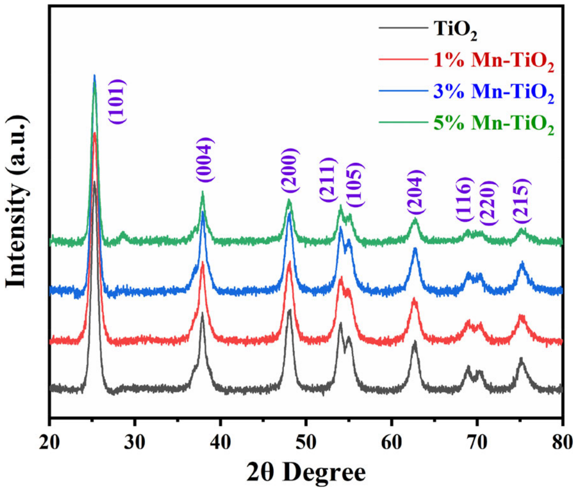


FIGURE 1 XRD pattern of pure TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2

2.3.1 | Photocatalytic degradation of brilliant green dye

We have prepared a 20 ppm brilliant green dye solution using distilled water at room temperature. From this prepared stock solution, 200 ml solution has been taken in the round bottom flask; to this, 100 mg of prepared catalyst has been added. This reaction mixture was stirred for 30 min. in dark to reach adsorption–desorption equilibrium. After this, the solution was transferred into the sunlight. 2 ml sample has been collected after a regular time interval, centrifuged, and performed UV–Visible spectral analysis from 200–800 nm wavelength and absorbance has been recorded for wavelength (λ_{max}) 625 nm for brilliant green.

2.3.2 | Photocatalytic degradation of mixture of dyes

We have prepared a 20 ppm solution of each dye (brilliant green, methylene blue and rhodamine B) using distilled water. By taking these three solutions in equal quantity, a 200 ml solution of mixture of brilliant green,

TABLE 1 Structural parameters of pure TiO_2 and Mn-doped TiO_2 nanoparticles

				Cell parameters			
Catalysts	**Standard d value**	**Observed d value**	**hkl plane**	**a (Å)**	**c (Å)**	**V (Å^3)**	**Crystallite size(nm)**
TiO_2	3.52	3.5147	(101)	3.78	9.52	136.02	9.927933
	2.37	2.38018	(004)				
	1.33	1.89052	(220)				
1% Mn-TiO_2	3.52	3.5201	(101)	3.775	9.4916	135.26	9.036106
	2.37	2.3729	(004)				
	1.33	1.8875	(220)				
3% Mn-TiO_2	3.52	3.5229	(101)	3.772	9.482	134.90	9.033568
	2.37	2.3705	(004)				
	1.33	1.8860	(220)				
5% Mn-TiO_2	3.52	3.5215	(101)	3.7854	9.494	136.04	8.944641
	2.37	2.3735	(004)				
	1.33	1.8927	(220)				

methylene blue and rhodamine B has been prepared. This prepared solution was taken in round bottom flask and 100 mg 5 mol% Mn-doped TiO_2 catalyst was added. After 30 min., the reaction mixture was transferred to direct sunlight, and after regular time interval the samples were collected. The absorbance of collected samples was recorded using a UV–visible spectrophotometer at the range of 200–800 nm wavelength.

3 | RESULT AND DISCUSSION

3.1 | Characterization

3.1.1 | X-ray diffraction study

X-ray diffraction patterns of undoped and Mn-doped TiO_2 nanocatalysts are shown in Figure 1. It is noted that all the diffraction peaks represented the anatase phase of TiO_2 with a characteristic high-intensity peak at $2\theta = 25.20°$ and other peaks correspond to 2θ values at 37.91, 47.98, 54.05, 55.12, 62.78, 68.94, 70.45 and 75.35° which can be indexed as (101), (004), (200), (211), (105), (204), (116), (220) and (215) planes of anatase TiO_2 (JCPDS card no.73–1764) respectively. Mostly, the XRD spectra have not shown any extra peaks corresponding to Mn. This indicated that the Mn may introduce in to TiO_2 lattice as substitution dopant by replacing Ti and O and not in the interstitial position of the TiO_2 lattice.[32,33]

The crystalline size of all prepared catalysts has been calculated on the basis of the Scherrer formula. The crystalline size of bare TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2 is 9.93, 9.04, 9.03, and 8.94 nm respectively. The Scherrer formula is as follows:

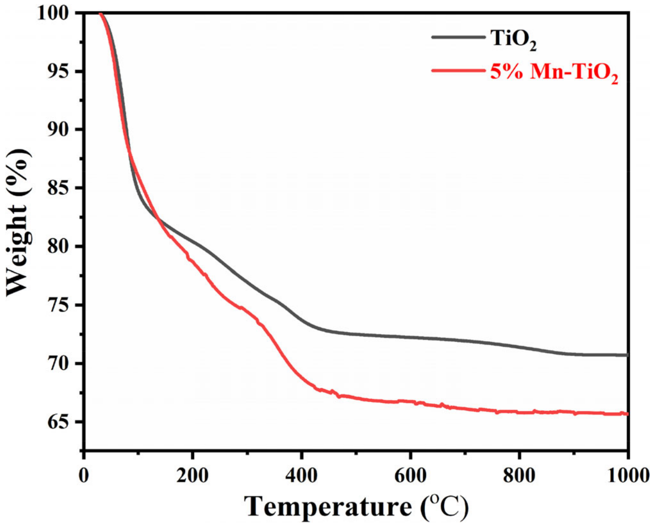


FIGURE 2 TGA of TiO_2 and 5 mol% Mn-doped TiO_2

$$D = \frac{k\lambda}{\beta \cos\theta}, \tag{1}$$

where D is the average size of the nanoparticle, λ is the wavelength, β is the full width at half maximum, and θ is Bragg's angle.

On the basis of crystalline size, we can say that on an increase in Mn doping, the size of the nanoparticle decreases, which results in an increase in the surface area of the catalyst and ultimately enrichment in photocatalytic activity. The structural parameters of pure TiO_2 and

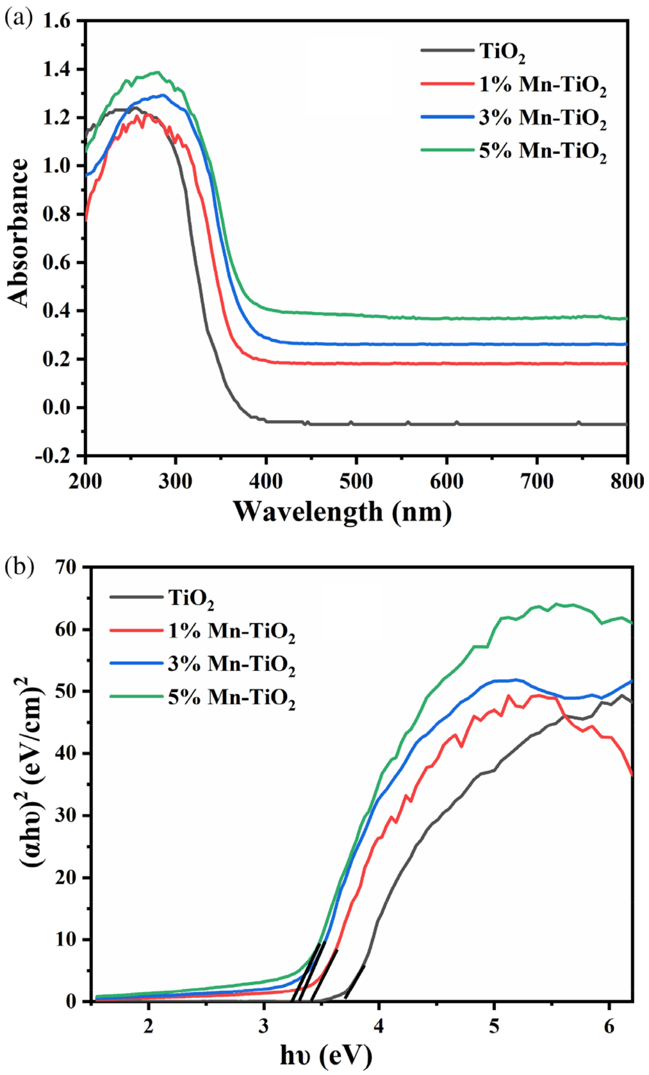


FIGURE 3 (a) UV–Visible absorption spectra; (b) plot of hυ versus αhυ^2 of bare TiO_2; and Mn-doped TiO_2

Mn-doped TiO_2 catalysts are shown in Table 1 and it is well matched with JCPDS 73–1764 data.

3.1.2 | Thermo gravimetric analysis

The thermogravimetric analysis plots of as-prepared pure TiO_2 and 5 mol% Mn-doped TiO_2 (before calcination) have been shown in Figure 2. The weight loss of TiO_2 from room temperature to 400°C is due to conversion from amorphous to crystalline phase.[34] In specific, after heating over 400°C, we do not observe any other phase than crystalline anatase TiO_2 this is prove on XRD analysis. The Thermo gravimetric analysis of Mn-TiO_2 is dividing in to three stages of weight loss. In stage first nearly 19% weight loss observed in between 30 and 180°C is due to loss of the residual solvent and water. The second weight loss which is about 12%, observed in between 126 and 380°C is due to loss of organic components. However, TiO_2 has shown less amount of weight loss as compared to Mn-doped TiO_2. Further, both Mn-doped TiO_2 and bare TiO_2 has not shown any significant weight loss after 400°C.

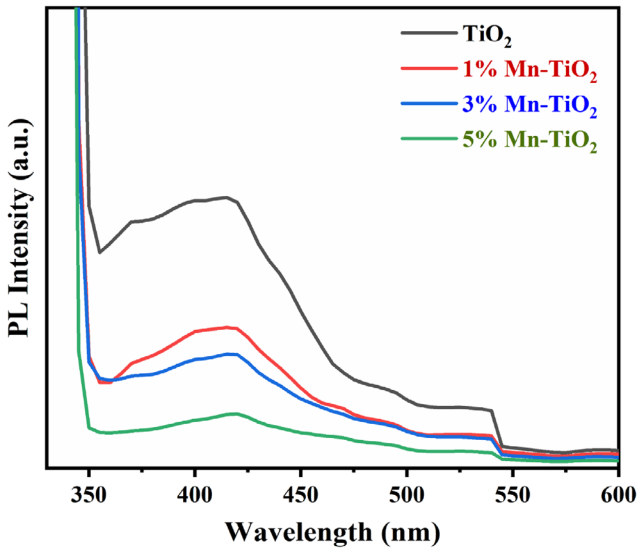


FIGURE 4 Photoluminescence spectra of bare TiO_2 and Mn-doped TiO_2 nanoparticles

As compared to bare TiO_2, Mn-doped TiO_2 has shown an overall 10% higher weight loss. The weight loss indicates that pure TiO_2 has early started to convert into its crystalline phase from the amorphous phase, whereas Mn-doped TiO_2 started later to convert into its crystalline form.

3.1.3 | UV–Visible spectroscopy study

The influence of doping on the UV–Vis spectra properties of the anatase TiO_2 is clear from Figure 3. The Mn-doped TiO_2 nanoparticles shows a remarkable change in their color, which depends on the concentration of dopant, as concentration of dopant increases color becomes light brown to light dark brown. From the UV–Vis spectra, the increase in absorption of Mn-doped TiO_2 in visible region has been observed which is due to their respective energy levels, the promotion of 3d electrons of doping Mn ions in to the conduction band of TiO_2.[35–37]

With the increase in doping, we observe that stronger absorption edges shifted to the right side of the spectrum, which results in a decrease in the band gap. As the percentage of doping increases band gap of prepared catalysts decreases from 3.7 to 3.2 eV. Due to decrease in band with absorption of lesser amount of energy can promotes electron to conduction band. It increases the photocatalytic activity of the prepared catalyst. On the

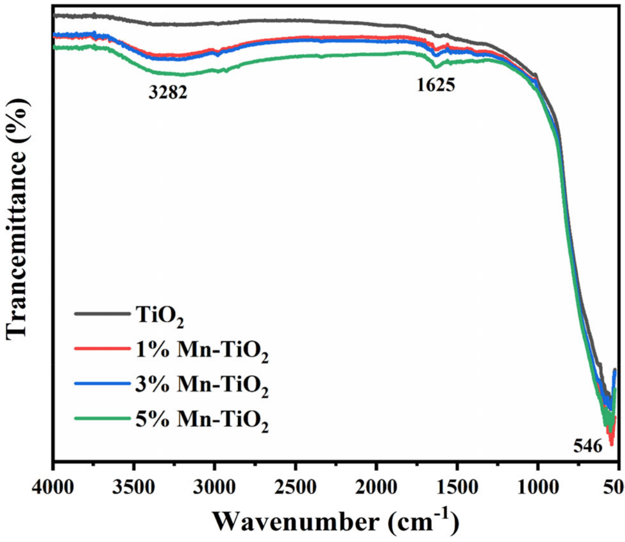


FIGURE 5 FTIR study of Mn-doped TiO_2 nanoparticles

basis of Figure 3b it is seen that 5 mol% Mn-doped TiO_2 has highest photocatalytic activity.

3.1.4 | Photoluminescence spectroscopy study

An important identifying tool for determining the existence of defects in a nanomaterial is PL spectroscopy. The photoluminescence spectra of pure TiO_2 and 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles at room temperature are shown in Figure 4. The PL spectra has been studied at an excitation wavelength of 330 nm. Two separate emission peaks have been identified in the spectra. The indirect band-to-band transition of TiO_2 nanoparticles from their conduction band to their valence band causes the UV emission.[38] The peak at 415 nm is related to self-trapped excitons.[38] The 490 nm peak is observed due to the charge transfer transition from Ti^{3+} to the TiO_6^{2-} octahedra associated with oxygen defects.[39] In this spectrum there is no additional peak of Mn or shifting of emission peak. On increasing Mn doping, the intensity of the emission peaks has been reduced. The oxygen vacancies in pure TiO_2 function as luminescence enhancers and boost emission intensity. The TiO_2 lattice is disturbed, the Ti–O bond is broken, and many oxygen vacancies are produced when Mn is doped. As the concentration of Mn in TiO_2 increases, the number of non-radiative oxygen vacancy centres also increases, nearby Mn^{2+}. Since there are more oxygen defects available, lesser photoexcited electrons are available to recombine with holes because they are entrapped and highly localized in those oxygen vacancies. Presence Mn resemblance a rise in non-radiative oxygen vacancy centres with trapped electrons, which causes a subsequent drop in emission intensity. Further, in addition to the non-radiative oxygen vacancies, the mobility of the carriers is another important factor influencing PL intensity. The mobility of the free carriers is decreased by dopants and deficiencies in the interior, grain boundary, and surface. When they get close to charged dopants or oxygen defect states, the mobile carriers disperse. Reduced mobility will result in more carriers being separated from one another, which lowers the intensity of the PL.[40]

3.1.5 | FTIR study

The FTIR spectra of Mn-doped TiO_2 nanoparticle is shown in Figure 5. The stretching and bending vibration of the hydroxyl group peak at 3282 cm^{-1} and the stretching vibration band intensity of Mn-doped TiO_2 is greater than pure TiO_2, indicating that TiO_2 has stronger absorption with Mn-doped TiO_2.[41] The absorption band in the prepared materials at 1625 cm^{-1} was associated with the stretching of the C–O–Ti bond. The peak at about 546 cm^{-1} is due to anatase TiO_2, which represents the bending vibration of Ti–O.

3.1.6 | FESEM and EDX study

The morphology and surface nature of the synthesized Mn-doped TiO_2 nanoparticles were studied by FESEM and obtained images of all samples are shown in Figure 6. The FESEM micrograph of all samples has shown the fine-grown crystals, which were gathered closely with each other. Further, the EDX analysis shows that obtained sample has the same elemental composition as per the proportion of precursors taken during the preparation.

3.1.7 | HRTEM study

The structural properties of prepared material Mn-doped TiO_2 nanoparticles have been further investigated by using HRTEM spectroscopy. The particle size for 5 mol% Mn-doped TiO_2 from the HRTEM images is varying from 4 to 14 nm as shown in Figure 7a. Clear lattice fringes for Mn-doped TiO_2 were obtained and shown in Figure 7b. Further, the presence of anatase phase of TiO_2 has been confirmed by the crystal lattice fringes having a d value of 0.352 nm which is corresponding to the spacing of (101) lattice plane of the anatase TiO_2 (JCPDS 73–1764). Furthermore, the selected area electron diffraction pattern shown in Figure 7c, matches with anatase TiO_2 and the brightness and intensity of polymorphic ring reveals the well crystalline nature. The average particle size of

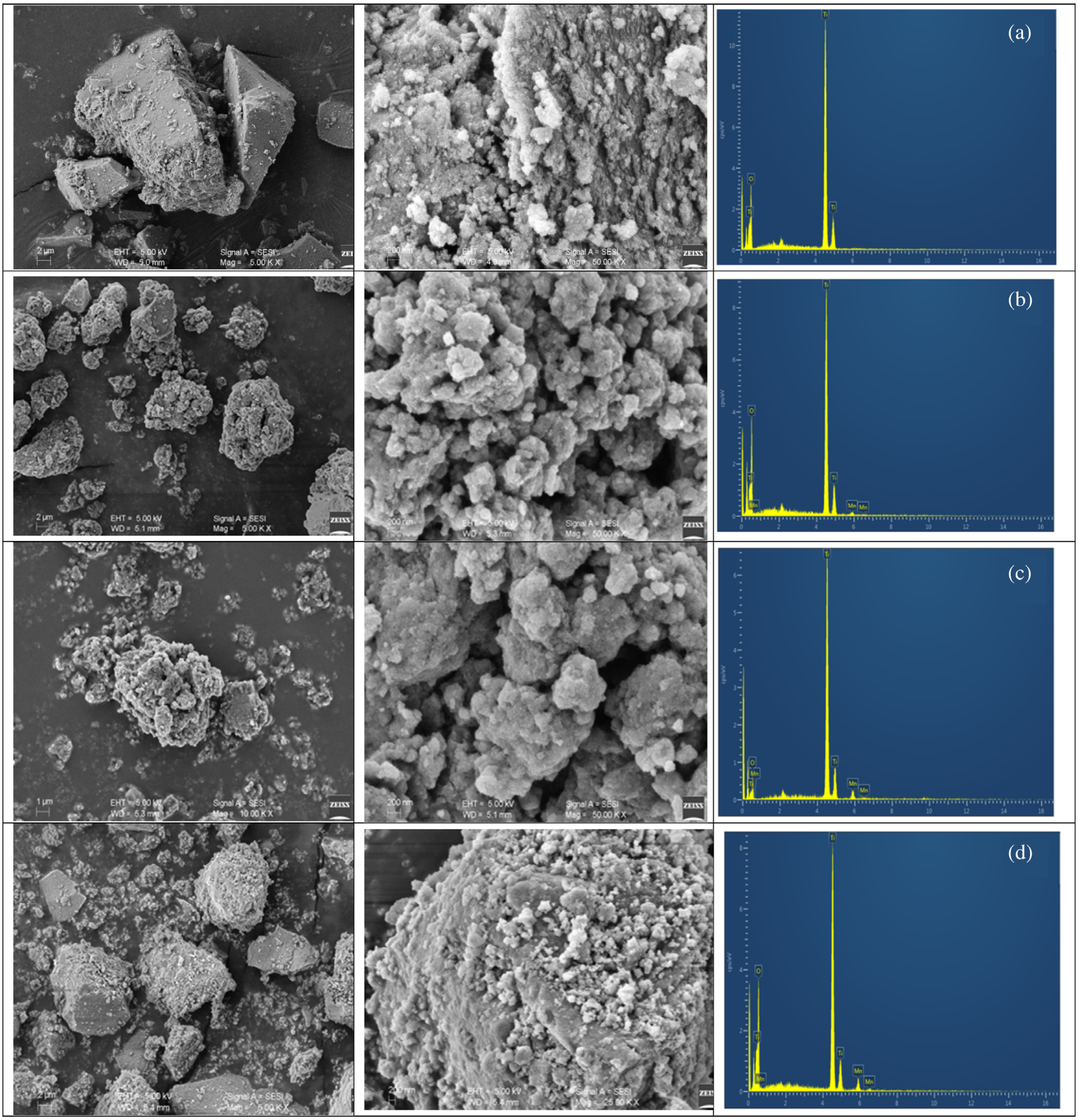


FIGURE 6 FESEM with EDX of (a) pure TiO_2; (b) 1 mol% Mn-doped TiO_2; (c) 3 mol% Mn-doped TiO_2; and (d) 5 mol% Mn-doped TiO_2 nanoparticles

the nanoparticles from HRTEM Figure 7d was found to be 8–10 nm, which is also matched with the XRD results.

3.1.8 | BET surface area analysis

The values of the specific surface area, pore volume, and pore diameter of pure TiO_2 and 5 mol% Mn-doped TiO_2 samples were measured using the Brunauer–Emmett–Teller (BET) equation following the Barrett–Joyner–Halenda method are summarized in Table 2. The N_2 adsorption–desorption for both the photocatalysts was consistent with Type IV isotherm (Figure 8), which is representative of mesoporous structures.[42–44] After doping with manganese, a significant increase in the specific surface area and pore volume of the samples has been

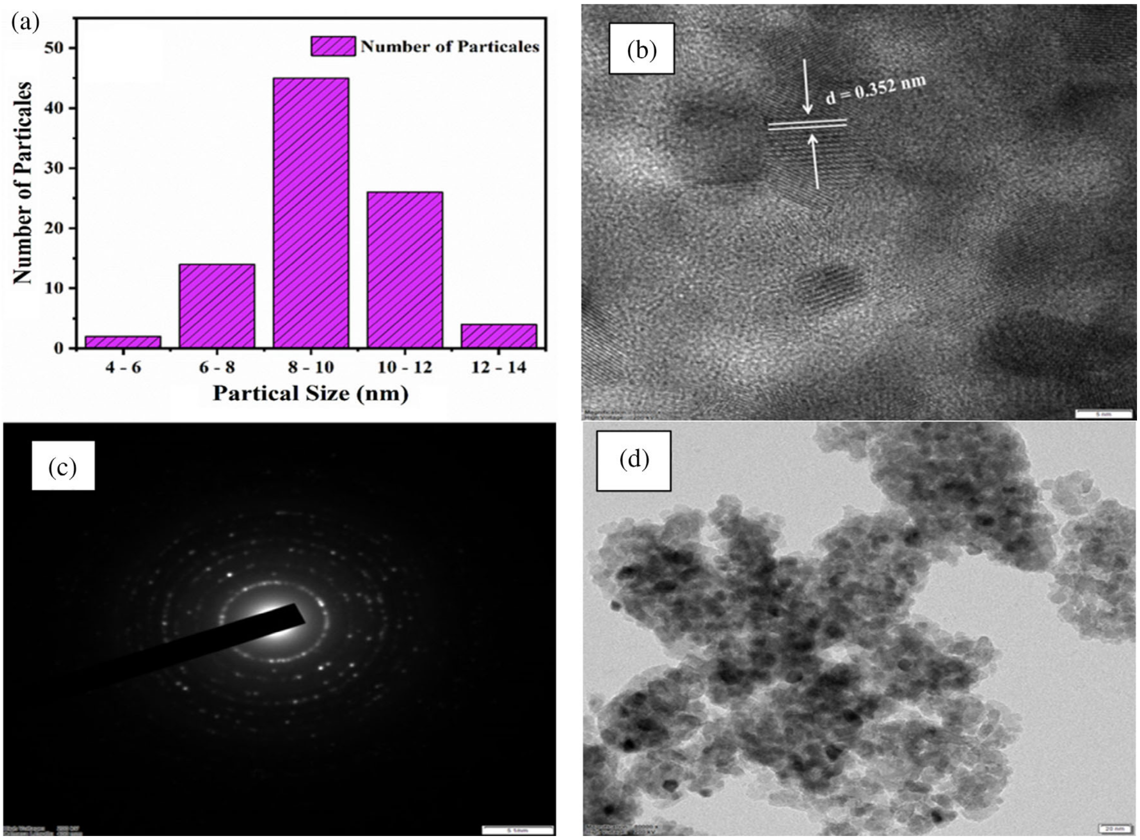


FIGURE 7 (a) Average particle size; (b) and (d) HRTEM image of 5 mol% Mn-doped TiO_2; and (c) SAED pattern of 5 mol% Mn-doped TiO_2 powder

TABLE 2 BET surface area, pore volume, and pore diameter of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticles

Sr. no.	Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	TiO_2	111.399	0.231848	7.83178
2	5% Mn-TiO_2	185.312	0.277406	5.63585

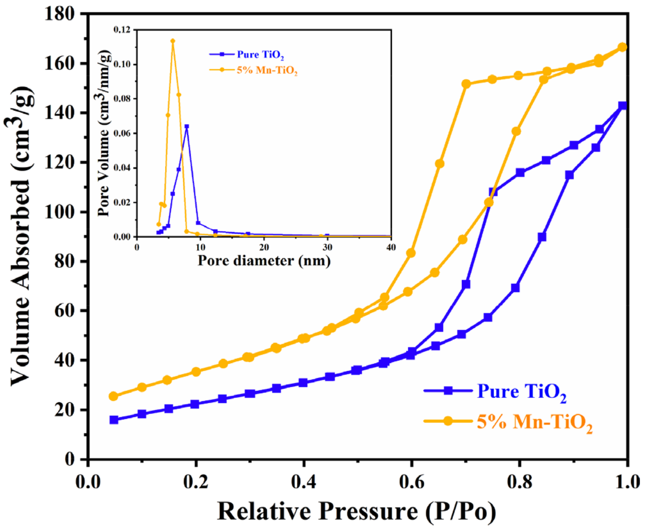


FIGURE 8 N_2 adsorption–desorption isotherm (inset, pore size distribution) of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticle

noticed. The BET surface area of 185.312 and 111.399 m^2/g was recorded for 5 mol% Mn-doped TiO_2 and bare TiO_2 respectively. Moreover, the pore diameter of pure TiO_2 is greater than 5 mol% Mn-doped TiO_2 and the pore volume of TiO_2 is less than 5 mol% Mn-doped TiO_2.

3.1.9 | XPS study

An XPS analysis of 5 mol% Mn-doped TiO_2 is shown in the Figure 9, which confirms the basic structure of the catalyst produced. Figure 9a shows the survey spectra, which shows the presence of Mn, Ti and O in the sample. The XPS spectrum of Mn 2p exhibited peaks at 642.2 and 653.8 eV, which were attributed to the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ levels, respectively, a finding that bears out the presence of Mn^{3+} is shown in Figure 9b.[45] From the

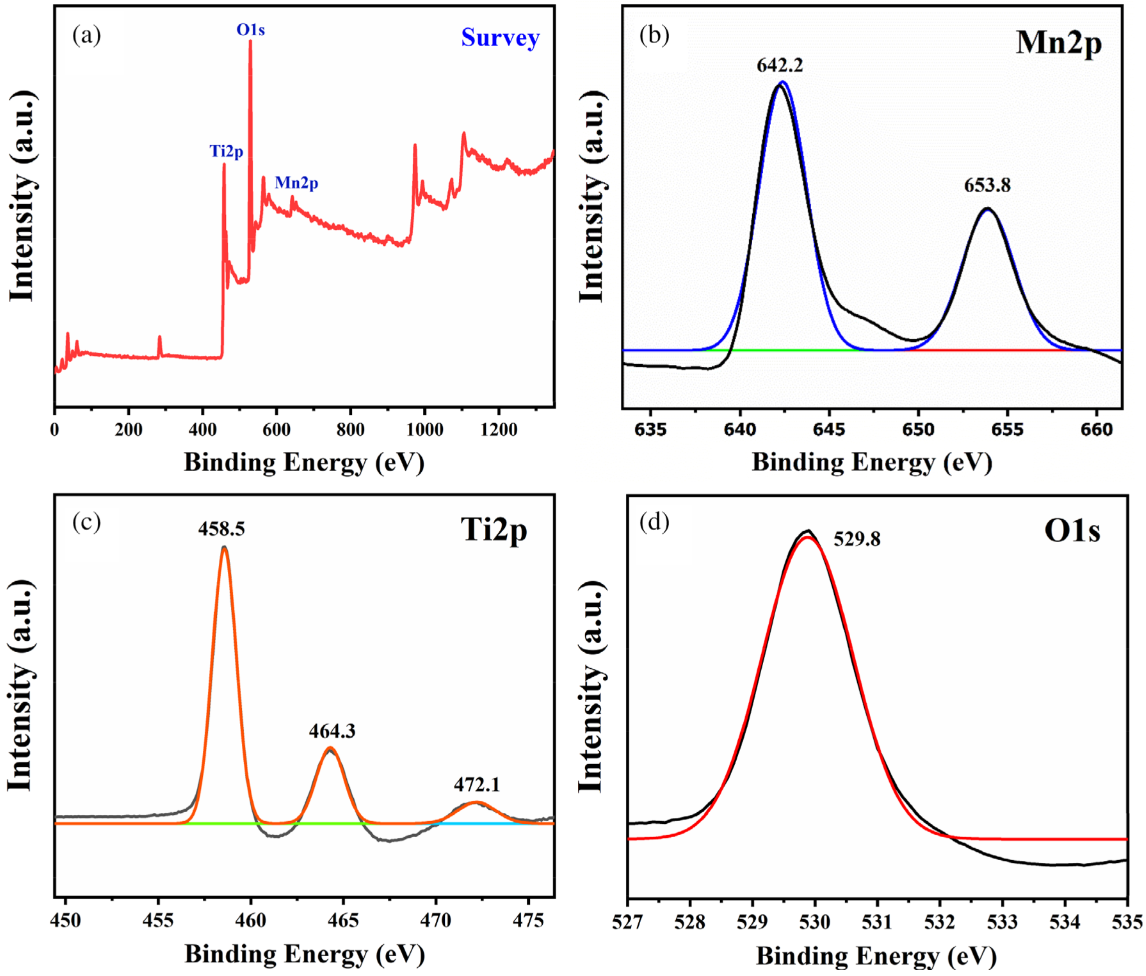


FIGURE 9 (a) XPS spectra of 5 mol% Mn-doped TiO_2, high-resolution spectra of (b) Ce 3d, (c) Ti 2p, and (d) O 1s

Figure 9c, the XPS spectrum of Ti 2p peaked at 458.5 and 464.3 eV, attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels, respectively, confirming the presence of Ti^{4+}. In addition, the difference between the two energy levels was approximately 6.0 eV and the 472.1 eV satellite peak is characteristic of TiO_2 compounds. Figure 9d shows O1s XPS spectrum peak at 529.8 eV, which is corresponds to the O-(Mn, Ti) lattice oxygen.[46]

3.2 | Photocatalytic degradation of brilliant green

The photocatalytic activity of synthesized nanoparticles has been explored for the degradation of brilliant green dye and a mixture of three dyes, namely methylene blue, brilliant green, and rhodamine B. Brilliant green is triarylmethane dye having the chemical formula $C_{27}H_{34}N_2O_4S$ and molecular weight 475.6 g/mol. It is used in dilute solution as a topical antiseptic and effective against gram positive microorganisms.

UV–Visible absorption spectra of degradation study of BG using 5 mol% Mn-doped TiO_2 with respect to irradiation time is shown in Figure 10a. The maximum absorption peak of brilliant green (BG) dye is at ~625 nm (λ_{max}). As the time increases from 0 to 180 min the peak intensity decreases gradually, also little shifting of peak to slightly lower wavelength is observed. The complete degradation of BG was observed after 180 min by using this catalyst. The plot of change in concentration of BG by using all prepared catalysts (such as 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and bare TiO_2) with respect to irradiation time has been shown in Figure 10b. The observation of experiment reveals that the concentration of BG has been nearly constant in the absence of photocatalyst and in the presence of visible light, suggests the thermodynamic stability of BG dye. The complete degradation of BG by using 5 mol % Mn-doped TiO_2 nanoparticles has required less time than that of 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 nanoparticles. This observation clearly indicates that the photocatalytic degradation

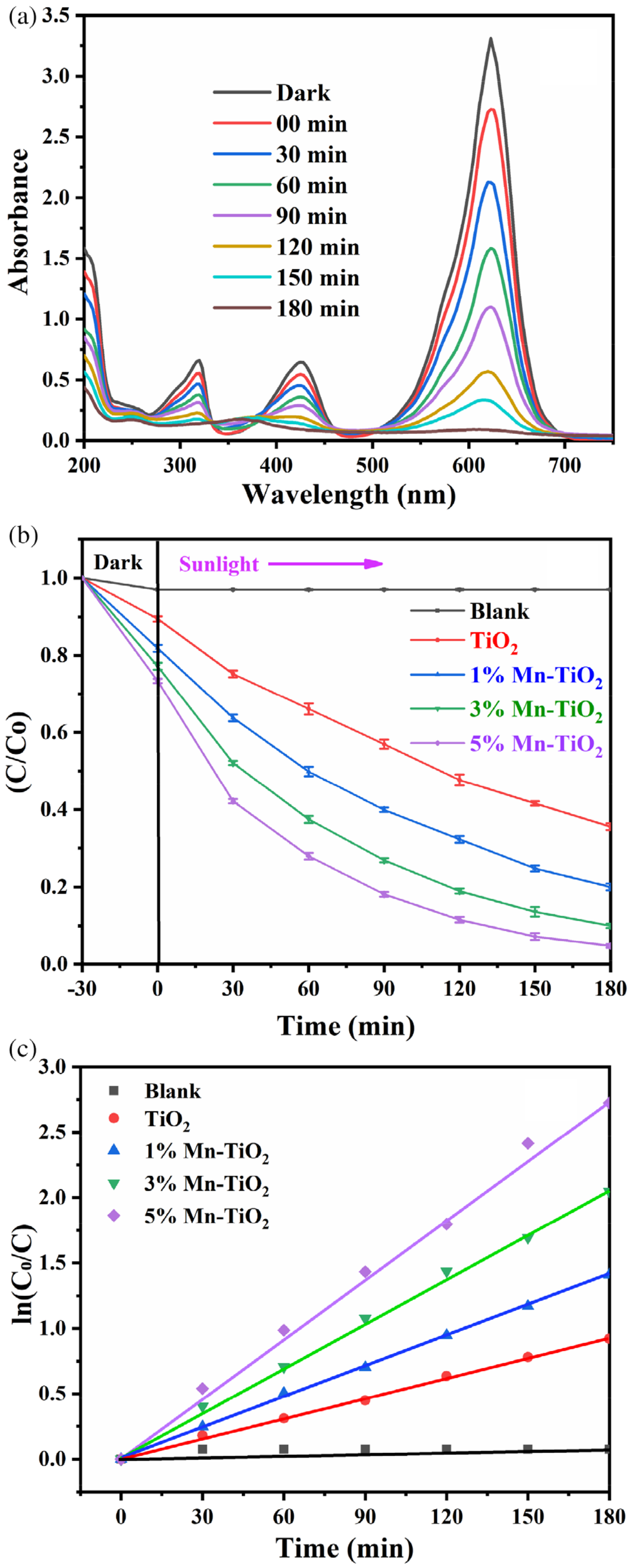


FIGURE 10 (a) UV–Visible spectra of BG at different time intervals using Mn-doped TiO_2 nanoparticle as catalyst, (b) change in concentration of BG by using different catalysts and without catalyst with irradiation time, and (c) corresponding graph of $\ln(C_0/C)$ of BG versus irradiation time

reaction of the Mn-doped TiO_2 nanoparticle is highly dependent upon the amount of Mn introduced into TiO_2 and the method used for synthesis of the catalyst preparation. Moreover, reaction kinetic has been shown in Figure 10c and results obtained were tabulated in Table 3 for photocatalytic degradation of BG by using prepared samples. As compared to other prepared catalysts, the higher rate constant (16.73×10^{-3} min^{-1}) for BG degradation using 5 mol% Mn-TiO_2 nanoparticles has been observed under visible light.

The effect of change in concentration of BG on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 nanoparticle has been studied by using 10–40 ppm BG solution. Figure 11a shows that complete degradation has been achieved for 10 ppm solution in 180 min., whereas 69, 55 and 28% degradation has been achieved of 20, 30, and 40 ppm solution respectively in same time by using 5 mol% Mn-doped TiO_2. Figure 11b shows the plot of d [BG]/dt versus time, on increasing the concentration of BG from 10 to 40 ppm, for time intervals of 0–30 min, 30–60 min, 60–90 min, and 90–120 min the change in concentration initially increases and then decreases. But for a time interval of 120–150 min, the trend is somewhat irregular.

The effectiveness of the photodegradation reaction largely depends upon the pH of the dye solution. The pH of the BG solution was adjusted using 1 N HCl to make a solution acidic and 1 N NaOH to make a solution basic. As shown in Figure 12, the rate of photocatalytic reaction was found higher in the basic medium (pH 12.0, 9.0) than that of the acidic medium (pH 5.0, 3.0). The different pH of the solution can change the surface charge on nanoparticles and, consequently, the potential of photocatalytic reactions. The mechanism of photocatalytic degradation is shown in Equations (2)–(7). The reactive species could be formed by the reactions shown in Equations (2)–(6), can be generated at specific potential and initiate the photocatalytic reaction (Equation 7).[47]

TABLE 3 Reaction kinetic parameters of photocatalytic degradation study of BG Mn-TiO_2 and bare TiO_2 nanoparticles

Catalyst	Initial Conc. of BG (%)	Final Conc. of BG (%)	Rate constant (min^{-1})
Blank	100	95.8	0.1×10^{-3}
TiO_2	100	57.8	5.7×10^{-3}
1% Mn-TiO_2	100	40.2	8.9×10^{-3}
3% Mn-TiO_2	100	27.6	12.69×10^{-3}
5% Mn-TiO_2	100	15.2	16.73×10^{-3}

Formation of $HO^{\bullet}$ is favored under basic condition and it may help for degradation under basic conditions.

$$\text{Mn}-\text{doped TiO}_2+h\nu\rightarrow\text{Mn}-\text{doped TiO}_2\left(e^-+h^+\right),\tag{2}$$

$$\text{Mn}-\text{doped TiO}_2(e^-)+O_2\rightarrow\text{Mn}-\text{doped TiO}_2+O_2{}^{-\bullet},\tag{3}$$

$$\text{Mn}-\text{doped TiO}_2(e^-)+O_2+H^+\rightarrow\text{Mn}-\text{doped TiO}_2+HO_2{}^{\bullet},\tag{4}$$

$$\text{Mn}-\text{doped TiO}_2\left(h^+\right)+H_2O\rightarrow\text{Mn}-\text{doped TiO}_2+H^++OH^{\bullet},\tag{5}$$

$$\text{Mn}-\text{doped TiO}_2\left(h^+\right)+OH^-\rightarrow\text{Mn}-\text{doped TiO}_2+OH^{\bullet},\tag{6}$$

$$\text{BG}+\text{Reactive species}\left(O_2{}^{-\bullet}/OH^{\bullet}/HO_2{}^{\bullet}\right)\rightarrow\text{Degradation Products}.\tag{7}$$

Furthermore, the photocatalytic degradation efficiency was evaluated by changing the amount of catalyst, that is, catalyst loading. Figure 13a shows the change in concentration of BG with irradiation time for the experiments carried out by using different catalyst loading, that is, from 0.25 to 1 g/L. The degradation efficiency increases with increase for catalyst loading. This is due to the fact that the higher amount of catalyst has higher active sites on the surface and consequently active sites

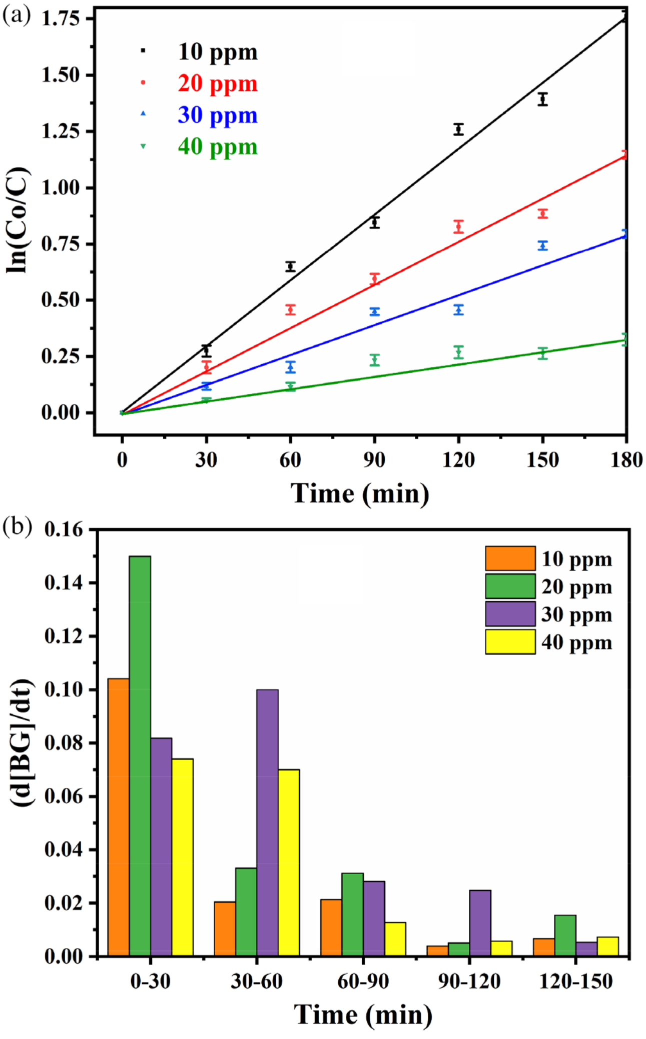


FIGURE 11 (a) Plot of percentage degradation of BG with different concentrations of dye solution by using 5 mol% Mn-doped TiO_2 nanoparticles with irradiation time and (b) corresponding plot of d[BG]/dt versus time

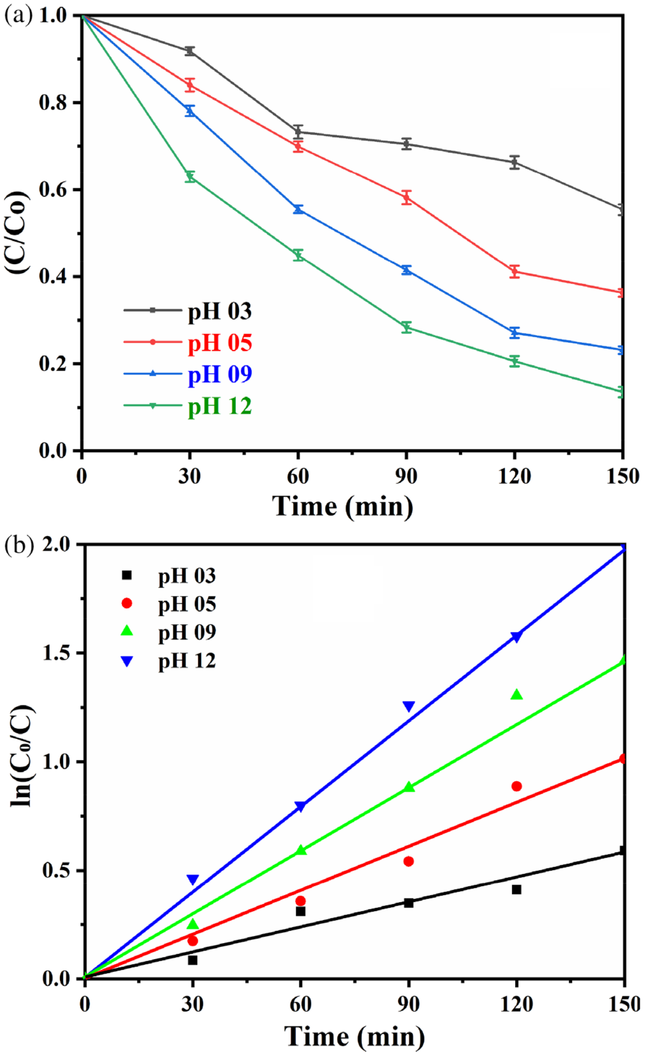


FIGURE 12 Effect of change in pH of BG dye solution: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ versus time by using 5 mol% Mn-doped TiO_2 nanoparticles

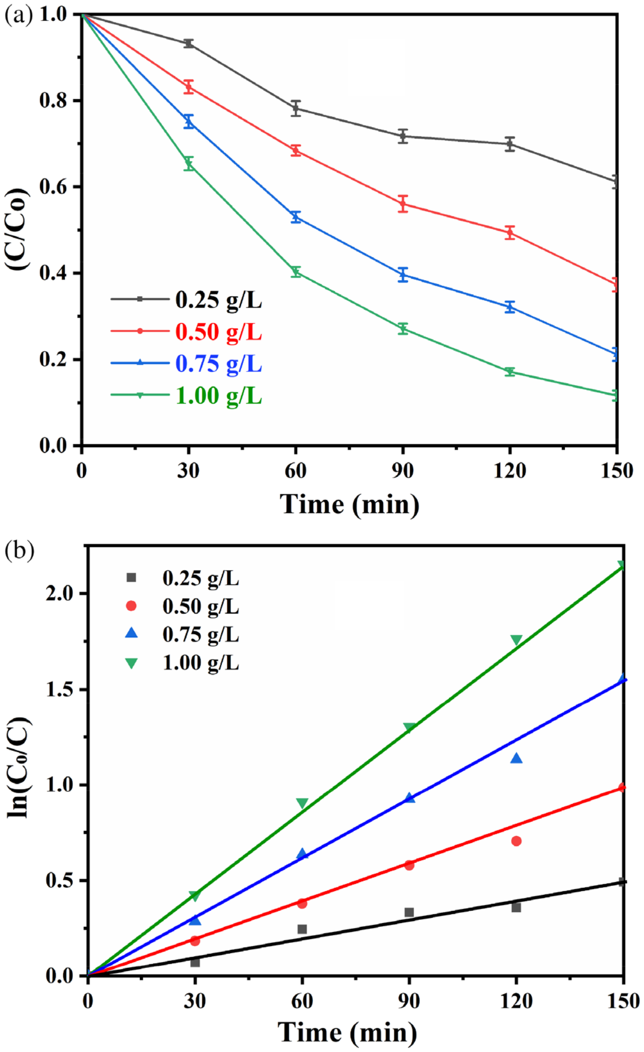


FIGURE 13 Effect of change in concentration of BG dye by using 5 mol% Mn-doped TiO_2 nanoparticles: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ vs. time

are involved for degradation reaction. The plot of $\ln(C_0/C)$ against time Figure 13b shows as the loading of catalyst increases it increases the photocatalytic activity.

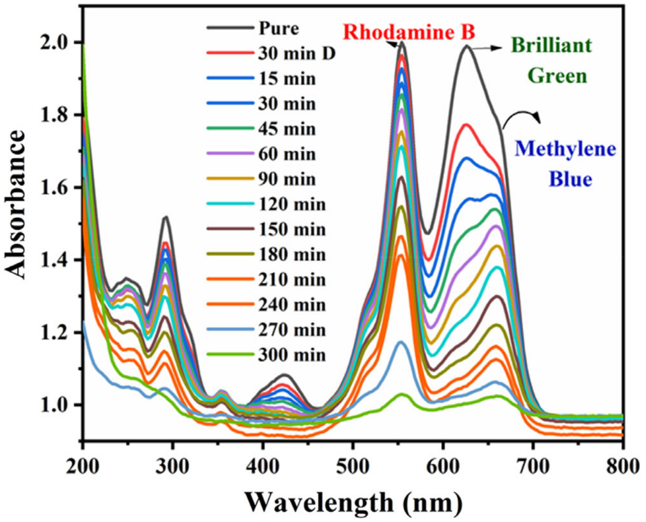


FIGURE 14 UV–Vis spectra of photocatalytic degradation of mixture of dyes (RhB, BG, and MB)

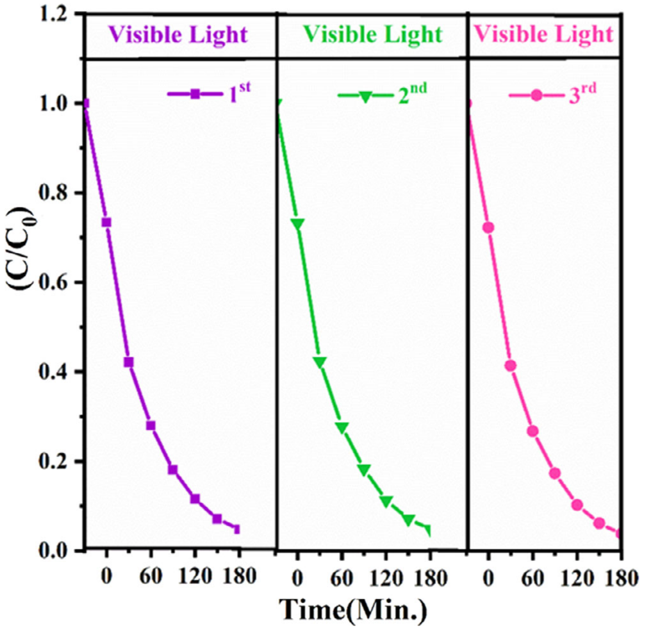


FIGURE 15 Reusability of catalyst

3.3 | Photocatalytic degradation of the mixture of dyes (RhB and BG, MB)

As per our photodegradation study of BG dye, it has been concluded that 5 mol% Mn-doped TiO_2 is more efficient in comparison with other prepared nanoparticles. Therefore, we have studied the photodegradation of a mixture of three dyes using 5 mol% Mn-doped TiO_2 nanoparticles and shown in Figure 14. As a representative of industrial dyestuff, an aqueous solution of a mixture of three dyes, that is, RhB, BG, and methylene blue (MB) is used. The control experiment (i.e., without using catalyst) reveals that the photodegradation of RhB and BG, MB is very slow under only visible light irradiation. Figure 14 shows a change in concentration of the mixture of dyes in the suspension of 5 mol% Mn-doped TiO_2 with respect to irradiation time. Absorption peaks have been observed at wavelengths ∼668, ∼544, and ∼625 nm, which are characteristic absorption peaks (λ_{max}) of MB, RhB and BG, respectively. Progress of the photodegradation reaction has been studied by measuring the absorbance at these wavelengths. In 300 min. Reaction time, almost complete degradation of these three dyes has been observed.

4 | REUSABILITY OF CATALYST

Reusability of prepared nanoparticles is one of the most significant features of catalyst effectiveness over practical reuses. Therefore, three cycles of photocatalytic degradation of BG were carried out using 5 mol% Mn-doped TiO_2 under direct sun light irradiation and the results obtained are shown in Figure 15. The almost same activity has been shown by nanoparticles for three cycles. This also confirms the stability of the catalyst under the reaction conditions.

5 | CONCLUSIONS

The photo catalytically active Mn-doped TiO_2 nanoparticles were successfully synthesized by using sol–gel method. Among the various nanoparticles, 5 mol% Mn-doped TiO_2 has shown the better efficacy for photodegradation of brilliant green (BG). Further, it has been successfully employed for the degradation of mixture of three dyes namely methylene blue (MB), rhodamine B (RB) and brilliant green (BG). The analysis of characterization of the catalysts, it has been confirm that 5 mol% Mn-doped TiO_2 act as a superior catalyst in the photocatalytic degradation. However, strong interaction of Mn in TiO_2 has been proved by FTIR. The UV–Visible absorption study shows that the 5 mol% Mn-doped TiO_2 catalyst has better visible light absorption than other prepared catalysts. The band gap 3.2, 3.3, 3.4, and 3.7 eV has been observed for 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 respectively. Further, TiO_2 has shown increased BET surface area on doping. Prepared catalysts have shown excellent photocatalytic activity for degradation of brilliant green dye and mixture of dyes. The study of different pH of solution, at basic pH catalyst has shown greater photocatalytic activity. Also, 5 mol% Mn-TiO_2 catalyst has been shown almost similar efficiency for three cycles. Rate constant of 5 mol% Mn-doped TiO_2 catalyst is nearly twice to that of bare TiO_2 for degradation of BG.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ORCID

Mangesh G. Bhosale https://orcid.org/0000-0002-1036-9018
Meghshyam K. Patil https://orcid.org/0000-0002-3144-5016

REFERENCES

[1] C. Fernández, M. S. Larrechi, M. P. Callao, *Trends Anal. Chem.* **2010**, *29*, 1202.
[2] C.-W. Siao, H.-L. Chen, L.-W. Chen, J.-L. Chang, T.-W. Yeh, C.-C. Chen, *J. Colloid Interface Sci.* **2018**, *526*, 322.
[3] Y.-C. Wang, A.-H. Lee, C.-C. Chen, *J. Taiwan Inst. Chem. Eng.* **2018**, *93*, 315.
[4] M. Barakat, *Arab. J. Chem.* **2011**, *4*, 361.
[5] D. Huang, S. Liao, W. Zhou, S. Quan, L. Liu, Z. He, J. Wan, *J. Phys. Chem. Solids* **2009**, *70*, 853.
[6] M. K. Patil, S. Shaikh, I. Ganesh, *Curr. Nanosci.* **2015**, *11*, 271.
[7] C.-W. Siao, W.-L. William Lee, Y.-M. Dai, W.-H. Chung, J.-T. Hung, P.-H. Huang, W.-Y. Lin, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *544*, 25.
[8] H.-L. Chen, F.-Y. Liu, X. Xiao, J. Hu, B. Gao, D. Zou, C.-C. Chen, *J. Colloid Interface Sci.* **2021**, *601*, 758.
[9] A.-H. Lee, Y.-C. Wang, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *533*, 319.
[10] Y. Yu, G. Chen, X. Wang, D. Jia, P. Tang, C. Lv, *RSC Adv.* **2015**, *5*, 74174.
[11] Y. Li, Y. Jiang, S. Peng, F. Jiang, *J. Hazard. Mater.* **2010**, *182*, 90.
[12] J. Zhang, X. Xiao, J. Nan, *J. Hazard. Mater.* **2010**, *176*, 617.
[13] H. Khan, D. Berk, *React. Kinet. Mech. Catal.* **2014**, *111*, 393.
[14] S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright, R. M. Lambert, *J. Am. Chem. Soc.* **2007**, *129*, 13790.
[15] M. Anpo, M. Takeuchi, *J. Catal.* **2003**, *216*, 505.
[16] D. Chatterjee, S. Dasgupta, J. Photochem, C. Photobiol, *Photochem. Rev.* **2005**, *6*, 186.
[17] J. Tian, Y. Leng, Z. Zhao, Y. Xia, Y. Sang, P. Hao, J. Zhan, M. Li, H. Liu, *Nano Energy* **2015**, *11*, 419.
[18] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, *J. Mol. Catal. A Chem.* **2000**, *161*, 205.
[19] N. Sharotri, D. Sud, *Desalination Water Treat.* **2016**, *57*, 8776.
[20] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, K. Ikeue, M. Anpo, *J. Photochem. Photobiol. A* **2002**, *148*, 257.
[21] D. Dvoranova, V. Brezova, M. Mazúr, M. A. Malati, *Appl. Catal.* **2002**, *37*, 91.
[22] T. J. Kemp, R. A. McIntyre, *Polym. Degrad. Stab.* **2006**, *91*, 165.
[23] P. Kapoor, S. Uma, S. Rodriguez, K. Klabunde, *J. Mol. Catal. A Chem.* **2005**, *229*, 145.
[24] M. Rauf, M. Meetani, S. Hisaindee, *Desalination* **2011**, *276*, 13.
[25] T. Jedsukontorn, T. Ueno, N. Saito, M. Hunsom, *J. Alloys Compd.* **2018**, *757*, 188.
[26] L. Zhang, D. He, P. Jiang, *Catal. Commun.* **2009**, *10*, 1414.
[27] H. Li, D. Wang, H. Fan, T. Jiang, X. Li, T. Xie, *Nano Res.* **2011**, *4*, 460.
[28] V. Binas, K. Sambani, T. Maggos, A. Katsanaki, G. Kiriakidis, *Appl. Catal.* **2012**, *113*, 79.
[29] E. S. Karafas, M. N. Romanias, V. Stefanopoulos, V. Binas, A. Zachopoulos, G. Kiriakidis, P. Papagiannakopoulos, *J. Photochem. Photobiol. A* **2019**, *371*, 255.
[30] V. Binas, D. Venieri, D. Kotzias, G. Kiriakidis, *J. Materiomics.* **2017**, *3*, 3.
[31] S. Paul, P. Chetri, A. Choudhury, *J. Alloys Compd.* **2014**, *583*, 578.
[32] R. Chauhan, A. Kumar, R. P. Chaudhary, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2012**, *98*, 256.
[33] S.-H. Nam, T. K. Kim, J.-H. Boo, *Catal. Today* **2012**, *185*, 259.
[34] M. Stucchi, A. Elfiad, M. Rigamonti, H. Khan, D. Boffito, *Ultrason. Sonochem.* **2018**, *44*, 272.

[35] H. Feng, M.-H. Zhang, E. Y. Liya, *Appl. Catal. A: Gen.* **2012**, *413*, 238.

[36] M. Xue, L. Huang, J.-Q. Wang, Y. Wang, L. Gao, J.-H. Zhu, Z.-G. Zou, *Nanotechnology* **2008**, *19*, 185604.

[37] G. Shao, *J. Phys. Chem. C* **2009**, *113*, 6800.

[38] B. Choudhury, A. Choudhury, *Curr. Appl. Phys.* **2013**, *13*, 1025.

[39] J. Liu, J. Li, A. Sedhain, J. Lin, H. Jian, *J. Phys. Chem. C* **2008**, *112*, 17127.

[40] B. Choudhury, A. Choudhury, *J. Lumin.* **2013**, *136*, 339.

[41] X. Ma, W. Zhou, Y. Chen, *Mater.* **2017**, *10*, 631.

[42] S. Smart, S. Liu, J. M. Serra, J. C. Diniz da Costa, A. Iulianelli, A. Basile, Porous ceramic membranes for membrane reactors. in *Handbook of Membrane Reactors*. Woodhead Publishing, Cambridge, England **2013**, p. 298.

[43] J. Choma, M. Kloske, M. Jaroniec, *J. Colloid Interface Sci.* **2003**, *266*, 168.

[44] W. H. M. Abdelraheem, M. K. Patil, M. N. Nadagouda, D. D. Dionysiou, *Appl. Catal. B: Environ.* **2019**, *241*, 598.

[45] Z. Xu, C. Li, N. Fu, W. Li, G. Zhang, *J. Appl. Electrochem.* **2018**, *48*, 1197.

[46] A. J. Moreira, J. O. Malafatti, T. R. Giraldi, E. C. Paris, E. C. Pereira, V. R. de Mendonca, V. R. Mastelaro, G. P. Freschi, *J. Environ. Chem. Eng.* **2020**, *8*, 104543.

[47] R. S. Sutar, R. P. Barkul, M. K. Patil, *Curr. Nanosci.* **2021**, *17*, 120.

How to cite this article: M. G. Bhosale, R. S. Sutar, S. B. Deshmukh, M. K. Patil, *J. Chin. Chem. Soc.* **2022**, 1. https://doi.org/10.1002/jccs.202200248

Received: 26 May 2022 | Revised: 19 July 2022 | Accepted: 31 July 2022
DOI: 10.1002/jccs.202200248

JCCS JOURNAL OF THE CHINESE CHEMICAL SOCIETY

ARTICLE

Photocatalytic efficiency of sol–gel synthesized Mn-doped TiO_2 nanoparticles for degradation of brilliant green dye and mixture of dyes

Mangesh G. Bhosale[1,2] | **Radhakrishna S. Sutar**[1] | **Sandip B. Deshmukh**[2] | **Meghshyam K. Patil**[1]

[1]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus, Osmanabad, India

[2]Department of Chemistry, Ramkrishna Paramhans Mahavidyalaya, Osmanabad, India

Correspondence
Meghshyam K. Patil, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus Osmanabad-413501(M. S.), India.
Email: meghshyam_patil@yahoo.com

Abstract

The Mn-doped TiO_2 nanoparticle photocatalysts have been prepared by a simple sol–gel method. 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles have been prepared by using a stoichiometric amount of manganese acetate and titanium isopropoxide as precursors of Mn and Ti respectively. The physico-chemical characterization of the prepared samples has been studied by x-ray diffraction (XRD), Brunauer–Emmett–Teller surface area analysis, field emission scanning electron microscope, energy dispersive x-ray analysis, high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, Ultraviolet–visible spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). XRD study reveals the formation of pure anatase phase of TiO_2 and decrease in crystalline size of TiO_2 on increasing the Mn doping content. TGA reveals minimum weight loss in the high-temperature region of 500–1,000°C, showing the thermal stability of the catalyst. FTIR study shows highly bonding in metal atoms. These samples have been tested for photocatalytic degradation of brilliant green dye. 5 mol% Mn-doped TiO_2 is having nearly four times more photocatalytic activity than pure TiO_2. In addition, Mn-doped TiO_2 has shown excellent photodegradation of a mixture of three dyes namely, rhodamine B, brilliant green, and methylene blue.

KEYWORDS

kinetic study, Mn-doped TiO_2, nanoparticles, photocatalytic activity, sol–gel method

1 | INTRODUCTION

Various industries such as the manufacture of textile, paint, leather, pesticides, fertilizers, pharmaceuticals, and so on are primarily responsible for water pollution. By means of these industries, various organic pollutants have been dumped into the water bodies. The aquatic life and human life may be largely affected by these organic pollutants, which are exceptionally difficult to be degraded or eliminated by nature.[1–3] Numerous predictable methods such as biological methods, chemical precipitation, and membrane filtration are suggested for wastewater treatment, but these methods may not be greatly possible. However, chemical precipitation causes several disadvantages, large chemical feeding such as lime, oxidants, or H_2S and physicochemical monitors

such as pH are essential for the effluent, the excessive chemical usually causes a secondary pollution issue. Membrane filtration is an alternative physical method for wastewater treatment,[4] but its utility is affected by factors such as particle size, solubility, diffusivity, and charge.

In several countries, economic growth and industrial development go hand in hand, for example, textile industries play an important role in many countries such as China, Bangladesh, Vietnam, India, Sri Lanka, etc. These industries use different raw materials such as cotton, synthetic and woolen fibers, and several synthetic and natural dyes and chemicals. Approximately 10,000 different synthetic dyes are available in the global market. The worldwide annual production of these dyes is over 700,000 tons. Nearly 200,000 tons of synthetic dyes are lost into the environment because of the inefficient dyeing process used in textile industries. According to the World Bank estimation, the textile dyeing and finishing treatment is having about 17%–20% share of the total industrial wastewater generated.[4–6]

To tackle water pollution, among the number of processes, one of the most effective processes is the use of heterogeneous photocatalyst.[7–10] The most effective heterogeneous photocatalyst is titanium dioxide, because of its interesting properties such as nontoxicity, low cost, strong oxidizing power, chemical, and biological inertness, reusability, porosity, phase transformation, crystallinity, availability in nano-size and in different morphology and so on.[11–14] TiO_2 has a large band gap of ~3.20 eV, hence it functions effectively under ultraviolet (UV) light irradiation and limits its applications in direct sunlight or visible light. Another obstacle is the larger recombination rate of photo-generated electrons and holes, which further limits its efficiency.[15] One of the major challenges is to make an innovative photocatalyst, which can absorb light in the visible region rather than the UV region. In this direction, our focus is to prepare a TiO_2 catalyst, which on modification can absorb visible light rather than UV light, and minimize its band gap.

Enormous research has been carried out during the last few decades for developing TiO_2 catalyst to increase its activity in the visible region, for the achievement of higher absorbance of visible light by TiO_2. This includes several methods such as metal and non-metal ion doping and surface sensitization of TiO_2 coupling which helps in narrowing the band gap.[16–19] In literature, the number of transition metals such as V, Cr, Fe, Mg, Co, Zn, and Mo has been used as a dopant in TiO_2, which results in the enhanced photocatalytic activity of TiO_2.[20–24] Among these, Mn is one of the effective doping elements, which results in the red shift in absorption wavelength due to the contraction in the band gap via the formation of new energy levels in between the Ti 3d states of the conduction band and the O 2p states of the valence band.[25] Zhang et al. reported the synthesis of MnO_2-doped anatase TiO_2 nanoparticles, which showed higher photocatalytic activity than Degussa P25.[26] Li et al. synthesized visible light active Mn-TiO_2 photocatalyst with controlled size for degradation of Rhodamine B (RhB).[27] Further, Mn-TiO_2 has been reported for the degradation of NO and acetaldehyde under visible irradiation.[28–32] In view of these results, there is a scope to develop a new method for the synthesis of Mn-doped TiO_2.

In this study, we have synthesized Mn-doped TiO_2 catalysts by the low-temperature sol–gel method. Prepared materials have been characterized by several techniques such as x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, Field Emission Scanning Electron Microscope (FESEM), energy dispersive x-ray analysis (EDX), High-Resolution Transmission Electron Microscopy (HRTEM), x-ray photoelectron spectroscopy (XPS), UV–Visible spectroscopy, Photoluminescence (PL) spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). Further, photocatalytic activity has been evaluated for the degradation of brilliant green dye in an aqueous solution and for the degradation of a mixture of dyes in an aqueous solution. Effect of various parameters such as concentration of dye, pH of a solution, and catalyst loading on the degradation of brilliant green has been evaluated.

2 | MATERIAL AND METHOD

2.1 | Synthesis of Mn-doped TiO_2 nanoparticles by sol gel method

The Mn-doped TiO_2 nanoparticles were prepared by using sol–gel method. Firstly, 5 ml of titanium isopropoxide and 5 ml of glacial acetic acid were taken in a clean round bottom flask and stirred for 15 min. To this solution separately prepared solution Tween 80 (0.2 ml) in 10 ml of distilled water was added slowly with constant stirring for 2 hr. To this resultant solution, 80 ml of distilled water was added slowly with constant stirring for 2 hr. Further, the stoichiometric amount of manganese acetate was added to a reaction mixture and stirred for 4 hr. pH of this solution is adjusted to 10 by adding ammonia solution with constant stirring and further stirred for 3 hr at 60°C for removing excess ammonia. The reaction mixture was cooled to room temperature and the supernatant liquid has been removed by decantation. Further, 80 ml of distilled water was added and the mixture was stirred for 3 hr at 60°C. The mixture was

filtered, washed with ethanol and obtained precipitate has been dried at 110°C for 12 hr. The obtained powder was crushed and calcined at 400°C for 5 hr. Light brown powder of Mn-doped TiO_2 nanoparticles has been formed. By this procedure, 1, 3, and 5 mol% Mn-doped TiO_2 have been synthesized. The same procedure was adopted for the synthesis of bare TiO_2, without the addition of manganese acetate.

2.2 | Characterization

The XRD spectra of all prepared samples were recorded by using Regaku diffractometer with Cu Kα (1.5418 Å). The diffraction data were collected in the 2θ range of 10–90° at the scanning rate of 2°/min. The crystalline size has been calculated by the Scherer equation. BET surface area, pore volume, and pore diameter of the bare TiO_2 and 5 mol% Mn-doped TiO_2 have been studied by N_2 adsorption measurement at −196°C using NOVA touch 4LX, Quntachrome, USA. UV–Vis absorption spectrum of the prepared catalysts was recorded in the range of 200–800 nm by using ELICO double beam SL210 UV–visible spectrophotometer. Photoluminescence measurement of all the prepared catalysts has been studied with 330 nm excitation wavelength (at 3.76 eV excitation energy) using a JASCO spectrofluorometer. FTIR spectra of the nanoparticles were recorded on Thermo Scientific Nicolet iS10 in the range of 400–4,000 cm^{-1} in transmission mode. High-resolution transmission electron microscopy (HRTEM) images of the samples were recorded on a JEOL JEM 2100 Plus. The FESEM images with EDX were recorded using Carl Zeiss Supra 55 scanning electron microscope with a field emission electron gun, to know the morphology and elemental composition respectively. XPS measurements of the prepared sample have been recorded on a Shimadzu (ESCA 3400) spectrometer having Mg Kα (1,253.6 eV) radiation as the excitation source. The TGA data were recorded on Mettler Toledo TGA1 thermogravimetric analyzer; it shows the thermal stability of the prepared catalysts.

2.3 | Photocatalytic activity

Photocatalytic degradation of Brilliant green in an aqueous solution has been studied by employing Mn-doped TiO_2 catalysts. Further, degradation of a mixture of three dyes (including brilliant green, rhodamine B, and methylene blue) in an aqueous solution under direct sunlight has been studied by using the most active 5 mol% Mn-doped TiO_2. Also, the effect of various parameters (such as pH of the solution, the concentration of the brilliant green, and catalyst loading) have been examined on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 for degradation of brilliant green. The pH of the solution was adjusted by adding an appropriate quantity of 1 N NaOH and 1 N HCl solutions. In the photocatalytic study, all the experiments are studied thrice and observed with almost similar results. The corresponding error bar has been shown within the figures.

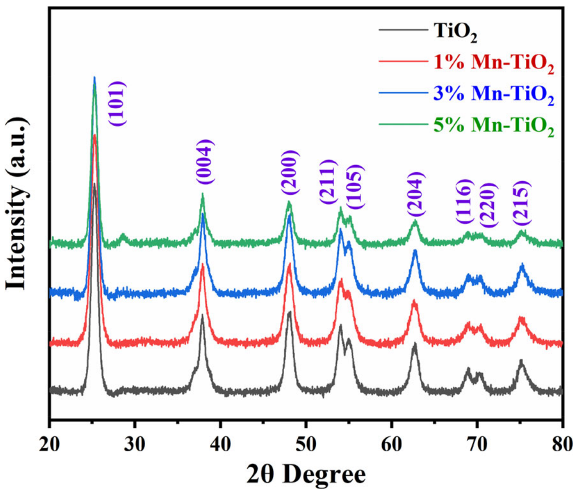


FIGURE 1 XRD pattern of pure TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2

2.3.1 | Photocatalytic degradation of brilliant green dye

We have prepared a 20 ppm brilliant green dye solution using distilled water at room temperature. From this prepared stock solution, 200 ml solution has been taken in the round bottom flask; to this, 100 mg of prepared catalyst has been added. This reaction mixture was stirred for 30 min. in dark to reach adsorption–desorption equilibrium. After this, the solution was transferred into the sunlight. 2 ml sample has been collected after a regular time interval, centrifuged, and performed UV–Visible spectral analysis from 200–800 nm wavelength and absorbance has been recorded for wavelength (λ_{max}) 625 nm for brilliant green.

2.3.2 | Photocatalytic degradation of mixture of dyes

We have prepared a 20 ppm solution of each dye (brilliant green, methylene blue and rhodamine B) using distilled water. By taking these three solutions in equal quantity, a 200 ml solution of mixture of brilliant green,

TABLE 1 Structural parameters of pure TiO_2 and Mn-doped TiO_2 nanoparticles

				Cell parameters			
Catalysts	**Standard d value**	**Observed d value**	**hkl plane**	**a (Å)**	**c (Å)**	**V (Å^3)**	**Crystallite size(nm)**
TiO_2	3.52	3.5147	(101)	3.78	9.52	136.02	9.927933
	2.37	2.38018	(004)				
	1.33	1.89052	(220)				
1% Mn-TiO_2	3.52	3.5201	(101)	3.775	9.4916	135.26	9.036106
	2.37	2.3729	(004)				
	1.33	1.8875	(220)				
3% Mn-TiO_2	3.52	3.5229	(101)	3.772	9.482	134.90	9.033568
	2.37	2.3705	(004)				
	1.33	1.8860	(220)				
5% Mn-TiO_2	3.52	3.5215	(101)	3.7854	9.494	136.04	8.944641
	2.37	2.3735	(004)				
	1.33	1.8927	(220)				

methylene blue and rhodamine B has been prepared. This prepared solution was taken in round bottom flask and 100 mg 5 mol% Mn-doped TiO_2 catalyst was added. After 30 min., the reaction mixture was transferred to direct sunlight, and after regular time interval the samples were collected. The absorbance of collected samples was recorded using a UV–visible spectrophotometer at the range of 200–800 nm wavelength.

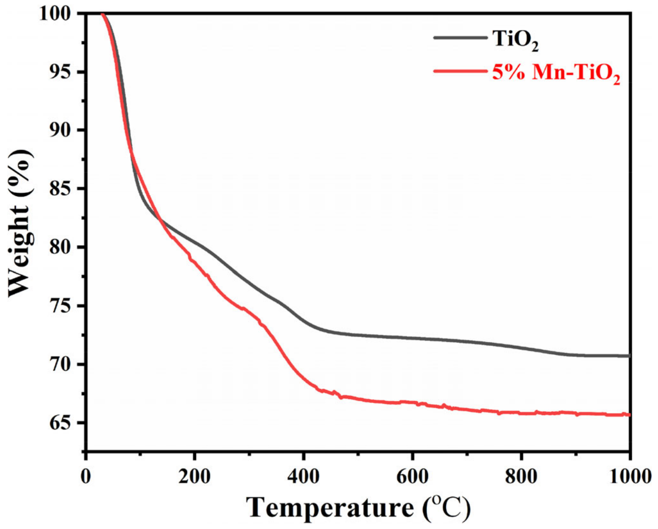


FIGURE 2 TGA of TiO_2 and 5 mol% Mn-doped TiO_2

3 | RESULT AND DISCUSSION

3.1 | Characterization

3.1.1 | X-ray diffraction study

X-ray diffraction patterns of undoped and Mn-doped TiO_2 nanocatalysts are shown in Figure 1. It is noted that all the diffraction peaks represented the anatase phase of TiO_2 with a characteristic high-intensity peak at $2\theta = 25.20°$ and other peaks correspond to 2θ values at 37.91, 47.98, 54.05, 55.12, 62.78, 68.94, 70.45 and 75.35° which can be indexed as (101), (004), (200), (211), (105), (204), (116), (220) and (215) planes of anatase TiO_2 (JCPDS card no.73–1764) respectively. Mostly, the XRD spectra have not shown any extra peaks corresponding to Mn. This indicated that the Mn may introduce in to TiO_2 lattice as substitution dopant by replacing Ti and O and not in the interstitial position of the TiO_2 lattice.[32,33]

The crystalline size of all prepared catalysts has been calculated on the basis of the Scherrer formula. The crystalline size of bare TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2 is 9.93, 9.04, 9.03, and 8.94 nm respectively. The Scherrer formula is as follows:

$$D = \frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

where D is the average size of the nanoparticle, λ is the wavelength, β is the full width at half maximum, and θ is Bragg's angle.

On the basis of crystalline size, we can say that on an increase in Mn doping, the size of the nanoparticle decreases, which results in an increase in the surface area of the catalyst and ultimately enrichment in photocatalytic activity. The structural parameters of pure TiO_2 and

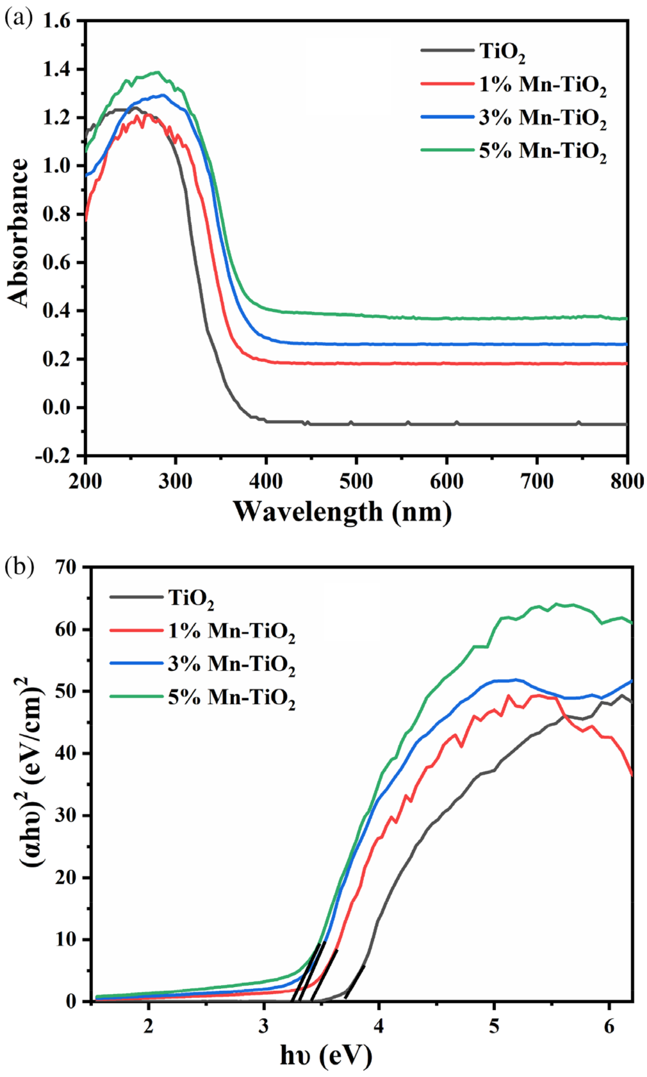


FIGURE 3 (a) UV–Visible absorption spectra; (b) plot of hυ versus $\alpha h\upsilon^2$ of bare TiO_2; and Mn-doped TiO_2

Mn-doped TiO_2 catalysts are shown in Table 1 and it is well matched with JCPDS 73–1764 data.

3.1.2 | Thermo gravimetric analysis

The thermogravimetric analysis plots of as-prepared pure TiO_2 and 5 mol% Mn-doped TiO_2 (before calcination) have been shown in Figure 2. The weight loss of TiO_2 from room temperature to 400°C is due to conversion from amorphous to crystalline phase.[34] In specific, after heating over 400°C, we do not observe any other phase than crystalline anatase TiO_2 this is prove on XRD analysis. The Thermo gravimetric analysis of Mn-TiO_2 is dividing in to three stages of weight loss. In stage first nearly 19% weight loss observed in between 30 and 180°C is due to loss of the residual solvent and water. The second weight loss which is about 12%, observed in between 126 and 380°C is due to loss of organic components. However, TiO_2 has shown less amount of weight loss as compared to Mn-doped TiO_2. Further, both Mn-doped TiO_2 and bare TiO_2 has not shown any significant weight loss after 400°C.

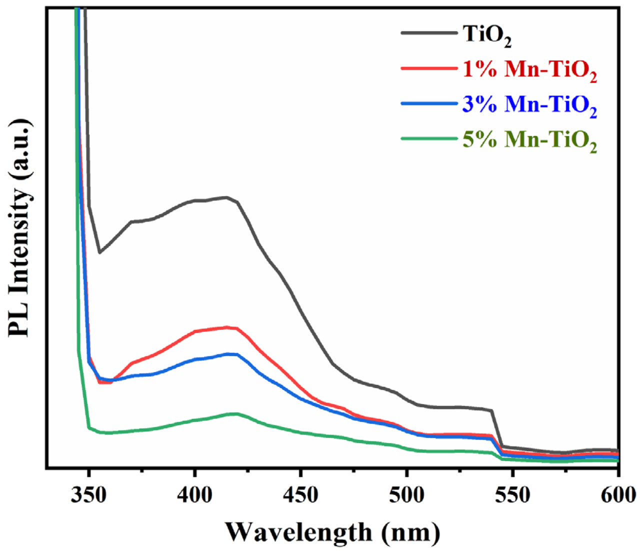


FIGURE 4 Photoluminescence spectra of bare TiO_2 and Mn-doped TiO_2 nanoparticles

As compared to bare TiO_2, Mn-doped TiO_2 has shown an overall 10% higher weight loss. The weight loss indicates that pure TiO_2 has early started to convert into its crystalline phase from the amorphous phase, whereas Mn-doped TiO_2 started later to convert into its crystalline form.

3.1.3 | UV–Visible spectroscopy study

The influence of doping on the UV–Vis spectra properties of the anatase TiO_2 is clear from Figure 3. The Mn-doped TiO_2 nanoparticles shows a remarkable change in their color, which depends on the concentration of dopant, as concentration of dopant increases color becomes light brown to light dark brown. From the UV–Vis spectra, the increase in absorption of Mn-doped TiO_2 in visible region has been observed which is due to their respective energy levels, the promotion of 3d electrons of doping Mn ions in to the conduction band of TiO_2.[35–37]

With the increase in doping, we observe that stronger absorption edges shifted to the right side of the spectrum, which results in a decrease in the band gap. As the percentage of doping increases band gap of prepared catalysts decreases from 3.7 to 3.2 eV. Due to decrease in band with absorption of lesser amount of energy can promotes electron to conduction band. It increases the photocatalytic activity of the prepared catalyst. On the

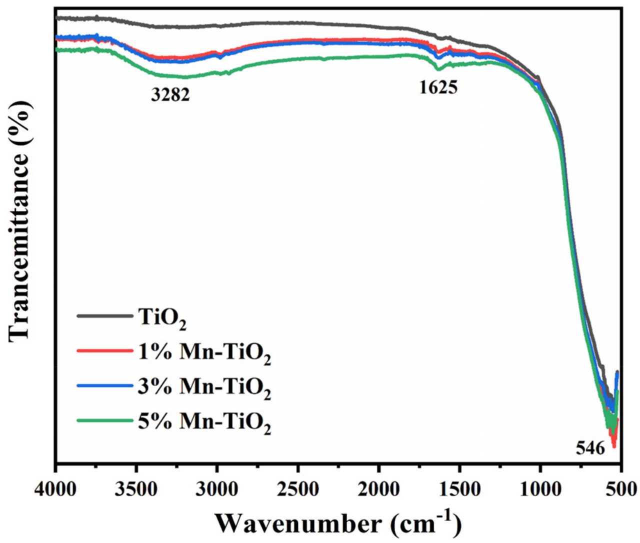


FIGURE 5 FTIR study of Mn-doped TiO_2 nanoparticles

basis of Figure 3b it is seen that 5 mol% Mn-doped TiO_2 has highest photocatalytic activity.

3.1.4 | Photoluminescence spectroscopy study

An important identifying tool for determining the existence of defects in a nanomaterial is PL spectroscopy. The photoluminescence spectra of pure TiO_2 and 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles at room temperature are shown in Figure 4. The PL spectra has been studied at an excitation wavelength of 330 nm. Two separate emission peaks have been identified in the spectra. The indirect band-to-band transition of TiO_2 nanoparticles from their conduction band to their valence band causes the UV emission.[38] The peak at 415 nm is related to self-trapped excitons.[38] The 490 nm peak is observed due to the charge transfer transition from Ti^{3+} to the TiO_6^{2-} octahedra associated with oxygen defects.[39] In this spectrum there is no additional peak of Mn or shifting of emission peak. On increasing Mn doping, the intensity of the emission peaks has been reduced. The oxygen vacancies in pure TiO_2 function as luminescence enhancers and boost emission intensity. The TiO_2 lattice is disturbed, the Ti–O bond is broken, and many oxygen vacancies are produced when Mn is doped. As the concentration of Mn in TiO_2 increases, the number of non-radiative oxygen vacancy centres also increases, nearby Mn^{2+}. Since there are more oxygen defects available, lesser photoexcited electrons are available to recombine with holes because they are entrapped and highly localized in those oxygen vacancies. Presence Mn resemblance a rise in non-radiative oxygen vacancy centres with trapped electrons, which causes a subsequent drop in emission intensity. Further, in addition to the non-radiative oxygen vacancies, the mobility of the carriers is another important factor influencing PL intensity. The mobility of the free carriers is decreased by dopants and deficiencies in the interior, grain boundary, and surface. When they get close to charged dopants or oxygen defect states, the mobile carriers disperse. Reduced mobility will result in more carriers being separated from one another, which lowers the intensity of the PL.[40]

3.1.5 | FTIR study

The FTIR spectra of Mn-doped TiO_2 nanoparticle is shown in Figure 5. The stretching and bending vibration of the hydroxyl group peak at 3282 cm^{-1} and the stretching vibration band intensity of Mn-doped TiO_2 is greater than pure TiO_2, indicating that TiO_2 has stronger absorption with Mn-doped TiO_2.[41] The absorption band in the prepared materials at 1625 cm^{-1} was associated with the stretching of the C–O–Ti bond. The peak at about 546 cm^{-1} is due to anatase TiO_2, which represents the bending vibration of Ti–O.

3.1.6 | FESEM and EDX study

The morphology and surface nature of the synthesized Mn-doped TiO_2 nanoparticles were studied by FESEM and obtained images of all samples are shown in Figure 6. The FESEM micrograph of all samples has shown the fine-grown crystals, which were gathered closely with each other. Further, the EDX analysis shows that obtained sample has the same elemental composition as per the proportion of precursors taken during the preparation.

3.1.7 | HRTEM study

The structural properties of prepared material Mn-doped TiO_2 nanoparticles have been further investigated by using HRTEM spectroscopy. The particle size for 5 mol% Mn-doped TiO_2 from the HRTEM images is varying from 4 to 14 nm as shown in Figure 7a. Clear lattice fringes for Mn-doped TiO_2 were obtained and shown in Figure 7b. Further, the presence of anatase phase of TiO_2 has been confirmed by the crystal lattice fringes having a d value of 0.352 nm which is corresponding to the spacing of (101) lattice plane of the anatase TiO_2 (JCPDS 73–1764). Furthermore, the selected area electron diffraction pattern shown in Figure 7c, matches with anatase TiO_2 and the brightness and intensity of polymorphic ring reveals the well crystalline nature. The average particle size of

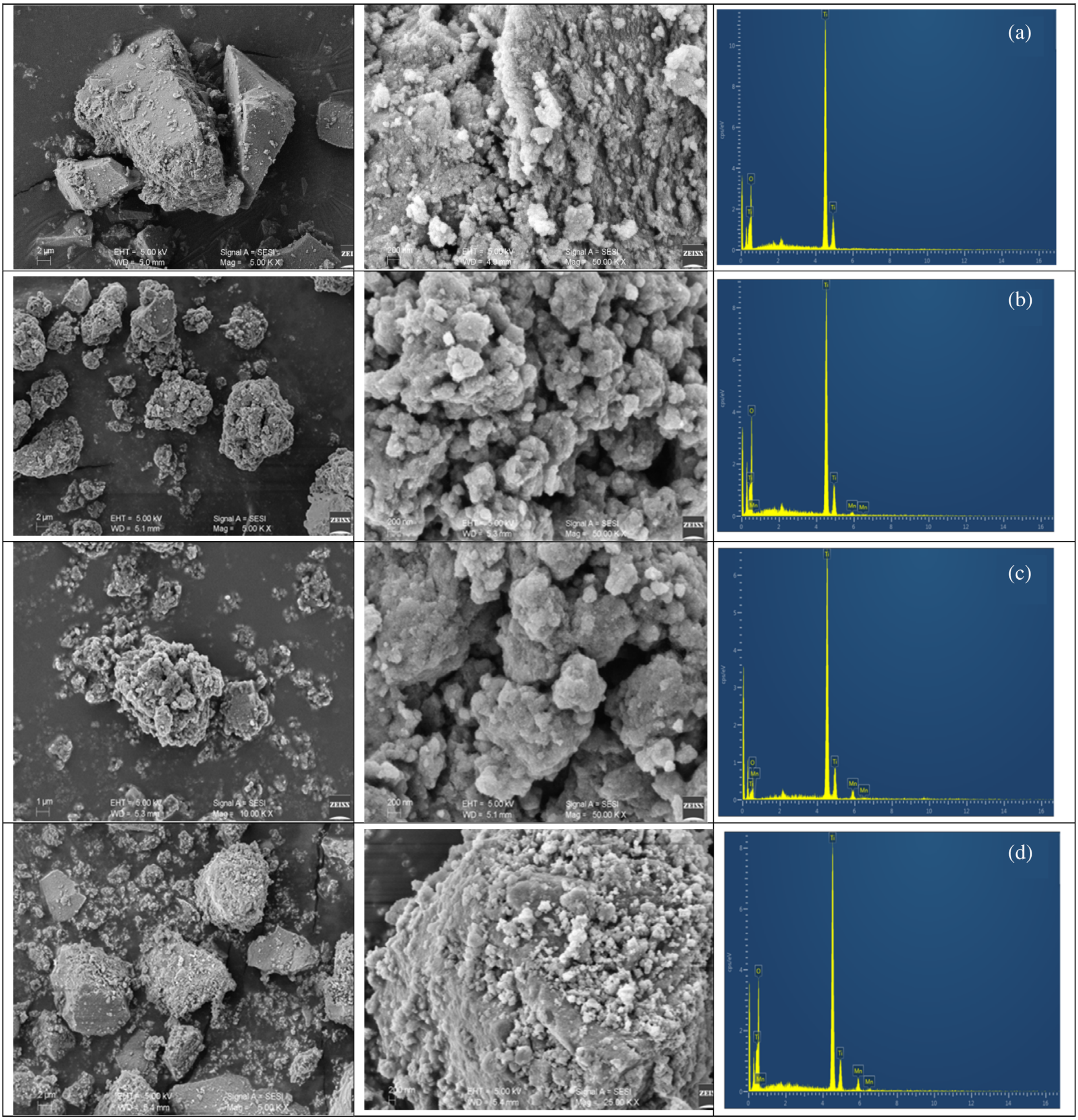


FIGURE 6 FESEM with EDX of (a) pure TiO_2; (b) 1 mol% Mn-doped TiO_2; (c) 3 mol% Mn-doped TiO_2; and (d) 5 mol% Mn-doped TiO_2 nanoparticles

the nanoparticles from HRTEM Figure 7d was found to be 8–10 nm, which is also matched with the XRD results.

3.1.8 | BET surface area analysis

The values of the specific surface area, pore volume, and pore diameter of pure TiO_2 and 5 mol% Mn-doped TiO_2 samples were measured using the Brunauer–Emmett–Teller (BET) equation following the Barrett–Joyner–Halenda method are summarized in Table 2. The N_2 adsorption–desorption for both the photocatalysts was consistent with Type IV isotherm (Figure 8), which is representative of mesoporous structures.[42–44] After doping with manganese, a significant increase in the specific surface area and pore volume of the samples has been

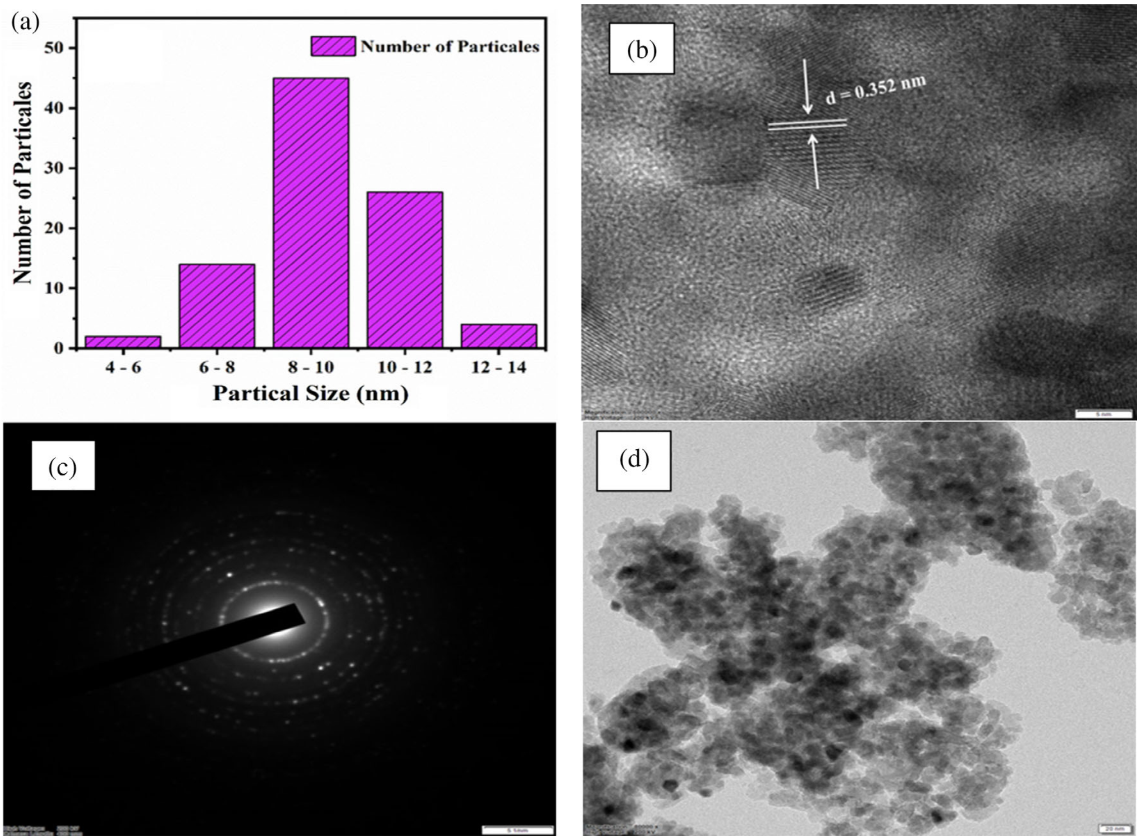


FIGURE 7 (a) Average particle size; (b) and (d) HRTEM image of 5 mol% Mn-doped TiO_2; and (c) SAED pattern of 5 mol% Mn-doped TiO_2 powder

TABLE 2 BET surface area, pore volume, and pore diameter of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticles

Sr. no.	Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	TiO_2	111.399	0.231848	7.83178
2	5% Mn-TiO_2	185.312	0.277406	5.63585

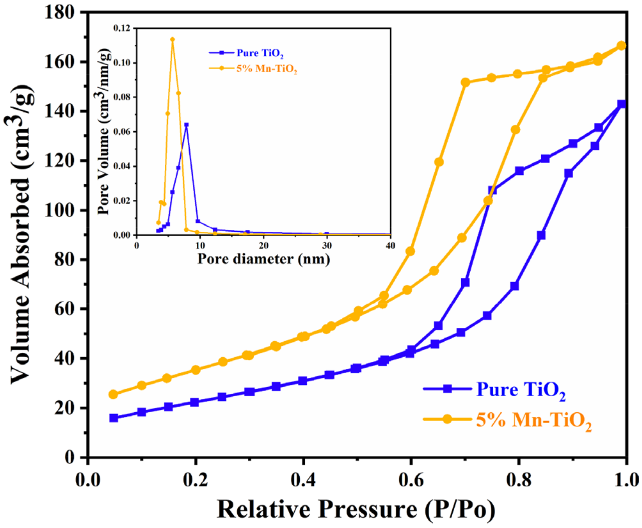


FIGURE 8 N_2 adsorption–desorption isotherm (inset, pore size distribution) of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticle

noticed. The BET surface area of 185.312 and 111.399 m^2/g was recorded for 5 mol% Mn-doped TiO_2 and bare TiO_2 respectively. Moreover, the pore diameter of pure TiO_2 is greater than 5 mol% Mn-doped TiO_2 and the pore volume of TiO_2 is less than 5 mol% Mn-doped TiO_2.

3.1.9 | XPS study

An XPS analysis of 5 mol% Mn-doped TiO_2 is shown in the Figure 9, which confirms the basic structure of the catalyst produced. Figure 9a shows the survey spectra, which shows the presence of Mn, Ti and O in the sample. The XPS spectrum of Mn 2p exhibited peaks at 642.2 and 653.8 eV, which were attributed to the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ levels, respectively, a finding that bears out the presence of Mn^{3+} is shown in Figure 9b.[45] From the

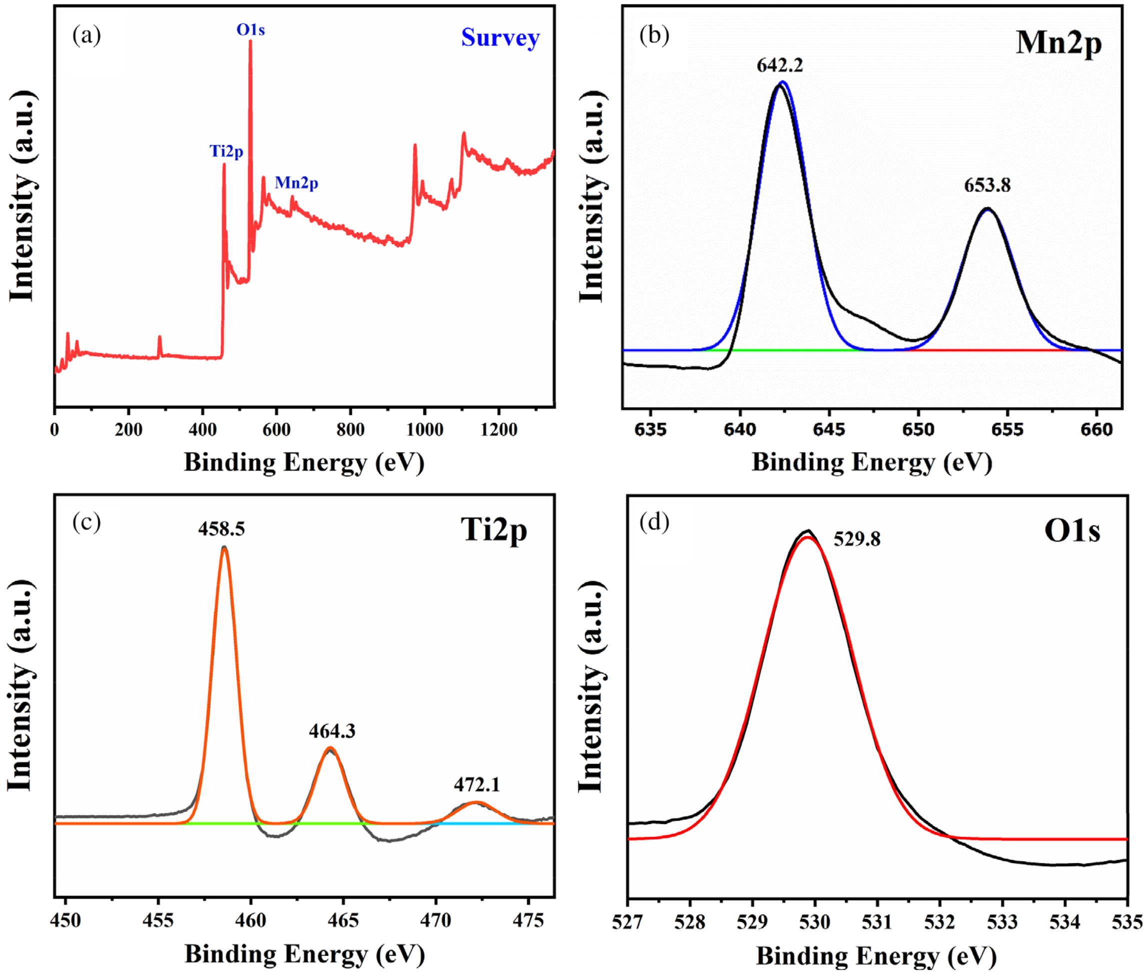


FIGURE 9 (a) XPS spectra of 5 mol% Mn-doped TiO_2, high-resolution spectra of (b) Ce 3d, (c) Ti 2p, and (d) O 1s

Figure 9c, the XPS spectrum of Ti 2p peaked at 458.5 and 464.3 eV, attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels, respectively, confirming the presence of Ti^{4+}. In addition, the difference between the two energy levels was approximately 6.0 eV and the 472.1 eV satellite peak is characteristic of TiO_2 compounds. Figure 9d shows O1s XPS spectrum peak at 529.8 eV, which is corresponds to the O-(Mn, Ti) lattice oxygen.[46]

3.2 | Photocatalytic degradation of brilliant green

The photocatalytic activity of synthesized nanoparticles has been explored for the degradation of brilliant green dye and a mixture of three dyes, namely methylene blue, brilliant green, and rhodamine B. Brilliant green is triarylmethane dye having the chemical formula $C_{27}H_{34}N_2O_4S$ and molecular weight 475.6 g/mol. It is used in dilute solution as a topical antiseptic and effective against gram positive microorganisms.

UV–Visible absorption spectra of degradation study of BG using 5 mol% Mn-doped TiO_2 with respect to irradiation time is shown in Figure 10a. The maximum absorption peak of brilliant green (BG) dye is at ~625 nm (λ_{max}). As the time increases from 0 to 180 min the peak intensity decreases gradually, also little shifting of peak to slightly lower wavelength is observed. The complete degradation of BG was observed after 180 min by using this catalyst. The plot of change in concentration of BG by using all prepared catalysts (such as 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and bare TiO_2) with respect to irradiation time has been shown in Figure 10b. The observation of experiment reveals that the concentration of BG has been nearly constant in the absence of photocatalyst and in the presence of visible light, suggests the thermodynamic stability of BG dye. The complete degradation of BG by using 5 mol % Mn-doped TiO_2 nanoparticles has required less time than that of 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 nanoparticles. This observation clearly indicates that the photocatalytic degradation

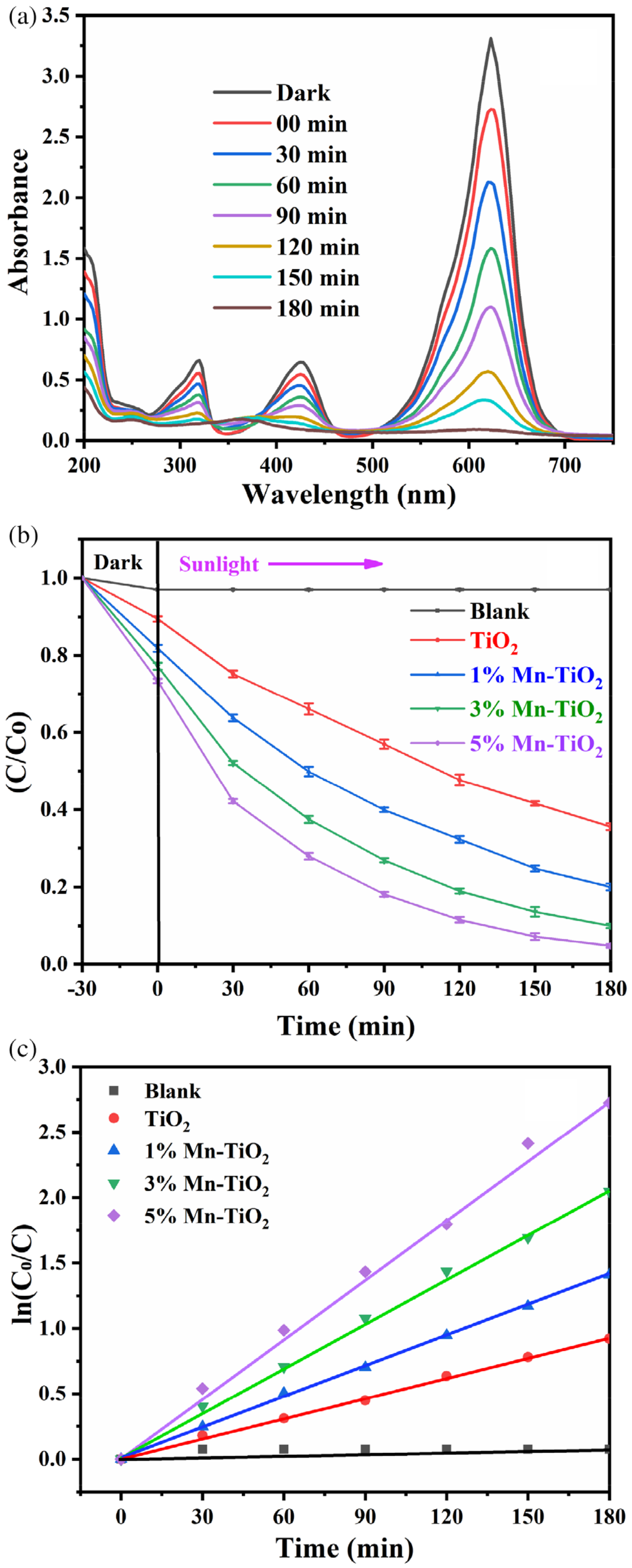


FIGURE 10 (a) UV–Visible spectra of BG at different time intervals using Mn-doped TiO_2 nanoparticle as catalyst, (b) change in concentration of BG by using different catalysts and without catalyst with irradiation time, and (c) corresponding graph of $\ln(C_0/C)$ of BG versus irradiation time

reaction of the Mn-doped TiO_2 nanoparticle is highly dependent upon the amount of Mn introduced into TiO_2 and the method used for synthesis of the catalyst preparation. Moreover, reaction kinetic has been shown in Figure 10c and results obtained were tabulated in Table 3 for photocatalytic degradation of BG by using prepared samples. As compared to other prepared catalysts, the higher rate constant (16.73×10^{-3} min^{-1}) for BG degradation using 5 mol% Mn-TiO_2 nanoparticles has been observed under visible light.

The effect of change in concentration of BG on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 nanoparticle has been studied by using 10–40 ppm BG solution. Figure 11a shows that complete degradation has been achieved for 10 ppm solution in 180 min., whereas 69, 55 and 28% degradation has been achieved of 20, 30, and 40 ppm solution respectively in same time by using 5 mol% Mn-doped TiO_2. Figure 11b shows the plot of d[BG]/dt versus time, on increasing the concentration of BG from 10 to 40 ppm, for time intervals of 0–30 min, 30–60 min, 60–90 min, and 90–120 min the change in concentration initially increases and then decreases. But for a time interval of 120–150 min, the trend is somewhat irregular.

The effectiveness of the photodegradation reaction largely depends upon the pH of the dye solution. The pH of the BG solution was adjusted using 1 N HCl to make a solution acidic and 1 N NaOH to make a solution basic. As shown in Figure 12, the rate of photocatalytic reaction was found higher in the basic medium (pH 12.0, 9.0) than that of the acidic medium (pH 5.0, 3.0). The different pH of the solution can change the surface charge on nanoparticles and, consequently, the potential of photocatalytic reactions. The mechanism of photocatalytic degradation is shown in Equations (2)–(7). The reactive species could be formed by the reactions shown in Equations (2)–(6), can be generated at specific potential and initiate the photocatalytic reaction (Equation 7).[47]

TABLE 3 Reaction kinetic parameters of photocatalytic degradation study of BG Mn-TiO_2 and bare TiO_2 nanoparticles

Catalyst	Initial Conc. of BG (%)	Final Conc. of BG (%)	Rate constant (min^{-1})
Blank	100	95.8	0.1×10^{-3}
TiO_2	100	57.8	5.7×10^{-3}
1% Mn-TiO_2	100	40.2	8.9×10^{-3}
3% Mn-TiO_2	100	27.6	12.69×10^{-3}
5% Mn-TiO_2	100	15.2	16.73×10^{-3}

Formation of HO$^\bullet$ is favored under basic condition and it may help for degradation under basic conditions.

$$\text{Mn}-\text{doped TiO}_2+h\nu \rightarrow \text{Mn}-\text{doped TiO}_2\left(e^-+h^+\right), \tag{2}$$

$$\text{Mn}-\text{doped TiO}_2(e^-)+O_2 \rightarrow \text{Mn}-\text{doped TiO}_2+O_2{}^{-\bullet}, \tag{3}$$

$$\text{Mn}-\text{doped TiO}_2(e^-)+O_2+H^+ \rightarrow \text{Mn}-\text{doped TiO}_2+HO_2{}^{\bullet}, \tag{4}$$

$$\text{Mn}-\text{doped TiO}_2\left(h^+\right)+H_2O \rightarrow \text{Mn}-\text{doped TiO}_2+H^++OH^{\bullet}, \tag{5}$$

$$\text{Mn}-\text{doped TiO}_2\left(h^+\right)+OH^- \rightarrow \text{Mn}-\text{doped TiO}_2+OH^{\bullet}, \tag{6}$$

$$\text{BG}+\text{Reactive species}\left(O_2{}^{-\bullet}/OH^{\bullet}/HO_2{}^{\bullet}\right) \rightarrow \text{Degradation Products}. \tag{7}$$

Furthermore, the photocatalytic degradation efficiency was evaluated by changing the amount of catalyst, that is, catalyst loading. Figure 13a shows the change in concentration of BG with irradiation time for the experiments carried out by using different catalyst loading, that is, from 0.25 to 1 g/L. The degradation efficiency increases with increase for catalyst loading. This is due to the fact that the higher amount of catalyst has higher active sites on the surface and consequently active sites

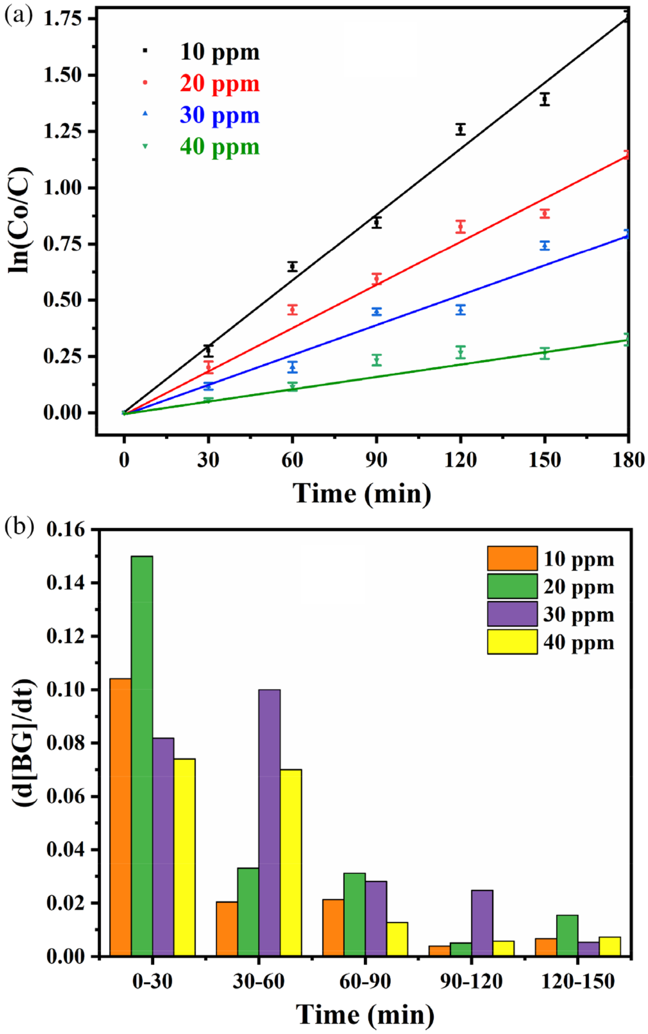


FIGURE 11 (a) Plot of percentage degradation of BG with different concentrations of dye solution by using 5 mol% Mn-doped TiO_2 nanoparticles with irradiation time and (b) corresponding plot of d[BG]/dt versus time

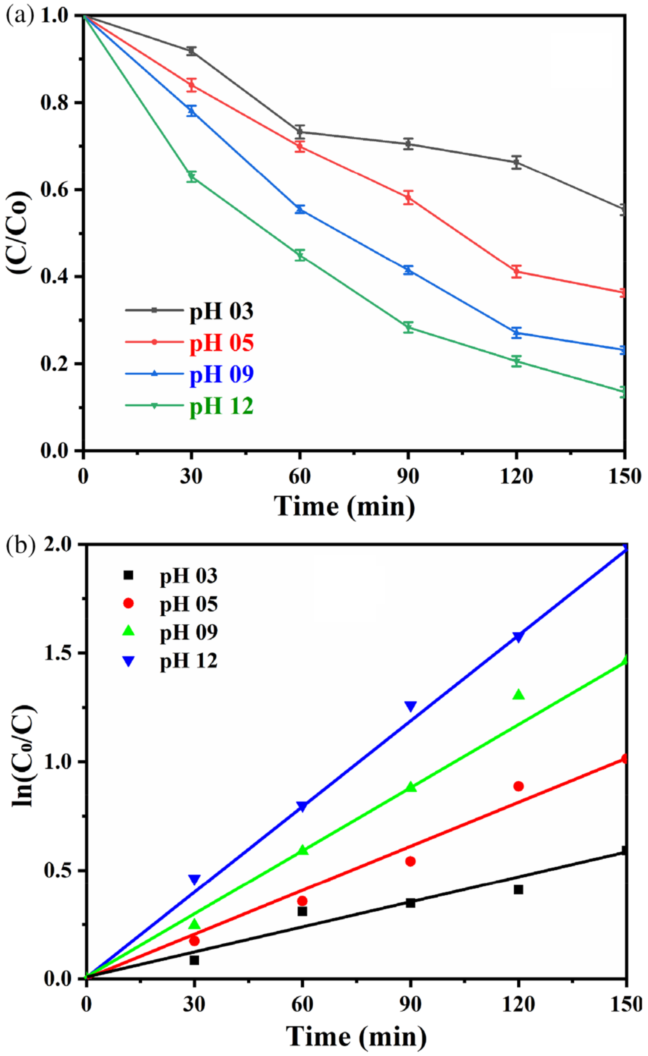


FIGURE 12 Effect of change in pH of BG dye solution: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ versus time by using 5 mol% Mn-doped TiO_2 nanoparticles

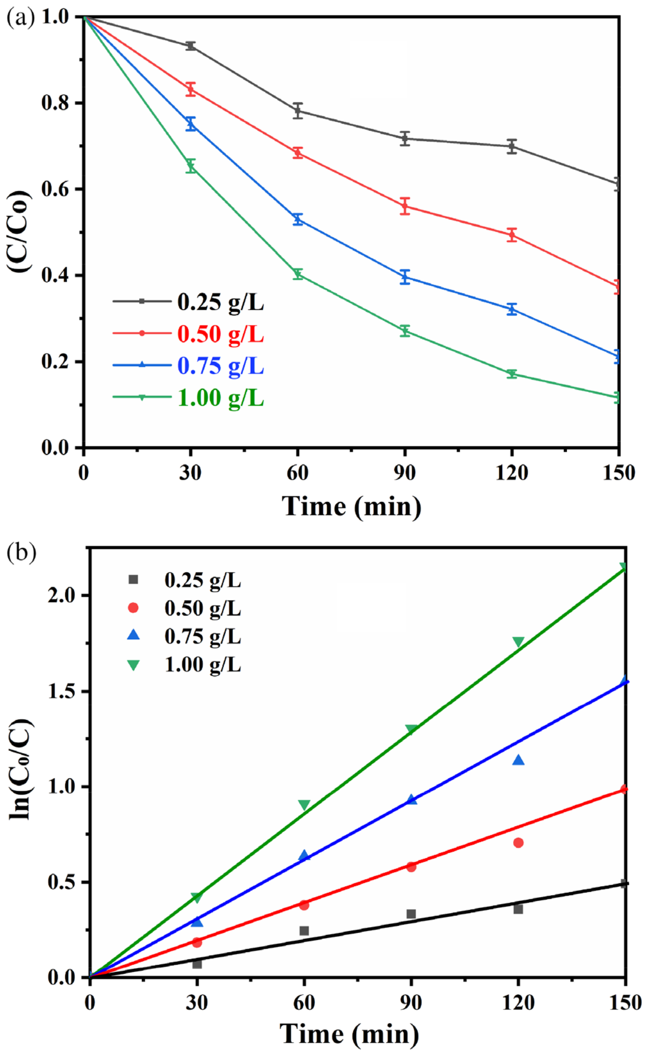


FIGURE 13 Effect of change in concentration of BG dye by using 5 mol% Mn-doped TiO_2 nanoparticles: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ vs. time

are involved for degradation reaction. The plot of $\ln(C_0/C)$ against time Figure 13b shows as the loading of catalyst increases it increases the photocatalytic activity.

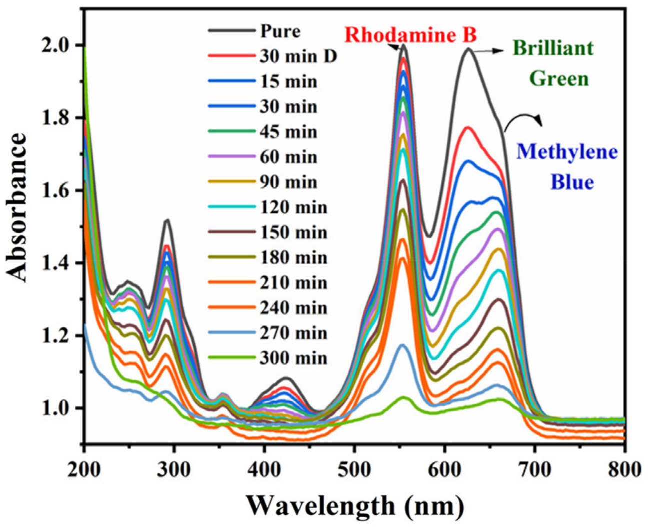


FIGURE 14 UV–Vis spectra of photocatalytic degradation of mixture of dyes (RhB, BG, and MB)

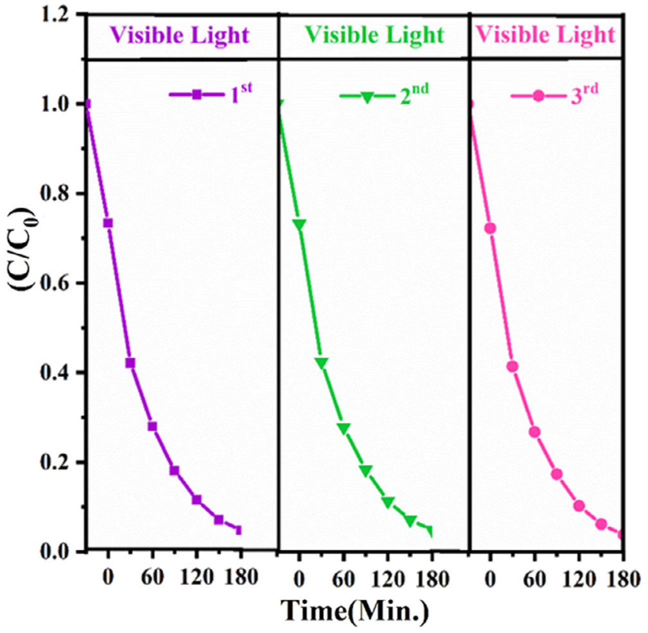


FIGURE 15 Reusability of catalyst

3.3 | Photocatalytic degradation of the mixture of dyes (RhB and BG, MB)

As per our photodegradation study of BG dye, it has been concluded that 5 mol% Mn-doped TiO_2 is more efficient in comparison with other prepared nanoparticles. Therefore, we have studied the photodegradation of a mixture of three dyes using 5 mol% Mn-doped TiO_2 nanoparticles and shown in Figure 14. As a representative of industrial dyestuff, an aqueous solution of a mixture of three dyes, that is, RhB, BG, and methylene blue (MB) is used. The control experiment (i.e., without using catalyst) reveals that the photodegradation of RhB and BG, MB is very slow under only visible light irradiation. Figure 14 shows a change in concentration of the mixture of dyes in the suspension of 5 mol% Mn-doped TiO_2 with respect to irradiation time. Absorption peaks have been observed at wavelengths ~668, ~544, and ~625 nm, which are characteristic absorption peaks (λ_{max}) of MB, RhB and BG, respectively. Progress of the photodegradation reaction has been studied by measuring the absorbance at these wavelengths. In 300 min. Reaction time, almost complete degradation of these three dyes has been observed.

4 | REUSABILITY OF CATALYST

Reusability of prepared nanoparticles is one of the most significant features of catalyst effectiveness over practical reuses. Therefore, three cycles of photocatalytic degradation of BG were carried out using 5 mol% Mn-doped TiO_2 under direct sun light irradiation and the results obtained are shown in Figure 15. The almost same activity has been shown by nanoparticles for three cycles. This also confirms the stability of the catalyst under the reaction conditions.

5 | CONCLUSIONS

The photo catalytically active Mn-doped TiO_2 nanoparticles were successfully synthesized by using sol–gel method. Among the various nanoparticles, 5 mol% Mn-doped TiO_2 has shown the better efficacy for photodegradation of brilliant green (BG). Further, it has been successfully employed for the degradation of mixture of three dyes namely methylene blue (MB), rhodamine B (RB) and brilliant green (BG). The analysis of characterization of the catalysts, it has been confirm that 5 mol% Mn-doped TiO_2 act as a superior catalyst in the photocatalytic degradation. However, strong interaction of Mn in TiO_2 has been proved by FTIR. The UV–Visible absorption study shows that the 5 mol% Mn-doped TiO_2 catalyst has better visible light absorption than other prepared catalysts. The band gap 3.2, 3.3, 3.4, and 3.7 eV has been observed for 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 respectively. Further, TiO_2 has shown increased BET surface area on doping. Prepared catalysts have shown excellent photocatalytic activity for degradation of brilliant green dye and mixture of dyes. The study of different pH of solution, at basic pH catalyst has shown greater photocatalytic activity. Also, 5 mol% Mn-TiO_2 catalyst has been shown almost similar efficiency for three cycles. Rate constant of 5 mol% Mn-doped TiO_2 catalyst is nearly twice to that of bare TiO_2 for degradation of BG.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ORCID

Mangesh G. Bhosale https://orcid.org/0000-0002-1036-9018

Meghshyam K. Patil https://orcid.org/0000-0002-3144-5016

REFERENCES

[1] C. Fernández, M. S. Larrechi, M. P. Callao, *Trends Anal. Chem.* **2010**, *29*, 1202.

[2] C.-W. Siao, H.-L. Chen, L.-W. Chen, J.-L. Chang, T.-W. Yeh, C.-C. Chen, *J. Colloid Interface Sci.* **2018**, *526*, 322.

[3] Y.-C. Wang, A.-H. Lee, C.-C. Chen, *J. Taiwan Inst. Chem. Eng.* **2018**, *93*, 315.

[4] M. Barakat, *Arab. J. Chem.* **2011**, *4*, 361.

[5] D. Huang, S. Liao, W. Zhou, S. Quan, L. Liu, Z. He, J. Wan, *J. Phys. Chem. Solids* **2009**, *70*, 853.

[6] M. K. Patil, S. Shaikh, I. Ganesh, *Curr. Nanosci.* **2015**, *11*, 271.

[7] C.-W. Siao, W.-L. William Lee, Y.-M. Dai, W.-H. Chung, J.-T. Hung, P.-H. Huang, W.-Y. Lin, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *544*, 25.

[8] H.-L. Chen, F.-Y. Liu, X. Xiao, J. Hu, B. Gao, D. Zou, C.-C. Chen, *J. Colloid Interface Sci.* **2021**, *601*, 758.

[9] A.-H. Lee, Y.-C. Wang, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *533*, 319.

[10] Y. Yu, G. Chen, X. Wang, D. Jia, P. Tang, C. Lv, *RSC Adv.* **2015**, *5*, 74174.

[11] Y. Li, Y. Jiang, S. Peng, F. Jiang, *J. Hazard. Mater.* **2010**, *182*, 90.

[12] J. Zhang, X. Xiao, J. Nan, *J. Hazard. Mater.* **2010**, *176*, 617.

[13] H. Khan, D. Berk, *React. Kinet. Mech. Catal.* **2014**, *111*, 393.

[14] S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright, R. M. Lambert, *J. Am. Chem. Soc.* **2007**, *129*, 13790.

[15] M. Anpo, M. Takeuchi, *J. Catal.* **2003**, *216*, 505.

[16] D. Chatterjee, S. Dasgupta, J. Photochem, C. Photobiol, *Photochem. Rev.* **2005**, *6*, 186.

[17] J. Tian, Y. Leng, Z. Zhao, Y. Xia, Y. Sang, P. Hao, J. Zhan, M. Li, H. Liu, *Nano Energy* **2015**, *11*, 419.

[18] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, *J. Mol. Catal. A Chem.* **2000**, *161*, 205.

[19] N. Sharotri, D. Sud, *Desalination Water Treat.* **2016**, *57*, 8776.

[20] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, K. Ikeue, M. Anpo, *J. Photochem. Photobiol. A* **2002**, *148*, 257.

[21] D. Dvoranova, V. Brezova, M. Mazúr, M. A. Malati, *Appl. Catal.* **2002**, *37*, 91.

[22] T. J. Kemp, R. A. McIntyre, *Polym. Degrad. Stab.* **2006**, *91*, 165.

[23] P. Kapoor, S. Uma, S. Rodriguez, K. Klabunde, *J. Mol. Catal. A Chem.* **2005**, *229*, 145.

[24] M. Rauf, M. Meetani, S. Hisaindee, *Desalination* **2011**, *276*, 13.

[25] T. Jedsukontorn, T. Ueno, N. Saito, M. Hunsom, *J. Alloys Compd.* **2018**, *757*, 188.

[26] L. Zhang, D. He, P. Jiang, *Catal. Commun.* **2009**, *10*, 1414.

[27] H. Li, D. Wang, H. Fan, T. Jiang, X. Li, T. Xie, *Nano Res.* **2011**, *4*, 460.

[28] V. Binas, K. Sambani, T. Maggos, A. Katsanaki, G. Kiriakidis, *Appl. Catal.* **2012**, *113*, 79.

[29] E. S. Karafas, M. N. Romanias, V. Stefanopoulos, V. Binas, A. Zachopoulos, G. Kiriakidis, P. Papagiannakopoulos, *J. Photochem. Photobiol. A* **2019**, *371*, 255.

[30] V. Binas, D. Venieri, D. Kotzias, G. Kiriakidis, *J. Materiomics.* **2017**, *3*, 3.

[31] S. Paul, P. Chetri, A. Choudhury, *J. Alloys Compd.* **2014**, *583*, 578.

[32] R. Chauhan, A. Kumar, R. P. Chaudhary, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2012**, *98*, 256.

[33] S.-H. Nam, T. K. Kim, J.-H. Boo, *Catal. Today* **2012**, *185*, 259.

[34] M. Stucchi, A. Elfiad, M. Rigamonti, H. Khan, D. Boffito, *Ultrason. Sonochem.* **2018**, *44*, 272.

[35] H. Feng, M.-H. Zhang, E. Y. Liya, *Appl. Catal. A: Gen.* **2012**, *413*, 238.

[36] M. Xue, L. Huang, J.-Q. Wang, Y. Wang, L. Gao, J.-H. Zhu, Z.-G. Zou, *Nanotechnology* **2008**, *19*, 185604.

[37] G. Shao, *J. Phys. Chem. C* **2009**, *113*, 6800.

[38] B. Choudhury, A. Choudhury, *Curr. Appl. Phys.* **2013**, *13*, 1025.

[39] J. Liu, J. Li, A. Sedhain, J. Lin, H. Jian, *J. Phys. Chem. C* **2008**, *112*, 17127.

[40] B. Choudhury, A. Choudhury, *J. Lumin.* **2013**, *136*, 339.

[41] X. Ma, W. Zhou, Y. Chen, *Mater.* **2017**, *10*, 631.

[42] S. Smart, S. Liu, J. M. Serra, J. C. Diniz da Costa, A. Iulianelli, A. Basile, Porous ceramic membranes for membrane reactors. in *Handbook of Membrane Reactors*. Woodhead Publishing, Cambridge, England **2013**, p. 298.

[43] J. Choma, M. Kloske, M. Jaroniec, *J. Colloid Interface Sci.* **2003**, *266*, 168.

[44] W. H. M. Abdelraheem, M. K. Patil, M. N. Nadagouda, D. D. Dionysiou, *Appl. Catal. B: Environ.* **2019**, *241*, 598.

[45] Z. Xu, C. Li, N. Fu, W. Li, G. Zhang, *J. Appl. Electrochem.* **2018**, *48*, 1197.

[46] A. J. Moreira, J. O. Malafatti, T. R. Giraldi, E. C. Paris, E. C. Pereira, V. R. de Mendonca, V. R. Mastelaro, G. P. Freschi, *J. Environ. Chem. Eng.* **2020**, *8*, 104543.

[47] R. S. Sutar, R. P. Barkul, M. K. Patil, *Curr. Nanosci.* **2021**, *17*, 120.

How to cite this article: M. G. Bhosale, R. S. Sutar, S. B. Deshmukh, M. K. Patil, *J. Chin. Chem. Soc.* **2022**, 1. https://doi.org/10.1002/jccs.202200248

Received: 26 May 2022 | Revised: 19 July 2022 | Accepted: 31 July 2022
DOI: 10.1002/jccs.202200248

JCCS JOURNAL OF THE CHINESE CHEMICAL SOCIETY

ARTICLE

Photocatalytic efficiency of sol–gel synthesized Mn-doped TiO_2 nanoparticles for degradation of brilliant green dye and mixture of dyes

Mangesh G. Bhosale[1,2] | **Radhakrishna S. Sutar**[1] | **Sandip B. Deshmukh**[2] | **Meghshyam K. Patil**[1]

[1]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus, Osmanabad, India

[2]Department of Chemistry, Ramkrishna Paramhans Mahavidyalaya, Osmanabad, India

Correspondence
Meghshyam K. Patil, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Sub-Campus Osmanabad-413501(M. S.), India.
Email: meghshyam_patil@yahoo.com

Abstract

The Mn-doped TiO_2 nanoparticle photocatalysts have been prepared by a simple sol–gel method. 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles have been prepared by using a stoichiometric amount of manganese acetate and titanium isopropoxide as precursors of Mn and Ti respectively. The physico-chemical characterization of the prepared samples has been studied by x-ray diffraction (XRD), Brunauer–Emmett–Teller surface area analysis, field emission scanning electron microscope, energy dispersive x-ray analysis, high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, Ultraviolet–visible spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). XRD study reveals the formation of pure anatase phase of TiO_2 and decrease in crystalline size of TiO_2 on increasing the Mn doping content. TGA reveals minimum weight loss in the high-temperature region of 500–1,000°C, showing the thermal stability of the catalyst. FTIR study shows highly bonding in metal atoms. These samples have been tested for photocatalytic degradation of brilliant green dye. 5 mol% Mn-doped TiO_2 is having nearly four times more photocatalytic activity than pure TiO_2. In addition, Mn-doped TiO_2 has shown excellent photodegradation of a mixture of three dyes namely, rhodamine B, brilliant green, and methylene blue.

KEYWORDS

kinetic study, Mn-doped TiO_2, nanoparticles, photocatalytic activity, sol–gel method

1 | INTRODUCTION

Various industries such as the manufacture of textile, paint, leather, pesticides, fertilizers, pharmaceuticals, and so on are primarily responsible for water pollution. By means of these industries, various organic pollutants have been dumped into the water bodies. The aquatic life and human life may be largely affected by these organic pollutants, which are exceptionally difficult to be degraded or eliminated by nature.[1–3] Numerous predictable methods such as biological methods, chemical precipitation, and membrane filtration are suggested for wastewater treatment, but these methods may not be greatly possible. However, chemical precipitation causes several disadvantages, large chemical feeding such as lime, oxidants, or H_2S and physicochemical monitors

such as pH are essential for the effluent, the excessive chemical usually causes a secondary pollution issue. Membrane filtration is an alternative physical method for wastewater treatment,[4] but its utility is affected by factors such as particle size, solubility, diffusivity, and charge.

In several countries, economic growth and industrial development go hand in hand, for example, textile industries play an important role in many countries such as China, Bangladesh, Vietnam, India, Sri Lanka, etc. These industries use different raw materials such as cotton, synthetic and woolen fibers, and several synthetic and natural dyes and chemicals. Approximately 10,000 different synthetic dyes are available in the global market. The worldwide annual production of these dyes is over 700,000 tons. Nearly 200,000 tons of synthetic dyes are lost into the environment because of the inefficient dyeing process used in textile industries. According to the World Bank estimation, the textile dyeing and finishing treatment is having about 17%–20% share of the total industrial wastewater generated.[4–6]

To tackle water pollution, among the number of processes, one of the most effective processes is the use of heterogeneous photocatalyst.[7–10] The most effective heterogeneous photocatalyst is titanium dioxide, because of its interesting properties such as nontoxicity, low cost, strong oxidizing power, chemical, and biological inertness, reusability, porosity, phase transformation, crystallinity, availability in nano-size and in different morphology and so on.[11–14] TiO_2 has a large band gap of ~3.20 eV, hence it functions effectively under ultraviolet (UV) light irradiation and limits its applications in direct sunlight or visible light. Another obstacle is the larger recombination rate of photo-generated electrons and holes, which further limits its efficiency.[15] One of the major challenges is to make an innovative photocatalyst, which can absorb light in the visible region rather than the UV region. In this direction, our focus is to prepare a TiO_2 catalyst, which on modification can absorb visible light rather than UV light, and minimize its band gap.

Enormous research has been carried out during the last few decades for developing TiO_2 catalyst to increase its activity in the visible region, for the achievement of higher absorbance of visible light by TiO_2. This includes several methods such as metal and non-metal ion doping and surface sensitization of TiO_2 coupling which helps in narrowing the band gap.[16–19] In literature, the number of transition metals such as V, Cr, Fe, Mg, Co, Zn, and Mo has been used as a dopant in $TiO_{2,}$ which results in the enhanced photocatalytic activity of $TiO_{2.}$[20–24] Among these, Mn is one of the effective doping elements, which results in the red shift in absorption wavelength due to the contraction in the band gap via the formation of new energy levels in between the Ti 3d states of the conduction band and the O 2p states of the valence band.[25] Zhang et al. reported the synthesis of MnO_2-doped anatase TiO_2 nanoparticles, which showed higher photocatalytic activity than Degussa P25.[26] Li et al. synthesized visible light active Mn-TiO_2 photocatalyst with controlled size for degradation of Rhodamine B (RhB).[27] Further, Mn-TiO_2 has been reported for the degradation of NO and acetaldehyde under visible irradiation.[28–32] In view of these results, there is a scope to develop a new method for the synthesis of Mn-doped TiO_2.

In this study, we have synthesized Mn-doped TiO_2 catalysts by the low-temperature sol–gel method. Prepared materials have been characterized by several techniques such as x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, Field Emission Scanning Electron Microscope (FESEM), energy dispersive x-ray analysis (EDX), High-Resolution Transmission Electron Microscopy (HRTEM), x-ray photoelectron spectroscopy (XPS), UV–Visible spectroscopy, Photoluminescence (PL) spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). Further, photocatalytic activity has been evaluated for the degradation of brilliant green dye in an aqueous solution and for the degradation of a mixture of dyes in an aqueous solution. Effect of various parameters such as concentration of dye, pH of a solution, and catalyst loading on the degradation of brilliant green has been evaluated.

2 | MATERIAL AND METHOD

2.1 | Synthesis of Mn-doped TiO_2 nanoparticles by sol gel method

The Mn-doped TiO_2 nanoparticles were prepared by using sol–gel method. Firstly, 5 ml of titanium isopropoxide and 5 ml of glacial acetic acid were taken in a clean round bottom flask and stirred for 15 min. To this solution separately prepared solution Tween 80 (0.2 ml) in 10 ml of distilled water was added slowly with constant stirring for 2 hr. To this resultant solution, 80 ml of distilled water was added slowly with constant stirring for 2 hr. Further, the stoichiometric amount of manganese acetate was added to a reaction mixture and stirred for 4 hr. pH of this solution is adjusted to 10 by adding ammonia solution with constant stirring and further stirred for 3 hr at 60°C for removing excess ammonia. The reaction mixture was cooled to room temperature and the supernatant liquid has been removed by decantation. Further, 80 ml of distilled water was added and the mixture was stirred for 3 hr at 60°C. The mixture was

filtered, washed with ethanol and obtained precipitate has been dried at 110°C for 12 hr. The obtained powder was crushed and calcined at 400°C for 5 hr. Light brown powder of Mn-doped TiO_2 nanoparticles has been formed. By this procedure, 1, 3, and 5 mol% Mn-doped TiO_2 have been synthesized. The same procedure was adopted for the synthesis of bare TiO_2, without the addition of manganese acetate.

2.2 | Characterization

The XRD spectra of all prepared samples were recorded by using Regaku diffractometer with Cu Kα (1.5418 Å). The diffraction data were collected in the 2θ range of 10–90° at the scanning rate of 2°/min. The crystalline size has been calculated by the Scherer equation. BET surface area, pore volume, and pore diameter of the bare TiO_2 and 5 mol% Mn-doped TiO_2 have been studied by N_2 adsorption measurement at −196°C using NOVA touch 4LX, Quntachrome, USA. UV–Vis absorption spectrum of the prepared catalysts was recorded in the range of 200–800 nm by using ELICO double beam SL210 UV–visible spectrophotometer. Photoluminescence measurement of all the prepared catalysts has been studied with 330 nm excitation wavelength (at 3.76 eV excitation energy) using a JASCO spectrofluorometer. FTIR spectra of the nanoparticles were recorded on Thermo Scientific Nicolet iS10 in the range of 400–4,000 cm^{-1} in transmission mode. High-resolution transmission electron microscopy (HRTEM) images of the samples were recorded on a JEOL JEM 2100 Plus. The FESEM images with EDX were recorded using Carl Zeiss Supra 55 scanning electron microscope with a field emission electron gun, to know the morphology and elemental composition respectively. XPS measurements of the prepared sample have been recorded on a Shimadzu (ESCA 3400) spectrometer having Mg Kα (1,253.6 eV) radiation as the excitation source. The TGA data were recorded on Mettler Toledo TGA1 thermogravimetric analyzer; it shows the thermal stability of the prepared catalysts.

2.3 | Photocatalytic activity

Photocatalytic degradation of Brilliant green in an aqueous solution has been studied by employing Mn-doped TiO_2 catalysts. Further, degradation of a mixture of three dyes (including brilliant green, rhodamine B, and methylene blue) in an aqueous solution under direct sunlight has been studied by using the most active 5 mol% Mn-doped TiO_2. Also, the effect of various parameters (such as pH of the solution, the concentration of the brilliant green, and catalyst loading) have been examined on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 for degradation of brilliant green. The pH of the solution was adjusted by adding an appropriate quantity of 1 N NaOH and 1 N HCl solutions. In the photocatalytic study, all the experiments are studied thrice and observed with almost similar results. The corresponding error bar has been shown within the figures.

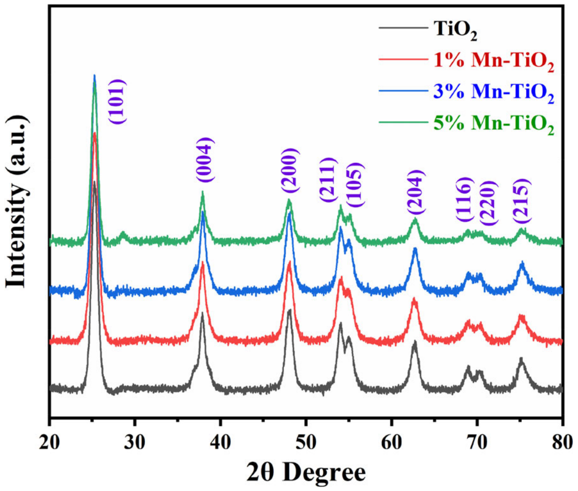


FIGURE 1 XRD pattern of pure TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2

2.3.1 | Photocatalytic degradation of brilliant green dye

We have prepared a 20 ppm brilliant green dye solution using distilled water at room temperature. From this prepared stock solution, 200 ml solution has been taken in the round bottom flask; to this, 100 mg of prepared catalyst has been added. This reaction mixture was stirred for 30 min. in dark to reach adsorption–desorption equilibrium. After this, the solution was transferred into the sunlight. 2 ml sample has been collected after a regular time interval, centrifuged, and performed UV–Visible spectral analysis from 200–800 nm wavelength and absorbance has been recorded for wavelength (λ_{max}) 625 nm for brilliant green.

2.3.2 | Photocatalytic degradation of mixture of dyes

We have prepared a 20 ppm solution of each dye (brilliant green, methylene blue and rhodamine B) using distilled water. By taking these three solutions in equal quantity, a 200 ml solution of mixture of brilliant green,

TABLE 1 Structural parameters of pure TiO_2 and Mn-doped TiO_2 nanoparticles

				Cell parameters			
Catalysts	**Standard d value**	**Observed d value**	**hkl plane**	**a (Å)**	**c (Å)**	**V ($Å^3$)**	**Crystallite size(nm)**
TiO_2	3.52	3.5147	(101)	3.78	9.52	136.02	9.927933
	2.37	2.38018	(004)				
	1.33	1.89052	(220)				
1% Mn-TiO_2	3.52	3.5201	(101)	3.775	9.4916	135.26	9.036106
	2.37	2.3729	(004)				
	1.33	1.8875	(220)				
3% Mn-TiO_2	3.52	3.5229	(101)	3.772	9.482	134.90	9.033568
	2.37	2.3705	(004)				
	1.33	1.8860	(220)				
5% Mn-TiO_2	3.52	3.5215	(101)	3.7854	9.494	136.04	8.944641
	2.37	2.3735	(004)				
	1.33	1.8927	(220)				

methylene blue and rhodamine B has been prepared. This prepared solution was taken in round bottom flask and 100 mg 5 mol% Mn-doped TiO_2 catalyst was added. After 30 min., the reaction mixture was transferred to direct sunlight, and after regular time interval the samples were collected. The absorbance of collected samples was recorded using a UV–visible spectrophotometer at the range of 200–800 nm wavelength.

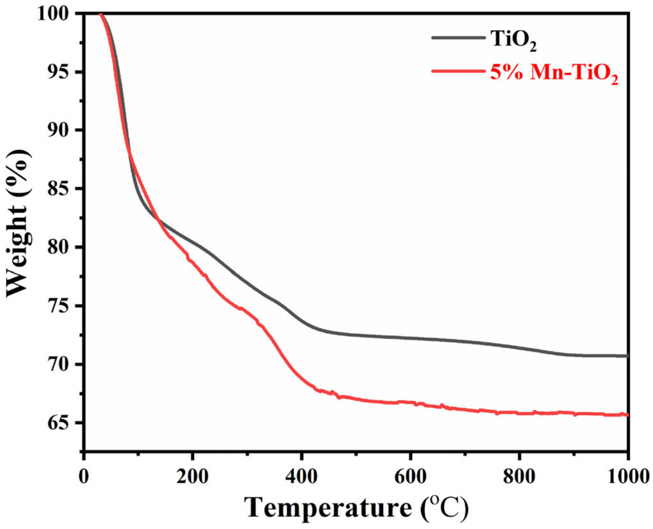


FIGURE 2 TGA of TiO_2 and 5 mol% Mn-doped TiO_2

3 | RESULT AND DISCUSSION

3.1 | Characterization

3.1.1 | X-ray diffraction study

X-ray diffraction patterns of undoped and Mn-doped TiO_2 nanocatalysts are shown in Figure 1. It is noted that all the diffraction peaks represented the anatase phase of TiO_2 with a characteristic high-intensity peak at $2\theta = 25.20°$ and other peaks correspond to 2θ values at 37.91, 47.98, 54.05, 55.12, 62.78, 68.94, 70.45 and 75.35° which can be indexed as (101), (004), (200), (211), (105), (204), (116), (220) and (215) planes of anatase TiO_2 (JCPDS card no.73–1764) respectively. Mostly, the XRD spectra have not shown any extra peaks corresponding to Mn. This indicated that the Mn may introduce in to TiO_2 lattice as substitution dopant by replacing Ti and O and not in the interstitial position of the TiO_2 lattice.[32,33]

The crystalline size of all prepared catalysts has been calculated on the basis of the Scherrer formula. The crystalline size of bare TiO_2, 1 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, and 5 mol% Mn-doped TiO_2 is 9.93, 9.04, 9.03, and 8.94 nm respectively. The Scherrer formula is as follows:

$$D = \frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

where D is the average size of the nanoparticle, λ is the wavelength, β is the full width at half maximum, and θ is Bragg's angle.

On the basis of crystalline size, we can say that on an increase in Mn doping, the size of the nanoparticle decreases, which results in an increase in the surface area of the catalyst and ultimately enrichment in photocatalytic activity. The structural parameters of pure TiO_2 and

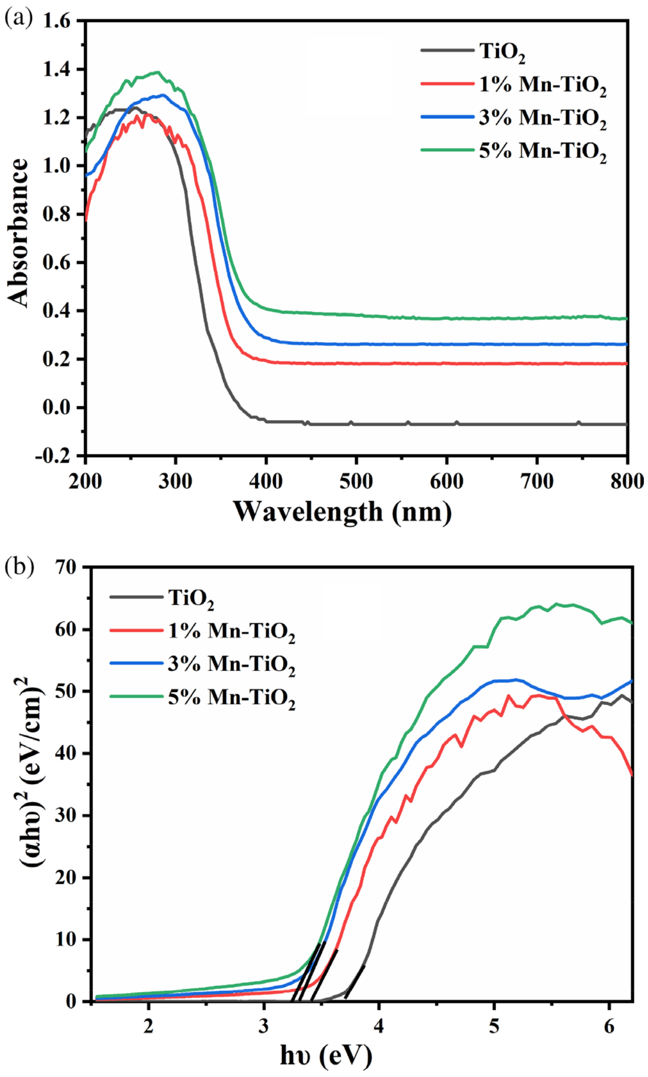


FIGURE 3 (a) UV–Visible absorption spectra; (b) plot of hυ versus $\alpha h\upsilon^2$ of bare TiO_2; and Mn-doped TiO_2

Mn-doped TiO_2 catalysts are shown in Table 1 and it is well matched with JCPDS 73–1764 data.

3.1.2 | Thermo gravimetric analysis

The thermogravimetric analysis plots of as-prepared pure TiO_2 and 5 mol% Mn-doped TiO_2 (before calcination) have been shown in Figure 2. The weight loss of TiO_2 from room temperature to 400°C is due to conversion from amorphous to crystalline phase.[34] In specific, after heating over 400°C, we do not observe any other phase than crystalline anatase TiO_2 this is prove on XRD analysis. The Thermo gravimetric analysis of Mn-TiO_2 is dividing in to three stages of weight loss. In stage first nearly 19% weight loss observed in between 30 and 180°C is due to loss of the residual solvent and water. The second weight loss which is about 12%, observed in between 126 and 380°C is due to loss of organic components. However, TiO_2 has shown less amount of weight loss as compared to Mn-doped TiO_2. Further, both Mn-doped TiO_2 and bare TiO_2 has not shown any significant weight loss after 400°C.

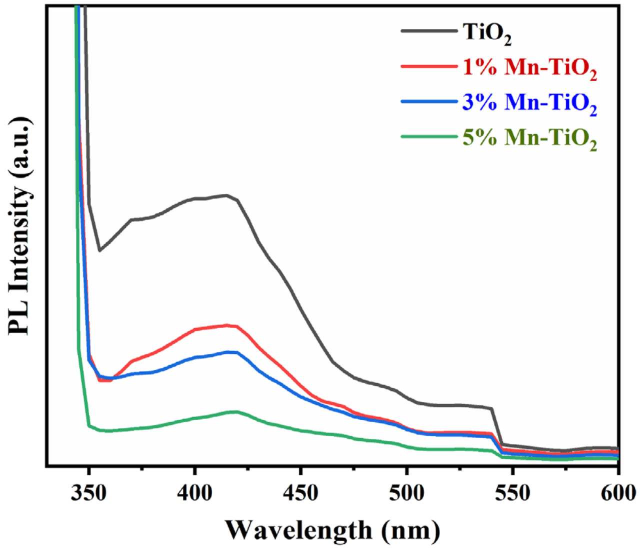


FIGURE 4 Photoluminescence spectra of bare TiO_2 and Mn-doped TiO_2 nanoparticles

As compared to bare TiO_2, Mn-doped TiO_2 has shown an overall 10% higher weight loss. The weight loss indicates that pure TiO_2 has early started to convert into its crystalline phase from the amorphous phase, whereas Mn-doped TiO_2 started later to convert into its crystalline form.

3.1.3 | UV–Visible spectroscopy study

The influence of doping on the UV–Vis spectra properties of the anatase TiO_2 is clear from Figure 3. The Mn-doped TiO_2 nanoparticles shows a remarkable change in their color, which depends on the concentration of dopant, as concentration of dopant increases color becomes light brown to light dark brown. From the UV–Vis spectra, the increase in absorption of Mn-doped TiO_2 in visible region has been observed which is due to their respective energy levels, the promotion of 3d electrons of doping Mn ions in to the conduction band of TiO_2.[35–37]

With the increase in doping, we observe that stronger absorption edges shifted to the right side of the spectrum, which results in a decrease in the band gap. As the percentage of doping increases band gap of prepared catalysts decreases from 3.7 to 3.2 eV. Due to decrease in band with absorption of lesser amount of energy can promotes electron to conduction band. It increases the photocatalytic activity of the prepared catalyst. On the

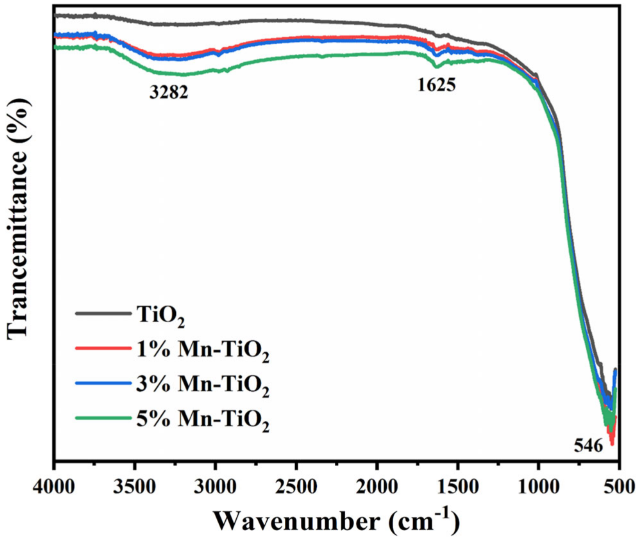


FIGURE 5 FTIR study of Mn-doped TiO_2 nanoparticles

basis of Figure 3b it is seen that 5 mol% Mn-doped TiO_2 has highest photocatalytic activity.

3.1.4 | Photoluminescence spectroscopy study

An important identifying tool for determining the existence of defects in a nanomaterial is PL spectroscopy. The photoluminescence spectra of pure TiO_2 and 1, 3, and 5 mol% Mn-doped TiO_2 nanoparticles at room temperature are shown in Figure 4. The PL spectra has been studied at an excitation wavelength of 330 nm. Two separate emission peaks have been identified in the spectra. The indirect band-to-band transition of TiO_2 nanoparticles from their conduction band to their valence band causes the UV emission.[38] The peak at 415 nm is related to self-trapped excitons.[38] The 490 nm peak is observed due to the charge transfer transition from Ti^{3+} to the TiO_6^{2-} octahedra associated with oxygen defects.[39] In this spectrum there is no additional peak of Mn or shifting of emission peak. On increasing Mn doping, the intensity of the emission peaks has been reduced. The oxygen vacancies in pure TiO_2 function as luminescence enhancers and boost emission intensity. The TiO_2 lattice is disturbed, the Ti–O bond is broken, and many oxygen vacancies are produced when Mn is doped. As the concentration of Mn in TiO_2 increases, the number of non-radiative oxygen vacancy centres also increases, nearby Mn^{2+}. Since there are more oxygen defects available, lesser photoexcited electrons are available to recombine with holes because they are entrapped and highly localized in those oxygen vacancies. Presence Mn resemblance a rise in non-radiative oxygen vacancy centres with trapped electrons, which causes a subsequent drop in emission intensity. Further, in addition to the non-radiative oxygen vacancies, the mobility of the carriers is another important factor influencing PL intensity. The mobility of the free carriers is decreased by dopants and deficiencies in the interior, grain boundary, and surface. When they get close to charged dopants or oxygen defect states, the mobile carriers disperse. Reduced mobility will result in more carriers being separated from one another, which lowers the intensity of the PL.[40]

3.1.5 | FTIR study

The FTIR spectra of Mn-doped TiO_2 nanoparticle is shown in Figure 5. The stretching and bending vibration of the hydroxyl group peak at 3282 cm^{-1} and the stretching vibration band intensity of Mn-doped TiO_2 is greater than pure TiO_2, indicating that TiO_2 has stronger absorption with Mn-doped TiO_2.[41] The absorption band in the prepared materials at 1625 cm^{-1} was associated with the stretching of the C–O–Ti bond. The peak at about 546 cm^{-1} is due to anatase TiO_2, which represents the bending vibration of Ti–O.

3.1.6 | FESEM and EDX study

The morphology and surface nature of the synthesized Mn-doped TiO_2 nanoparticles were studied by FESEM and obtained images of all samples are shown in Figure 6. The FESEM micrograph of all samples has shown the fine-grown crystals, which were gathered closely with each other. Further, the EDX analysis shows that obtained sample has the same elemental composition as per the proportion of precursors taken during the preparation.

3.1.7 | HRTEM study

The structural properties of prepared material Mn-doped TiO_2 nanoparticles have been further investigated by using HRTEM spectroscopy. The particle size for 5 mol% Mn-doped TiO_2 from the HRTEM images is varying from 4 to 14 nm as shown in Figure 7a. Clear lattice fringes for Mn-doped TiO_2 were obtained and shown in Figure 7b. Further, the presence of anatase phase of TiO_2 has been confirmed by the crystal lattice fringes having a d value of 0.352 nm which is corresponding to the spacing of (101) lattice plane of the anatase TiO_2 (JCPDS 73–1764). Furthermore, the selected area electron diffraction pattern shown in Figure 7c, matches with anatase TiO_2 and the brightness and intensity of polymorphic ring reveals the well crystalline nature. The average particle size of

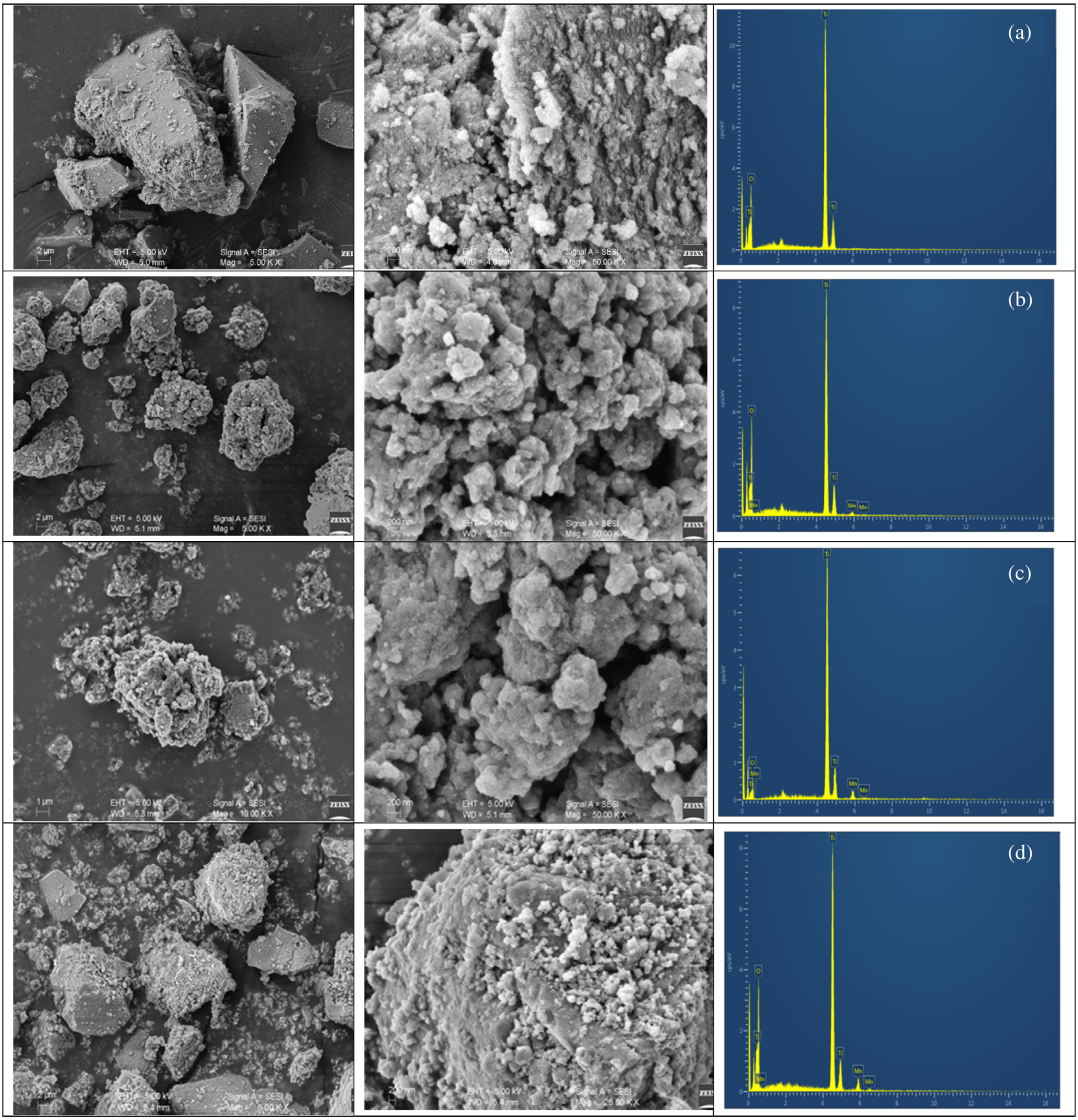


FIGURE 6 FESEM with EDX of (a) pure TiO_2; (b) 1 mol% Mn-doped TiO_2; (c) 3 mol% Mn-doped TiO_2; and (d) 5 mol% Mn-doped TiO_2 nanoparticles

the nanoparticles from HRTEM Figure 7d was found to be 8–10 nm, which is also matched with the XRD results.

3.1.8 | BET surface area analysis

The values of the specific surface area, pore volume, and pore diameter of pure TiO_2 and 5 mol% Mn-doped TiO_2 samples were measured using the Brunauer–Emmett–Teller (BET) equation following the Barrett–Joyner–Halenda method are summarized in Table 2. The N_2 adsorption–desorption for both the photocatalysts was consistent with Type IV isotherm (Figure 8), which is representative of mesoporous structures.[42–44] After doping with manganese, a significant increase in the specific surface area and pore volume of the samples has been

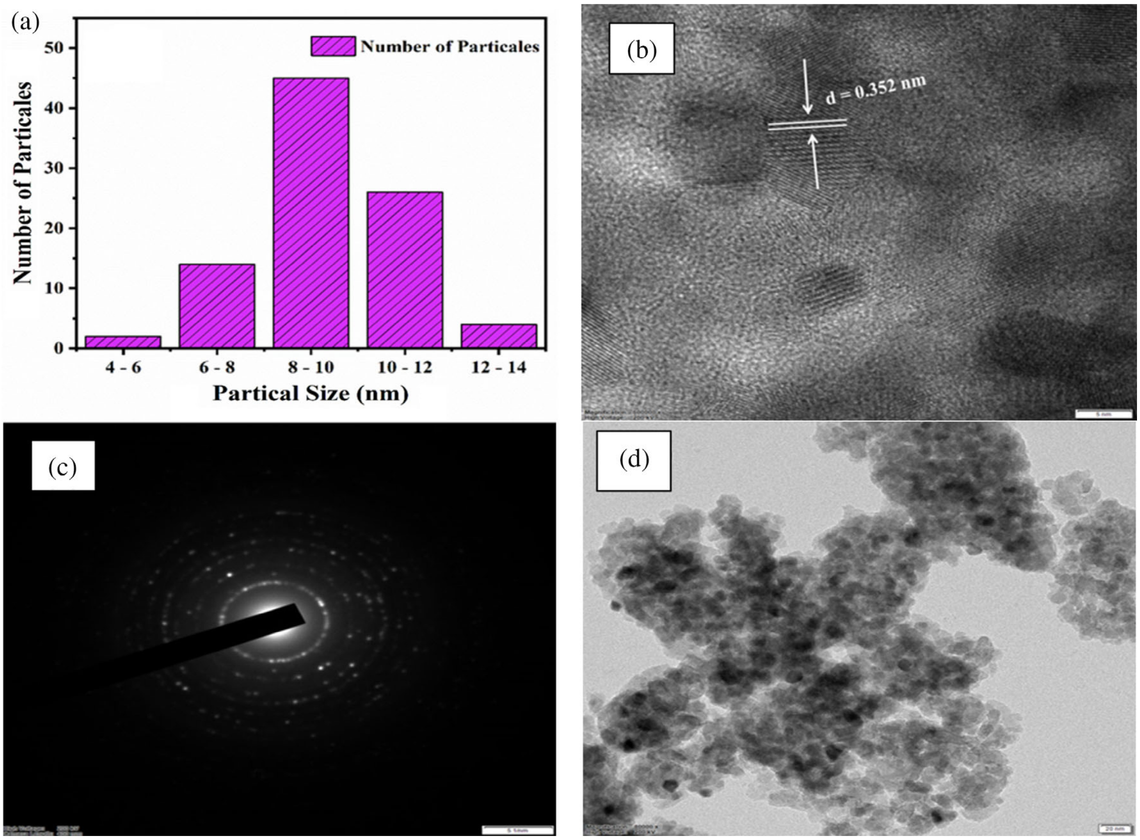


FIGURE 7 (a) Average particle size; (b) and (d) HRTEM image of 5 mol% Mn-doped TiO_2; and (c) SAED pattern of 5 mol% Mn-doped TiO_2 powder

TABLE 2 BET surface area, pore volume, and pore diameter of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticles

Sr. no.	Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	TiO_2	111.399	0.231848	7.83178
2	5% Mn-TiO_2	185.312	0.277406	5.63585

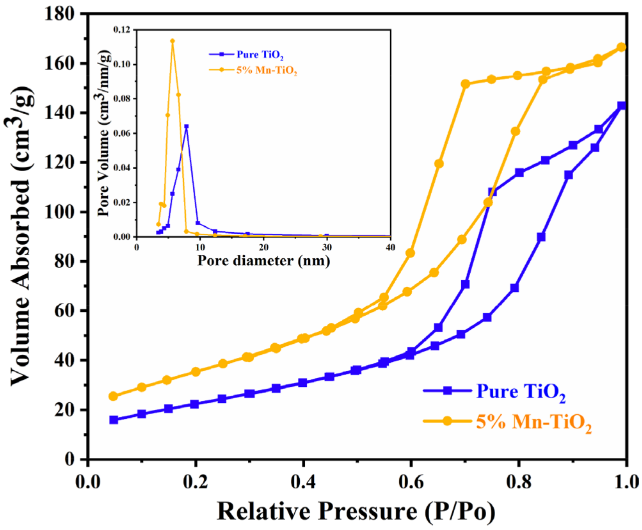


FIGURE 8 N_2 adsorption–desorption isotherm (inset, pore size distribution) of bare TiO_2 and 5% Mn-doped TiO_2 nanoparticle

noticed. The BET surface area of 185.312 and 111.399 m^2/g was recorded for 5 mol% Mn-doped TiO_2 and bare TiO_2 respectively. Moreover, the pore diameter of pure TiO_2 is greater than 5 mol% Mn-doped TiO_2 and the pore volume of TiO_2 is less than 5 mol% Mn-doped TiO_2.

3.1.9 | XPS study

An XPS analysis of 5 mol% Mn-doped TiO_2 is shown in the Figure 9, which confirms the basic structure of the catalyst produced. Figure 9a shows the survey spectra, which shows the presence of Mn, Ti and O in the sample. The XPS spectrum of Mn 2p exhibited peaks at 642.2 and 653.8 eV, which were attributed to the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ levels, respectively, a finding that bears out the presence of Mn^{3+} is shown in Figure 9b.[45] From the

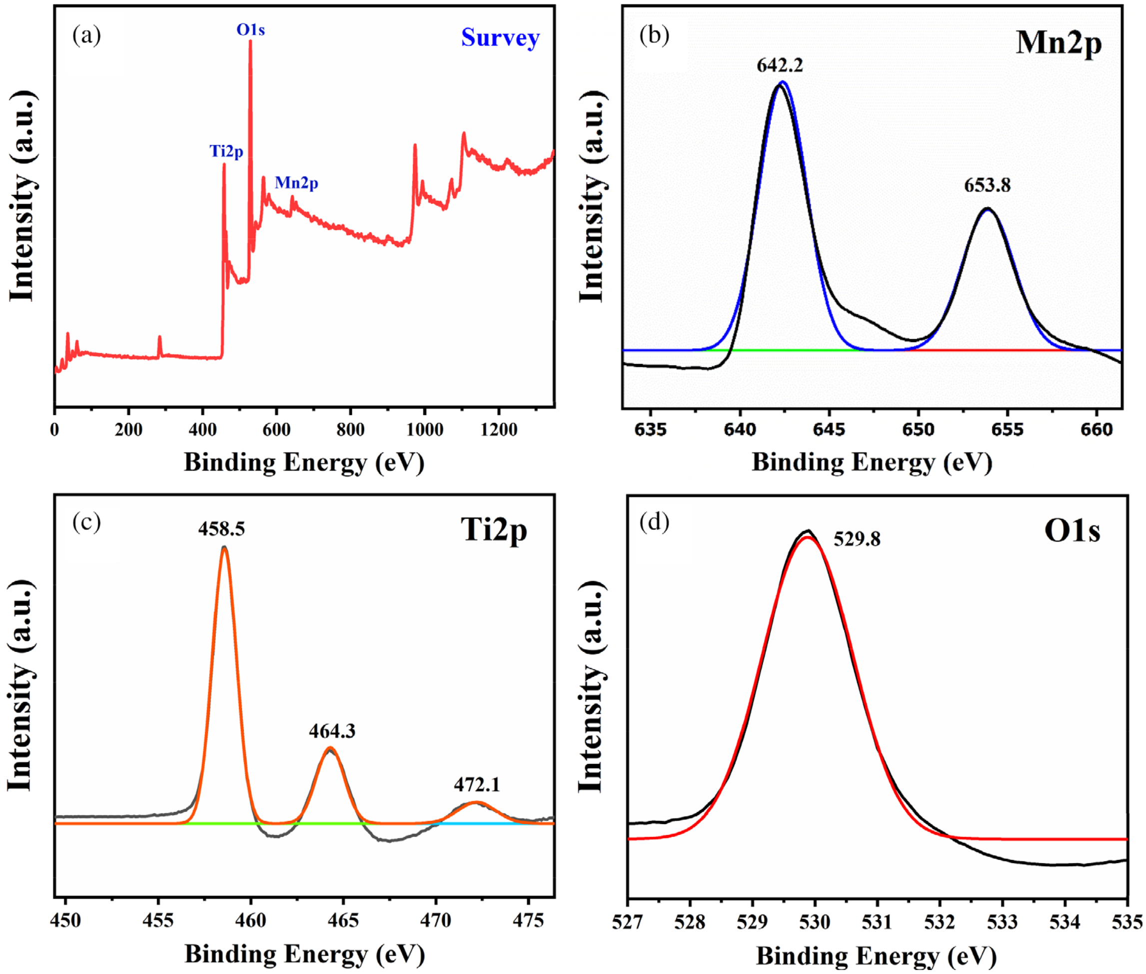


FIGURE 9 (a) XPS spectra of 5 mol% Mn-doped TiO_2, high-resolution spectra of (b) Ce 3d, (c) Ti 2p, and (d) O 1s

Figure 9c, the XPS spectrum of Ti 2p peaked at 458.5 and 464.3 eV, attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels, respectively, confirming the presence of Ti^{4+}. In addition, the difference between the two energy levels was approximately 6.0 eV and the 472.1 eV satellite peak is characteristic of TiO_2 compounds. Figure 9d shows O1s XPS spectrum peak at 529.8 eV, which is corresponds to the O-(Mn, Ti) lattice oxygen.[46]

3.2 | Photocatalytic degradation of brilliant green

The photocatalytic activity of synthesized nanoparticles has been explored for the degradation of brilliant green dye and a mixture of three dyes, namely methylene blue, brilliant green, and rhodamine B. Brilliant green is triarylmethane dye having the chemical formula $C_{27}H_{34}N_2O_4S$ and molecular weight 475.6 g/mol. It is used in dilute solution as a topical antiseptic and effective against gram positive microorganisms.

UV–Visible absorption spectra of degradation study of BG using 5 mol% Mn-doped TiO_2 with respect to irradiation time is shown in Figure 10a. The maximum absorption peak of brilliant green (BG) dye is at ~625 nm (λ_{max}). As the time increases from 0 to 180 min the peak intensity decreases gradually, also little shifting of peak to slightly lower wavelength is observed. The complete degradation of BG was observed after 180 min by using this catalyst. The plot of change in concentration of BG by using all prepared catalysts (such as 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and bare TiO_2) with respect to irradiation time has been shown in Figure 10b. The observation of experiment reveals that the concentration of BG has been nearly constant in the absence of photocatalyst and in the presence of visible light, suggests the thermodynamic stability of BG dye. The complete degradation of BG by using 5 mol % Mn-doped TiO_2 nanoparticles has required less time than that of 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 nanoparticles. This observation clearly indicates that the photocatalytic degradation

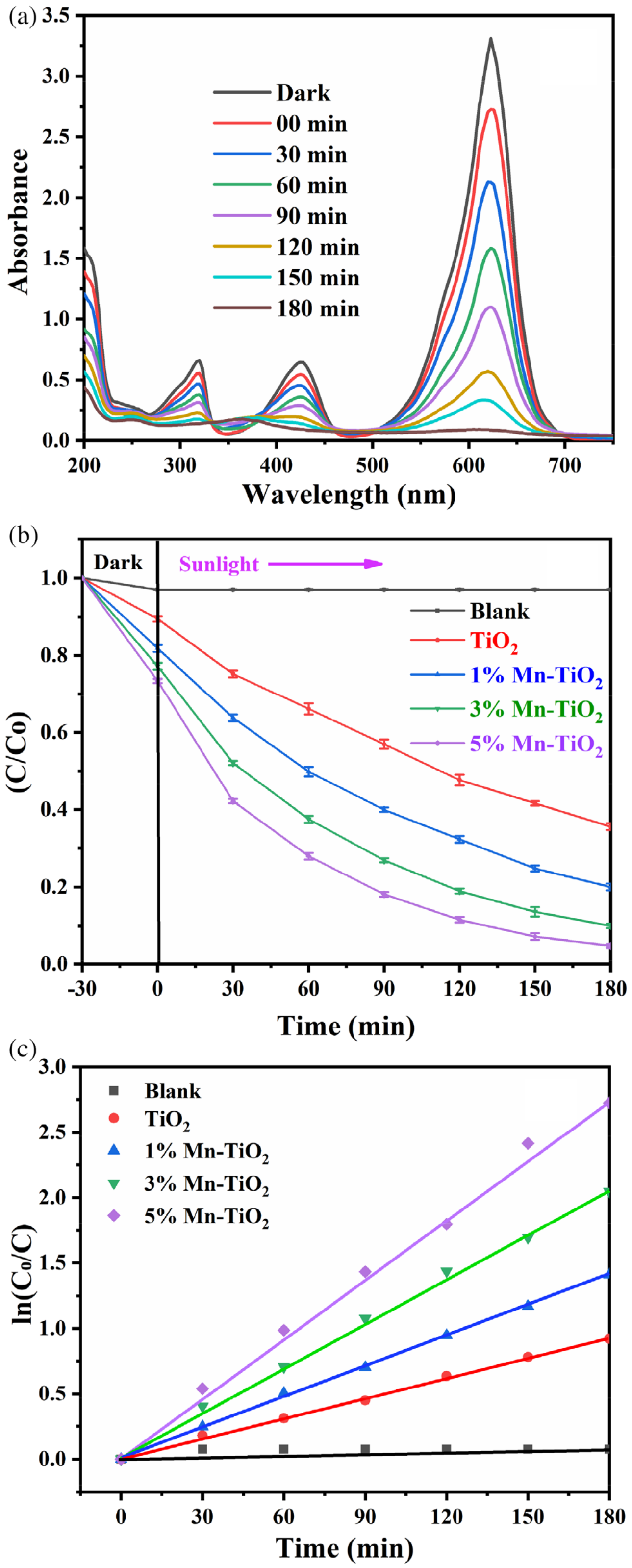


FIGURE 10 (a) UV–Visible spectra of BG at different time intervals using Mn-doped TiO_2 nanoparticle as catalyst, (b) change in concentration of BG by using different catalysts and without catalyst with irradiation time, and (c) corresponding graph of $\ln(C_0/C)$ of BG versus irradiation time

reaction of the Mn-doped TiO_2 nanoparticle is highly dependent upon the amount of Mn introduced into TiO_2 and the method used for synthesis of the catalyst preparation. Moreover, reaction kinetic has been shown in Figure 10c and results obtained were tabulated in Table 3 for photocatalytic degradation of BG by using prepared samples. As compared to other prepared catalysts, the higher rate constant (16.73×10^{-3} min^{-1}) for BG degradation using 5 mol% Mn-TiO_2 nanoparticles has been observed under visible light.

The effect of change in concentration of BG on photocatalytic efficiency of 5 mol% Mn-doped TiO_2 nanoparticle has been studied by using 10–40 ppm BG solution. Figure 11a shows that complete degradation has been achieved for 10 ppm solution in 180 min., whereas 69, 55 and 28% degradation has been achieved of 20, 30, and 40 ppm solution respectively in same time by using 5 mol% Mn-doped TiO_2. Figure 11b shows the plot of d [BG]/dt versus time, on increasing the concentration of BG from 10 to 40 ppm, for time intervals of 0–30 min, 30–60 min, 60–90 min, and 90–120 min the change in concentration initially increases and then decreases. But for a time interval of 120–150 min, the trend is somewhat irregular.

The effectiveness of the photodegradation reaction largely depends upon the pH of the dye solution. The pH of the BG solution was adjusted using 1 N HCl to make a solution acidic and 1 N NaOH to make a solution basic. As shown in Figure 12, the rate of photocatalytic reaction was found higher in the basic medium (pH 12.0, 9.0) than that of the acidic medium (pH 5.0, 3.0). The different pH of the solution can change the surface charge on nanoparticles and, consequently, the potential of photocatalytic reactions. The mechanism of photocatalytic degradation is shown in Equations (2)–(7). The reactive species could be formed by the reactions shown in Equations (2)–(6), can be generated at specific potential and initiate the photocatalytic reaction (Equation 7).[47]

TABLE 3 Reaction kinetic parameters of photocatalytic degradation study of BG Mn-TiO_2 and bare TiO_2 nanoparticles

Catalyst	Initial Conc. of BG (%)	Final Conc. of BG (%)	Rate constant (min^{-1})
Blank	100	95.8	0.1×10^{-3}
TiO_2	100	57.8	5.7×10^{-3}
1% Mn-TiO_2	100	40.2	8.9×10^{-3}
3% Mn-TiO_2	100	27.6	12.69×10^{-3}
5% Mn-TiO_2	100	15.2	16.73×10^{-3}

Formation of $HO^{\bullet}$ is favored under basic condition and it may help for degradation under basic conditions.

$$\mathrm{Mn-doped\ TiO_2} + h\nu \rightarrow \mathrm{Mn-doped\ TiO_2}\left(e^{-} + h^{+}\right), \tag{2}$$

$$\mathrm{Mn-doped\ TiO_2}(e^{-}) + O_2 \rightarrow \mathrm{Mn-doped\ TiO_2} + O_2^{-\bullet}, \tag{3}$$

$$\begin{aligned} &\mathrm{Mn-doped\ TiO_2}(e^{-}) + O_2 + H^{+} \\ &\rightarrow \mathrm{Mn-doped\ TiO_2} + HO_2^{\bullet}, \end{aligned} \tag{4}$$

$$\begin{aligned} &\mathrm{Mn-doped\ TiO_2}\left(h^{+}\right) + H_2O \\ &\rightarrow \mathrm{Mn-doped\ TiO_2} + H^{+} + OH^{\bullet}, \end{aligned} \tag{5}$$

$$\begin{aligned} &\mathrm{Mn-doped\ TiO_2}\left(h^{+}\right) + OH^{-} \\ &\rightarrow \mathrm{Mn-doped\ TiO_2} + OH^{\bullet}, \end{aligned} \tag{6}$$

$$\begin{aligned} &\mathrm{BG} + \mathrm{Reactive\ species}\left(O_2^{-\bullet}/OH^{\bullet}/HO_2^{\bullet}\right) \\ &\rightarrow \mathrm{Degradation\ Products}. \end{aligned} \tag{7}$$

Furthermore, the photocatalytic degradation efficiency was evaluated by changing the amount of catalyst, that is, catalyst loading. Figure 13a shows the change in concentration of BG with irradiation time for the experiments carried out by using different catalyst loading, that is, from 0.25 to 1 g/L. The degradation efficiency increases with increase for catalyst loading. This is due to the fact that the higher amount of catalyst has higher active sites on the surface and consequently active sites

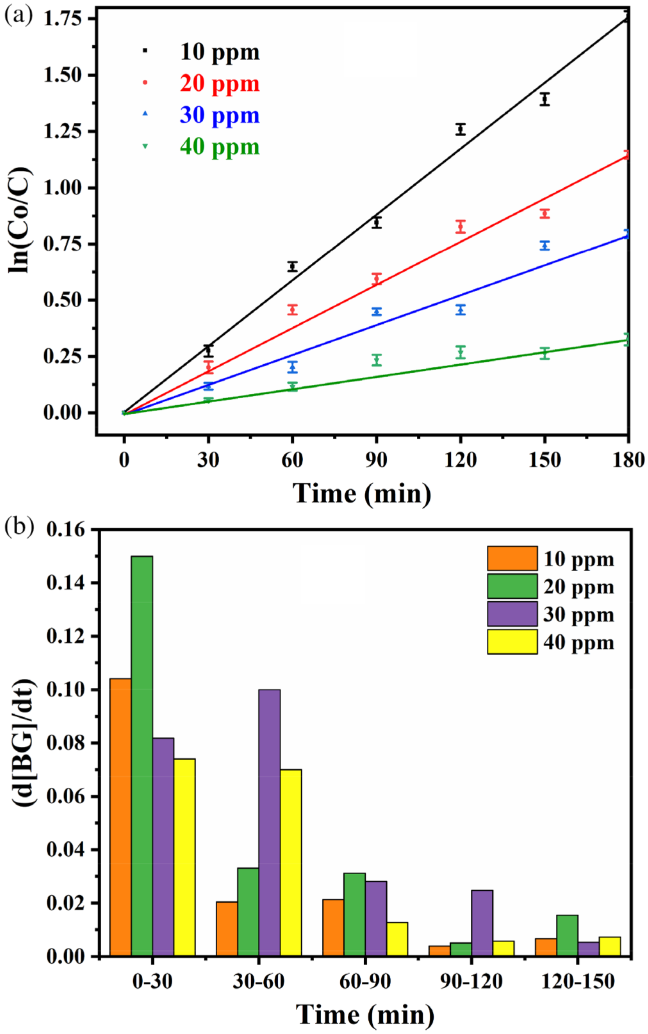


FIGURE 11 (a) Plot of percentage degradation of BG with different concentrations of dye solution by using 5 mol% Mn-doped TiO_2 nanoparticles with irradiation time and (b) corresponding plot of d[BG]/dt versus time

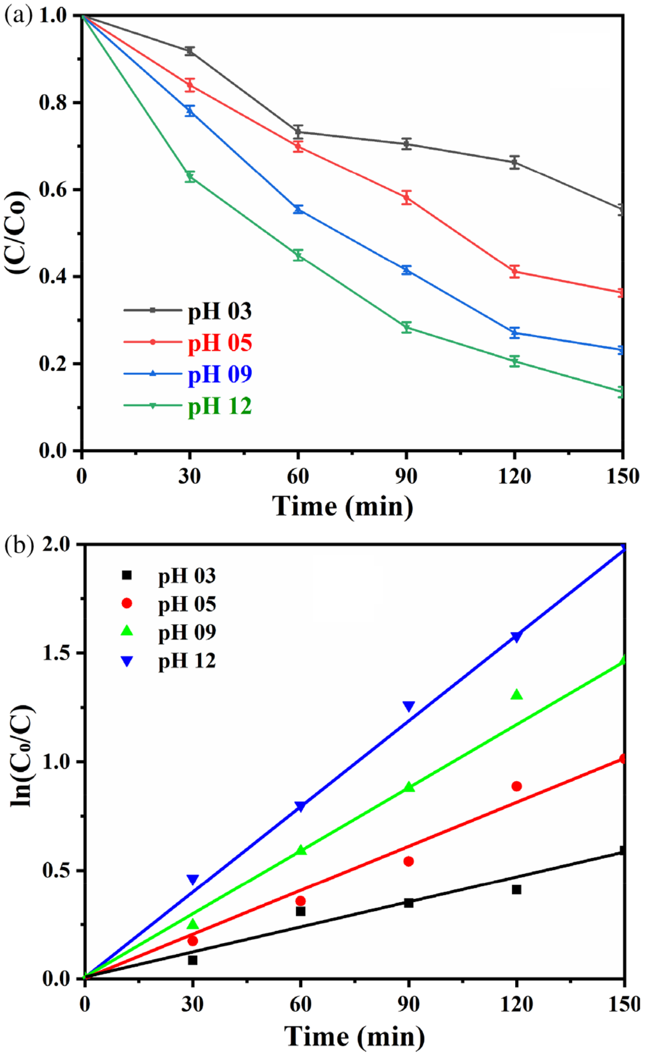


FIGURE 12 Effect of change in pH of BG dye solution: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ versus time by using 5 mol% Mn-doped TiO_2 nanoparticles

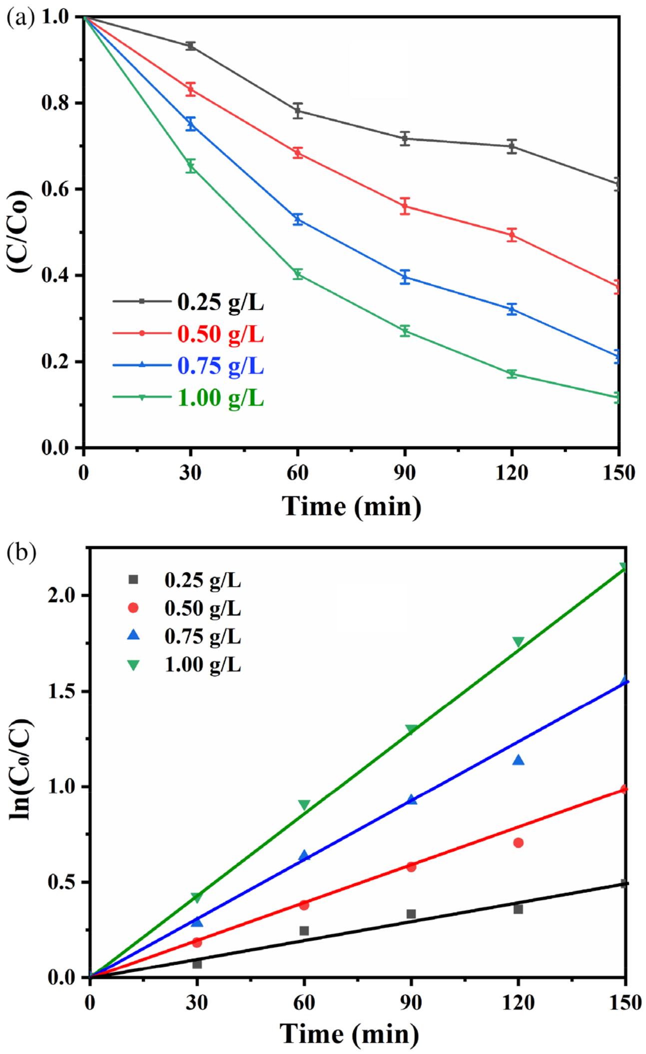


FIGURE 13 Effect of change in concentration of BG dye by using 5 mol% Mn-doped TiO_2 nanoparticles: (a) plot of (C/C_0) versus time and (b) plot of $\ln(C_0/C)$ vs. time

are involved for degradation reaction. The plot of $\ln(C_0/C)$ against time Figure 13b shows as the loading of catalyst increases it increases the photocatalytic activity.

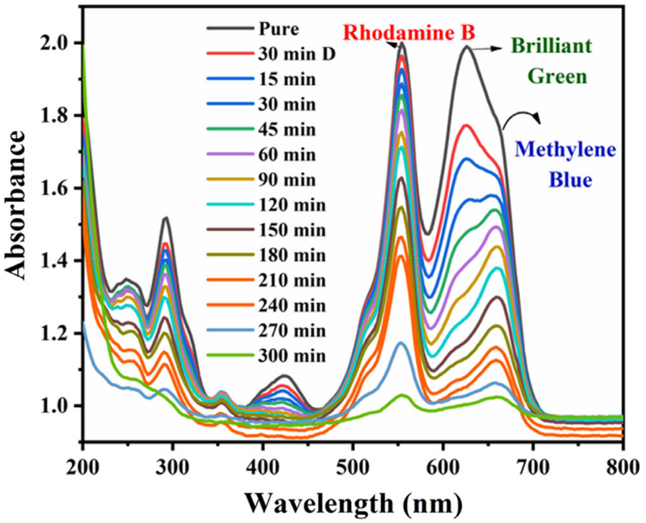


FIGURE 14 UV–Vis spectra of photocatalytic degradation of mixture of dyes (RhB, BG, and MB)

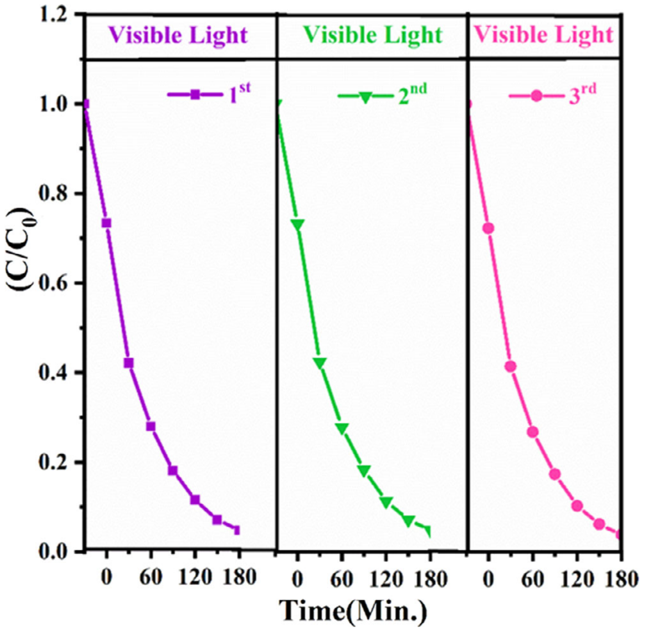


FIGURE 15 Reusability of catalyst

3.3 | Photocatalytic degradation of the mixture of dyes (RhB and BG, MB)

As per our photodegradation study of BG dye, it has been concluded that 5 mol% Mn-doped TiO_2 is more efficient in comparison with other prepared nanoparticles. Therefore, we have studied the photodegradation of a mixture of three dyes using 5 mol% Mn-doped TiO_2 nanoparticles and shown in Figure 14. As a representative of industrial dyestuff, an aqueous solution of a mixture of three dyes, that is, RhB, BG, and methylene blue (MB) is used. The control experiment (i.e., without using catalyst) reveals that the photodegradation of RhB and BG, MB is very slow under only visible light irradiation. Figure 14 shows a change in concentration of the mixture of dyes in the suspension of 5 mol% Mn-doped TiO_2 with respect to irradiation time. Absorption peaks have been observed at wavelengths ∼668, ∼544, and ∼625 nm, which are characteristic absorption peaks (λ_{max}) of MB, RhB and BG, respectively. Progress of the photodegradation reaction has been studied by measuring the absorbance at these wavelengths. In 300 min. Reaction time, almost complete degradation of these three dyes has been observed.

4 | REUSABILITY OF CATALYST

Reusability of prepared nanoparticles is one of the most significant features of catalyst effectiveness over practical reuses. Therefore, three cycles of photocatalytic degradation of BG were carried out using 5 mol% Mn-doped TiO_2 under direct sun light irradiation and the results obtained are shown in Figure 15. The almost same activity has been shown by nanoparticles for three cycles. This also confirms the stability of the catalyst under the reaction conditions.

5 | CONCLUSIONS

The photo catalytically active Mn-doped TiO_2 nanoparticles were successfully synthesized by using sol–gel method. Among the various nanoparticles, 5 mol% Mn-doped TiO_2 has shown the better efficacy for photodegradation of brilliant green (BG). Further, it has been successfully employed for the degradation of mixture of three dyes namely methylene blue (MB), rhodamine B (RB) and brilliant green (BG). The analysis of characterization of the catalysts, it has been confirm that 5 mol% Mn-doped TiO_2 act as a superior catalyst in the photocatalytic degradation. However, strong interaction of Mn in TiO_2 has been proved by FTIR. The UV–Visible absorption study shows that the 5 mol% Mn-doped TiO_2 catalyst has better visible light absorption than other prepared catalysts. The band gap 3.2, 3.3, 3.4, and 3.7 eV has been observed for 5 mol% Mn-doped TiO_2, 3 mol% Mn-doped TiO_2, 1 mol% Mn-doped TiO_2 and pure TiO_2 respectively. Further, TiO_2 has shown increased BET surface area on doping. Prepared catalysts have shown excellent photocatalytic activity for degradation of brilliant green dye and mixture of dyes. The study of different pH of solution, at basic pH catalyst has shown greater photocatalytic activity. Also, 5 mol% Mn-TiO_2 catalyst has been shown almost similar efficiency for three cycles. Rate constant of 5 mol% Mn-doped TiO_2 catalyst is nearly twice to that of bare TiO_2 for degradation of BG.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ORCID

Mangesh G. Bhosale https://orcid.org/0000-0002-1036-9018

Meghshyam K. Patil https://orcid.org/0000-0002-3144-5016

REFERENCES

[1] C. Fernández, M. S. Larrechi, M. P. Callao, *Trends Anal. Chem.* **2010**, *29*, 1202.
[2] C.-W. Siao, H.-L. Chen, L.-W. Chen, J.-L. Chang, T.-W. Yeh, C.-C. Chen, *J. Colloid Interface Sci.* **2018**, *526*, 322.
[3] Y.-C. Wang, A.-H. Lee, C.-C. Chen, *J. Taiwan Inst. Chem. Eng.* **2018**, *93*, 315.
[4] M. Barakat, *Arab. J. Chem.* **2011**, *4*, 361.
[5] D. Huang, S. Liao, W. Zhou, S. Quan, L. Liu, Z. He, J. Wan, *J. Phys. Chem. Solids* **2009**, *70*, 853.
[6] M. K. Patil, S. Shaikh, I. Ganesh, *Curr. Nanosci.* **2015**, *11*, 271.
[7] C.-W. Siao, W.-L. William Lee, Y.-M. Dai, W.-H. Chung, J.-T. Hung, P.-H. Huang, W.-Y. Lin, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *544*, 25.
[8] H.-L. Chen, F.-Y. Liu, X. Xiao, J. Hu, B. Gao, D. Zou, C.-C. Chen, *J. Colloid Interface Sci.* **2021**, *601*, 758.
[9] A.-H. Lee, Y.-C. Wang, C.-C. Chen, *J. Colloid Interface Sci.* **2019**, *533*, 319.
[10] Y. Yu, G. Chen, X. Wang, D. Jia, P. Tang, C. Lv, *RSC Adv.* **2015**, *5*, 74174.
[11] Y. Li, Y. Jiang, S. Peng, F. Jiang, *J. Hazard. Mater.* **2010**, *182*, 90.
[12] J. Zhang, X. Xiao, J. Nan, *J. Hazard. Mater.* **2010**, *176*, 617.
[13] H. Khan, D. Berk, *React. Kinet. Mech. Catal.* **2014**, *111*, 393.
[14] S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright, R. M. Lambert, *J. Am. Chem. Soc.* **2007**, *129*, 13790.
[15] M. Anpo, M. Takeuchi, *J. Catal.* **2003**, *216*, 505.
[16] D. Chatterjee, S. Dasgupta, J. Photochem, C. Photobiol, *Photochem. Rev.* **2005**, *6*, 186.
[17] J. Tian, Y. Leng, Z. Zhao, Y. Xia, Y. Sang, P. Hao, J. Zhan, M. Li, H. Liu, *Nano Energy* **2015**, *11*, 419.
[18] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, *J. Mol. Catal. A Chem.* **2000**, *161*, 205.
[19] N. Sharotri, D. Sud, *Desalination Water Treat.* **2016**, *57*, 8776.
[20] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, K. Ikeue, M. Anpo, *J. Photochem. Photobiol. A* **2002**, *148*, 257.
[21] D. Dvoranova, V. Brezova, M. Mazúr, M. A. Malati, *Appl. Catal.* **2002**, *37*, 91.
[22] T. J. Kemp, R. A. McIntyre, *Polym. Degrad. Stab.* **2006**, *91*, 165.
[23] P. Kapoor, S. Uma, S. Rodriguez, K. Klabunde, *J. Mol. Catal. A Chem.* **2005**, *229*, 145.
[24] M. Rauf, M. Meetani, S. Hisaindee, *Desalination* **2011**, *276*, 13.
[25] T. Jedsukontorn, T. Ueno, N. Saito, M. Hunsom, *J. Alloys Compd.* **2018**, *757*, 188.
[26] L. Zhang, D. He, P. Jiang, *Catal. Commun.* **2009**, *10*, 1414.
[27] H. Li, D. Wang, H. Fan, T. Jiang, X. Li, T. Xie, *Nano Res.* **2011**, *4*, 460.
[28] V. Binas, K. Sambani, T. Maggos, A. Katsanaki, G. Kiriakidis, *Appl. Catal.* **2012**, *113*, 79.
[29] E. S. Karafas, M. N. Romanias, V. Stefanopoulos, V. Binas, A. Zachopoulos, G. Kiriakidis, P. Papagiannakopoulos, *J. Photochem. Photobiol. A* **2019**, *371*, 255.
[30] V. Binas, D. Venieri, D. Kotzias, G. Kiriakidis, *J. Materiomics.* **2017**, *3*, 3.
[31] S. Paul, P. Chetri, A. Choudhury, *J. Alloys Compd.* **2014**, *583*, 578.
[32] R. Chauhan, A. Kumar, R. P. Chaudhary, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2012**, *98*, 256.
[33] S.-H. Nam, T. K. Kim, J.-H. Boo, *Catal. Today* **2012**, *185*, 259.
[34] M. Stucchi, A. Elfiad, M. Rigamonti, H. Khan, D. Boffito, *Ultrason. Sonochem.* **2018**, *44*, 272.

[35] H. Feng, M.-H. Zhang, E. Y. Liya, *Appl. Catal. A: Gen.* **2012**, *413*, 238.

[36] M. Xue, L. Huang, J.-Q. Wang, Y. Wang, L. Gao, J.-H. Zhu, Z.-G. Zou, *Nanotechnology* **2008**, *19*, 185604.

[37] G. Shao, *J. Phys. Chem. C* **2009**, *113*, 6800.

[38] B. Choudhury, A. Choudhury, *Curr. Appl. Phys.* **2013**, *13*, 1025.

[39] J. Liu, J. Li, A. Sedhain, J. Lin, H. Jian, *J. Phys. Chem. C* **2008**, *112*, 17127.

[40] B. Choudhury, A. Choudhury, *J. Lumin.* **2013**, *136*, 339.

[41] X. Ma, W. Zhou, Y. Chen, *Mater.* **2017**, *10*, 631.

[42] S. Smart, S. Liu, J. M. Serra, J. C. Diniz da Costa, A. Iulianelli, A. Basile, Porous ceramic membranes for membrane reactors. in *Handbook of Membrane Reactors*. Woodhead Publishing, Cambridge, England **2013**, p. 298.

[43] J. Choma, M. Kloske, M. Jaroniec, *J. Colloid Interface Sci.* **2003**, *266*, 168.

[44] W. H. M. Abdelraheem, M. K. Patil, M. N. Nadagouda, D. D. Dionysiou, *Appl. Catal. B: Environ.* **2019**, *241*, 598.

[45] Z. Xu, C. Li, N. Fu, W. Li, G. Zhang, *J. Appl. Electrochem.* **2018**, *48*, 1197.

[46] A. J. Moreira, J. O. Malafatti, T. R. Giraldi, E. C. Paris, E. C. Pereira, V. R. de Mendonca, V. R. Mastelaro, G. P. Freschi, *J. Environ. Chem. Eng.* **2020**, *8*, 104543.

[47] R. S. Sutar, R. P. Barkul, M. K. Patil, *Curr. Nanosci.* **2021**, *17*, 120.

How to cite this article: M. G. Bhosale, R. S. Sutar, S. B. Deshmukh, M. K. Patil, *J. Chin. Chem. Soc.* **2022**, 1. https://doi.org/10.1002/jccs.202200248

J. Chem. Sci. (2022)134:81
https://doi.org/10.1007/s12039-022-02074-w

REGULAR ARTICLE

Zinc ferrite as reusable and green catalyst for synthesis of quinoxaline derivatives

GANESH BABURAO PUND[a], SAMBHAJI TUKARAM DHUMAL[b], MADHAV JANARDAN HEBADE[c], MAZAHAR FAROOQUI[d] and BHAGWANSING SHIVSING DOBHAL[c,*]
[a]Department of Chemistry, Dr. Rafiq Zakariya College for Women, Aurangabad, MS 431001, India
[b]Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad, MS 413501, India
[c]Department of Chemistry, Badrinarayan Barwale Mahavidyalaya, Jalna, MS 431213, India
[d]Department of Chemistry, Maulana Azad College of Arts Science and Commerce, Aurangabad, MS 431001, India
E-mail: drbsdobhal@gmail.com

MS received 17 February 2022; revised 27 May 2022; accepted 2 June 2022

Abstract. A convenient method for synthesis of quinoxaline has been accomplished by cyclo condensation of substituted phenacyl bromides with *o*-phenylenediamines in $ZnFe_2O_4$ as a bimetallic and eco-friendly catalyst. The auxiliary benefits of the current protocol include short reaction time, mild reaction conditions, reusability of catalyst, ambient temperature, a wide substrate scope, a simple work-up procedure, good yields, and no chromatographic separation. Similarly, it was observed that under these reaction conditions, we had achieved all the above-mentioned benefits easily as compared to already known methods for the synthesis of quinoxalines. Therefore, this methodological approach will generate new pathways to synthesize the derivatives of quinoxalines on the industrial scale too.

Keywords. $ZnFe_2O_4$; Quinoxaline; Bimetallic catalyst; Green synthesis.

1. Introduction

Nowadays, the development of eco-friendly methodology in the field of synthetic organic chemistry prompts the synthesis of various heterocyclic scaffolds due to their prominent biological activities and importance in medicinal chemistry. The chemistry and applications of quinoxaline derivatives have recently attracted a lot of attention due to their uses as synthetic intermediates and their biological importance as antiviral,[1] anti-HIV,[2] antibacterial,[3] anticancer,[4] sensing of ions,[5,6] and kinase inhibition,[7] etc.

As illustrated in Figure 1, the quinoxaline ring scaffold was present as a major structural motif in many medicinal compounds such as chloroquinoxaline, quinacillin, levomycin, actinomycin varencline, clofazimine, echinomycin, brimonidine, and sulphonamide. Derivatives of quinoxalines also have a variety of uses in electroluminescent materials,[8] organic semiconductors,[9] dyes,[10] and chemically controlled switches.[11] Considering the importance of quinoxaline, we have planned for the synthesis of quinoxaline using a green technique.

Green synthesis has turned into an important method for expediting drug discovery and development procedures. Another goal of the green chemistry protocol is to develop sustainable chemical transformations using heterogeneous catalyst reactions.[12] Heterogeneous catalysis is preferred in industrial processes over homogeneous catalysis because product extraction and catalyst recovery are simpler in heterogeneous catalysis.[13] Based on green chemistry, developing innovative methodologies for comparatively nontoxic and recyclable catalysts that reduce the amount of energy and time needed to achieve separation can result in considerable economic and environmental advantages. Hence, the well-known chemical and biological significance of quinoxalines

---

*For correspondence

Supplementary Information: The online version contains supplementary material available at https://doi.org/10.1007/s12039-022-02074-w.

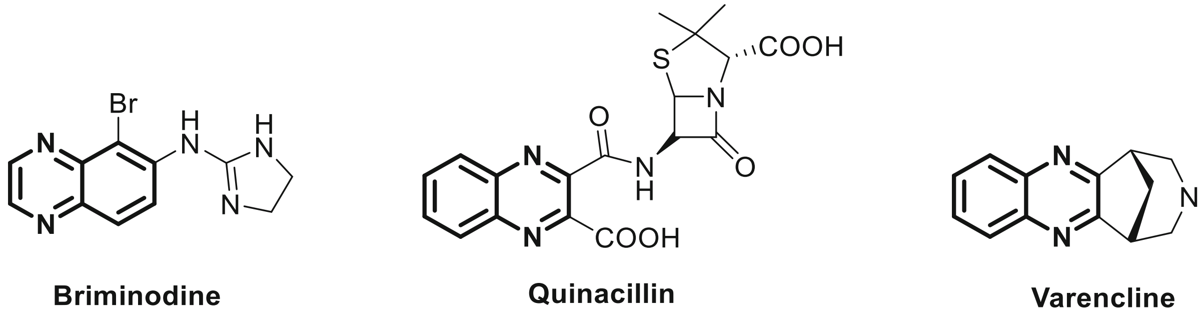


Figure 1. Some quinoxaline derivatives with pharmacological activities.

has attracted organic chemists to develop an ideal method for synthesizing quinoxalines and their derivatives.

Because of the importance of these molecules, many catalysts for the synthesis of quinoxaline have been described, including citric acid,[14] hypervalent iodine (III) in PEG-400,[15] alumina-supported heteropolyoxometalates,[16] CAN,[17] $Ga(ClO_4)_3$,[18] TMSCl,[19] Amberlite IR-120H,[20] DABCO,[21] Miceller SDS,[22] Catalyst free approach,[23] Phosphomolybdic acids,[24] $Co(OAc)_2$-Phen/Carbon-800,[25] Cu-Al catalysts,[26] Fe_3O_4@APTES@MOF-199,[27] Ni-Nanoparticles,[28] Co-Nanoparticles,[29] ZrO_2-Al_2O_3,[30] SO_4^{2-}/ZrO_2-TiO_2,[31] Ruthenium−*p*-cymene complexes,[32] Perlite–SO_3H nanoparticles,[33] Mn/Al_2O_3,[34] g-C_3N_4/Ni Nanocomposite,[35] Cobalt complex,[36] AuCNT,[37] and Camphor sulfonic acid,[38] etc.

However, the described processes had one or more kind of drawbacks, such as Amberlite IR-120H,[20] Phosphomolybdic acid,[24] ZrO_2-Al_2O_3,[30] Rutile phase nano TiO_2[31] catalyzed reactions required high temperature, the $Co(OAc)_2$-Phen/Carbon-800[25] and Cobalt complex[36] required longer reaction time while in AuCNT[37] catalyst used gold is very costly, and DABCO[21] catalyst is non-recyclable. Considering above mentioned drawbacks, there is still a need to design an appropriate environmentally benign synthetic protocol.

Zinc Ferrite ($ZnFe_2O_4$) is a bimetallic heterogeneous and very stable catalyst in which the counter anionic O^{2-} and the Fe^{3+} cation, respectively, operate as Lewis base and Lewis acid.[39] Additionally, the catalyst can be easily recovered from the reaction mixture and reused, making the method more cost-effective. The use of $ZnFe_2O_4$ nanoparticles in the synthesis of quinoxaline is described in this work.

By considering all the above aspects regarding synthetic methods, we have reported an effective and convenient process for synthesizing quinoxalines by condensation of phenacyl bromides with *o*-phenylenediamine utilizing $ZnFe_2O_4$ nanoparticles as a green and recyclable heterogeneous catalyst.

2. Experimental

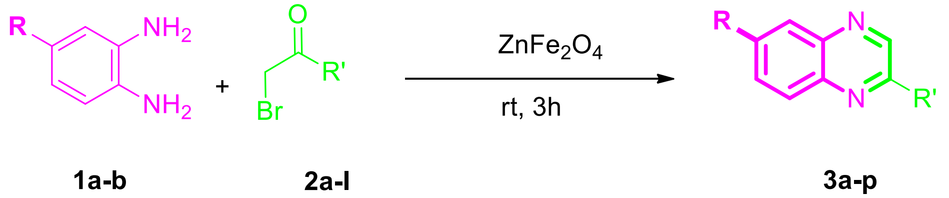
2.1 *General experimental procedure for the synthesis of quinoxalines*

10 mol% of $ZnFe_2O_4$ catalyst was added to a mixture of an *o*-phenylenediamine (1 mmol) and phenacyl bromide (1 mmol) in DMF (5 mL), and then the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was recovered by simple filtration. The crude product was purified by crystallization using ethanol to afford the pure quinoxaline. The melting points of the obtained products (**3a-p**) in this study were in good agreement with those previously reported in the literature.[40–44]

2.2 *Spectroscopic data*

2-(4-Bromophenyl)quinoxaline (***3f***) The compound (**3f**) was synthesized by Zinc Ferrite catalyzed reaction between *o*-phenylenediamine (**1a**) and 4-bromophenacyl bromide (**2f**) as pale yellow solid; yield 95%; M.p. 139-140 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.76 (d, J = 12 Hz, 1H), 7.78 (s, 1H), 7.81 (d, J = 3 Hz, 2H), 8.08 (d, J = 3 Hz, 1H), 8.13 (d, J = 9 Hz, 3H), 9.30 (s, 1H, quinazolyl-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 125.14, 129.15, 129.32, 129.75, 129.97, 130.64, 132.51, 142.96, 150.81; HRMS (ESI$^+$) calcd. for $C_{14}H_9BrN_2$ $(M+H)^+$: 285.0024; found 285.0020.

2-(4-Chlorophenyl)-7-methylquinoxaline (***3n***) The compound (**3n**) was synthesized by Zinc Ferrite catalyzed reaction between 4-methyl-*o*-



R= a=H, **R'** = a=Ar-H, b=Ar-4-NO_2, c=Ar-3-NO_2,
d=Ar-4-CN, e=Ar-3,4-dichloro,
f=Ar-4-Br, g=Ar-4-Cl, h=Ar-4-F,
i=Naphthyl, j=Ar-4-CH_3, k=Ar-3-OCH_3,
l=Ar-4-OCH_3.
R= b=CH_3, **R'** = a=Ar-H, g=Ar-4-Cl, b=Ar-4-NO_2,
f=Ar-4-Br.

Scheme 1. Synthesis of quinoxalines using $ZnFe_2O_4$ catalyst.

phenylenediamine (**1b**) and 4-chlorophenacyl bromide (**2g**) as brown solid; yield 94%; M.p. 113-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.61 (s, 3H, CH_3), 7.54 (d, J = 6 Hz, 2H), 7.60 (d, J = 6 Hz, 1H), 7.91 (d, J = 9 Hz, 1H), 8.03-8.15 (m, 3H, Ar-H), 9.25 (s, 1H, quinazolyl-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 22.03, 128.55, 128.77, 129.23, 129.49, 132.37, 132.95, 135.49, 141.21, 142.11, 142.91, 149.93, 150.65; HRMS (ESI$^+$) calcd. for $C_{15}H_{11}ClN_2$ $(M+H)^+$: 255.0689; found 255.0683.

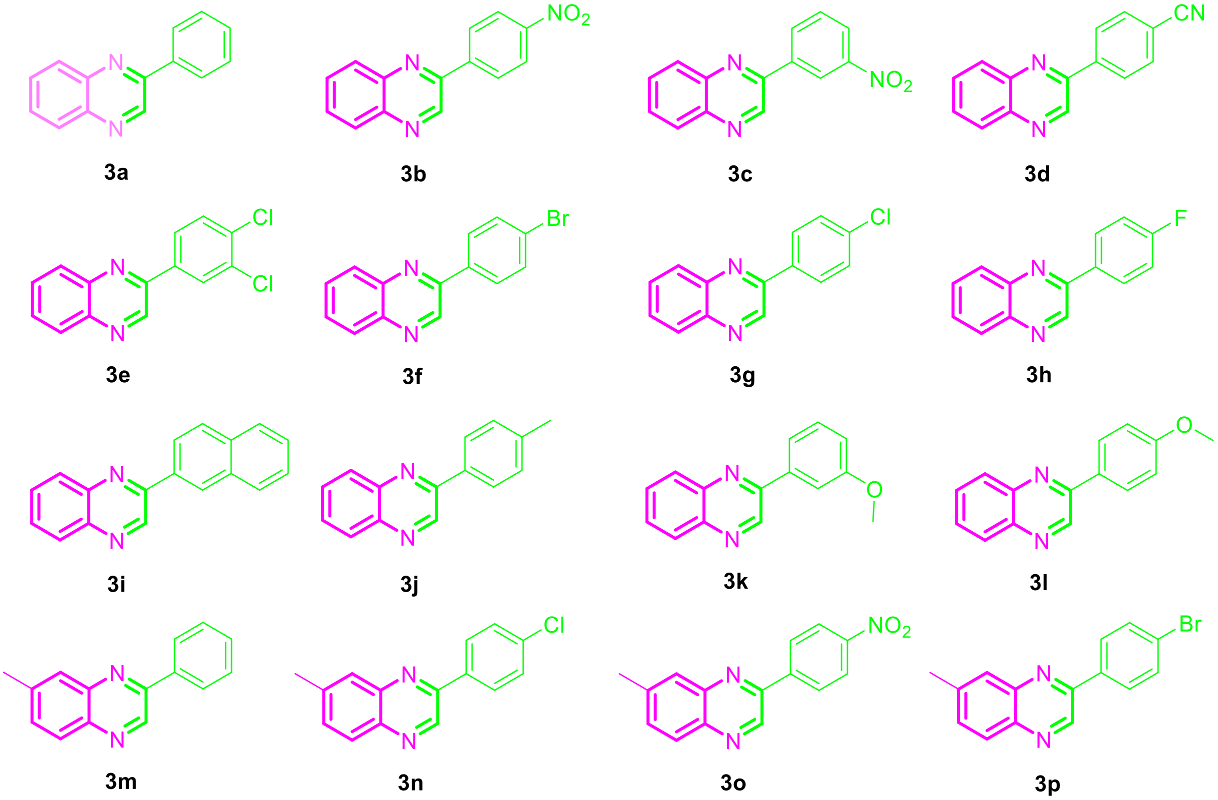
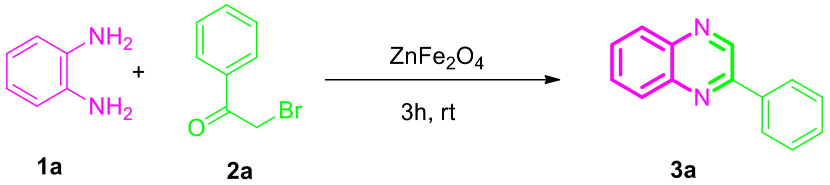


Figure 2. Structures of all the synthesized quinoxalines (**3a-p**).



Scheme 2. Model reaction for the synthesis of quinoxaline using $ZnFe_2O_4$ catalyst.

3. Results and Discussion

In this procedure, a mixture of phenacyl bromides (**2a-l**) (1 mmole), *o*-phenylenediamines (**1a-b**) (1 mmol), and $ZnFe_2O_4$ was stirred at room temperature for 3 h which afforded quinoxalines (**3a-p**) with excellent yields and high purity, which is outlined in the Scheme 1. The structures of all the synthesized quinoxalines (**3a-p**) are shown in Figure 2.

Optimization of the reaction parameters was performed by general model reaction of *o*-phenylenediamine (**1a**) and phenacyl bromide (**2a**) as shown below (Scheme 2).

Firstly, we studied reactions in various solvents like dioxane, dimethylformamide, dichloromethane, and acetonitrile as aprotic solvents and ethanol, methanol, glycerol, PEG-400, and water as protic solvents. It is observed that when we use dimethylformamide as a solvent, the yield of quinoxaline is high (Table 1, entry 3). Although, the reaction in different solvents like acetonitrile, dichloromethane, 1,4-dioxane, glycerol, PEG-400, ethanol, methanol,

Table 1. Screening of reaction condition with respect to solvent and catalyst loading **3a**[a].

Entry	Solvent	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	Dimethylformamide	No catalyst	5	NR
2	Dimethylformamide	5% $ZnFe_2O_4$	4	89
3	Dimethylformamide	10% $ZnFe_2O_4$	3	95
4	Dimethylformamide	15% $ZnFe_2O_4$	4	94
5	Dimethylformamide	20% $ZnFe_2O_4$	4	90
6	Acetonitrile	10% $ZnFe_2O_4$	3.5	83
7	Dichloromethane	10% $ZnFe_2O_4$	3	72
8	Ethanol	10% $ZnFe_2O_4$	3	65
9	Methanol	10% $ZnFe_2O_4$	3	62
10	Water	10% $ZnFe_2O_4$	10	59
11	1,4-Dioxane	10% $ZnFe_2O_4$	4	70
12	PEG-400	10% $ZnFe_2O_4$	4	61
13	Glycerol	10% $ZnFe_2O_4$	4	60

[a]Reaction conditions: Phenacyl bromide (0.001 mol), *o*-phenylenediamine (0.001 mol), 10% $ZnFe_2O_4$ in 5 mL DMF, at room temperature for 3 h. [b]Isolated yields, NR: No Reaction.

Table 2. Comparative study of $ZnFe_2O_4$ with other metal oxides.

Entry	Catalyst (10 mol%)	Time (h)	Yield (%)	Condition
1	ZnO	3	58	DMF
2	MgO	3	38	DMF
3	CuO	3	44	DMF
4	ZrO_2	3	54	DMF
5	α-Fe_2O_3	3	64	DMF
6	β-Fe_2O_3	3	59	DMF
7	$ZnFe_2O_4$	3	95	DMF

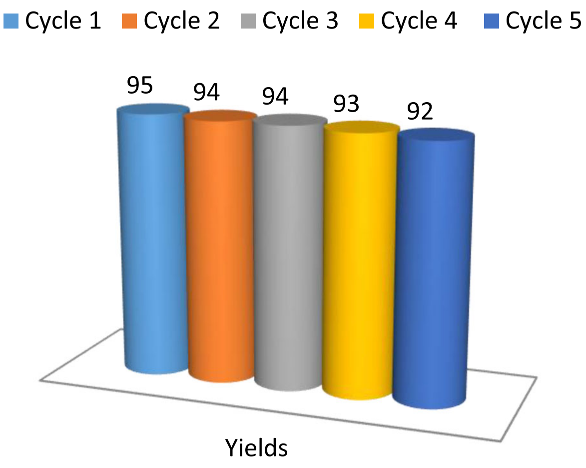
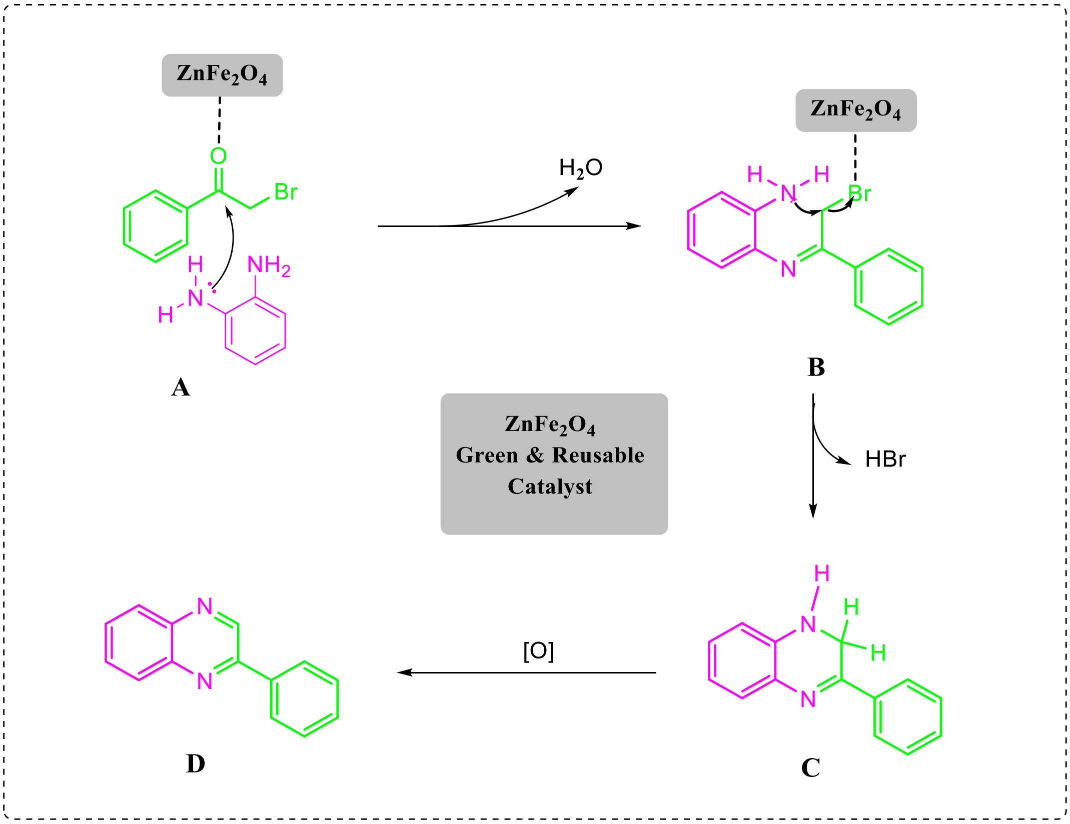


Figure 3. The recyclability of $ZnFe_2O_4$ ^{a} in the synthesis of quinoxalines.

and water gave less yield as compared to dimethylformamide (Table 1, entries 6-13).

The solvent is crucial to the catalyst's activity and efficacy; when protic solvents are present, the product yield is lower than when aprotic solvents are present. We noticed that when we changed the solvent in the reaction, the percentage yield changed, and after further examination, we established that dimethylformamide is a good solvent for this conversion. We have also examined catalyst loading, and the findings are summarised in Table 1. The results showed that a catalyst loading of 10% $ZnFe_2O_4$ is suitable for the intended conversion. While decreasing to 5 mol% and increasing 15, 20 mol% $ZnFe_2O_4$ did not result in a significant increase in product yield (Table 1, entries 2, 4, and 5).

When the standard reaction was carried out in the absence of $ZnFe_2O_4$, there was no conversion of reactants to products after 5 h of stirring at room temperature under optimal conditions (Table 1, entry 1). This result motivates us to investigate the methods for synthesizing quinoxalines from substituted phenacyl bromides and *o*-phenylenediamines using a 10 mole% $ZnFe_2O_4$ catalyst and dimethylformamide (DMF) as the solvent under an optimized reaction condition. We have also examined the comparative study of Zinc ferrite with other metal oxides for the synthesis of quinoxaline. According to a study, Zinc ferrite ($ZnFe_2O_4$) is a prominent catalyst for the efficient and facile synthesis of quinoxaline. The results are disclosed in (Table 2, entry 1-7).



Scheme 3. A plausible mechanism for the synthesis of quinoxaline derivatives.

We also studied the recyclability of $ZnFe_2O_4$ in dimethylformamide solvent for 3 h at room temperature for model reactions such as *o*-phenylenediamine (**1a**) and phenacyl bromide (**2a**), with the findings displayed in Figure 3.

Recovery and extending the reusability of a heterogeneous catalyst are crucial factors in its practical application. As a result, a series of studies were conducted to recover and reuse $ZnFe_2O_4$ for the reaction between o-phenylenediamine (**1a**) and phenacyl bromide (**2a**) under optimal reaction conditions. After completion of the reaction, the reaction mixture was diluted with 10 mL ethyl acetate followed by filtration to recover the catalyst. The recovered catalyst was washed with water and acetone before being dried in a desiccator and utilized in a subsequent reaction.

The plausible mechanism for the synthesis of quinoxaline, as shown in Scheme 3, involves the activation of the carbonyl group of phenacyl bromide over $ZnFe_2O_4$ indicated as **A**, followed by the dehydration and dehalogenation of *o*-phenylenediamine, resulting in the formation of cyclic product **C**, which is easily oxidized in air to form desired product **D**.

4. Conclusions

In conclusion, we developed an eco-friendly, simple, convenient, and efficient procedure for the synthesis of quinoxalines from the various phenacyl bromides and *o*-phenylenediamines using $ZnFe_2O_4$ as a reusable catalyst under mild reaction conditions. The advantages of the presented method include high yield, ease of handling, inexpensive catalyst, simple procedure and work-up, cleaner reaction profile, short reaction time, and no need for column chromatography, which make it a useful and appealing process for the rapid synthesis quinoxaline derivatives as biologically interesting compounds. It would be one of the potential methodologies for the synthesis of quinoxaline derivatives. It may also be viable for large-scale industrial level too, as we have used the greener and recyclable catalyst for the synthesis, which could be recovered and regenerated easily. Therefore, the method must be cost-effective for the industry to scale up rapidly.

Supplementary Information (SI)

Full experimental detail, HRMS/MS, ^1H, and ^{13}C NMR spectra. Supplementary information is available at www.ias.ac.in/chemsci.

Acknowledgements

The author G.B.P. is very much thankful to the Council for Scientific and Industrial Research (CSIR), New Delhi, for the award senior research fellowship. File No. 08/613(0005)/2018-EMR-I.

Declarations

Conflict of interest The authors declare no conflict of interest.

References

1. Montana M, Montero V, Khoumeri O and Vanelle P 2020 Quinoxaline derivatives as antiviral agents: A systematic review *Molecules* **25** 1
2. Patel S B, Patel B D, Pannecouque C and Bhatt HG 2016 Design, synthesis and anti-HIV activity of novel quinoxaline derivatives *Eur. J. Med. Chem.* **117** 230
3. Ammar Y A, Farag A A, Ali A M, Hessein S A, Askar A A, Fayed E A, et al. 2020 Antimicrobial evaluation of thiadiazino and thiazolo quinoxaline hybrids as potential DNA gyrase inhibitors; design, synthesis, characterization and morphological studies *Bioorg. Chem.* **99** 103841
4. Kaushal T, Srivastava G, Sharma A and Negi A 2019 An insight into medicinal chemistry of anticancer quinoxalines *Bioorg. Med. Chem.* **27** 16
5. Dey S K, Kobaisi M A and Bhosale S V 2018 Functionalized Quinoxaline for chromogenic and fluorogenic anion sensing *ChemistryOpen* **7** 934
6. Srivani D, Gupta A, La D D, Bhosale R S, Puyad A L, Xiang W, et al. 2017 Small molecular non-fullerene acceptors based on naphthalenediimide and benzoisoquinoline-dione functionalities for efficient bulk-heterojunction devices *Dye Pigm.* **143** 1
7. Kim Y B, Kim Y H, Park J Y and Kim S K 2004 Synthesis and biological activity of new quinoxaline antibiotics of echinomycin analogues *Bioorg. Med. Chem. Lett.* **14** 541
8. Thomas J, Velusamy M, Lin Jiann T, Chuen C H and Tao Y T 2005 Chromophore-labeled quinoxaline derivatives as efficient electroluminescent materials *Chem. Mater.* **17** 1860
9. Liu Y, Liu J, Chen D, Wang X, Liu Z, Liu H, et al. 2019 Quinoxaline-based semiconducting polymer dots for in vivo nir-ii fluorescence imaging *Macromolecules* **52** 5735
10. Chang D W, Lee H J, Kim J H, Park S Y, Park S M, Dai L and Baek J B 2011 Novel quinoxaline-based organic sensitizers for dye-sensitized solar cells *Org. Lett.* **13** 3880
11. Pashazadeh R, Pander P, Lazauskas A, Dias FB and Grazulevicius JV 2018 Multicolor luminescence switching and controllable thermally activated delayed fluorescence turn on/turn off in Carbazole-Quinoxaline-Carbazole triads *J. Phys. Chem. Lett.* **9** 1172

12. Corma A and Garcia H 1997 Organic reactions catalyzed over solid acids *Catal. Today* **38** 257
13. Margelefsky E L, Zeidan R K and Davis M E 2008 Cooperative catalysis by silica-supported organic functional groups *Chem. Soc. Rev.* **37** 1118
14. Mahesh R, Dhar A K, Sasank T, Thirunavukkarasu S and Devadoss T 2011 Citric acid: An efficient and green catalyst for rapid one pot synthesis of quinoxaline derivatives at room temperature *Chin. Chem. Lett.* **22** 389
15. Lin PY, Hou RS, Wang HM, Kang IJ and Chen LC 2009 Hypervalent iodine(iii) sulfonate mediated synthesis of quinoxalines in liquid PEG-400 *J. Chin. Chem. Soc.* **56** 683
16. Ruiz D M, Autino J C, Quaranta N, Vazquez P G and Romanelli G P 2012 An efficient protocol for the synthesis of quinoxaline derivatives at room temperature using recyclable alumina-supported heteropolyoxometalates *Sci. World. J.* 174784
17. More S V, Sastry M and Yao C F 2006 Cerium (IV) ammonium nitrate (CAN) as a catalyst in tap water: A simple, proficient and green approach for the synthesis of quinoxalines *Green Chem.* **8** 91
18. Pan F, Chen T M, Cao J J, Zou J P and Zhang W 2012 $Ga(ClO_4)_3$-catalyzed synthesis of quinoxalines by cycloaddition of α-hydroxyketones and *o*-phenylenediamines *Tetrahedron Lett.* **53** 2508
19. Wan J P, Gan S F, Wu J M and Pan Y 2009 Water mediated chemoselective synthesis of 1,2-disubstituted benzimidazoles using o-phenylenediamine and the extended synthesis of quinoxalines *Green Chem.* **11** 1633
20. Kamal A, Babu K S, Hussaini S A, Mahesh R and Alarifi A 2015 Amberlite IR-120H, an efficient and recyclable solid phase catalyst for the synthesis of quinoxalines: A greener approach *Tetrahedron Lett.* **56** 2803
21. Meshram H M, Ramesh P, Santosh Kumar G and Chennakesava Reddy B 2010 One-pot synthesis of quinoxaline-2-carboxylate derivatives using ionic liquid as reusable reaction media *Tetrahedron Lett.* **51** 4313
22. Ghosh P and Mandal A 2013 Sodium dodecyl sulfate in water: Greener approach for the synthesis of quinoxaline derivatives *Green Chem. Lett. Rev.* **6** 45
23. Kumar K, Mudshinge S R, Goyal S, Gangar M and Nair V A 2015 A catalyst free, one pot approach for the synthesis of quinoxaline derivatives via oxidative cyclisation of 1,2-diamines and phenacyl bromides *Tetrahedron Lett.* **56** 1266
24. Tejeswararao D 2016 Synthesis of quinoxaline using silica supported phosphomolybdic acid as reusable heterogeneous catalyst *Asian J. Chem.* **28** 2353
25. Panja D, Paul B, Balasubramaniam B, Gupta R K and Kundu S 2020 Application of a reusable Co-based nanocatalyst in alcohol dehydrogenative coupling strategy: Synthesis of quinoxaline and imine scaffolds *Catal. Commun.* **137** 105927
26. Nakhate A V, Rasal K B, Deshmukh G P, Gupta S S and Mannepalli L K 2017 Synthesis of quinoxaline derivatives from terminal alkynes and o-phenylenediamines by using copper alumina catalyst *J. Chem. Sci.* **129** 1761
27. Sajjadifar S, Amini I and Karimian M 2021 Synthesis and Characterization of Fe_3O_4@APTES@MOF-199 Magnetic nanocatalyst and its application in the synthesis of Quinoxaline derivatives *Iran J. Catal.* **11** 59
28. Kumar A, Kumar S, Saxena A, De A and Mozumdar S 2008 Ni-nanoparticles: an efficient catalyst for the synthesis of quinoxalines *Catal. Commun.* **9** 778
29. Rajabi F, Alves D and Luque R 2015 An efficient and recyclable nanoparticle-supported Cobalt catalyst for Quinoxaline synthesis *Molecules* **20** 20709
30. Thimmaraju N and Shamshuddin M 2016 Synthesis of 2,4,5-trisubstituted imidazoles, quinoxalines and 1,5-benzodiazepines over eco-friendly and highly efficient ZrO_2-Al_2O_3 catalyst *RSC Adv.* **6** 60231
31. Shelke S V, Dhumal S T, Karale A Y, Deshmukh T R and Patil M K 2022 A Facile synthesis of Quinoxalines by SO_4^{2-}/ZrO_2-TiO_2 as efficient and recyclable heterogeneous catalyst *Synth. Commun.* **52** 597
32. Sindhuja D, Gopiraman M, Vasanthakumar P, Bhuvanesh N and Karvembu R 2021 Ruthenium –p-cymene complexes with acylthiourea, and its heterogenized form on graphene oxide act as catalysts for the synthesis of quinoxaline derivatives *J. Organomet. Chem.* **949** 121933
33. Rouhani M and Ramazani A 2018 Perlite-SO_3H nanoparticles: very efficient and reusable catalyst for three-component synthesis of *N*-cyclohexyl-3-aryl-quinoxaline-2- amine derivatives under ultrasound irradiation *J. Iran. Chem. Soc.* **15** 2375
34. Rekha M, Kathyayini H and Nagaraju N 2013 Catalytic activity of manganese oxide supported on alumina in the synthesis of quinoxalines *Front. Chem. Sci. Eng.* **7** 415
35. Rashidizadeh A and Ghafuri H 2019 g-C_3N_4/Ni Nanocomposite: An efficient and eco-Friendly recyclable catalyst for the synthesis of Quinoxalines *Proceedings* **9** 20
36. Shee S, Ganguli K, Jana K and Kundu S 2018 Cobalt complex catalyzed atom-economical synthesis of Quinoxaline, Quinoline and 2-Alkylaminoquinoline derivatives *Chem. Commun.* **54** 6883
37. Shah N, Gravel E, Jawale D V, Doris E and Namboothiri I N 2014 Synthesis of Quinoxalines by a carbon nanotube–Gold nanohybrid-catalyzed cascade reaction of vicinal diols and keto alcohols with diamines *ChemCatChem* **7** 57
38. Kaur G, Singh A, Kaur N and Banerjee B 2021 A general method for the synthesis of structurally diverse quinoxalines and pyrido-pyrazine derivatives using camphor sulfonic acid as an efficient organo-catalyst at room temperature *Synth. Commun.* **51** 1121
39. Khazaei A, Ranjbaran A, Abbasi F, Khazaei M and Moosavi-Zare A R 2015 Synthesis, characterization and application of $ZnFe_2O_4$ nanoparticles as a heterogeneous ditopic catalyst for the synthesis of pyrano[2,3-d] pyrimidines *RSC Adv.* **5** 13643
40. Harsha K B, Rangappa S, Preetham H D, Swaroop T R, Gilandoust M, Rakesh K S and Rangappa K S 2018 An Easy and efficient method for the synthesis of Quinoxalines using recyclable and heterogeneous nanomagnetic-supported acid catalyst under solvent-free condition *ChemistrySelect* **3** 5228

41. Jadhav S A, Sarkate A P, Shioorkar M G and Shinde D B 2017 Expeditious one-pot multicomponent microwave-assisted green synthesis of substituted 2-phenyl Quinoxaline and 7-bromo-3-(4-ethylphenyl) pyrido[2,3-b]pyrazine in water–PEG and water–ethanol *Synth. Commun.* **47** 1661
42. Khalafy J, Habashi B P, Marjani A P and Moghadam P N 2012 The synthesis of 2-arylquinoxaline derivatives *Curr. Chem. Lett.* **1** 139
43. Lian M, Li Q, Zhu Y, Yin G and Wu A 2012 Logic design and synthesis of quinoxalines via the integration of iodination/oxidation/cyclization sequences from ketones and 1,2-diamines *Tetrahedron* **68** 9598
44. Tanwar B, Purohit P, Naga Raju B, Kumar D, Kommi D N and Chakraborti A K 2015 An “all-water” strategy for regiocontrolled synthesis of 2-aryl quinoxalines Babita *RSC Adv.* **3** 10715

June 2022 - May - 2023

ARTICLE IN PRESS

Infectious Diseases Now xxx (xxxx) xxx

Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

ELSEVIER

Infectious Diseases Now

Short communication

Prevalence of Entamoeba histolytica among schoolchildren in Dilla town, Gedeo zone, Ethiopia

Mequanint Abate[a], Feleke Eriso[a], Vikas B. Kalyankar[b], Nitin D. Padwal[c], Suresh Chandra Singh[d], Vijay Upadhye[e], Atul Shivajirao Humbe[f], Swati Dilip Jadhav[g], Sunil Tulshiram Hajare[a,*]

[a] Department of Biology, College of Natural and Computational Sciences, Dilla University, Dilla 419, SNNPR, Ethiopia
[b] Department of Zoology, Toshniwal Arts, Commerce and Science College, Sengaon, SRTMU, Nanded, India
[c] Department of Zoology, Shankarrao Patil Mahavidyalaya, Bhoom, Dist Osmanabad (MS), India
[d] Project In Charge, TB & COVID Antigen Development Centre, Gujarat, India
[e] Deputy Director & Associate Professor (CD4D), Parul Institute of Applied Sciences, Vadodara, Gujarat, India
[f] Department of Zoology, SGRG Shinde College, Paranda, Dist. Osmanabad, (India)
[g] Department of Zoology, RP College, Osmanabad, (India)

ARTICLE INFO

Article history:
Received 19 April 2022
Revised 25 June 2022
Accepted 15 September 2022
Available online xxxx

Keywords:
Entamoeba histolytica
Antigen detection test
Ethiopia
Prevalence
Schoolchildren

ABSTRACT

Background: To measure the prevalence of Entamoeba histolytica (E. histolytica) infections and associated risk factors among schoolchildren in Dilla town, Gedeo zone Ethiopia.
Methods: A total of 501 schoolchildren were recruited by random sampling. Microscopically positive samples for E. histolytica cysts were further characterized using the E. histolytica II antigen detection kit. Univariate and multivariate logistic regression models were employed to analyze associations between E. histolytica infections, age, sex and study setting.
Results: Overall prevalence of E. histolytica was 13.17%. Hand washing before eating, hand washing after defecation, mother's occupation, and awareness about amebiasis were the factors associated with parasite prevalence.
Conclusion: Prevalence of E. histolytica in the study population was high. Health promotion campaigns to create awareness about health and hygiene are clearly needed.

Introduction

Entamoeba histolytica infection in children is a major public health issue, particularly in the developing countries of Africa. Even though several protozoan species of the Entamoeba genus (E. coli, E. dispar, E. moshkovskii, E. hartmanni and E. polecki…) infect humans, only E. histolytica is considered pathogenic [1]. While most infections are asymptomatic, they can lead to severe infection with amebic colitis and amebic liver abscess. E. histolytica infection prevalence differs from one age group to another, and is at its highest during the first 15 years of life [8].

According to a WHO report, every year diarrhea contributes to more than one out of ten (13 %) child deaths in Ethiopia [2]. According to a survey report on 97 communities of Ethiopia, overall prevalence of Entamoeba histolytica infections in schoolchildren approaches 15.0 % [3]. In that country, intestinal parasitic infections (IPIs) including Entamoeba infections, are more prevalent in rural areas due to poverty, illiteracy, poor hygiene, lack of access to potable water and a hot and humid tropical climate [4,5].

Amebiasis is endemic in developing African countries, particularly Ethiopia. In a resource-limited setting, due to its affordability and accessibility, microscopy remains the diagnostic tool for Entamoeba infections, even though it which cannot differentiate E. histolytica, the cause of invasive amebiasis, and E. dispar, which is considered to be a harmless commensal. In this investigation, we aimed to assess the prevalence of E. histolytica in fresh stool specimens obtained from elementary school children in Dilla, Ethiopia.

2. Material and Methods

2.1. Study setting

The study was conducted in the town of Dilla (Gedeo Zone) which is located 359 km southeast of Addis Ababa (the Ethiopian capital) and 87 km from Hawasa (the SNNPR capital).

---

* Corresponding author at: Biotechnology, College of Natural and Computational Sciences, Dilla University, Dilla- 419, Ethiopia.
E-mail address: sunilhajare@gmail.com (S.T. Hajare).

https://doi.org/10.1016/j.idnow.2022.09.016
2666-9919/

Please cite this article as: M. Abate, F. Eriso, V.B. Kalyankar et al., Prevalence of Entamoeba histolytica among schoolchildren in Dilla town, Gedeo zone, Ethiopia, Infectious Diseases Now, https://doi.org/10.1016/j.idnow.2022.09.016

2.2. Study population and research design

A school-based cross-sectional study was conducted to establish by simple random and stratified sampling the prevalence of E. histolytica infection and associated risk factors among schoolchildren in Dilla. All in all, 10,772 students (grade 1 to grade 8) were registered in the three selected schools.

We used the following formula to calculate the common multiplier.

P = t/T: P = common multiplier; t = Study sample size; T = total number of students.

2.3. Sample size determination

The sample size was determined by the standardized formula [6].

n = Z2*P(1-P) X deff d2.

Where n = sample size, Z = Standard normal deviate (1.96), which corresponds to 95 % confidence interval P = prevalence of E. histolytica from a previous study (P = 32 %) [7] and d = precision (d = 0.04).

deff = Design effect (deff = 1.5).

Based on the above formula:

$N = 1.5*(1.96)^2 *0.32(1-0.32) = 1.96^2 *0.32*0.68*1.5 = 501.$

$\mathbf{(0.05)^2\ (0.05)^2}$

Finally, 501 students at all grade levels in three elementary schools participated in the study.

2.4. Eligibility criteria

Were included: students who signed informed consent and agreed to deliver stool specimens, students who had not received any antiphrastic treatments in the days prior to sampling.

2.5. Stool samples and data collection

Data were obtained through structured and semi-structured interviews (questionnaires administered by the researchers to students) and by stool examination analysis. The stool samples were processed by direct wet smear and formalin ethyl acetate sedimentation technique, followed by iodine staining, and examined via microscopy. Microscopically positive samples for E. histolytica cysts were further by using the E. histolytica II (TechLab, Inc., Blacksburg, VA) detection kit according to the manufacturer's instructions [8].

2.6. Statistical analysis

All statistical analyses were performed using SPSS version 20. Variables of interest were calculated by binary logistic regression and multivariate logistic regression analysis. The level of significance was set at < 0.05 with a 95 % confidence interval.

3. Results

3.1. Socio-demographic characteristics of the study subjects

Five hundred and one school children were recruited and included in the analysis, with a 100 % response rate. There were 248 (49.5 %) males and 253 (50.5 %) females. The participants ranged in age from five to eighteen years; 170 (50.9 %) were grade level 1 to 4. Regarding the fathers, 128 (25.6 %) had received higher education; as for the mothers, in 110 cases (32.9 %), educational level was limited to reading and writing. Moreover, 34.5 percent of the fathers were merchants, while 35.5 percent of the mothers were housewives.

3.2. Environmental and behavioral factors

A large majority (86.62 %) of the students had tap water as their source of drinking water. Concerning drinking water storage, 64.67 % of the households used a jerrican, 15.96 % kept their water containers uncovered, and 78.04 % did not treat their drinking water by chlorine or boiling. As regards toilets, 84.43 % had facilities at home (in and around the compound), but among the households with toilets, 71.86 % were devoid of water access. Most (77.84 %) households had no sewage disposal facility, 20.01 % of the students did not generally wash their hands before eating, and only 21.95 % had the habit of washing hands with soap after defecation. Most of them (73.85 %) had the habit of eating unwashed fruit. While 88.62 % were aware of the importance of nail trimming, only 25.14 % showed awareness about amoebiasis (Table 1).

3.3. Prevalence of E. Histolytica

Microscopy and E. histolytica II antigen detection kit were used to test single stool specimens from 501 asymptomatic school children aged 5 to 18 years. Microscopy was positive in 126 (25.14 %) stool samples for E. histolytica, and the antigen detection test was positive in 66 (13.17 %) of stool specimens.

3.4. Association of risk factors with E. Histolytica infection among school children

Multivariate logistic regression analysis confirmed the following: Hand washing before eating, hand washing after defecation, mother's occupation and awareness of ameba were significantly associated ($p < 0.05$) with prevalence of E. histolytica (Table 2, 3).

Table 1
Environmental and behavioral risk factors of E.histolytica infection among schoolchildren.

Variable	Category	Frequency	Percent
Source of drinking water	Tap	434	86.62
	Ground water	67	12.7
Water storage	Tank	90	17.96
	Jerrican	324	64.67
	Baldy	51	10.17
	Clay spot	36	7.18
Status of water container	Covered	421	84.03
	Uncovered	80	15.97
Treatment of water at home	Yes	110	21.95
	No	391	78.04
Presence of latrine at home	Yes	423	84.43
	No	78	15.56
Access to water in latrine	Yes	304	71.86
	No	-	-
Sewage disposal	Garbage pit	111	22.15
	Outside the compound	390	77.84
Hand washing before eating	Yes	400	79.9
	No	101	20.1
Handwashingafter defecation	No	161	32.13
	Water only	230	45.90
	Water and soap	110	21.95
Habit ofeating unwashed fruits	Yes	370	73.85
	No	131	26.14
Habit of nail trimming	Yes	444	88.62
	No	57	11.37
Awareness of ameba	Yes	126	25.14
	No	375	74.85

Table 2
Univariate and multivariate analysis of socio-demographic factors.

Variables	Category	Total exam ined	EH +VE	EH -Ve	COR (95 % CI)	AOR (95 % CI)	p- value
Father's educational status	Unable to write and read	71	4	67	1	1	
	Able to write and read only	105	13	92	1.247(0.584, 2.543)	0.767 (0.327, 3.34)	0.812
	Elementary school	88	9	79	1.382(0.580,3.294)	0.956 (0.204, 4.409)	0.947
	Secondary school	108	20	88	2.289(0.729, 7.239)	1.013 (0.195,6.190)	0.915
	Higher education	128	20	108	0.841(0.259, 1.56)	0.645 (0.214, 1.767)	0.38
Mother's educational status	Unable to write and read	61	6	21	1	1	
	Able to write and read only	143	17	93	1.241(0.341,4.252)	0.59(0.042, 8.12)	0.814
	Elementary school	96	9	52	2.144(0.951,4.753)	0.879 (0.195, 4.341)	0.762
	Secondary school	118	20	66	2.237(0.881,5.756)	0.640 (0.146, 2.998)	0.465
	Higher education	83	14	36	1.286(0.582,2.843)	0.715 (0.195, 2.634)	0.618
Father's occupation	Merchant	173	26	147	1	1	
	Government worker	164	27	137	0.899(0.398,2.063)	0.956 (0.235, 3.741)	0.89
	Day laborer	73	4	69	0.769(0.327,1.765)	1.210 (0.269, 5.298)	0.92
	Farmer	91	9	82	1.43(0.42,5.134)	1.749 (0.339, 8.912)	0.567
Mother's occupation	Housewife	177	24	153	1	1	
	Merchant	158	27	131	2.823(0.768,8.440)	1.942(0.310, 16.231)	0.67
	Government worker	62	10	52	2.117(0.579,7.768)	1.285(0.151, 11.074)	0.821
	Day laborer	58	1	57	1.087(0.263,4.618)	0.493 (0.038, 6.614)	0.613
	Farmer	46	4	42	4.35(2.7,7.02)	**2.41(1.53,3.82)**	**0.034**

EH = *E. histolytica;* COR = Crude odds ratio; AOR = Adjusted odds ratio.

Table 3
Association of behavioral and environmental factors with prevalence of *E. histolytica.*

Variable	Category	Total exam ined	EH +ve	EH -ve	COR (95 %CI)	AOR (95 %CI)	p- value
Source of drinking water	Tap	468	63	405	0.95(0.73,1.25)	0.487(0.67,1.18)	0.79
	Ground water	33	3	30	1	1	
Water storage	Tank	104	12	57	1	1	
	Jerrican	312	45	163	0.448(0.094,2.94)	0.212(0.037,1.242)	0.096
	Baldy	51	7	27	0.435(0.178,1. 275)	0.213(0.044,1.072)	0.081
	Clay spot	34	2	21	0.368(0.072,1.956)	0.179(0.028,1.161)	0.071
Status of water container	Covered	471	63	251	0.704(0.201,2.473)	0.653(0.162,2.664)	0.651
	Uncovered	30	3	17	1	1	
Treatmentof water at home	Yes	127	16	69	1.03(0.98,1.18)	1.10(0.80,1.40)	0.44
	No	374	50	199	1	1	
Presenceof latrine at home	Yes	501	435	268			
	No		-	-			
Presenceof water in latrine	Yes	204	29	107	0.8(0.61,1.05)	0.77(0.32,1.88)	0.765
	No	297	37	161	1	1	
Sewage disposal	Garbage pit	168	26	86	0.84(0.58,1.22)	0.71(0.43,1.151)	0.067
	Outside the compound	333	40	182	1	1	
Handwashing before feeding	Yes	400	60	340	0.91(0.82,1.01)	**0.85(0.74,0.98)**	**0.02**
	No	101	6	95	1	1	
Handwashing after defecation	No	159	22	137	1	1	
	Water only	235	34	201	1.06(0.85,1.32)	1.07(0.73,1.58)	0.267
	Water and soap	107	10	97	1.14(0.91,1.41)	**0.57(0.4,0.81)**	**0.04**
Habit of eating unwashed fruits	Yes	312	43	269	0.84(0.58,1.22)	10.71(0.43,1.151)	0.254
	No	189	23	163	1	1	
Dirty materials in the fingers	Yes	160	16	144	1.22(1.01,1.44)	1.03(0.92,1.15)	0.77
	No	344	50	294	1	1	
Habitofnail trimming	Yes	456	64	392	0.269(0.061,1.148)	4.539(0.879,23.43)	0.083
	No	45	2	43	1	1	
Awareness of ameba	Yes	105	9	96	1.02(0.85,1.34)	0.4(0.3,0.7)	0.03
	No	396	57	339	1	1	

EH = *E. histolytica;* COR = Crude odds ratio; AOR = Adjusted odds ratio.

4. Discussion

In our study, both microscopy detection and antigen detection were used, and overall prevalence of *E. histolytica* infection with the latter was 13.17 %. These findings confirmed a trend of high risk of E. histolytica infection among schoolchildren as shown in other local studies (12.9 % prevalence rate of E. histolytica by using microscopy) [4]. Our results are likewise congruent with overseas studies, which reported E. histolytica prevalence by using PCR in parts of India and Bangladesh [9,10].

However, higher prevalence of E. histolytica among schoolchildren was recorded in Bahir Dar (24.5 %) [11], Gurage Zone of Ethiopia (27.3 %) [12], Western Gojjam 17.1 % [13] and Chencha town, Southern Ethiopia (16.5 %) [14]. These discrepant results may be due to differences in the laboratory techniques applied. Most of the studies identifying E. histolytica infection in Ethiopia did not distinguish between the two separate species, E.histolytica and E. dispar. The present study represents the first attempt to use a commercial antigen detection kit in addition to routine microscopy so as to estimate the prevalence of E. histolytica among schoolchildren in Dilla province. Some samples that were positive by microscopy were negative when tested by antigen detection; these samples may belong to other classes of other common amoebas. To conclude, these findings show that the diagnostic sensitivity and specificity of microscopic examination to detect E. histolytica in stools is low [15,16].

The prevalence rate in the present study was incongruent with the high prevalence of protozoa infections (42.%) recorded in regions of Mexico by serology [17], and in Cairo, Egypt (38 %) [18], using stool antigen detection. These discrepancies have been attributed to diversified research settings and different participant characteristics. Some types of parasites mainly affect children with specific living conditions [19]. In addition to socioeconomic status, demographic factors (age, gender…) have been associated with distinct patterns of IPI prevalence [11].

This study corroborates the observation that while E. histolytica infection is often more prevalent in male than in female students, the gender difference is generally not significant. Previous studies identified web of risk factors associated with high prevalence of E. histolytica and other parasitic infections. To summarize, drinking water contamination, poor personal hygiene, lack of regular hand washing habits, poor geographical and personal hygiene are strongly associated with E. histolytica infection [11].

Using multivariate analysis, the present study confirmed that mother's occupations, hand washing before eating, hand washing after defecation [13] and awareness of amoebiasis were significantly associated with E. histolytica infection [10,13].

5. Conclusion

E. histolytica infection prevalence in the study setting was high. There is an urgent need for E. histolytica prevention and control through nationwide health development programs that would involve policy-makers, health organs and educational organizations, the common objective being to increase public awareness about IPIs and personal hygiene.

6. Limitation

Due to lack of laboratory facilities using PCR, this study could not determine the prevalence of E. histolytica at a molecular level.

Availability of data and materials

All data generated during the study have been included in the paper. Raw data can be obtained from the corresponding author upon reasonable request.

Ethical approval

The study protocol was approved by Dilla University Ethical Committee (DUEC Ref Du/120/2021). Oral consent had been taken from school directors. Informed consent was obtained from all students recruited in the study. Written informed consent was obtained from the parents. The questionnaires concerning the prevalence of study were recorded during sample collection. Apart from these, students were asked to fill the questionnaire and assist during sample collection.

CRediT authorship contribution statement

Mequanint Abate: Conceptualization, Methodology, Investigation. **Feleke Eriso:** Conceptualization, Methodology, Supervision. **Vikas B. Kalyankar:** Data curation, Writing – original draft. **Nitin D. Padwal:** Data curation, Writing – original draft, Writing – review & editing. **Suresh Chandra Singh:** Data curation, Writing – original draft, Writing – review & editing. **Vijay Upadhye:** Data curation, Writing – original draft, Writing – review & editing. **Atul Shivajirao Humbe:** Writing – review & editing. **Swati Dilip Jadhav:** Writing – review & editing. **Sunil Tulshiram Hajare:** Conceptualization, Methodology, Writing – review & editing.

References

[1] Tanyuksel M, Petri WAJR. Laboratory diagnosis of amebiasis. Clin Microbiol Rev 2003;16(4):713–29.

[2] World Health Organization. Diarrhoeal Disease; 2017. https://www.who.int/news-room/fact-sheets/detail/diarrhoeal-disease (last Verified on 19/04/2022).

[3] Erko B, Birrie H, Tedla S. Amoebiasis in Ethiopia. Trop Geogr Med 1995:47(1):30–2.

[4] Mengistu Legesse BE. Prevalence of intestinal parasite among school children in rural area close to the Southeast of Lake Langano, Ethiopia. *Ethiop J Health Dev* 2004;18(2):116–20.

[5] Beyene A, Hailu T, Faris K, Kloos H. Current state and trends of access to sanitation in Ethiopia and the need to revise indicators to monitor progress in the post-2015 era. BMC Public Health 2015;15:451. https://doi.org/10.1186/s12889-015-1804-4.

[6] Biostatistics DWW. Google Scholar. a Foundation for Analysis in the Health Science. New York: John Wiley & Sons; 1999.

[7] Eriso F. Intestinal parasitic infections in elementary schools children at Dilla town and its peripheral villages. J Infect Endem Dis 2014;4(2):88–95.

[8] Haque R, Mollah NU, Ali IK, et al. Diagnosis of amebic liver abscess and intestinal infection with the TechLab *Entamoeba histolytica* II antigen detection and antibody tests. J Clin Microbiol 2000;38(9):3235–9. https://doi.org/10.1128/JCM.38.9.3235-3239.2000.

[9] Nath J, Ghosh SK, Singha B, Paul J. Molecular epidemiology of amoebiasis: a cross-sectional study among North East Indian population. PLOS Negl Trop Dis 2015;9(12):e0004225.

[10] Mondal D, Minak J, Alam M, et al. Contribution of enteric infection, altered intestinal barrier function, and maternal malnutrition to infant malnutrition in Bangladesh. Clin Infect Dis 2012;54(2):185–92.

[11] Hailegebriel T. Prevalence of intestinal parasitic infections and associated risk factors among students at Dona Berber primary school, Bahir Dar, Ethiopia. BMC Infect Dis 2017;17(1):362. https://doi.org/10.1186/s12879-017-2466-x.

[12] Melesse Birmeka KU, Petros B. Prevalence and determinants of intestinal parasitic infections among primary schoolchildren in Gurage zone, south central Ethiopia. E-Cronicon. Microbiology 2017;8(2):59–70.

[13] Andualem AM. Parasitic infection and associated factors among the primary school children in Motta town, western Amhara, Ethiopia *Am J Public Health Res* 2014;2(6):248–54.

[14] Abossie A, Seid M. Assessment of the prevalence of intestinal parasitosis and associated risk factors among primary school children in Chencha town, Southern Ethiopia. *BMC Public Health* 2014;14:166. https://doi.org/10.1186/1471-2458-14-166.

[illegible] Haque R, Neville LM, Hahn P, Petri WA. Rapid diagnosis of Entamoeba infection by using Entamoeba and Entamoeba histolytica stool antigen detection kits. J Clin Microbiol 1995;33(10):2558–61.

[illegible] Haque R, Petri WA. Diagnosis of amebiasis in Bangladesh. Arch Med Res [illegible]

[illegible] Alvarado-Esquivel C, Hernandez-Tinoco J, Sanchez-Anguiano LF. Seroepidemiology of Entamoeba histolytica infection in general population in rural Durango, Mexico. J Clin Med Res 2015;7(6):435–9.

[18] Abd-Alla MD, Ravdin JI. Diagnosis of amoebic colitis by antigen capture ELISA in patients presenting with acute diarrhoea in Cairo, Egypt. Trop Med Int Health 2002;7(4):365–70.

[19] [illegible] Prevalence of intestinal parasitoses in [illegible] J Pediatr (Rio J) [illegible]

महाराष्ट्रातील कॉंग्रेस पक्षाची सकलजनवादी राजकारणा पासूनची अलिप्तता

डॉ. नितिन हरिदास गायकवाड
राज्यशास्त्र विभाग प्रमुख रामकृष्ण परमहंस महाविदयालय, उस्मानाबाद ४१३५०१

घोषवारा :– महाराष्ट्राच्या राजकारणात यशवंतराव चव्हाण यांनी सकलजनवाद बहुजनवाद या संकल्पना मुळे महाराष्ट्राची एक राजकीय चौकट तयार केले होती. परंतु १९७० नंतर ही राजकीय चौकट कोलमडण्यास सुरुवात झाली मराठा वर्चस्ववादी राजकारणाची सुरुवात झाली यामधुन इतर जाती गटामध्ये असुरक्षितता, राजकीय समावेशाच्या मर्यादा अधिक गुंतागुंतीच्या होत गेल्या याच दशकात शिवसेना, कॉंग्रेस अंतर्गत नेतृत्व स्पर्धा गटांचे यामुळे पर्यायी राजकारण उभे राहु लागले ९०च्या दशकात त्यास अधिक चालना मिळाले त्र्याहत्तर व चौ–याहत्तर घटनादुरुतीने सर्व गटांच्या स्थानिक स्वराज्य संरक्षात नेतृत्वाची संधी मिळाली.

मुख्य शब्द :– यशवंतराव चव्हाण, बहुजन, सकलजनवाद, महाराष्ट्र कॉंग्रेस पक्ष, मराठा, वर्चस्ववाद,

प्रस्तावना :–

महाराष्ट्र हा पुरोगामी राज्य म्हणुन नेहमी ओळखला गेला कारण स्वातंत्र्य पुर्व कालखंडात महाराष्ट्रातील समाजसुधारकांनी समाज सुधारणे साठी व्यापक प्रयत्न केले यामधुनच फुले, आगरकर, रानडे, गोखले, शाहु महाराज, यांच्या समाजसुधारणे मुळे महाराष्ट्रास पुरोगामीत्व मिळाले याच टप्यावर राष्ट्रीय सभेला नेतृत्व व दिशा देण्याची संधी ही काही कालावधी साठी टिळकांच्या स्वरुपाने मिळाली टिळकांनी राष्ट्रावादास अधिक पाठिंबा दिला व राजकीय स्वातंत्र्यास महत्व दिले. शाहु महाराजांनी सत्यशोधक समाजाचे काम पुढे नेले यामधुन राष्ट्रीय सभेच्या नेतृत्वामध्ये अभिजन वर्गाचा सहभाग व सामान्यांचा सहभाग असे गट तयार झाले यामध्येच महाराष्ट्रात १९३० नंतर डॉ. बाबासाहेब आंबेडकरांना मिळालेली दलित वर्गाची साथ तर केशवराव जेधे यांना शेतकरी कुणबी वर्गाची साथ यामुळे स्वातंत्र्य पुर्व कालखंडात विरोषत हा १९३५ च्या कायदयावर झाालेल्या निवडणुकीत कॉंग्रेस पक्षास बहुमत मिळाले असले तरी वर्ग व गट कॉंगेस अंतर्गत तयार झाले होते. स्वातंत्र्यानंतर कॉंग्रेस पक्षांने महाराष्ट्रभर आपल प्रभाव निर्माण केला असे दिसते यमाध्ये यशवंतराव चव्हाण यांच्या नेतृत्वाने महाराष्ट्रात सकलजनवाद बहुजनवादी राजकारणाची चौकट तयार केले. यशवंतराव चव्हाणांच्या नेतृत्वानंतर महाराष्ट्रातील सर्व विभागांना नेतृत्वाची संधी मिळाली परंतु १९७० च्या दशकांनंतर महाराष्ट्राचे राजकरण बदलत गेले यामध्ये विविध घटक कारणीभूत दिसतात याच टप्यामध्ये कॉंग्रेस पक्षा पासून महाराष्ट्रातील जनाधार तुटत गेला कॉंग्रेस पक्षात मराठा संरंजामदार पध्दत सुरु झाली तर ९० च्या दशकात मराठा इतर जात समुहानी आपआपले राजकीय अभिसरणे तयार केली यास मंडळ राजकारण, दिल्लीतील नेतृत्व गटबाजी इ. कारणे दिसतात. प्रस्तुत शोध निबंधात महाराष्ट्रातील कॉंग्रेस पक्षाने उभारलेली सकलजनवादी राजकारणाची चौकट का संपुष्टात आली व कॉंग्रेस पक्षाने या बहुजवादी प्रतिमेपासून का अलिप्तता दाखविली याचा शोध घेण्याचा प्रयत्न केला आहे.

उदिदष्टे :–

१. सकलजनवादी, बहुजनवाद या संकल्पनेचा अभ्यास करणे

२. कॉंग्रेस पक्षानी यशवंतराव चव्हाण यांच्या तयार केलेल्या बहुजनवादी राजकीय चौकटीपासून अलिप्त धोरण का स्विकारले. याचा अभ्यास करणे.

सकलजनवादाची संकल्पना :–

महाराष्ट्राच्या राजकारणात यशवंतराव चव्हाण यांचे राजकारण व समाज जोडणी ही या सकल जनवादावर आधारलेली आहे जयतलेले यांनी यशवंतराव चव्हाणांची जी मुलाखत घेतली त्यामध्ये सकलवादी विचार दिसुन येतो सकल याचा अर्थ व्यापक सर्वाचा समावेश असणे किंवा

सर्वसमावेशकता तसेच सांस्कृतिक व सामाजिक ऐक्यासाठी सकलजन ही सकल्पना वापरली जाते यामधुन राजकारणास जी सामान्य मराठी माणसाची अधिमान्यता यशवंतराव चव्हाण यांच्या नेतृत्वातील कॉंग्रेस पक्षास मिळत गेली राजकिय आघाडी व्यक्ती स्वातंत्र्य आर्थिक विकास उत्पादन साधनांचे वितरण सेवांचे वितरण या मुदया भोवती लोकशही तत्वावर यशवंतराव चव्हाण यांचा सकलजवादाचे राजकारण उभे केले त्यास लोकप्रिय अर्थाने बहुजन राजकारण म्हणतात (पवार प्रकाश : २०१६) केवळ संख्यात्मक दृष्टीने बहुजन या संकल्पनेचा अर्थ संकुचित तयार होतो सर्वसमाज बांधणी ही यशवंतराव चव्हाण यांनी बहुजन याच सकल्पनेतुन केली आहे.

बहुजन या शब्दात महाराष्ट्रातील सर्व जाती गटाचा सहभाग आहे अगदी उच्च जाती मराण मराठा इतर समुहामध्ये ऐक्य सलेखा यामुळे तयार झाल होता. यशवंतराच चव्हाण यांनी उच्च जाती, मराठा, नवबौध्द, ओबीसी इ. समुहांचे राजकीय समावेशन घडवुन आण ले यामध्ये शहरी . ग्रामीण . मराठी व्यापरी, उदयोजक अशा विविधा टप्यामधुन सकलजनांच्या राजकारणाची उभारणी केले व यामधुन सकलजनांच्या राजकारणाची उभारणी केले व यामधुन एक राजकीय समाज तयार करेन (पवार प्रकाश : २०१६) केशवराव जेथे व गाडगीळ यांनी यशवंतराव चव्हाण यांच्या अधीच्या राजकारणात ब्राम्हण ब्राम्हणेत्तर दुफळी न तयार करता कृषक समाज . समाजवादी विकास याची पाठराखन केले होती यशवंतराव चव्हाण यांनी महाराष्ट्राच्या राजकारण या दुफळीचे उत्तर सकलजनवाद यामधुन दिले व महाराष्ट्र उभारणीमध्ये सर्व समुह एकत्रित केले. यशवंतराव चव्हाण यांचे नेतृत्व होते. तो पर्यंत महाराष्ट्राचे मुख्यमंत्रीपद विदर्भ, मराठवाडा, तसेच मराठात्तर व्यक्तीस मिळाले होते. त्यांच्या मंत्रिमंडामधील सर्व जाती समुहांना प्रतिनिधीत्व मिळत होते. परंतु १९७० नंतर महाराष्ट्रातील सकलजनावर संपुष्टात येऊन मराठा घराणी तयार झाले (पवार प्रकाश २०१६ : ६५—६७) या घराण्यामुळे महाराष्ट्राच्या राजकारणात दलित, ओबीसी समुह दुर्लक्षीत होत राहिल व कॉंग्रेस पासुन अंतर राखण्यासाची सुरुवात होत गेली.

यशवंतराव चव्हाण यांच्या बहुजन संकल्पातेली नैसर्गिक साधनांचे वितरण, लोकशाही मुख्य, शेती, उदयोग, न्याय क्षेत्रातील समझोता संपुष्टात आल सहकार चळवळीने महाराष्ट्राची आर्थिक प्रगती दिसत होती परंतु साधन संपत्तीचे वितरण असुनही सर्व समावेशक ग्रामीण घटकापर्यंत पोहचले नव्हते. सरकार हा खाजगी क्षेत्राकडे वळण्यास सुरुवात झाली यामुळे सामान्य माणसाचा राजकारणावरील विश्वास कमी झाल अधिमान्यता जी यशवंतराव चव्हाण यांनी बहुजन यामधुन तयार केले होती ती संपुष्टात आली अधिमान्यता मिळवण्यासाठी पर्यायी साधने वर्चस्व शक्ती आले त्यामुळे १९९०नंतर कॉंग्रेसचा जनाधार कमी होत गेलं.

राजकारणातील संस्थात्मक अधार नष्ट झाला :—

महाराष्ट्राच्या राजकारणास संस्थात्मक आधार होता तो सहाजिकच १९६० नंतर तयार झालेल्य स्थानिक स्वराज्य संस्था चा यामध्ये यशवंतराव चव्हाण यांच्या बहुजनवादी संकल्पनाने कॉंग्रेस पक्षाचा पाया विस्तारण सर्व समावेशक राजकीय सहभागास संधी मिळाली महाराष्ट्रातील सर्व जाती गट समुह यामध्ये सहभागी झाले व सतेचे सहभागी झाले सतेचे विकेंद्रीकरण घडुन आले. यामध्ये शेतकरी कामगार पक्ष समाजवादी पक्ष हे ग्रामीण भागात पोहचते नव्ते या मधुन ग्रामीण भागात कॉंग्रेस पक्षास व्यापक संस्थात्मक राजकारणाच्या साधन बनल्या या सर्वांना कर्ज पुरवठा करणारी जिल्हा. मध्यवर्ती बॅक ही महत्वाची केद्र बनले यामधुनही कॉंग्रेस पक्षाचा जनाधार मजबुत होता परंतु सत्तरच्या दशकानंतर कॉंग्रेस मधील अंतर्गत राजकारण, स्पर्धात्मक, सहकारातील दोष यामुळे संस्थात्मक अधार असुनही कॉंग्रेस पक्ष जनाधार टिकवून ठेवण्यास असमर्थ ठरला

सामाजिक स्थित्यंतर :— पक्षीय स्पर्धात्मक राजकारणात विविध समाजघटक महत्वाचे असतात त्यांचे परस्पर संबंध तयार झाले होते. त्यामध्ये सत्तरच्या दशकानंतर बदल होत गेले १९७०पुर्वी महाराष्ट्राच्या राजकारणाची सुत्रे बहुतअंश पध्दतीने मराठा नेतृत्वाकडे होती बिगर मराठा जातीचा कॉंग्रेसत्व मोठया प्रमाणावर पाठिंबा होता. ही समिकरणे १९९० च्या दशकात फिसकटत गेले. ;पळशीकर १९९६ : १७६ — १७८) सर्व समाज घटकांना चव्हाण यांच्या सकलजनवादी भुमीकेने समावुन घेतले होते परंतु नंतरच्या नेतृत्वाने राजकीय समावेशन थांबवले शिवसेना, भाजप यामुळे इतर समुहांना प्रथमच पर्याय उपलब्ध झाला महाराष्ट्राच्या सामाजिक रचनेत अन्य मागास

ओबीसी ब्राम्हणेत्तर जाती संख्येने छोटया आहेत. तरीही शेती व्यवसायात असणा—या काही ओबीसी जातीसमुहातील गटांनी स्वतंत्र राजकारण उभारले कॉंग्रेस व राष्ट्रवादी कॉंग्रेस पक्षातील मराठा धर्मिक नेतृत्वामुळे ओबीसी समुह शिवसेना, भाजपा या राजकीय पक्षांकडे आकर्षित झाला. त्र्याहत्तर व चौ—याहतराव्या घटनादुरुस्तानी स्थानिक शासनात सहभागाची संधी मिळण्यास सुरुवात झाल्यामुळे या वर्गाच्या राजकीय महत्वकांक्षा वाढीस लागल्या व मराठा नेतृत्वासमोर प्रश्न, तसेच सर्वसमावेश धोरणा संबंधी आग्रह धरला तरीही वर्चस्ववादी राजकारणामुळे ओबीसी, दलित, बहुजन, समुह १९९० च्या दशकानंतर पर्यायी राजकारण उभे करु पाहत आहेत.

आर्थिक धोरणातील बदल व स्पर्धात्मकता :— ९० च्या दशकात नव आर्थिक धोरण स्विकारले त्यामुळे २०१०पर्यंत महाराष्ट्रातही नव मध्यवर्ग सक्षम पध्दतीने उभा राहिला सहकार चळवळीचे रुपांतर खाजगी व्यवसायामध्ये झाले. यामुळे या मध्यवर्गास आर्थिक शक्तीचे महत्व नव्याने समुजुन आले जुना शोषीत आश्रीत ओळख पुसुन नवीन राजकीय सत्तेवरील नियंत्रण स्थापन करण्याची महत्वकांक्षा सर्व वर्ग गटात तयार झाली यामुळे महाराष्ट्रातही सामाजिक अभियांत्रीकीचे प्रयोग निर्माण झाले सामाजिक प्रश्नांची योग्य मांडणी, सर्वसमावेश धोरण या आधारावर महाराष्ट्राचे सत्ताकारण उभारले जात आहे असे दिसते.

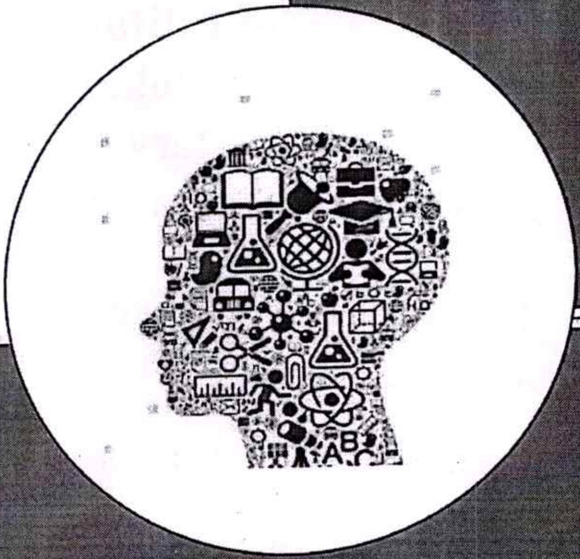
समारोप :— महाराष्ट्राच्या राजकारणात यशवंतराव चव्हाण यांनी सकलजनवाद, बहुजनवाद या संकल्पना मुळे महाराष्ट्राची एक राजकीय चौकट तयार केले होती. या चौकटीमध्ये महाराष्ट्राच्या सर्व विभागांना नेतृत्वाची संधी मिळाले तसेच दलित ओबीसी ब्राम्हण मराठा या सर्व जाती गटांना प्रतिनिधीत्व ही मिळत होते. परंतु १९७० नंतर ही राजकीय चौकट कोलमडण्यास सुरुवात झाले मराठा वर्चस्ववादी राजकारणाची सुरुवात झाले यामधुन इतर जाती गटामध्ये असुरक्षितता, राजकारणातील सहभागाच्या मर्यादा अधिक होत गेल्या याच दशकात शिवसेना, कॉंग्रेस अंतर्गत नेतृत्व स्पर्धा गटांचे यामुळे पर्यायी राजकारण उभे राहु लागले ९०च्या दशकात त्यास अधिक चालना मिळाले त्र्याहत्तर व चौ—याहत्तर घटनादुरुतीने सर्व गटांच्या स्थानिक स्वराज्य संरक्षात नेतृत्वाची संधी मिळाली व राजकीय महत्वकांक्षा वाढीस लागल्या या मधुनच सामाजिक अभियांत्रिकी तयार झाली बहुजन जाती गट ज्या राजकीय पक्षाकडे जनाधार देईल त्या पक्षाचा महाराष्ट्र विधानसभेमध्ये सत्ता स्थापनेच्या दाव्यास बळ मिळताना दिसते आहे थोडक्यात कॉंग्रेस पक्षाने यशवंतराव चव्हाण यांच्या बहुजन संकल्पनेपासुन अलिप्त झाल्यामुळे दलित ओबीसी या जाती गटाचा विश्वास संपुष्टात आल यामधुनच जनाधार हळूहळू कमी होताना दिसतो आहे.

संदर्भ :—

१ पवार प्रकाश, २०१६, कॉंग्रेसपुढील आव्हाने आणि भाजपचा उदय डायमंड पब्लिकेशन्स, पुणे.
२ पळशीकर सुहास, १९९८, जात व महाराष्ट्रातील सत्ताकारण, सुगावा प्रकाशन पुणे,
३ फडके य. दि., १९८२, राजकारणाचे बदल ते रंगरुप.
४ पळशीकस सुहास, १९९६, महाराष्ट्रातील सत्तांतर, ग्रंथाली प्रकाशन, मुंबई.
५. गायकवाड नितीन, २०२१, नवआर्थिक धोरणानंतर भारतीय राजकारणातील बदल, एज्युकेशन पब्लिशर औरंगाबाद.
५. भोळे, बेडकिहाळ, २००३, बदलता महाराष्ट्र, डॉ. बाबासाहेब आंबेडकर अकादमी, सातारा.

ISSN No 2347-7075
Impact Factor- 7.328
Volume-3 Issue-1

INTERNATIONAL JOURNAL of ADVANCE and APPLIED RESEARCH



Publisher: P. R. Talekar
Secretary,
Young Researcher Association
Kolhapur(M.S), India

Young Researcher Association

International Journal of Advance and Applied Research (IJAAR)
Peer Reviewed Bi-Monthly

ISSN – 2347-7075
Impact Factor –7.328
Vol.3 Issue-1 Sept-Oct- 2022

International journal of advance and applied research (IJAAR)

A Multidisciplinary International Level Referred and Peer Reviewed Journal

Volume-3 *Issue-1*

Chief Editor

P. R. Talekar
Secretary,
Young Researcher Association, Kolhapur(M.S), India

Editorial & Advisory Board

Published by: Young Researcher Association, Kolhapur, Maharashtra, India

International Journal of Advance
and Applied Research (IJAAR)
Peer Reviewed Bi-Monthly

ISSN – 2347-7075
Impact Factor –7.328
Vol.3 Issue-1 Sept-Oct-2022

CONTENTS

International Journal of Advance and Applied Research
www.ijaar.co.in
ISSN – 2347-7075
Peer Reviewed
Vol.3 No.1
Impact Factor – 7.328
Bi-Monthly
Sept – Oct 2022

PERFORMANCE EVALUATION OF PMFBY IN MAHARASHTRA STATE

Dr. N. B. Kale[1] Asst. Prof. B. K. Nagare[2]
[1]HOD, Dept. of Commerce, Tuljabhani Mahavidylaya, Tuljapur
[2]HOD, Dept. of Commerce, R. P. College, Osmanabad
Email: balajinagare@gmail.com
Corresponding Author- **Dr. N. B. Kale**
Email id: balajinagare@gmail.com

DOI- 10.5281/zenodo.7267018

Introduction:

`Maharashtra is a 15th rank India in agricultural output. In 2019, agriculture and allied sectors like forestry, logging and fishing represented 13.12% of the GDP. Maharashtra took 3rd rank in population as a compare to other states. At the time of independence, more than one-half of the national income was contributed by agricultural. At the same time, more than 70% of total population was depended on agriculture. The agriculture secures faces the lot of challenges due to uncertainties in agriculture i.e. natural and artificial hazards especially Maharashtra state. Still, more people in India make money for their livelihood from this sector, than from all other economic sectors. In rural India, households that depend upon income from agriculture (either self-employed or as agricultural workforce) accounted from nearly 70% of the population. According to the World Bank collection of development indicator, employment in agriculture in India was reported 41. 49 percent in 2020. All this facts & figures show that, the need for the development of agricultural sector in India. Maharashtra has reached the stage of self-sufficiency but it is still cursed by nature. This poses a great risk to state farmers in agricultural production and on their way. It has been observed that fluctuations in crop production in the Indian also in Maharashtra subcontinent are mainly due to natural uncertainties such as droughts, floods, cyclones, storms, landslides, earthquakes etc. The government of India was introduced crop Insurance scheme to face these challenges.

Pradhan Mantri Fasal Bima Yojana (PMFBY) is the one of the largest crop insurance scheme, which was introduced in Feb. 2016. In this study, main focused on performance of PMFBY in Maharashtra state from last five years.

Objectives of the study

The objectives of concern study are as follows.

1. To study about crop insurance schemes in Maharashtra
2. To measure the performance of crop insurance scheme in Maharashtra
3. To analyzed the farmers participation, area insured and gross premium of crop insurance scheme
4. To suggest to upgrade the performance of crop insurance scheme in Maharashtra

Research methodology

Data Collection: This is an analytical study; hence, Secondary data is an impetrate and powerful tool for the research. Researcher as complete research work is carried out on the basis of secondary data. The secondary data is collected through newspapers, magazine, government reports and internet. For accomplishing the objectives of the study, three years data is collected and analyzed it.

Research area: The present study deals with the Performance evaluation of PMFBY. For justify the subject & detailed study proposes, PMFBY are selected in Maharashtra.

Limitations of the study: In this study, only PMFBY was selected and only five years performance was measured of the agriculture insurance scheme. Other crop insurance schemes are not taken into account.

Pradhan Mantri Fasal Bima Yojana (PMFBY)

Pradhan Mantri Fasal Bima Yojana (PMFBY) is one of the world's largest and important crop insurance programs. It's aimed to providing risk cover to Indian farmers. It was launched in early 2016 with the key feature being a highly subsidized and affordable premium to farmers. Under the scheme, only 2% premium of maximum to pay farmers during Kharif sowing, 1.5% during Rabi sowing for food and oilseed crops, whereas for annual commercial crops they have to pay a maximum of 5%. As a same, the Government of India and state government shared equally pay the subsidy on farmer's premium of actuarial premium rate. The National Agricultural Insurance Scheme (NAIS) as well as the modified NAIS has combined into PMFBY.

Performance evaluation of PMFBY in Maharashtra

The performance of crop insurance scheme especially PMFBY measured with the help of indicates. From last five years, performance was evaluated from 2018 to 2022. It includes farmer's participation, Area insured, Premium paid and Sum insured by farmers as well as government subsidy.

Farmer's participation:

From Kharif 2018-2022 and Rabi 2018-2021, total of 2.59 crore farmer applications have been approved under the scheme of PMFBY. In the Kharif Season 2018 to 2022, total of 2.56 crore and in Rabi season 42.86 lac farmers were participated from last five years. During 2018 to 2022, the participation of farmers was increased by 2.06 per cent only. Also, as a compare 2019 to 2018, farmer's participation was decline by -22.91 per cent, in the year 2019 to 2020, farmer's participation was decline by -10.17 per cent. The number of insured farmers has declined in a last five years regularly. Table no 01 shows the detailed performance in farmer's participation under PMFBY in Maharashtra from 2018 to 2022.

Table No 01: Performance indicators in Farmers participation in PMFBY from 2018 to 2022

Year	Farmers coved in Kharif Season	Farmers coved in Rabi Season	Total	% Increase/ decries
2018	4593623	2401852	6995475	
2019	4736089	656565	5392654	-22.91
2020	4277749	566532	4844281	-10.17
2021	3607307	661615	4268922	-11.89
2022	4356649	-	4356649	2.06
Total	21571417	4286564	25857981	-42.91

Source: PMFBY Report 2018 to 2022

Area covered:

The total area insured in kharif and Rabi taken together has 34411.22 thousand hectors from 2018 to 2022. The area under PMFBY has decline by 39.85 per cent from 2018 to 2022.

As a compared to Rabi season, in Kharif season 2018 to 2022, the area covered under PMFBY has more. Following table 02 indicates the performance in Area Covered in PMFBY in Maharashtra state from 2018 to 2022.

Table No 02: Performance indicators in Area covered in PMFBY from 2018 to 2022

Year	Area covered in Kharif Season (Thousand Hect.)	Area covered in Rabi Season (Thousand Hect.)	Total	% Increase/ decries
2018	5675.5	3177.38	8852.88	
2019	6748.29	805.17	7553.46	-14.68

2020	5784.23	735.88	6520.11	-13.68
2021	4875.38	845.84	5721.22	-12.25
2022	5763.55		5763.55	0.74
Total	28846.95	5564.27	34411.22	-39.87

Source: PMFBY Report 2018 to 2022

Premium and Government Subsidy:

The premium paid by the farmers from 2018 to 2022 had 271494.43 lac and state and central government had paid 375848.25 lac in that period. The gross premium has increased from year to year. During 2018 to 2020 but after 2020 the gross premium has decline During 2018 to 2022, the state and central government commonly paid the subsidy under these schemes. The subsidy paid by the state and central government on PMFBY had 88.06 per cent, 87.18 per cent, 90.21 per cent, 90.21 per cent and 85.14 per cent in the year 2018 to 2022 respectively. The following table 03 shows the performance in Premium and Govt. subsidy in PMFBY in Maharashtra state from 2018 to 2022.

Table No 03: Performance indicators in Premium and Govt. subsidy in PMFBY from 2018 to 2020

Year	State/Central Govt. Subsidy (in Lac.)	Farmers Premium (in Lac.)	Gross Premium (In Lac.)	Subsidy Paid In percent by Govt.
2018	371228.22	50357.99	421586.21	88.06
2019	395192.18	58103.16	453295.34	87.18
2020	490201.68	53226.08	543427.76	90.21
2021	407158.99	44203.38	451362.37	90.21
2022	375848.25	65603.82	441452.07	85.14
Total	**2039629.32**	**271494.43**	**2311123.75**	**88.25**

Source: PMFBY Report 2018 to 2020

Sum Insured:

As compared to 2018, the total sum insured all over the Maharshtra has decline from Rs 2769711.03 lac to Rs 2537512.06 lac in 2019, a decline of about -8.38 per cent. Similarly, it has decline during 2019 to 2020, 2020 to 2021 but it was increased in 2021 to 2022 up to 27.06 per cent. The total value of sum insured under PMFBY in Maharashtra was Rs. 12751100.28 lac, a increased average rate has 4.71 per cent during 2018 to 2022. Table no. 03 indicates the performance of PMFBY in Sum Insured.

Table No 03: Performance indicators in Sum Insured in PMFBY from 2018 to 2022

Year	Sum Insured in Kharif Season	Sum Insured in Rabi Season	Total	% Increase /Decries
2018	1980272.67	789438.36	2769711.03	
2019	2314747.44	222764.62	2537512.06	-8.38
2020	2217942.99	251619.1	2469562.09	-2.68
2021	1895414.99	295314.51	2190729.5	-11.29
2022	2783585.6	-	2783585.6	27.06
Total	**11191963.69**	**1559136.59**	**12751100.28**	4.71

Source: PMFBY Report 2018 to 2022

Conclusion:

As per the performance evaluate of PMFBY during 2018 to 2021 in Maharashtra state, it is clearly indicates that, the number of farmers participation, area covered under PMFBY and sum insured had decline from last four year but in 2021-2022 was increased. Apart from Premium and government subsidy had increased. There is need to motivate the farmers towards crop insurance scheme. It is possible when the ground level motivation camp will be organized to door to door in every village.

Bibliography

1. Ashok Gulati, (Feb. 2018), Crop Insurance in India: Key Issues and Way Forward, Working paper NO. 352
2. Singh, G. (2010), "Crop Insurance in India", IIM Ahmedabad, Working Paper. No. 2010-06- 01
3. Ministry of Agriculture & farmers welfare Govt. of India; PMFBY Progress and achievement 2016 to 2021 report
4. https://pmfby.gov.in/adminStatistics/dashboard
5. https://pmfby.gov.in/pdf/New%20Schemes-english_.pdf
6. https://pmfby.gov.in/ext/rpt/ssfr_17
7. Hazell, P., Pomareda, C., and Valdes, A. (1986), "Crop Insurance for Agricultural Development", John Hopkins University Press, Baltimore, USA Harms, S.C, "History of Crop Insurance in the United States", Retrieved from

Impact Factor-8.575 (SJIF) ISSN-2278-9308

B.Aadhar

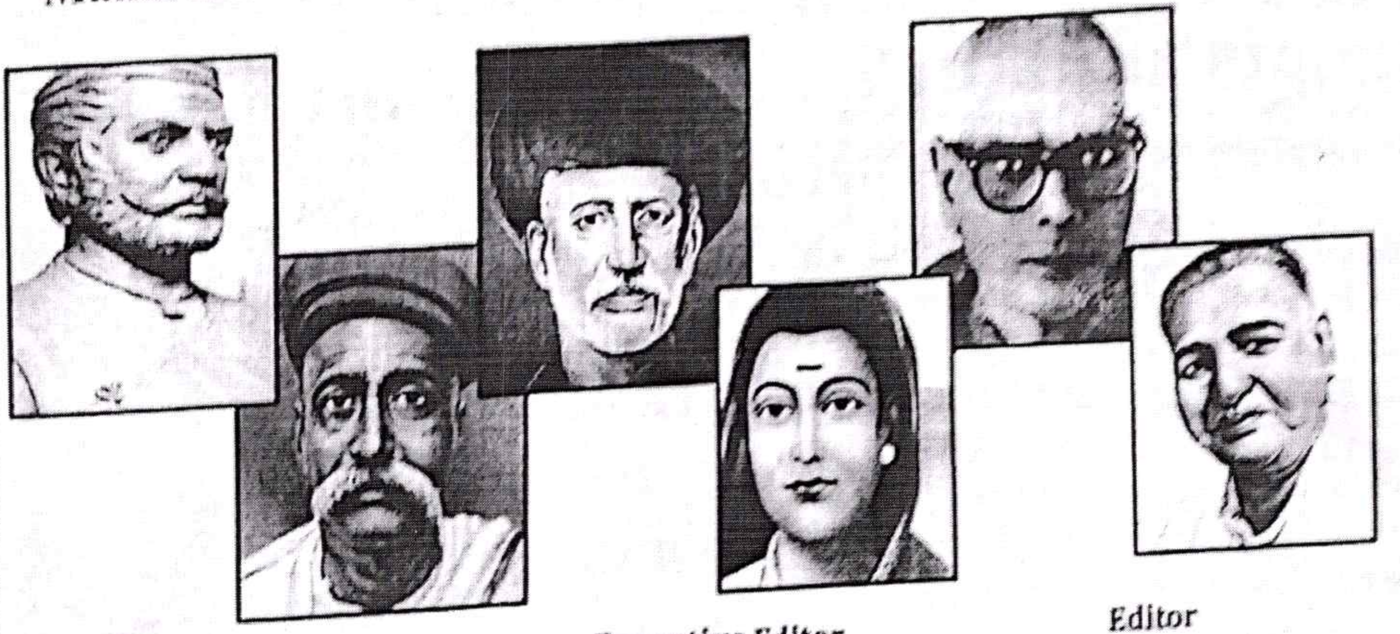
Peer-Reviewed & Refreed Indexed

Multidisciplinary International Research Journal

October-2022

(CCCLXXII) 372

Maharashtra's Contribution to the Indian Freedom Struggle



Chief Editor
Prof. Virag S. Gawande
Director
Aadhar Social
Research & Development
Training Institute Amravati

Executive Editor
Dr. M.N. Kolpuke
Principal
Maharashtra Mahavidyalaya,
Nilanga Dist. Latur

Editor
Dr. Subhash G. Benjalwar
Head, Department of History,
Maharashtra Mahavidyalaya,
Nilanga Dist. Latur

This Journal is indexed in :

- Scientific Journal Impact Factor (SJIF)
- Cosmos Impact Factor (CIF)
- International Impact Factor Services (IIFS)

Aadhar International Publication

For Details Visit To : www.aadharsocial.com

स्वातंत्र्य सेनानी पद्मावतीबाई हरोलीकर यांचे भारतीय स्वातंत्र्य लढ्यातील योगदान

प्रा.डॉ. विकास मोहन सरनाईक
इतिहास विभाग,रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद. ,मेल- sarnaik.viki@gmail.com

भारतामध्ये प्राचीन काळापासुन समाजाच्या सर्व क्षेत्रात स्त्रियांना दुय्यम स्थान होते. या दुय्यमत्वाच्या परंपरेला ब्रिटीश राजवटीबरोबर आलेल्या आधुनिक विचारांनी आव्हान दिले. त्यातून स्त्रियांच्या बंधमुक्तीच्या लढ्याला सुरुवात झाली. परिणामत: स्त्रियांना पुरुषांच्या बरोबरीने हक्क व अधिकार मिळण्यास सुरुवात झाली. स्त्रिया या कोणत्याही समाजाचा अर्धा भाग किंबहुना अर्धी ताकद असतात. कोणत्याही समाजाच्या ताकदीचा पूर्ण वापर केल्याशिवाय सामाजिक, आर्थिक व राजकीय बदल शक्य नसतात. या जाणिवेतूनच भारतामध्ये ब्रिटिश राजवटीत स्त्रीहक्काचा लढा सुरु झाला. भारताच्या स्वातंत्र्य लढ्याच्या पहिल्या दोन टप्प्यात म्हणजेच मवाळ व जहाल युगात स्त्रियांचा स्वातंत्र्य लढ्यातील सहभाग मर्यादित होता. इ.स.१९२० नंतर भारतीय स्वातंत्र्यचळवळीच्या पटलावरती महात्मा गांधीचा उदय झाला. त्यांनी शेतकरी, कामगार, महिला या समाजघटकात जागृती निर्माण करुन त्यांना स्वातंत्र्यलढ्यात सहभागी करुन घेतले.[1]

इ.स. १९३० च्या सविनय कायदेभंग चळवळीच्या दरम्यान त्यांनी महिलांना आवाहन केले की, "स्त्रियांना अबला म्हणणे ही त्यांची बदनामी असुन तो पुरुष जातीने त्यांच्यावर केलेला अन्याय आहे." गांधीजींच्या या आवाहनामुळे घराबाहेर न जाणाऱ्या स्त्रिया, बुरखा वापरणाऱ्या स्त्रिया, विधवा, अविवाहित मुली अशा सवळ्यास सर्वजणी चळवळीत सामिल झाल्या.[2]निदर्शने व मोर्चे काढुन तुरुंगवास ही सहन करु लागल्या. कित्येक महिलांनी आपले संपुर्ण आयुष्य देशसेवेसाठी अर्पण केले. यातील मॅडम कामा, पंडिता रमाबाई, सरोजनी नायडु अशा प्रसिद्ध व उच्च शिक्षित स्त्रियांची दखल इतिहासकारांनी घेतली. मात्र देशसेवेसाठी आपले आयुष्य खर्ची घातलेल्या सर्व सामान्य स्त्रियांची नोंद इतिहासाने घेतली नाही. म्हणूनच पदमावतीबाई हरोलीकर या दुर्लक्षित स्वातंत्र्य सेनानीच्या कार्याचा थोडक्यात आढावा घेण्याचा प्रयत्न प्रस्तुत लेखात केला आहे.

पूर्वायुष्य:

रमा उर्फ पद्मावती यांचा जन्म ब्राह्मण कुटुंबात इ.स.१८९२ मध्ये मुंबई येथे झाला. त्यांच्या वडिलांचे नाव त्रिंबक काशिनाथ चित्रे असे होते, ते टिळक भक्त होते. त्यामुळे देशप्रेमाचे बाळकडू त्यांना वडिलांकडून मिळाले होते. तत्कालीन रुढीप्रमाणे त्यांचा बालविवाह पुण्यातील कुवळेकर कुटुंबात झाला. त्यानंतर त्या सत्यभामा कुवळेकर या नावाने ओळखल्या जाऊ लागल्या. दुर्दैवाने वयाच्या १४ व्या वर्षीच त्या विधवा झाल्या. विधवेचे जीवन जगण्यापेक्षा तिने शिक्षण घ्यावे असे त्यांच्या सासऱ्यांचा आग्रह होता. त्यामुळे रमा उर्फ सत्यभामा पुण्याला रमाबाई रानडे यांनी स्थापन केलेल्या 'सेवा-सदनात' या शाळेत जाऊ लागल्या.[3]

स्वातंत्र्य लढ्यातील योगदान :

इ.स.१९२० मध्ये त्या ५वीच्या वर्गात शिकत असताना किर्लोस्कर नाट्यगृह पुणे येथे महात्मा गांधींची सभा होती. त्या सभेला ज्या मोजक्या १०-१५ स्त्रिया हजर होत्या. त्यामध्ये सत्यभामाबाईचा समावेश होता. सभेतील स्त्रियांना उद्देशून महात्माजी म्हणाले, 'भगिनींनो आपण देशाची अर्धी शक्ती आहात. स्वातंत्र्याच्या चळवळीतही तुमचा अर्धा हिस्सा असला पाहिजे. खरे सौंदर्य हे उत्तम प्रकृती, चेहऱ्यावर व डोळ्यात निर्भयता, चारित्र्यसंपन्नता यात असते. दागिन्यांनी नटूनसजून सौंदर्यशालिनी होता येत नाही. शालिनतेबरोबरच कणखरही बनणे आवश्यक आहे. गांधीजींच्या या विचारांचा सत्यभामाबाई कुवळेकर यांच्यावर खूप प्रभाव पडला. त्यातून व सासऱ्यांच्या आग्रहामुळे सत्यभामेबाईनी आपले बगुड्या, अंगठी, कुडी, माळ हे दागिने उतरवून ते सर्व स्वातंत्र्य लढ्यासाठी गांधीजींच्या हातात ठेवले. गांधीजींना पदस्पर्श करुन ती म्हणाली, 'आज मी माझे स्त्रीधन आपल्या स्वाधीन केले आहे व 'आजन्म सोने वापरणार नाही' अशी शपथ घेतली. त्यानंतर मंगळसुत्रातील सोन्याच्या दोन वाट्या सोडून

त्यांनी कधीही सोने वापरले नाही. गांधीजींच्या प्रभावातून सत्यभामेने कॉंग्रेसच्या चळवळीला स्वातंत्र्य मिळेपर्यंत वाहून घेण्याचे ठरविले व ते पाळलेही.

इ.स.१९२०च्या चळवळीत सत्यभामाबाईंनी आर्थिक स्वावलंबित्वासाठी 'सुतकमिटी' स्थापन केली व या माध्यमातुन स्वतः बरोबरच समाजातील इतर गरजु महिलांना रोजगार मिळवून दिला .हे काम करीत असतानाच त्यांचामुद्रक व प्रकाशक व्यंकटराव हरोलीकरांशी संपर्क आला. व्यंकटराव हे देशभक्त शंकरराव देव यांनी पुण्यात 'स्वराज्य' नावाचे वर्तमानपत्र सुरू केले होते. त्याचे मुद्रक व प्रकाशक होते. ५मे, १९२७ च्या स्वराज्यच्या अंकात 'क्रांतीखेरीज स्वराज्य नाही' असा अग्रलेख संपादक देव यांनी लिहिला होता. सोलापूर व तळेगाव येथे गणपती विसर्जनाच्या निमित्ताने जातीय दंगली झाल्या. त्या विषयाला धरून १५सप्टेंबर, १९२७ च्या अंकात 'निदान धर्मयुद्ध करा' असा लेख प्रसिद्ध झाला. त्यामुळे भारतीय दंड संहितेच्या १२१व १२४ह्या कलामान्वये राजद्रोह व खुनाला चिथावणी दिली म्हणून शंकरराव व व्यंकटराव हरोलीकर ह्या संपादक व प्रकाशकांना दोन वर्षांची सक्तमजुरीची शिक्षा झाली. व्यंकटराव हरोलीकरांना महारोगाची बाधा झाल्याने शिक्षा पूर्ण होण्यापूर्वीच त्यांना तुरुंगातून सोडून दिले. त्यानंतर ते पुण्याला एका वाड्यात राहात. व्यंकटराव सुटले व आजारी आहेत हे समजल्यामुळे कार्यकर्ते त्यांच्या भेटीला जात. सत्यभामाबाई कुवळेकरही त्यांना भेटायला गेल्यानंतर त्यांना दिसले की, त्यांच्याजवळ कोणी जात नसे. ते आपल्या जखमा स्वताच स्वच्छ करत होते. त्यांचे जेवण, कपडे भांडी ते स्वतःच करतात, हे पाहून दुसऱ्या दिवशी सकाळीच त्या व्यंकटरावांच्या घरी गेल्या. त्यांचे कपडे धुतले, भांडी घासून स्वयंपाक केला व जखमा धुवून मलमपट्टीही केली सततच्या संपर्कामुळे यांच्याकडे पाहण्याचा समाजाचा दृष्टिकोन नकारात्मक होवु नये म्हणुन पदमावतीबाईंनी व्यंकटेश यांच्याशी विवाह केला. त्यांनी चळवळीचे व समाजउद्धाराचे कार्य पुढे निरंतर सुरू ठेवले.त्यांच्या या कार्यास पती व्यंकटेश यांची साथ मिळाली. कारण ते स्वताही चळवळीचे धडाडीचे कार्यकर्ते होते.

पदमावतीबाईच्या स्वातंत्र्यलढ्यातील कार्याची दखल म्हणुन इ.स.१९२१-२२ मध्ये महाराष्ट्र प्रांतिक कमिटीचे सदस्यत्व देण्यात आले. तर अखिल भारतीय कॉंग्रेस कार्यकारिणीवरही त्या इ.स.१९३२साली निवडून गेल्या होत्या.त्यांना अखिल भारतीय कॉंग्रेस कमिटीचे सदस्यत्व देण्यात आले. इ.स.१९३० मध्ये सविनय कायदेभंग चळवळीत त्यांनी 'संपूर्ण स्वातंत्र्याचा ठराव' वाचून कायदेभंग केला. त्याबद्दल त्यांना दोन वर्षांची सक्तमजुरीची शिक्षा झाली. शिक्षा संपल्यानंतर गांधी विचारानुसार त्यांनी खेडयाकडेजावुन ग्रामीण समाजाच्या उद्धाराचे कार्य आरंभीले. या कार्यासाठीत्यांनी सोलापुर जिल्हयातील सांगोला तालुक्यातील एकतपुर,मंगेवाडी इत्यादी खेडी निवडली व येथील विकास करण्यासाठी त्यांनी त्या भागात 'राष्ट्रीय युवती संघ' स्थापन केला.

इ.स.१९३७ मध्ये हिंदुस्थानात प्रांतिक स्वायत्ततेच्या कायद्यानुसार निवडणुका होऊन अकरापैकी नऊ प्रातांत कॉंग्रेस सत्तेवर आली. कॉंग्रेस कार्यकर्त्यांनी ह्या निवडणुकीसाठी पद्मावतीबाईंना स्त्रियांसाठी राखीव असलेल्या मतदारसंघात उमेदवारी द्यावी म्हणून सूचना केली. दुर्दैवाने निष्ठावान देशभक्त व गांधींच्या विचारांनी प्रभावित कार्यकर्तीला प्रदेश कॉंग्रेस नेते व अखिल भारतीय कॉंग्रेस समितीनेही उमेदवारी नाकारली. यामुळे सर्वांना आश्चर्य वाटले व धक्का बसला. व्यंकटेशरावांना तर हा पद्मावतीबाईंच्या कामाचा अपमान वाटला. अशातच इ.स.१९३९ साली आजारपण बळावल्याने व्यंकटरावांचा मृत्यू झाला. पतीची साथ गमावल्यावरही सत्यभामाबाई निराश झाल्या नाहीत. त्यांनी गांधींच्या विचाराने देशसेवेचे कार्य निरंतर सुरूच ठेवले. त्यांच्या या कार्याची दखल घेवुनच इ.स.१९४० च्या वैयक्तिक सत्याग्रहामध्ये महाराष्ट्रातुन त्यांची निवड झाली व त्या 'महाराष्ट्रातील पहिल्या महिला वैयक्तिक सत्याग्रही ठरल्या'. या चळवळीत त्यांना तीन महिने तुरूंगवास सहन करावा लागला .त्यांच्या याकार्यामुळेचइ.स.१९४२च्या लढ्यामध्ये स्थानिकांना प्रोत्साहीत करू नये म्हणुन सरकारने त्यांना चलेजाव आंदोलनात भाग घेण्यापूर्वीच स्थानबद्ध केले व आंदोलन शांत झाल्यानंतर इ.स.१९४४ मध्ये त्यांना सोडण्यात आले. सुटकेनंतर त्यांनी सोलापूर जिल्ह्यात कॉंग्रेसचा विधायक कार्यक्रम राबवण्यास सुरुवात केली. इ.स.१९४६ ते १९४८ पर्यंत त्यांनी पंढरपूर नगर परिषदेच्या शिक्षण समितीच्या अध्यक्ष म्हणून कार्य केले. ज्या स्वातंत्र्यासाठी त्यांनी आयुष्य वेचले त्यानंतर त्या जवळ जवळ पन्नास वर्ष हयात होत्या. स्वातंत्र्यानंतर त्या 'सर्वोदय' गटाबरोबर काम करु लागल्या. सर्वोदयाच्या माध्यमातून मुळशी तालुक्यातील शिंदेवाडी गाव सुधारण्यासाठी त्यानी अविश्रांत काम केले.जयसिंगपूर व कोल्हापूर येथेही गांधीजींच्या विधायक कार्यक्रमाप्रमाणे काम केले. इ.स.१९५९ पर्यंत जयसिंगपूर व कोल्हापूर जिल्ह्यात सर्वोदयाचे काम केले. व्यंकटेशरावांची सर्व संपत्ती सरकारने इ.स.१९२७ साली जप्त केली

होती, ती काँग्रेस सरकारकडे विनंती अर्ज केल्यास परत मिळेल तेव्हा, शक्य तेवढ्या लवकर तसा अर्ज करावा अशी विनंती मुख्यमंत्री बाळासाहेब खेर यांनी पद्मावतीबाईंना केली. त्यावेळी त्यांनी 'आर्थिक बाबतीत कुणाकडे हात पसरून, माझ्या पतीने उच्च ध्येयाने प्रेरीत होऊन केलेल्या त्यागाला मी कमीपणा आणणार नाही.' असे बाणेदार उत्तर दिले. स्वातंत्र्यसैनिक म्हणून त्यांना व व्यंकटेशरावांची पत्नी म्हणून अशी दोन निवृत्तीवेतने त्यांना भारत सरकार व महाराष्ट्र सरकार यांच्याकडून मिळणार होती. पण तीही त्यांनी नाकारली.[४] आज स्वातंत्र्यसैनिक म्हणून एक महिन्याची शिक्षा भोगलेल्यांना निवृत्तीवेतन मिळालेले स्त्री-पुरुष पाहिले आहेत. त्यांची संख्या वर्षे जातील तशी कमी न होता वाढतच आहे. ज्यामध्ये ढोंगीपणा आणि भ्रष्टाचाराने शिरकाव केला आहे.[५]ह्या पार्श्वभूमीवर खरे स्वातंत्र्यसैनिक कसे गांधीवादी विचारसरणीच्या मुशीत तयार झालेले होते हे लक्षात येते. शेवटपर्यंत त्यांनी कोणत्याही मानपत्राचा स्वीकार केला नाही.आयुष्याच्या शेवटपर्यंत त्यांनी आपला स्वाभिमान गांधी विचार जोपासले. व राष्ट्रसेविका म्हणून आयुष्य कंठीत केले.

संदर्भ:

१. गांधी एम. के. काशीनाथ त्रिवेदी (अनु.) *'सत्य के प्रयोग अथवा आत्मकथन'* नवजीवन प्रकाशन मंदिर, अहमदाबाद, पहिली आवृत्ती, १९५७, पृ.११६.)

२. चंद्र बिपिन, काळे डॉ. एम.व्ही.(अनु.), *'इंडिया स्ट्रगल फॉर इंडिपेंडन्स'*, के सागर पब्लिकेशन पुणे, चौथी आवृत्ती २०१०, पृ. ३१७.

३ .*दैनिक लोकसत्ता,* चतुरंग, पुणे आवृत्ती, १५/०९/२०१३, पृ. ५.

४.www.rutugandha.com *ऋतुगंध: बहर शब्दसाहित्याचा*– एक समर्पित जीवन, 27/02/2018.

५. टिकेकर अरुण, *'सामाजिक आणि सांस्कृतिक पडझडीचा आलेख –कालांतर'*, रोहन प्रकाशन, पुणे दुसरी आवृत्ती, २०१७, पृ.७५.

15

बदलत्या जागतिक राजकारणाच्या संदर्भात भारताचे परराष्ट्र धोरण

डॉ.नितीन हरीदास गायकवाड
सहाय्यक प्राध्यापक, राज्यशास्त्र विभाग प्रमुख,
रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद

****

प्रस्तावना :

कोणत्याही देशाचे परराष्ट्र धोरण त्या देशाचे हितसंबंध काय आहेत व उद्दिष्टे काय आहेत यावर ठरत असते. याखेरीज आंतरराष्ट्रीय स्तरावरील परिस्थितीप्रमाणे व देशाच्या शक्तीप्रमाणेही हे धोरण ठरते. भूराजकीय व सामरिक बाबी कायम राहत असल्यामुळे काही हितसंबंध व उद्दिष्टे फारशी बदलत नाहीत. पण धोरण निश्चिती करणारे नेतृत्व त्याच्या विचारांप्रमाणे उद्दिष्टे व ती गाठण्याच्या प्रक्रियेत बदल करू शकत असल्याने परराष्ट्र धोरणात कमीअधिक बदल होऊ शकतो. आंतरराष्ट्रीय परिस्थिती जशी बदलत गेली आहे तसेच भारताची सत्तास्थितीही बदलली आहे. एका दुर्बल कृषिप्रधान देशाचे रूपांतर आता औद्योगिकदृष्ट्या विकसनशील, प्रगत व विजिगीषु देशात झालेले आहे आणि परराष्ट्र धोरण हे गटनिरपेक्षतेकडून स्वतंत्र धोरणाकडे वळलेले आहे. विशेषत: १९९० नंतर सोव्हिएत युनियनच्या पतनानंतर व शीतयुद्ध संपल्यानंतर गटनिरपेक्षतेचे महत्त्व संपलेच. जागतिकीकरणाच्या व उदारीकरणाच्या रेट्यात परराष्ट्र धोरणात व त्याच्या अंमलबजावणीत भारताला महत्त्वाचे बदल करावे लागले. अनेक नव्या आंतरराष्ट्रीय व प्रादेशिक संस्था व संघटनांमुळे बहुपक्षीय राजनयाला अधिक महत्त्व आले. म्हणजेच परराष्ट्र धोरण हे अधिक गुंतागुंतीचे झाले असून भारताच्या परराष्ट्र धोरणार बदलत्या आंतरराष्ट्रीय घडामोडीचा प्रभाव पडलेला दिसतो.

उद्दिष्टे :

१. बदलत्या जागतिक परिस्थितीचा अभ्यास करणे.

२. भारताच्या परराष्ट्र धोरणात बदलत्या जागतिक परिस्थितीचा प्रभावाचा अभ्यास करणे.

बदलते जागतिक परिस्थितील राजकारण :

१९९१ मध्ये सोविएत रशियाच्या विघटनाबरोबरच अमेरिका आणि सोविएत रशियामधील शीतयुद्धाचे राजकारण संपुष्टात आले. द्विध्रुवीकरणावर आधारित शीतयुद्धकालीन सत्ता–समतोल व्यवस्था कोसळली. यामुळे जगात लोकशाहीकरणाची प्रक्रिया गतिशील बनली. तसेच त्या काळातनिर्माण झालेल्या लष्करी गटांची जागा विभागीय व्यापार संघांनी घेतली. अमेरिका आणि बहुतांश पश्चिम युरोपीय राष्ट्रांनी आर्थिक हितसंबंधांना आपल्या परराष्ट्र धोरणामध्ये अग्रक्रम दिला. विचारसरणीपेक्षा हितसंबंध महत्त्वाचे बनले.शीत–युद्धाच्या समाप्तीबरोबरच संयुक्त राष्ट्र संघटनेची भूमिका आंतरराष्ट्रीय राजकारणात वाढली. शीतयुद्धाचे राजकारण, लष्करी संघटनांचे जाळे यामुळे संयुक्त राष्ट्र संघटनेची भूमिका मर्यादित झाली होती.

शीतयुद्धकालीन विश्वयरचना कोसळल्या बरोबरच एक नवीन विश्वरचना आकाराला आली. ही विश्ववरचना एकध्रुवीय आहे की, बहुध्रुवीय आहे याबात मतभेद असले तरी सुरुवातीच्या काळात ती अमेरिका केंद्रित असल्याचे दिसून येऊ लागले. परराष्ट्र धोरणात पुढील बदल घडून आले.

समाजवादी समाजाच्या उभारणीच्या स्वप्नातून आधुनिक भांडवलशाही समाजाच्या निर्मितीकडे परराष्ट्र धोरणाचा कल वाढू लागला.

परराष्ट्र धोरणात राजकीय हितसंबंधा ऐवजी आर्थिक हितसंबंधांना प्राधान्य देण्याचे निश्चित करणे.

तिसऱ्या जगाच्या हितसंबंधा ऐवजी राष्ट्रीय हितसंबंधाला प्राधान्य.

पश्चिम विरोधी परराष्ट्र धोरणाचा त्याग करणे.

आदर्शवादापेक्षा वास्तववादावर भर देणे.

बहुध्रुवीय विश्वासाठी प्रयत्न करणे.

बदलती जागतिक नवीन विश्वरचनाचा भारताच्या परराष्ट्र धोरणावर परिणाम :

१९९० नंतर जगाची शीतयुद्धोत्तर काळात नवीन

विश्वरचनामुळे जागतिक स्तरावर परराष्ट्र धोरणात बदल घडून आले. परिणामी भारतीय अर्थव्यवस्था समाजवादी अर्थव्यवस्थेमधून भांडवलशाही अर्थव्यवस्थेत परार्वातत होत असताना भारताने आर्थिक उदारीकरण आणि खाजगीकरणाचे धोरण आखले गेले आणि टप्याटप्याने अर्थव्यवस्था मुक्तन करून तिला जागतिक अर्थव्यवस्थेशी संलग्न केले गेले. या अनुषंगाने भारताच्या परराष्ट्र धोरणाच्या क्षेत्रात महत्त्वपूर्ण बदल करणे क्रमप्राप्त झाले. स्वातंर्त्योत्तर नेहरुंच्या वैचारिक प्रभावाने प्रेरित परराष्ट्र धोरण मागे पडले असून हितसंबंधांना विचारसरणीपेक्षाही प्राधान्य देणारे नवीन परराष्ट्र धोरण आखण्यात आले आहे. या परराष्ट्र धोरणामध्ये राजकीय उद्दिष्टांपेक्षा आर्थिक आणि व्यापारी हितसंबंध साधण्याचा उद्दिष्टाला प्राधान्य देण्यात आले आहे. परराष्ट्र धोरण वास्तववादी आणि व्यावसायिकतेकडे झुकले गेले. तसेच संरक्षण क्षेत्रात शीतयुद्धकालीन संभ्रमावस्था बाजूला सारून अधिकाधिक स्पष्टता आणण्याचा प्रयत्न केला गेला. याचे स्पष्ट प्रतिबिब हे भारताच्या आण्विक धोरणात उमटलेले दिसते. भारताने अणुबॉम्ब न बनविण्याची किंवा अण्वस्त्रांविषयी असलेल्या तिरस्काराची नेहरूंपासून चालत आलेली परंपरा खंडित करत १९९८ साली भारताला अण्वस्त्रधारी राष्ट्र म्हणून घोषित केले. अण्वस्त्र क्षेत्रात असलेली संभ्रमावस्था ही १९७४ पासून सुरू होती. १९७४ साली भारताने अणुचाचणी करून भारताकडे अणुबॉम्ब बनविण्याची क्षमता असल्याचे सिद्ध केले. मात्र अणुबॉम्ब बनविला नाही किंवा स्वत:ला अण्वस्त्रधारी राष्ट्र म्हणून घोषितही केले नाही. असे न करण्यामागे शीतयुद्ध काळापासून परराष्ट्र आणि संरक्षण क्षेत्रात चालू असलेली वैचारिक संभ्रमावस्थेची परांपराच प्रामुख्याने जबाबदार होती. ही संभ्रमावस्था नवीन विश्वरचनेत खंडित झालेली दिसून येते.

या नवीन विश्वरचनेमध्ये एखादे राष्ट्र इतर राष्ट्रांना आपल्या हितसंबंधानुसार वागण्यासाठी कोणत्या मर्यादेपर्यंत प्रभावित करू शकते. तर एखादे राष्ट्र इतर राष्ट्रांनी त्यांच्या हितसंबंधाच्या पूर्ततेसाठी टाकलेला प्रभाव कोणत्या मर्यादेपर्यंत थोपवू शकते यावर त्या राष्ट्राची आंतरराष्ट्रीय राजकारणाची पत ठरवू शकते. या दोन्ही तत्वानुसार भारताने आपले हितसंबंध आणि परराष्ट्र धोरण निश्चीत करण्याच्या दृष्टीने मार्गक्रम केलेला आहे. हे करत असताना भारताला दहशतवादी कारवाया आणि फुटीरवाद्यांच्या हालचालींमुळे धोक्यात आलेली अंतर्गतसुरक्षा, पाकिस्तानकडून प्रत्यक्ष–अप्रत्यक्षपणे सुरक्षाक्षेत्रात दिली जाणारी आव्हाने, चीनच्या विस्तारवादी आणि घुसखोर धोरणांचे आव्हान, भारताच्या पूर्वेकडील आणि पश्चितमेकडील समुद्रमार्गाच्या संरक्षणाचे आव्हान निर्माण झालेले दिसून येते. याचा विचार करून नवीन विश्वरचनामध्ये भारताने आपले परराष्ट्र धोरण अवलंबले होते.

एकविसाव्या शतकात प्रवेश केल्यानंतर अल्पावधीतच अमेरिकेच्या वर्ल्ड ट्रेड सेंटरच्या ट्विन टॉवर झालेल्या दहशतवादी हल्ल्यांनी जागतिक राजकारणाची दिशा पुन्हा बदललेली दिसते. ९/११च्या त्या एका घटनेने जागतिक राजकारणाची दिशाच बदलली असून अनेक समीकरणे बदलली आहेत. जुनी मोडली, नवीन तयार झाली. सुरुवातील अमेरिका आणि भारत यांचे परराष्ट्र संबंध सौदाहार्यपूर्ण नव्हते पण आज दोन्ही देशांमध्ये मैत्री संबध मजबूत होत असताना दिसते.

भारताने बदलत्या आंतरराष्ट्रीय राजकारणानुसार पूर्वेकडे पहा धोरण ते पूर्वेकडील सक्रीय धोरण असा बदल झाला तसेच परराष्ट्र धोरणात 'नेबरहूड फर्स्ट' धोरण राबवले. या धोरणानुसार भारताने शेजारी देशाशी संबंध बदलत्या आंतरराष्ट्रीय राजकारणानुसार सहकार्य धोरण अवलबंताना भारत–बांगलादेशा संबंधात बांगलाभूमीतून भारतीय बंडखोरांनी विकलेल्या भारतविरोधी कारवाया, बांगलादेशातून भारतात होणारे अवैध स्थलांतर, ईशान्येकडील सामाजिक तणाव, सरहदीवर होणारी तस्करी, तिस्ता नदीच्या पाण्याचे वाटप इ. प्रश्न, अफगाणिस्तानमधील सध्याची भारताच्या सुरक्षिततेची भूमिका, भारत–पाकिस्तान संबंधात संशयाचे वातावरण, भारताने श्रीलंकेच्या बाबत बहुध्रुवीय दृष्टीकोन, नेपाळ —भारत आणि भारत–भूतानच्या परराष्ट्र धोरणाची पुनर्रचना अशा अनेक मुद्दयांना सोडवण्यासाठी बदलत्या राजकारणात भारताने शेजारील राष्ट्रांना प्राधान्य दिलेले दिसते.

बदल्या आंतरराष्ट्रीय राजकारणात काही वर्षांपासून इंडो–पॅसिफिक प्रदेशाचा मुद्दा विविध कारणांनी सतत चर्चेत राहिलेला आहे. भारताने आपल्या परराष्ट्र धोरणात इंडो– पॅसिफिक प्रदेशाला सर्वसमावेशक, मुक्त, एकात्मिक आणि संतुलित स्थान मानतो. हिंद महासागर आणि पॅसिफिकमधील सामरिक आंतर–संबंध, समान

आव्हाने आणि संधी यावर भारत सातत्याने भर दिलेला आहे. पण अमेरिकेला मुक्त इंडो–पॅसिफिक हवे आहे तर चीनच्या या प्रदेशातील भूमिकेवर नियंत्रण ठेवण्याचा प्रयत्न करत आहे आणि आसियान देश इंडो–पॅसिफिकला एक समन्वयवादी मॉडेल म्हणून पाहत असल्याचे दिसते.

भारताच्या परराष्ट्र धोरणात बदलत्या आंतरराष्ट्रीय राजकारणात इंडो–पॅसिफिकचा प्रभाव पडलेला आहे. भारताचे अमेरिका, ऑस्ट्रेलिया, जपान आणि इंडोनेशिया प्रत्यक्षात इंडो–पॅसिफिकला आशिया–पॅसिफिक प्लस भारत म्हणून पाहत असून भारताला आशिया–पॅसिफिकच्या धोरणात्मक गतिशीलतेमध्ये समाकलित करण्याचा प्रयत्न केला आहे.

१६६० च्या दशकात भारताने लूक ईस्ट पॉलिसी सादर केली एक नवीन संकल्पना ज्याचा उद्देश देशाच्या ईशान्येला इंडो पॅसिफिक प्रदेशाचे प्रवेशद्वार बनवणे आणि भारताच्या विस्तारित शेजार्यांशी मजबूत संबंध निर्माण करण्यात मदत करणे हे होते. त्यानंतरच्या शासन प्रणालीच्या परराष्ट्र धोरणात लूक ईस्ट पॉलिसी मुख्य केंद्र राहिलेले दिसते. २०१४ च्या भारताच्या ईशान्य राज्यांसाठी विकासाच्या संधी निर्माण करणे हे घ्क्ट ईस्ट धोरणाचे उद्दिष्ट राबवले. अशा प्रकारे वाणिज्य, संस्कृती आणि कनेक्टिव्हिटी –हे तीन 'सी' भारताच्या सध्याच्या अॅक्ट ईस्ट धोरणाचे आधारस्तंभ असल्याचे दिसते. या धोरणाचा प्रभाव भारतीय परराष्ट्र धोरणावर पडला आहे.

भारताचे अॅक्ट ईस्ट धोरण त्याच्या पूर्वेकडील अभिमुखतेचे केंद्रस्थान आहे आणि ते इंडो–पॅसिफिकशी जवळून जोडलेले आहे. गेल्या काही वर्षांमध्ये ASEAN आणि त्याच्याशी संबंधित संरचना, जसे की ARF, EAS, आणि ADMM+, तसेच जपान, दक्षिण कोरिया, ऑस्ट्रेलिया आणि पॅसिफिक बेटे या पूर्वेकडील देशांकडे भारताचा दृष्टीकोन एक व्यापक धोरणात्मक प्रतिबद्धता बनली आहे. भारत आणि ASEAN यांच्यातील सहकार्याने व्यापार आणि गुंतवणूक, कनेक्टिव्हिटी, ऊर्जा, संस्कृती, लोक संपर्क आणि सागरी सुरक्षा यासह आर्थिक आणि धोरणात्मक मुद्द्यांपासून पुढे गेले आहे.

निष्कर्ष :

१. बदलत्या जागतिक राजकारणात भारताचे परराष्ट्र धोरण देशांतर्गत आर्थिक प्राधान्यांशी जोडण्यासाठी आणि आर्थिक विकासाची सुप्त क्षमता प्रत्यक्षात उतरवण्यासाठी आणि जगातील एक मोठी आर्थिक सत्ता बनण्यासाठी एक साधन म्हणून आर्थिक मुत्सदेगिरीचा अधिक प्रभावीपणे उपयोग करणे अनिवार्य झाले आहे.

२. आंतरराष्ट्रीय वाटाघाटी आणि परराष्ट्र धोरणातील उद्दोष्टांमध्ये आर्थिक मुत्सहेगिरीचा एक भाग म्हणून आर्थिक चिंतनाला स्थान दिले आहे.

३. जागतिकीकरणाच्या बदलत्या अमेरिका आणि रशियाबरोबरील भारताच्या संबंधांत अनेक महत्त्वाचे बदल घडून आले.

४. बदलत्या जागतिकरणाच्या धोरणात भारत –अमेरिका संबंध मैत्रीत परिवर्तित होत आहेत. पाकिस्तानविषयक अमेरिकेच्या भूमिकेत बदल झाला आहे.

५. भारताची भूमिका व्यापक होत असून आंतरराष्ट्रीय पातळीवरील सहसंबंधात भारताचे योगदान संयमी व विकसनशील झाले आहे.

६. जागतिकीकरणाच्या व उदारीकरणाच्या रेट्यात परराष्ट्र धोरणात व त्याच्या अंमलबजावणीत भारताला महत्त्वाचे बदल करावे लागले. परराष्ट्र धोरणात आर्थिक व व्यापारी राजनयाचे महत्त्व वाढले.

७. भारताच्या परराष्ट्र धोरणात विविध देश, संघटना, हिंदी महासागर क्षेत्र अशा विविध घटकांची परराष्ट्र धोरणात बदल झालेले आहे.

संदर्भ सूची :

१. डॉ.शैलेन्द्र देवळाणकर, (एफ्रिल २०१६) " मो!दी कालखंडात भारताचे परराष्ट्र धोरण व संरक्षण धोरण: उपलब्धी विपुल आव्हाने बाकी", व्ही.पी.एम. दिशा, वर्ष विसावे, अंक ४.

२. गाडगीळ.ज. ने. , (१६६४) "नवभारताचे शिल्पकार", राजहंस प्रकाशन, पुणे

१. अ कुमार महेंद्र, लाल नंदा, (२०२०), "आंतरराष्ट्रीय राजनिती के सैद्धांतिक पक्ष", शिवलाल अग्रवाल अँण्ड कंपनी, आगार रोड.

३. नीता पाटील, "सिव्हिल न्यूक्लियर डील –भारत–अमेरिका अणुकरारातील डॉ. अनिल काकोडकरांचे योगदान"साधना साप्ताहिक,२० डिसेंबर २०१६

४. कुलकर्णी प्रसाद, (२० मे२०१८), "वास्तववादातील भारत–चीन संबंध", आंतरराष्ट्रीय सारीपाट राजकारण, अर्थविश्व, महाराष्ट्र टाईम्स

५. एशियन न्युज डायजेस्ट, ४–१० जून २०००

६. कोसिंग्ज रेकॉर्ड, एप्रिल २००१

Peer reviewed Journal Impact Factor: 7.265 ISSN-2230-9578

Journal of Research and Development

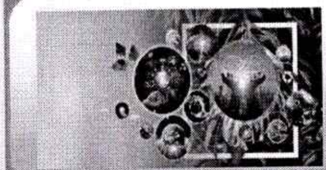
A Multidisciplinary International Level Referred Journal

November 2022 Volume-14 Issue-20

Chief Editor

Dr. R. V. Bhole

'Ravichandram' Survey No-101/1, Plot
No-23, Mundada Nagar, Jalgaon (M.S.)



Address
'Ravichandram' Survey No-101/1, Plot, No-23, Mundada Nagar, Jalgaon (M.S.) 425102

CONTENTS

'Journal of Research & Development'
A Multidisciplinary International Level Referred and Peer Reviewed Journal,
Impact Factor-7.265, ISSN: 2230-9578, November 2022, Volume-14 Issue-20

Journal of Research and Development

A Multidisciplinary International Level Referred and Peer Reviewed Journal

November-2022 Volume-14 Issue-20

Published by-Chief Editor, Dr. R. V. Bhole, (Maharashtra)

'Journal of Research & Development'
A Multidisciplinary International Level Referred and Peer Reviewed Journal,
Impact Factor-7.265, ISSN: 2230-9578, November 2022, Volume-14 Issue-20

Role of PMFBY in Agricultural Development in Marathwada Region

Dr. N. B. Kale [1]Asst. Prof. N. B. Nagare[2]
[1]HOD, Dept. of Commerce, Tuljabhani Mahavidylaya, Tuljapur
[2]HOD, Dept. of Commerce,R. P. College, Osmanabad
Email:kalenetaji123@gmail.com

Abstract

Marathwada is a one of the region of Maharashtra state. It is known as a drought prone area. More than 50 per cent population are affected due to short rainfall and other Natural hazard. At the same time, more than 70% of total population was depended on agriculture. So the government of India introduced PMFBY in Feb. 2016 for agriculture development. Pradhan Mantri Fasal Bima Yojana (PMFBY) is the one of the largest crop insurance scheme, which is helps to agriculture development. In this study, main focused on performance of PMFBY and agriculture development in marathwada region in Maharashtra state. For detailed study, we collected the secondary data about PMFBY and analyzed on the four indicates I.e. Farmer's participation, Area covered, Premium and Government Subsidy and Sum Insured.

Keywords: Insurance, Marathwada Region, Maharashtra, Agriculture development, Government subsidy, Role of PMFBY

Introduction:

Marathwada is a one of the region of Maharashtra state. It is known as a drought prone area. More than 50 per cent population are affected due to short rainfall and other Natural hazard. At the same time, more than 70% of total population was depended on agriculture. The agriculture secures faces the lot of challenges due to uncertainties in agriculture i.e. natural and artificial hazards especially Marathwada region in Maharashtra state. Still, more people in Marathwada region make money for their livelihood from this sector, than from all other economic sectors.

Marathwada region has totally depended on agriculture and the agriculture sectors continue affected due to Natural hazard. The Government of India has developed various strategies to reduce agricultural risk and uncertainty. Mainly in it include providing tax remission, waiving off loans and interest, drought or flood relief measures, etc. Even so, a major problem with such types of relief is that such measures be dependent primarily on government policy as well as resources. However, these measures provide some guarantee and security in case of uncertainty, it is possible to expect some relief as the government is on their side when farmers are at a loss.

Although all the above matters are being done at the government level, the problems of the farmers are increasing day by day. In the first six months of 2020 in Maharashtra, 310 farmers have committed suicide in Marathwada. This number is lower than in the last six years. In the first six months, 413 farmers committed suicide. Drought-hit Marathwada farmer suicide is a serious problem, Aurangabad Division, Jalna, Parbhani, Beed, Osmanabad, Nanded, Latur and Hingoli are the eight Marathwada districts under Aurangabad Division. Beed district has the highest number of suicides this year, followed by Osmanabad with 56, Jalna and Nanded with 53. There have been 20 suicides in Hingoli.

Pradhan Mantri Fasal Bima Yojana (PMFBY) is the one of the largest crop insurance scheme, which is helps to agriculture development. PMFBY was introduced in Feb. 2016. In this study, main focused on performance of PMFBY and agriculture development in marathwada region in Maharashtra state.

Objectives of the study

The objectives of concern study are as follows.

1. To study about role of crop insurance schemes in Agriculture development
2. To measure the performance of crop insurance scheme for agriculture development

3. To analyze the farmers' participation, area insured and gross premium of crop insurance scheme

Research methodology

Data Collection: This is an analytical study; hence, Secondary data is an important and powerful tool for the any type of research. Researcher conducted his research work is on the basis of secondary data. The secondary data is collected through newspapers, magazine, government reports and internet. For accomplishing the objectives of the study, three years data is collected and analyzed it.

Research area: The present study deals with the role of PMFBY and agriculture development. For justify the subject & detailed study proposes, PMFBY are selected in Marathwada region.

Limitations of the study: In this study, only PMFBY was selected and only five years performance was measured of the agriculture insurance scheme in Marathwada region in Maharashtra stae. Other crop insurance schemes are not taken into account.

Pradhan Mantri Fasal Bima Yojana (PMFBY)

Pradhan Mantri Fasal Bima Yojana (PMFBY) is one of the world's largest and important crop insurance scheme. It's aimed to providing risk cover to Indian farmers. PMFBY was launched in early 2016 with the key feature being a highly subsidized and affordable premium to farmers. Under the scheme, only 2% premium of maximum to pay farmers during Kharif sowing, 1.5% during Rabi sowing for food and oilseed crops, whereas for annual commercial crops they have to pay a maximum of 5%. As a same, the Government of India and state government shared equally pay the subsidy on farmer's premium of actuarial premium rate. The National Agricultural Insurance Scheme (NAIS) as well as the modified NAIS has combined into PMFBY.

Role of PMFBY in Agriculture development in Marathwada region

The role of crop insurance scheme especially PMFBY measured with the help of some indicators. It includes farmer's participation, Area insured, Premium paid and Sum insured by farmers as well as government subsidy. The performance are evaluated in Kharif seasoan 2018-2020 and Rabi Seasoan 2018-2021 of Marathwada region in Maharashtra state.

Farmer's participation:

During last three years, in Kharif 2018-2020 and Rabi 2018-2021, total of 1.11 crore farmers participated under PMFBY in Marathwada Region. The more farmers were participated in Kharif seasoan as a compare to Rabi seasaon. In kharif-2018, total 31.56 lac, Kharif-2019, total 28.15 lac and Kharif-2020, total 25.33 farmers were participated during last three years. It shows the participation of farmers are decreased in Marathwada region.

As per the PMFBY report 2018 to 2020, the Latur district took frist place in farmers participation with 22.58 lac farmers. Also, Bid and Nanded district took second and third place in participation respectively.

As per agriculture census, there had a total number of 3480702 frames, which is averagely 1851785 farmers participated in Marathwada region in Kharif and rabi season under PMFBY. It shows that 52.20 per cent farmers had participated in PMFBY during last three years and it is helpful to agriculture development.

Area covered:

The total area insured in kharif and Rabi taken together has 14451.66 thousand hectors from 2018 to 2021. The area under PMFBY has decreased year to year. As a compared to Rabi season, in Kharif season 2018 to 2021, the area covered under PMFBY has more. Following chart 02 indicates the performance in Area Covered in PMFBY in Marathwada region from 2018-19 to 2020-21.

As per PMFBY report, it shows that Bid, Latur and Osmanabad took first, second and third place in area covered under PMFBY in Marathwada region during 2018-19 to 2020-21. As per agriculture census, total agriculture area has 52361.7 thousand hectors and only 14451.66 thousand hectors area under PMFBY in Marathwada region. It indicates that only 27.60 per cent area were covered under PMFBY in Marathwada region.

Premium and Government Subsidy:

The premium paid by the farmers from 2018 to 2021 had 110575.98 lac and state and central government had paid 1099843.71 lac in that period. The gross premium has increased from year to year. During 2018 to 2021, the state and central government commonly paid subsidy under PMFBY has 90.86 per cent. The government of India plays most important role through provide subsidy for insuring crops.

Sum Insured:

The total sum insured in Marathwada rgion has increased regularly during 2018-19 to 2020-21. the total value of sum insured under PMFBY has Rs.5,073,874.10 lac from last three years in Marathwada region and Rs. 12,751,100.28 lac in Maharashtra state. Bed, Latur and Osmanabad stood a first, second and third rank in sum insured. As a compare to Maharashtra, 40 per cent value of sum insured in Marathwada region. So it is clearly indicates that, the government always tray to develop agriculture sectors.

Conclusion:

As per the performance evaluate of PMFBY during 2018 to 2021 in Marathwada region, the number of farmers participation, area covered under PMFBY and sum insured had declined from last four year but in 2021-2022 was increased. Apart from Premium and government subsidy had increased. There is need to motivate the farmers towards crop insurance scheme. It is possible when the ground level motivation camp will be organized door to door in every village. On the basis of conclusion, there is need too much more efforts in PMFBY to sustainable development in agriculture.

Bibliography

1. Ashok Gulati, (Feb. 2018), Crop Insurance in India: Key Issues and Way Forward, Working paper NO. 352
2. Singh, G. (2010), "Crop Insurance in India", IIM Ahmedabad, Working Paper. No. 2010-06- 01
3. Ministry of Agriculture & farmers welfare Govt. of India; PMFBY Progress and achievement 2016 to 2021 report
4. https://pmfby.gov.in/adminStatistics/dashboard
5. https://pmfby.gov.in/pdf/New%20Schemes-english_.pdf
6. https://pmfby.gov.in/ext/rpt/ssfr_17
7. Hazell, P., Pomareda, C., and Valdes, A. (1986), "Crop Insurance for Agricultural Development", John Hopkins University Press, Baltimore, USA Harms, S.C, "History of Crop Insurance in the United States", Retrieved from

UGC CARE LISTED
ISSN No. 2394-5990

इतिहासाचार्य वि. का. राजवाडे मंडळ, धुळे
या संस्थेचे त्रैमासिक

।। संशोधक ।।

पुरवणी अंक ११ – डिसेंबर २०२२ (त्रैमासिक)

● **शके १९४४**   ● **वर्ष : ९०**   ● **पुरवणी अंक : ११**

✵ प्रकाशक ✵

श्री. संजय मुंदडा
कार्याध्यक्ष, इ. वि. का. राजवाडे संशोधन मंडळ, धुळे ४२४००१
दूरध्वनी (०२५६२) २३३८४८, ९४०४५७७०२०

कार्यालयीन वेळ
सकाळी ९.३० ते १.००, सायंकाळी ४.३० ते ८.०० (रविवारी सुट्टी)

मूल्य रु. १००/-
वार्षिक वर्गणी रु. ५००/-, आजीव वर्गणी रु. ५०००/- (१४ वर्षे)

विशेष सूचना : संशोधक त्रैमासिकाची वर्गणी चेक/ड्राफ्टने
'संशोधक त्रैमासिक राजवाडे मंडळ, धुळे' या नावाने पाठवावी.

अक्षरजुळणी : सौ. सीमा शिंत्रे, वारजे-माळवाडी, पुणे ५८.

महाराष्ट्र राज्य साहित्य आणि संस्कृती मंडळाने या नियतकालिकेच्या प्रकाशनार्थ अनुदान दिले आहे. या नियतकालिकेतील लेखकांच्या विचारांशी मंडळ व शासन सहमत असेलच असे नाही.

INDEX

A study on Awareness of M-banking in Marathwada region

Dr. Kale N. B.
Head, Dept. of Commerce,
Tuljabhavani College, Tuljapur,
Email: kalenetaji123@gmail.com

Mr. Nagare B. K.
Head, Dept. of Commerce,
R. P. College, Osmanabad

Abstract :

Mobile banking is the act of making financial transactions on a mobile device such as cell phone, tablet etc. Today's Bank became a pocket bank because of the 4G remote portable innovation structure and also mobile banking service provided through bank apps and other private apps such as PhonePe, Paytm, BHIM, Google Pay, WhatsApp Pay etc. As of Jan. 2022, there were about 658 million internet users and about 1.2 billion mobile banking subscribers in India. In Q1 2022, customers made 15.6 billion mobile based payments whereas Net Banking. In terms of value, INR 44.68 trillion was transacted though mobile banking. So day to day, Mobile banking becomes popular all over the India. Mine study focused on the awareness of M-banking and its services in Marathwada region. For justify the subject primary data was collect from eight district of Marathwada region through Google survey form and secondary data of mobile banking transactions. Marathwada Region in Maharashtra state was surveyed. We used convenience sampling methods to reach 200 samples and data was analysis and interpreted on that basis.

Keywords: Mobile Banking, Awareness, Marathwada region, m-banking services

Introduction :

Day-to-day Mobile technology made much more progress. Tomorrow's mobile device today became an outdated. Mobile technology is that goes where the user goes. Therefore, Mobiles became a whole world connected device. There are each and every facility are available on Cell phone. Mobile banking is a one of the most recent activity of Mobile technology.

Mobile banking is the act of making financial transactions on a mobile device such as cell phone, tablet etc. Throughout the mobile banking, banks provided various services are provided to users such as fund transfer form one account to another, Account balance information on a click, electronic bill payment, remote check deposits, P2P payments and other services. Today's Bank became a pocket bank because of the 4G remote portable innovation structure and also mobile banking service provided through bank apps and other private apps such as PhonePe, Paytm, BHIM, Google Pay, WhatsApp Pay etc. Anywhere, anytime you can connected to bank for banking services. In late 1990, first joint effort did a German organization Paybox and Deutsche bank for mobile banking. In decade of the 21 century, some developing nation began presenting Mobile banking services. So, Mobile banking is a new recent trend in banking and financial industries.

As of Jan. 2022, there were about 658 million internet users and about 1.2 billion mobile banking subscribers in India. In Q1 2022, customers made 15.6 billion mobile based payments whereas Net Banking. In terms of value, INR 44.68 trillion was transacted though mobile banking. So day to day, Mobile banking becomes popular all over the India.

Mine study focused on the awareness of M-banking and its services in Marathwada region. For justify the subject primary data was collect from eight district of Marathwada region through Google survey form and secondary data of mobile banking transactions.

Rationale of the study :

Bharati Motwani, SukhjeetMatharu, Sharda Haryani el 2016, in their study "A comparative study of mobile banking services in public and private sector banks" they recomanded the following things to improve the use of mobile banking.

l Training courses to be conducted to the customers to encourage the usage of mobile banking.

l Provide the manual to customer about information of usages of mobile banking.

Anayasi and Otubu 2009, in their study "Mobile phone technology in Banking system: its economic effect" they observes effects on economy due to mobile banking. They observe that, Mobile banking helps economic development when extension of mobile banking business to all remote areas.

Also, why Mobile banking used by customers?, How Mobile banking service provider and customers trust on each other? What are the technological issues came in Mobile banking services? etc. issues know in this study.

Review of literature:

In literature, many connected examinations are available, which for the most part centers on study of mobile banking services. Specialists utilized different terms for mobile banking services, Amin et al., 2006 alluded mobile managing an account as pocket keeping banking, Vyas, 2009;Rao et al. 2003, explained that banks need innovation and creativity in their banking facility to gain competitive edge, Gupta, 1999;pegu, 2000;Dasgupta, 2002, suggested that the assures a bright future of mobile banking in India. Nidhi S. & Neena Sinha, 2016, the study on impact of age on mobile banking etc. there are various researchers was such on mobile banking and hug number of literature available.

Research Methodology :

The conducting the study and achieving objectives of study, analytical research mythology is used.

Objectives of the study :

1. To study about awareness about M-banking
2. To study about the factors affecting the mobile banking
3. To study the rate of use of M-banking
4. To give suggestions based on the study.

Sample Selections:

In Marathwada region has 8 district headquarters, from that on the basis of convenience sampling 200 respondents were selected from district headquarter as a sample.

Data Collection, analysis and interpretation:

This is an analytical study; hence, Primary and Secondary data is used. The primary data has collected from 200 respondents through the Google survey from in eight district of Marathwada region and secondary data has collected during 2018 to 2020 of Mobile banking transaction in India. The collected data was analyzed using Adv. Ms-Excel software and the following results were found in below.

A) Personal Information :

The total no of respondents were 100, out of which the men were 144 and 56 were women respondents. 08% respondents were below 20 years followed by 14% respondent in the 20-30 years age. There were 38% of respondents from the 30-40 years age group, 27% respondent

ISSN No. 2394-5990

from the 40-50 years age group and 13% respondent from above 50 years age group. On the basis of education level, 32% respondents are graduates, 42% post graduates and 26% are professionals.

The category of income and the results indicates that 06% respondents earn of less then Rs.2,00,000, followed by 51% of respondents in a group of Rs.2,00,001-Rs.4,00,000 and 19% are between Rs.4,00,001-Rs.6,00,000 and 13% for those between Rs.6,00,001-Rs.10,00,000 and 11% in the range above Rs.10,00,000.

B) Awareness about Mobile banking :

T.1. Do you know, can make banking transactions through Mobile?

Response	Frequency	Percent
Yes	165	82.5%
No	35	17.5%
Total	200	100%

Interpretation: it is represented that awareness of banking transaction through Mobile is 82.5% and 17.5% respondents are not know about it.

T.2. Do you know, your bank provide the M-Banking App?

Response	Frequency	Percent
Yes	116	58%
No	85	42%
Total	200	100%

Interpretation: the above table indicates that 58% are aware of the bank provide M-banking app and 42% are not.

T.3 Are you use any mobile banking app for banking transaction?

Response	Frequency	Percent
Yes	97	48.5
No	103	51.5
Total	200	100%

Interpretation: from the above table 51.5% respondents are not using M-banking app.

T.4 which types of M-banking Application is you used?

Response	Frequency	Percent
Bank app	16	16.49
PhonePe	28	28.86
PayTm	38	39.18
Google Pay	12	12.37
Other	03	03.10
Total	97	100%

Interpretation: Above table show that the use of M-banking application, 39.18% respondent used Paytm followed by 39.18% used PhonePe and only 16.49% are used bank app for M-banking.

T.5 How many time do you used M-banking per months?

Mobile Banking transaction per month	Response
01 to 10	29%
11 to 20	53%
Above 21	18%

Interpretation: As per above table Maximum 53% of people used M-banking 11 to 20 time in a month followed by 29% used M-banking 01 to 10 times per month and only 18% respondents said they used above 21 time.

T.6 Which types of banking transaction are you do through M-banking?

Response	Percent
Fund transfer	58.25%
Bill payment	69.34%
Access to account information	24.57%
Other services	17.48%
All of the above	37.45%

Interpretation: the above table shows that, 69.34% respondent used M-banking for Bill payment followed 58.25% used for fund transfer and 37.45% respondent used all of the bank services.

T.7 Do you need any training for M-banking?

Response	Frequency	Percent
Yes	147	73.50%
No	53	26.50%
Total	200	100%

Interpretation: From the above table 73.5% respondents are need for training for M-banking.

T.8 Are you interested to take training of M-banking?

Response	Frequency	Percent
Yes	154	77.00%
No	46	23.00%
Total	200	100%

Interpretation: 77.00% respondents are interested in training for M-banking.

T.9 How do you know about M-banking application?

Sources	Responded
Bank Broucher	17.25
Newspaper advertising	04.50
Electronic means	37.25
Family and friend	41.38
Do Not Know	15.46
Other	03.47

Interpretation: Most of the respondents said about M-banking app through family and friend 41.38% followed through Electronic means 37.25%. The 17.25% of Bank broucher and Newspaper adverting is 04.50% and 3.47 respectively.

T.10 Reasons of not using M-banking App

Problems	Response %
Do not know how to operate	45.75
Not interested	25.26
Difficult to operate	38.25
Bad Network	12.50
Not feel Secured	36.25
Mobile Handset operating	27.75

Interpretation: from the above table represents that 45.75% people do not know to how to operate M-banking app. 38.25% for difficult to operate and 36.25 of the people have not feel secured about M-banking.

Conclusion :

The present study indicates that peoples are aware about M-banking in Marathwada region is 82.5% and 58% about bank provide M – banking app and only 48.5% used M-banking application for day to day banking transaction. The M-banking users used various applications for mobile banking in that 39.18% customers used Paytm, 28.86% used PhonePe and only 16.49% used bank app. And they used maximum 53% of M-banking 11 to 20 times in a month. About the use of M-banking services, most of the people are used M-banking for Bill payment and fund transactions. It is also depicted that the various factors affected to using m-banking is Do not know how to operate (45.75%), difficult to operate (38.25%) and not feel secured (36.25%). Most of the respondent said, there is need to m-banking training and 77.00% respondents are interested in training for M-banking. Taken into account above conclusion it is suggested that need of free cost m-banking training is provide to customers and there is need to increase the an awareness among the customers about M-banking.

References :

- Sadhana S. Thatte & Dr. S. M. Kulkarni (2019): A study on awareness of M-banking app in rural areas of Jalgoan district, https://www.researchgate.net/publication/333973639
- Al Shifa, Dr. Madhav Hajmadi (2020): A study of M-banking with reference to Customer satisfaction in bank Nizwa, Oman, https://www.researchgate.net/publication/343850290

- Awasthi (2015): Impact of technology in Banking sector, New Delhi; Shroff Publisher and Distributer PVT LTD.
- Dr. HemaDivya (2018). A study on Digital Payments in India with perspective of customers adoption, International Journal of Pune and Applied Mathematics, V.118 no 24.
- Mr. B Sambamurthy (Jan. 2014): RBI Report on M. Banking, https://rbidocs.rbi.org.in/rdocs/PublicationReport/Pdfs/TMB070214BF.pdf
- Dr.HemaDivya. (2018). A Study on Degital Payments in India with perspective of consumers adoption. International Journal of Pure and Applied Mathematics, V.118 no 24.
- https://rbidocs.rbi.org.in/rdocs/Content/PDFs/87665.pdf
- Vaidya (2011): "Emerging Trends on Functional Utilization of Mobile Banking in Developed Markets in Next 3–4 Years"
- Tiwari, Rajnish and Buse, Stephan(2007): The Mobile Commerce Prospects: A Strategic Analysis of Opportunities in the Banking Sector, Hamburg University Press (E-Book as PDF to be downloaded)
- Tiwari, Rajnish; Buse, Stephan and Herstatt, Cornelius (2007): Mobile Services in Banking Sector: The Role of Innovative Business Solutions in Generating Competitive Advantage, in: Proceedings of the International Research Conference on Quality, Innovation and Knowledge Management, New Delhi, pp. 886–894.
- Tiwari, Rajnish; Buse, Stephan and Herstatt, Cornelius (2006): Customer on the Move: Strategic Implications of Mobile Banking for Banks and Financial Enterprises, in: CEC/EEE 2006, Proceedings of the 8th IEEE International Conference on E-Commerce Technology and The 3rd IEEE International Conference on Enterprise Computing, E-Commerce, and E-Services (CEC/EEE'06), San Francisco, pp. 522–529.
- Tiwari, Rajnish; Buse, Stephan and Herstatt, Cornelius (2006): Mobile Banking as Business Strategy: Impact of Mobile Technologies on Customer Behaviour and its Implications for Banks, in: Technology Management for the Global Future – Proceedings of PICMET '06.
- Owens, John and Anna Bantug-Herrera (2006): Catching the Technology Wave: Mobile Phone Banking and Text-A-Payment in the Philippines

■■■

NCICST-2022
National Conference on 'Innovations & Challenges in Science & Technology'
In Association with International Journal of Scientific Research in Science and Technology
Volume 9 | Issue 15 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)

Intramural Investigation of Pollen in Osmanabad

H. A. Kamble1, B. V. More2
[1]Department of Botany, R.P. Mahavidyalaya, Osmanabad, Maharashtra, India
[2]Department of Zoology, R. P. Mahavidyalaya, Osmanabad, Maharashtra, India

ABSTRACT

A present investigation deals with the monthly frequency of pollen in the intramural environment of cattle shed. A systematic aeropalynological investigation was carried out from 01 January 2017 to 31 December 2017. This investigation was conducted by using volumetric Tilak air sampler in the intramural environment of cattle shed.

In the present investigation 26 pollen types were found. The Grass pollen contribute highest percentage (41.54%), Cyperus rotundus (15.33%), Moringa oleifera (8.62%), Poaceae (7.71%), Parthenium hysterophorus (6.22%). Frequency of pollen grains shows seasonal variation.

KEYWORDS: Pollen, Intramural environment, Grass pollen.

I. INTRODUCTION

Pollen grains are produced by flowering plants and found in the air. Pollen grains are male gametophytes of Angiosperms. Pollen grains are of variable in size, ranging from 3μm to 250 μm. Wind borne pollen range from 10 μm to 100 μm (1). 'Palynology' is a science for pollen and spore studies and its application(2). Pollen grains are widely known to be the cause of various allergic complaints like hay fever, eczema, asthma and urticaria(3). So it is important to monitor airborne pollen, their emission patterns through systematic air sampling.

II. MATERIAL AND METHOD

In the present investigation was carried out with the help of volumetric air sampler (4).

SAMPLING METHOD:

Samples were collected by using continuously operating Tilak air sampler. Sampler was kept at constant height of 2 meters above ground level. Air was sampled at the rate of 5 liters per minute and inside placed transparent cello tape coated with adhesive petroleum jelly was collected and changed every 8 days at about 6 p.m. The exposed transparent cello tape was cut into 8 equal parts each parts representing 24 hrs. trace area. These eight parts of tape were again cut into 2 parts, each representing 12 hrs. trace area of day and night accordingly. The transparent cello tape pieces were mounted on slides, with the help ofglycerine jelly as a mountant.

SCANNING:

Scanning of pollen was done regularly scanned under microscope (10 x 45 eye pieces and objectives lens combination of the microscope). The identification of the trapped pollen types was done based on 1) Morphological characters 2) Visual identification by comparison with reference slides.

STUDY SITE:

Investigation of pollen studies were carried out at Osmanabad a district of Maharashtra State, India. Osmanabad is located at 18°19'10"N latitude and 76°4'25"E longitude and situated at 652 meters above sea level(5).

CLIMATIC CONDITION:

Graphical presentation show climatic conditions.

III. RESULTS

In the intramural environment of cattle shed total 26 pollen types were found.These pollen types and their percentage contribution to the total air palynosdporaare as fallow *Acalypha hispida*(1.08%), *Amaranthus viridis*(2.74 %), *Argemon mexicana*(0.5 %), *Azadirachta indica*(0.91 %), *Bougainvillea spectabilis*(0.91 %), *Caesalpinia pulcherrima*(0.91 %), *Casuarina equisetifolia*(0.83 %), *Cassia fistula*(0.75 %) ,*Cocos nucifera*(0.91 %), *Cyperus rotundus*(15.33 %), *Datura metel*(1.07 %), *Eucalyptus globulus*(0.41 %), *Euphorbia* sp.(0.91 %), *Grass*(41.54 %), *Helianthus annuus*(0.25%), *Hibiscus rosa-sinensis*(0.33 %), *Lantana camera*(0.41%),*Leucaena leucocephala*(0.91 %),*Mangifera indica*(0.50 %), *Moringa oleifera*(8.62 %), *Parthenium hysterophorus*(6.22 %), *Poaceae*(7.71%), *Ricinus communis*(2.99 %), *Sorghum sp.*(0.58 %), *Syzygium cumini*(0.25 %) *and* Unidentified pollen(2.40 %). Unidentified pollen category includes those pollen grains types whose identification is not clear due to the following reason attach and mix with other particles, semitransparent, rupture wall, etc.

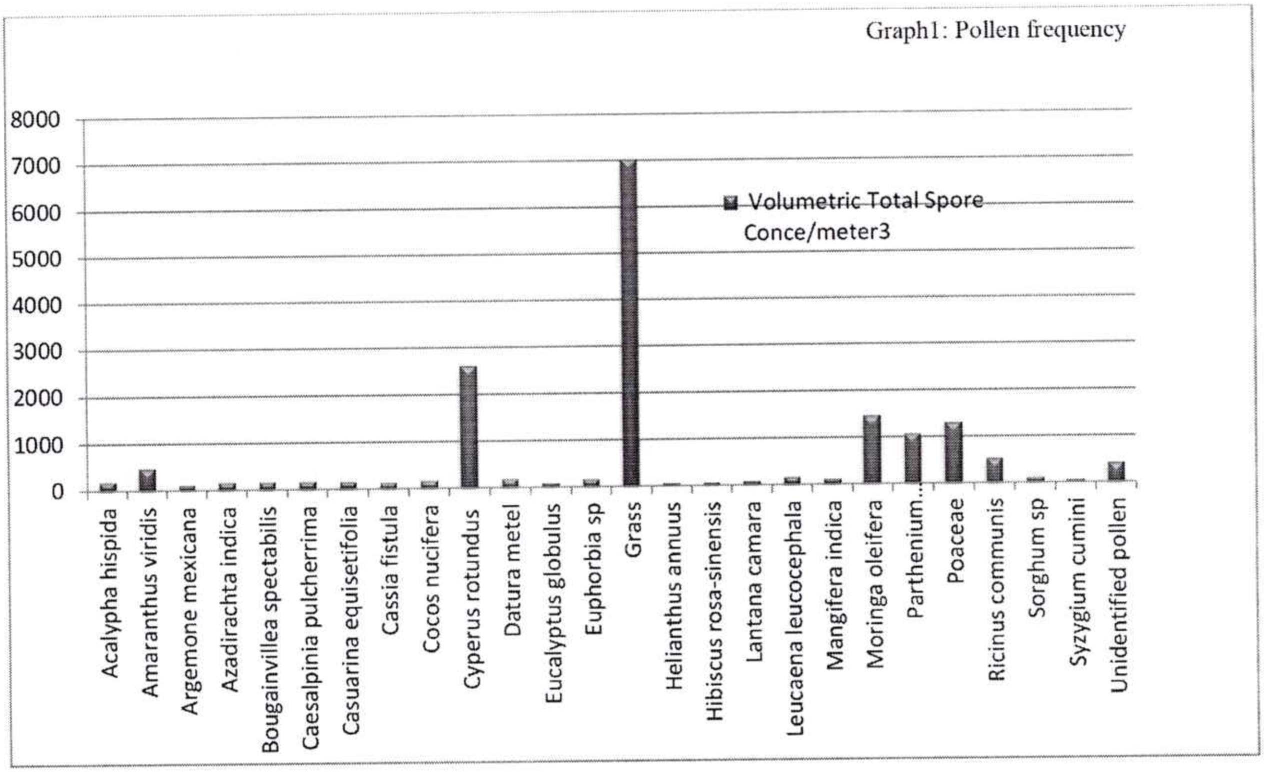
Grass pollen contributed highest percentage of contribution (41.54%) to the total palynospora. The size of grass pollens were > 50 μm. Second highest contributor was *Cyprus rotundus* contributed (15.33%) to the total air palynospora. Third contributor was *Moringa oleifera*contributed *(8.62%)* to the total air palynospora. Pollen grains are two types Anemophilous and Entomophilous (6). Anemophilous pollen were abundant in the air as compare to Entomophilous pollens. Pollen availability is correlated with meteorological factors such as wind speed, rainfall etc. and flowering season.

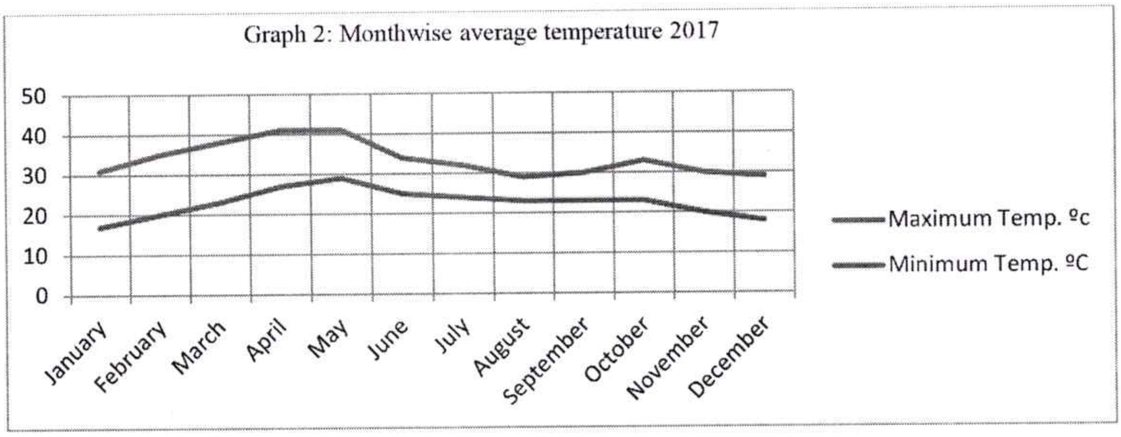
Table 1: Monthly frequency of various aerial Pollen of intramural atmosphere trapped in Tilak Air Sampler from 1 Jan 2017 to 31st Dec 2017

Sr. No.	Pollen grains	Jan	Feb	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Total	Volumetric Total Spore Concentration Per m^3	Percentage Contribution to the Total Air Palynospora
1	*Acalypha hispida*	2	2	1	1	1	-	-	1	1	1	1	2	13	182	1.08
2	*Amaranthus viridis*	3	2	1	1	1	1	1	8	7	3	3	2	33	462	2.74
3	*Argemon mexicana*	1	2	1	1	1	-	-	-	-	-	-	-	6	84	0.50
4	*Azadirachta indica*	3	4	2	2	-	-	-	-	-	-	-	-	11	154	0.91
5	*Bougainvillea spectabilis*	2	2	1	1	2	3	-	-	-	-	-	-	11	154	0.91
6	*Caesalpinia pulcherrima*	3	2	-	-	-	1	1	-	-	1	1	2	11	154	0.91
7	*Casuarina equisetifolia*	2	1	2	2	3	-	-	-	-	-	-	-	10	140	0.83
8	*Cassia fistula*	-	-	2	2	1	2	-	-	1	1	-	-	9	126	0.75

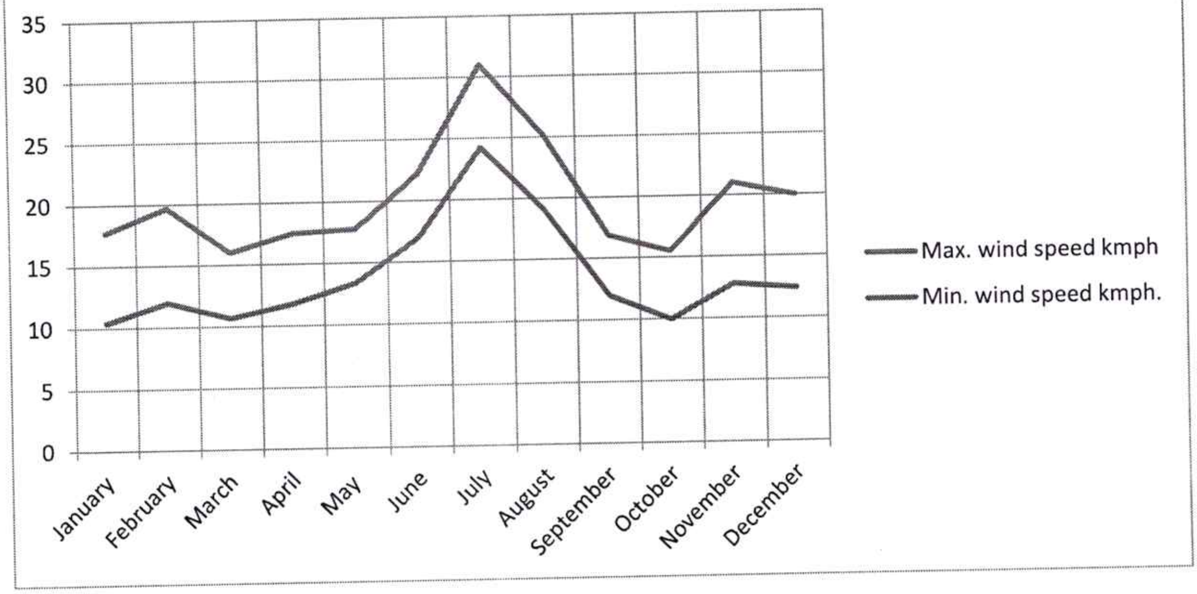
9	*Cocos nucifera*	1	1	1	-	-	-	1	1	2	1	1	2	11	154	0.91
10	*Cyperus rotundus*	12	8	4	1	1	6	7	32	35	36	22	21	185	2590	15.33
11	*Datura metel*	1	1	1	-	-	-	1	1	2	2	2	2	13	182	1.07
12	*Eucalyptus globulus*	1	1	-	-	-	-	-	-	-	1	1	1	5	70	0.41
13	*Euphorbia* sp.	1	1	1	-	-	-	-	1	2	2	1	2	11	154	0.91
14	Grass	50	36	19	8	5	6	15	66	107	98	55	36	501	7014	41.54
15	*Helianthus annuus*	-	-	-	-	-	-	-	-	1	1	1	-	3	42	0.25
16	*Hibiscus rosa-sinensis*	-	-	-	-	-	-	-	1	2	1	-	-	4	56	0.33
17	*Lantana camara*	1	-	-	-	-	-	-	-	2	1	-	1	5	70	0.41
18	*Leucaena leucocephala*	-	-	-	-	-	-	-	1	2	2	2	4	11	154	0.91
19	*Mangifera indica*	-	2	2	2	-	-	-	-	-	-	-	-	6	84	0.50
20	*Moringa oleifera*	9	11	14	20	15	3	2	4	6	8	6	6	104	1456	8.62
21	*Parthenium hysterophorus*	2	1	2	1	1	1	1	16	18	12	14	6	75	1050	6.22
22	Poaceae	9	7	4	2	1	1	4	13	20	15	10	7	93	1302	7.71
23	*Ricinus communis*	2	2	2	1	1	2	2	3	6	8	4	3	36	504	2.99
24	*Sorghum* sp.	1	-	-	-	-	-	-	2	2	-	-	2	7	98	0.58

25	*Syzygium cumini*	-	1	1	1	-	-	-	-	-	-	-	-	3	42	0.25
26	Unidentified pollen	2	2	3	2	2	2	2	3	4	3	2	2	29	406	2.40
	Total Pollen grains	108	89	64	48	35	28	37	153	220	197	126	101	1206	16884	99.99

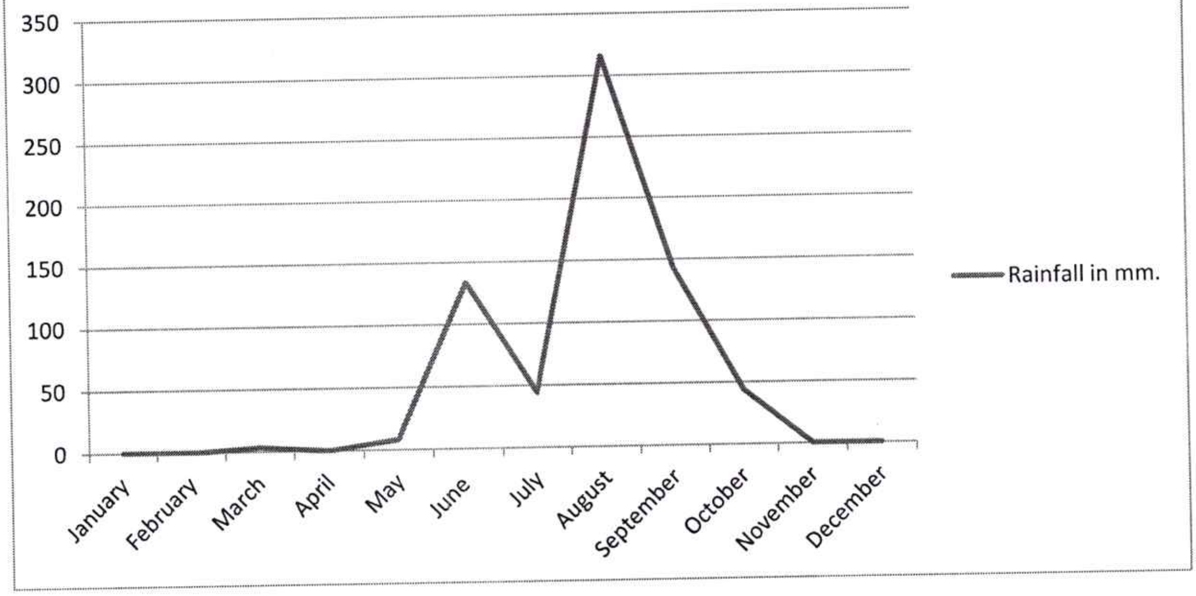

Graph1: Pollen frequency


Graph 2: Monthwise average temperature 2017

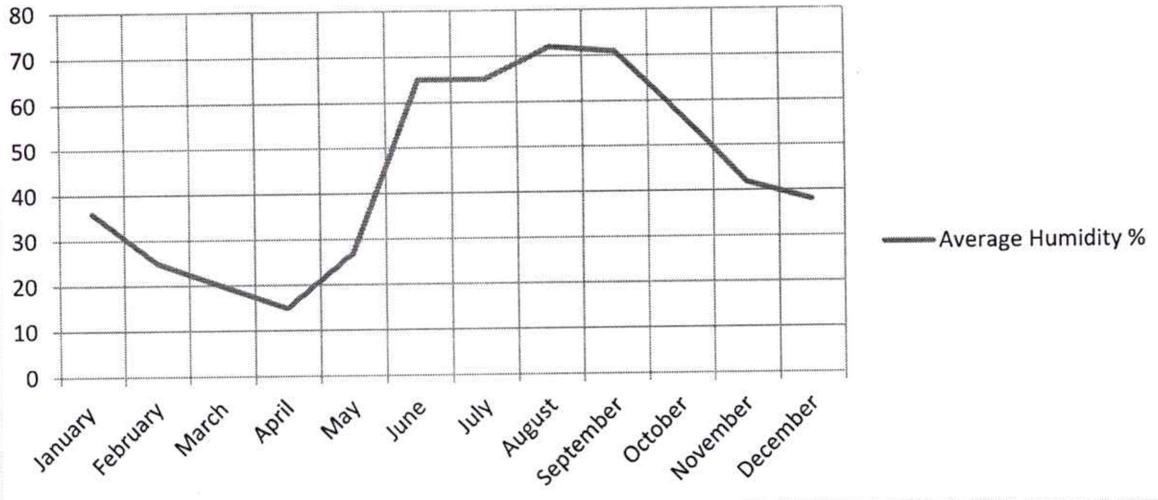
Graph 3: Monthwise average wind speed 2017



Graph 4: Monthwise average rainfall (mm) 2017.



Graph 5: Monthly Average Humidity % 2017.



IV. DISCUSSION AND CONCLUSION

Pollen grains are categorized into two major types Anemophilous and Entomophilous. In this investigation total 26 pollen types were found. Entomophilous plant species such as *Hibiscus rosa-sinensis, Lantana camera, and Bougainvillea spectabilis* also contribute to the airspora. Anemophilous pollen types were abundant in the air as compare to Entomophilous pollens. Pollen availability is correlated with meteorological factors such as rainfall, wind speed etc. and flowering season and vegetation.

Most of pollen grains concentration observed in the month of August to January due to rainy season. Grass pollen contribute highest percentage (41.54%), *Cyperus rotundus*(15.33%) second highest and third highest *Moringa oleifera(8.62%)* because *Moringa* plants were higher in number around the cattle shed.

V. REFERENCES

[1]. Gregory, P.H. 1973. The microbiology of the atmosphere.2nd ed., Leonard Hill, Aylesbury.
[2]. Hyde, H.A. and Adams, K. 1958.An atlas of air-borne pollen grains. Mac Millan, London.
[3]. Mandal, S. and Chanda, S. 1981.Aeroallergens of West Bengal in the context of environmental pollution and respiratory allergy.Biol. Mem.6 : 1-61.
[4]. Nair, P.K.K. 1963. An analysis of atmospheric pollen, fungal spores and other vegetative matter at Vellore, Madras State (South India). Indian J . Med. Res.51 : 447 - 452.
[5]. Tilal, S.T. and Kulkarni, R.L. 1970.A new air sampler. Experimential boil. 26 : 443.
[6]. Kamble, H.A. and Yeragi S.S. 2019. A Study of atmospheric pollen in Osmanabad. Review of research J. Vol-8 Issue-9.
[7]. Tilak, S.T. 1982.Aerobiology.VaijayantiPrakashan, Aurangabad.

"Structural and Optical Studies on Phosphorous doped TiO_2 nanoparticles"

Sandip B. Deshmukh[a*], Dhananjay V. Mane[b], Mangesh G. Bhosale[a], Maheshkumar L. Mane[c], Jalindar D. Ambekar[d]

a. *Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad. 413 501, Maharashtra, India.*

b. *Department of Chemistry, Shri Chhatrapati Shivaji Mahavidyalaya, Omerga 413 606, Maharashtra, India.*

c. *Department of Physics, Shikshan Maharshi Guruvarya R. G. Shinde Mahavidyalaya, Paranda 413 502, Maharashtra, India.*

d. *Centre for Materials for Electronics Technology (C-MET), Pune 411 008, Maharashtra, India.*

**Corresponding author*

Abstract

The pure anatase phase tetragonal structured Phophorous doped TiO_2 nanoparticles were successfully synthesized at room temperature by using simple sol–gel method. The structural, optical properties of the materials are investigated thoroughly by various spectral techniques (XRD, EDAX, FT-IR, and UV-DRS) and electron microscopy (FESEM and HRTEM). The experimental results suggest that, the P doped TiO_2 influenced the structural, morphological, and optical properties significantly. UV-DRS studies investigate that the doping of P ion can directly shift band gap of semiconductors into the visible region. The energy band gap decreases from 3.2 to 2.0 eV as the doping of mole % of P increases as 1, 3 and 5 mole %. P doping can effectively decrease the recombination rate of photogenerated charges in TiO_2.

1. Introduction

Heterogeneous photocatalysis has shown distinctive advantages in degradation [1]. TiO_2 semiconductor is extensively used as raw materials of ointment, paint, sunscreen, and toothpaste [2- 4]. Semiconductor photocatalysis has attracted wide attention in the field of water splitting, CO_2 reduction and pollution degradation [5-12] after the Honda and Fujishima's discovery of water photolysis on TiO_2 [13]. Now days, TiO_2 is still regarded as one of the most significant photocatalysts due to its long-term stability, low cost and nontoxicity [14-15]. However, the exploitation of visible light is limited due to the large band gap. The band gap of anatase TiO_2 is 3.2 eV and it is in the UV region. Moreover, the high resistance and high carrier recombination rate are also the disadvantages of TiO_2 photocatalyst [15,16]. To enhance the lifetime of photogenerated electron–hole pairs and decrease the band gap, various methods and techniques have been developed such as metal ion and nonmetal ion doping[17,18], with several foreign ions[19, 20], hybridization with carbon materials[21,22], co-doping, and surface sensitization by noble metal [23]. Nonmetal ion doping has made great success in the field of modifying photocatalyst such as N [24 – 27] and S [28-30]. The doping of nonmetal ion can directly shift band gap of semiconductors, resulting improved visible excited photocatalytic efficiency [31-33]. Comparing with other nonmetal elements, phosphorus has distinctive advantages on improving photocatalytic efficiency. P doping can effectively decrease the recombination rate of photogenerated charges in TiO_2 [34,35]. On the other hand, it has been reported by many researchers that moderate oxygen vacancies on photocatalyst can result in the formation of unpaired electrons and avoid the electron hole recombination [36, 37].

2 Materials and method

2.1 Materials

Nanocrystalline P doped TiO_2 was synthesized by using the sol-gel technique. In this work Analytical grade titanium(IV)tetraisopropoxide (TTIP) ($TiOCH(CH_3)_{24}$ 97% Sigma Aldrich), Orthophosphoric acid (H_3PO_4), Oleic acid ($C_{18}H_{34}O_2$), ammonia (NH_3) and absolute ethyl alcohol (C_2H_5OH) were used for the synthesis.

2.2 Synthesis of P doped TiO_2 nanoparticles

Optimum compositions (0.0 mole %, 1 mole %, 3 mole % and 5 mole %) of P doped TiO_2 nanoparticles were prepared by sol-gel method at room temperature.

5ml Oleic acid was taken in a 250 mL round-bottom flask. The content was stirred at 120^0C for 10 min. followed by the addition of 10 mL TTIP and 200 mL distilled water (DW); white precipitate of titanium hydroxide was formed. The content was stirred at room temperature for 1 h. Then, the content was filtered and re-slurred in 200 mL DW and the pH of the solution was adjusted to 10 by using an ammonia solution. After that, the content was stirred at 60^0C for 3 h. The stoichiometric quantity of orthophosphoric acid (H_3PO_4) was added into the above solution. The content was again stirred for 3 h at 60^0C. Then, the content was filtered and washed with 50 mL DW and 10 mL ethyl alcohol. After that, the residue was dried at 100^0C and annealed in air at 500^0C for 5 h. After annealing, the residue resulted in the off white colored P doped TiO_2 nanoparticles.

2.3 Characterization

The prepared powder samples were characterized by powder X-ray diffraction technique. XRD data of the samples were collected in the 2θ range of $10^0 – 90^0$ in step scan mode at a rate of 0.2^0/min using ULTIMA IV, Rigaku Corporation, Japan diffractometer with source Cu Kα (Kα1 = 1.5406 and Kα1 = 1.5444 Å) radiation. Nicolet iS10, Thermo Scientific, USA Fourier Transform Infrared spectrometer was used to record FTIR spectra of the nanoparticles in the range of 400 cm^{-1} to 4000 cm^{-1} with the transmission mode. The surface morphology of samples was investigated by using filed emission Scanning Electron Microscopy (FE-SEM) Hitachi S-4800 system with EDAX analysis was performed to determine the elemental composition of the samples. A JEOL JEM2100F field emission gun-transmission electron microscope (HR-TEM 200kV) operating at 200 kV with resolution (Point: 0.19 nm Line: 0.1 nm) and magnification (50X – 1.5 X) was employed for generating HR-TEM image of the nanoparticles. UV–Visible diffuse reflectance spectra of all the samples were recorded in the range of 200 nm – 800 nm, using an ELICO – SL159 UV–Visible spectrometer.

3 Results and discussion

3.1 X-ray diffraction analysis (XRD)

Figure 1 suggests the phase formation and crystalline structure of bare TiO_2 and various concentrations of P doped TiO_2 nanoparticles X-ray diffraction analysis was performed on the precursor material at room temperature using Cu-Kα radiations (λ=1.5406 Å). Fig. 4.11 shows XRD spectra of all the samples. The X-ray diffraction peaks (101), (004), (200), (105), (211), (204), (116), (220), and (215) of bare TiO_2 corresponding to diffraction angles at $2\theta = 25.4°$, 38.02°, 48.14°, 54.12°, 55.18°, 62.81°, 68.71°, 70.28°, and 75.30° could be attributed to the anatase phase TiO_2, respectively (JCPDS 21-1272). No peak phase assigned to P was observed with doping concentration, the crystal structure of doped TiO_2 samples shows stability of anatase phase when compared with that of bare TiO_2 sample. The average crystallite size of all the samples was calculated from the Full Width at Half Maximum (FWHM) (β) of all major diffraction peaks of anatase, using the Debye-Scherer method [38]. The obtained results of the average crystallite size (D) changed after P doping was tabulated in **Table 1**. The variation of crystallite size with P mole% was shown in **Figure 2** and it is observed that due to P doping crystallite size decreases.

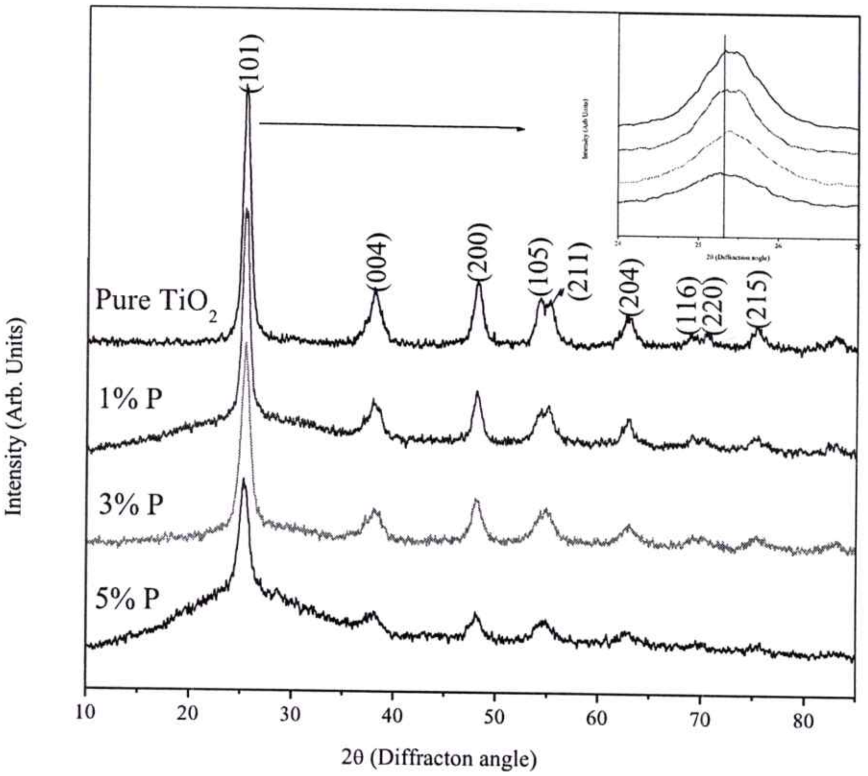


Figure 1: X-ray Diffraction Pattern for bare TiO_2 and P-doped TiO_2 nanoparticles

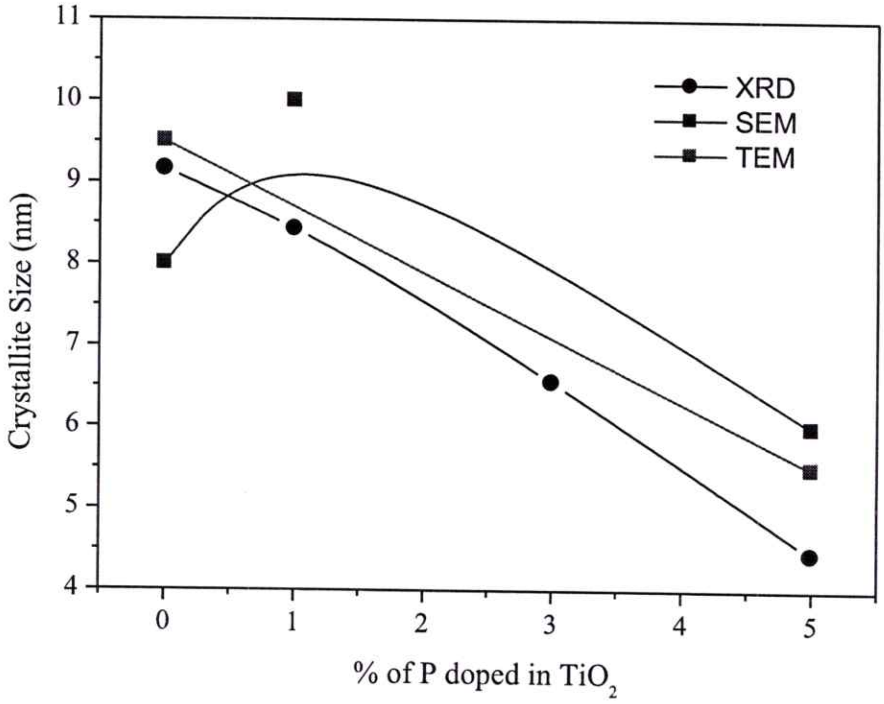


Figure 2: Variation of crystallite size with % of P doped in TiO_2 nanoparticles

Table 1: The average crystallite size

Bare TiO2			1 % P			3 % P			5 % P		
2θ	β	D (nm)	2θ	β	D (nm)	2θ	β	D (nm)	2θ	β	D (nm)
25.41	0.81	10.03	25.38	0.89	9.14	25.41	1.10	7.38	25.19	2.97	2.74
38.03	1.28	6.58	37.95	1.56	5.39	38.00	1.67	5.03	27.97	1.62	5.07
48.14	0.91	9.53	48.12	0.83	10.52	48.14	1.07	8.16	48.10	1.45	5.99
54.13	0.79	11.34	54.74	1.53	5.86	54.76	1.73	5.19	54.70	2.23	4.02
62.81	1.16	8.01	62.84	0.83	11.26	62.96	1.32	7.05			
Average D (nm)		9.10			8.43			6.56			4.45

3.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of bare and 1, 3 and 5 mole% P are shown in **Figure 3**. The FTIR of bare and various mole% of TiO_2 shown broad bands at 3240 and 1640 cm^{-1} is corresponding to the -OH stretching and bending vibrations of chemical adsorbed water and hydroxyl groups [39]. As the mole% of P increases, these bands became broader and stronger than that for the bare TiO_2 [40]. The P doping is responsible for high adsorption capacity of the TiO_2 due to their large surface area. The absorption bands shown at 1040, 1095, and 1125 cm^{-1} is attributed to the doped materials, signifying the chemical environment of the P in the TiO_2. These bands are corresponding to P-O vibration [41]. The broad peak at 1095 cm^{-1} is attributed to the ν3 vibration of the phosphate ions coordinated with TiO_2. The ν2 vibration of the phosphate in a bidentate state (associating at surface) is shown band at 1125 cm^{-1}, and the peak at 1040 cm^{-1} is related to Ti-O-P framework vibrations [42]. It means that P perhaps would exist in the surface as bidentate phosphate and Ti-O-P bonds forming in the lattice [43]. The broad adsorption peak present at 800 cm^{-1} for all materials is assigned to Ti-O-Ti vibration if Ti is in octahedral environment [44].

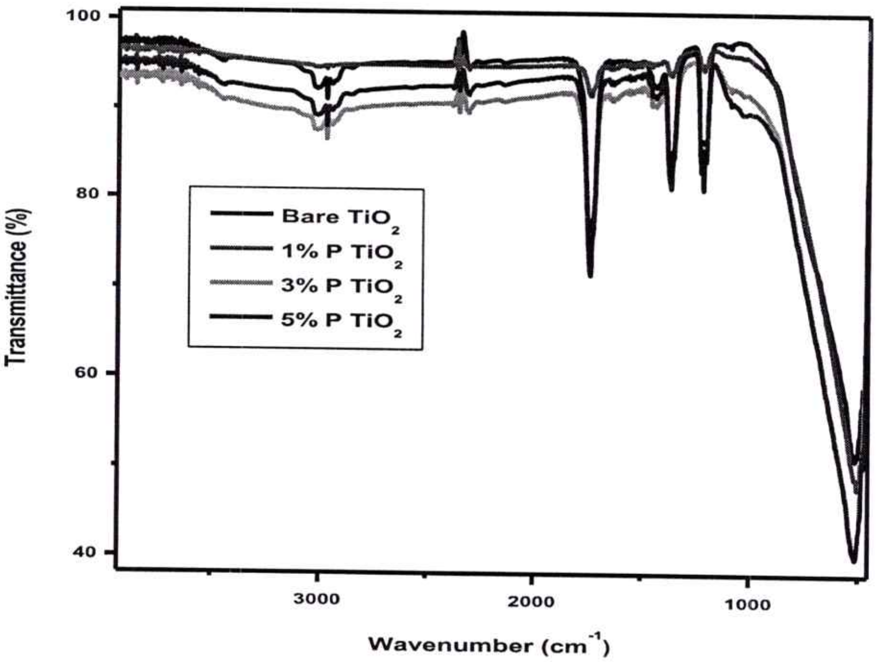


Figure 3: FTIR spectra of bare TiO_2 and P-doped TiO_2 nanoparticles

3.3 Field emission scanning electron microscopy (FESEM)

Morphology of bare TiO_2, 1 mole% and 5 mole % P doped TiO_2 synthesized by using *sol-gel* method and calcined at 500 °C is shown in **Figure 4** (a), (c)and (e) FESEM images shown the surface. It is apparent from these images that the P doped TiO_2 were included of non-spherical particles with an average diameter of 5 - 10 nm of its particle size. The size of particles was estimated by measuring the diameter of the particles from Gaussian fitting of Histograms. **Figure 4** (b, d, f) represents the particle size distribution Gaussian fitting of Histograms, and average particle size is determined. The histogram shows an average size distribution is 8 nm. The average particle size determined from Gaussian fitting is in close concurrence with the particle size calculated from XRD analysis. The P doped TiO_2 is compared with the bare TiO_2, the diameter and morphology did not change significantly because the amount of P doped on TiO_2 was very less, so the TiO_2 doped of P in the SEM image is difficult to observe effectively. The variation of particle size with mole % of P is shown in **Figure 4**

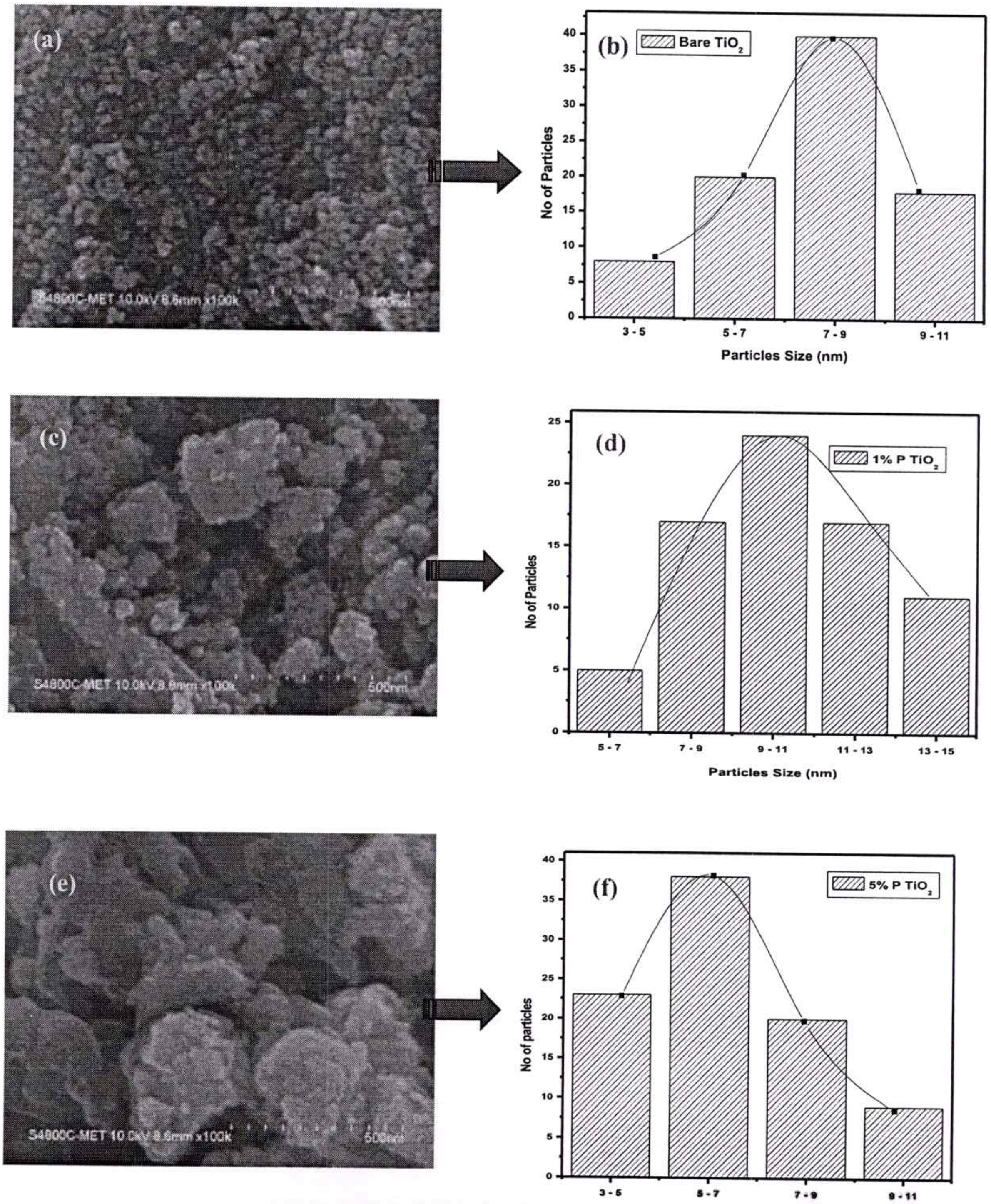
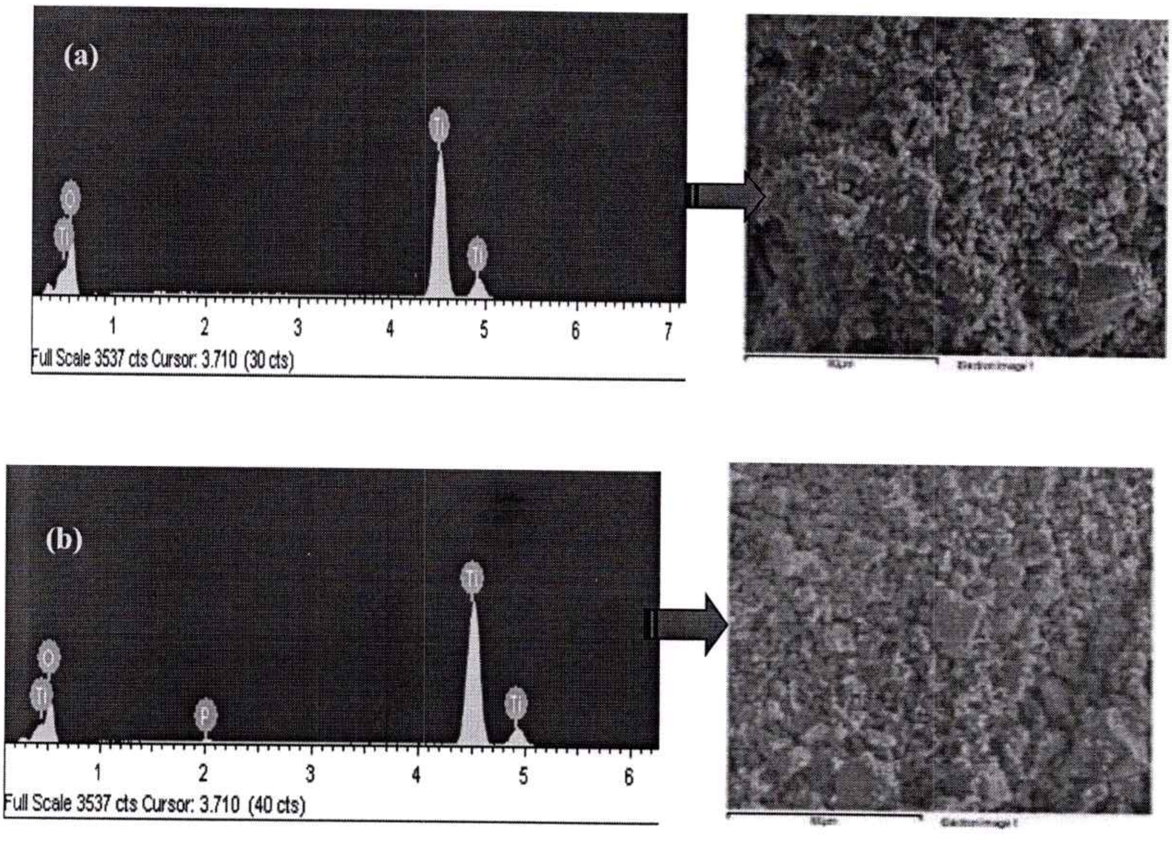


Figure 4: FESEM images of (a) bare TiO_2, (c) 1% P doped TiO_2 and (e) 5% P doped TiO_2 and corresponding histograms of samples (b), (d) and (f)

3.4 EDAX analysis

The elemental composition of P doped TiO_2 spheres with varying amounts of P doping calcined at 500 °C was analyzed using EDAX. EDAX was used to determine the elemental composition of the nanoparticles and the representative patterns are shown in **Figure 5**(a), (b) and (c). These patterns reveal the presence of Ti, P, O elements in the doped samples element. It can be observed that the intensity of the P peak corresponding to emission lines at 2.0 keV($K\alpha 1$) increases with increasing P doping by comparing the EDAX spectra of the P doped samples with that of bare TiO_2. The presence of a 0.3, 0.4, 0.5, 0.6, 4.5 and 4.9 keV ($L\alpha 1$) peaks are attributed to the Ti and O. In **Figure 5** (a), only Ti and O elements were detected in bare TiO_2 powder, while in **Figure 5** (b) and (c), P was detected in addition to Ti and O elements. P doped TiO_2, indicating that P was successfully doped on the TiO_2. Elemental composition of Ti, O and P in weight% and atomic% shown in **Table 2**.



ISSN NO : 1006-6748

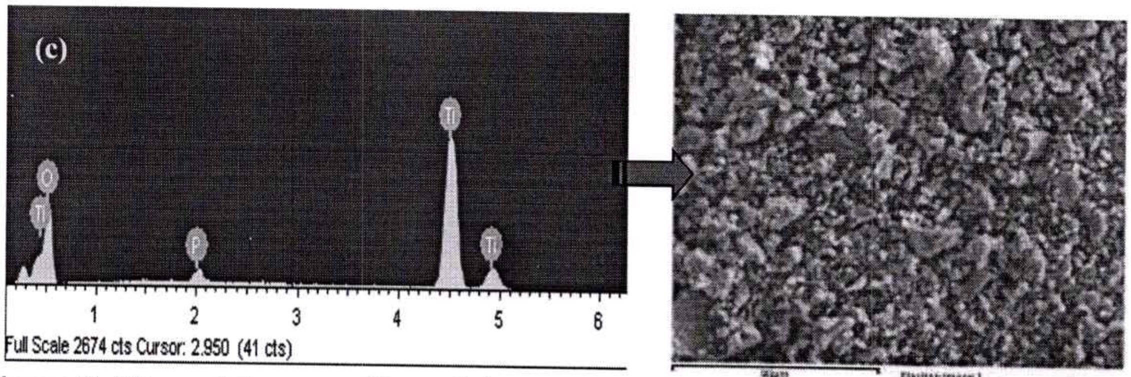


Figure 5: Elemental composition of (a) bare TiO_2, (b) 1% P, and (c) 5% P doped TiO_2 nanoparticles and the representative patterns of EDAX

Table 2: Elemental composition in weight% and atomic%

Sample	Element	Weight%	Atomic%
Bare TiO_2	O K	22.78	46.90
	Ti K	77.22	53.10
	P L	0	0
1 mole % P	O K	18.57	40.52
	Ti K	81.10	59.10
	P L	0.33	0.38
5 mole % P	O K	17.29	38.49
	Ti K	82.06	61.51
	P L	1.42	1.45
Total		100%	

3.5 High resolution transmission electron microscopy (HR-TEM)

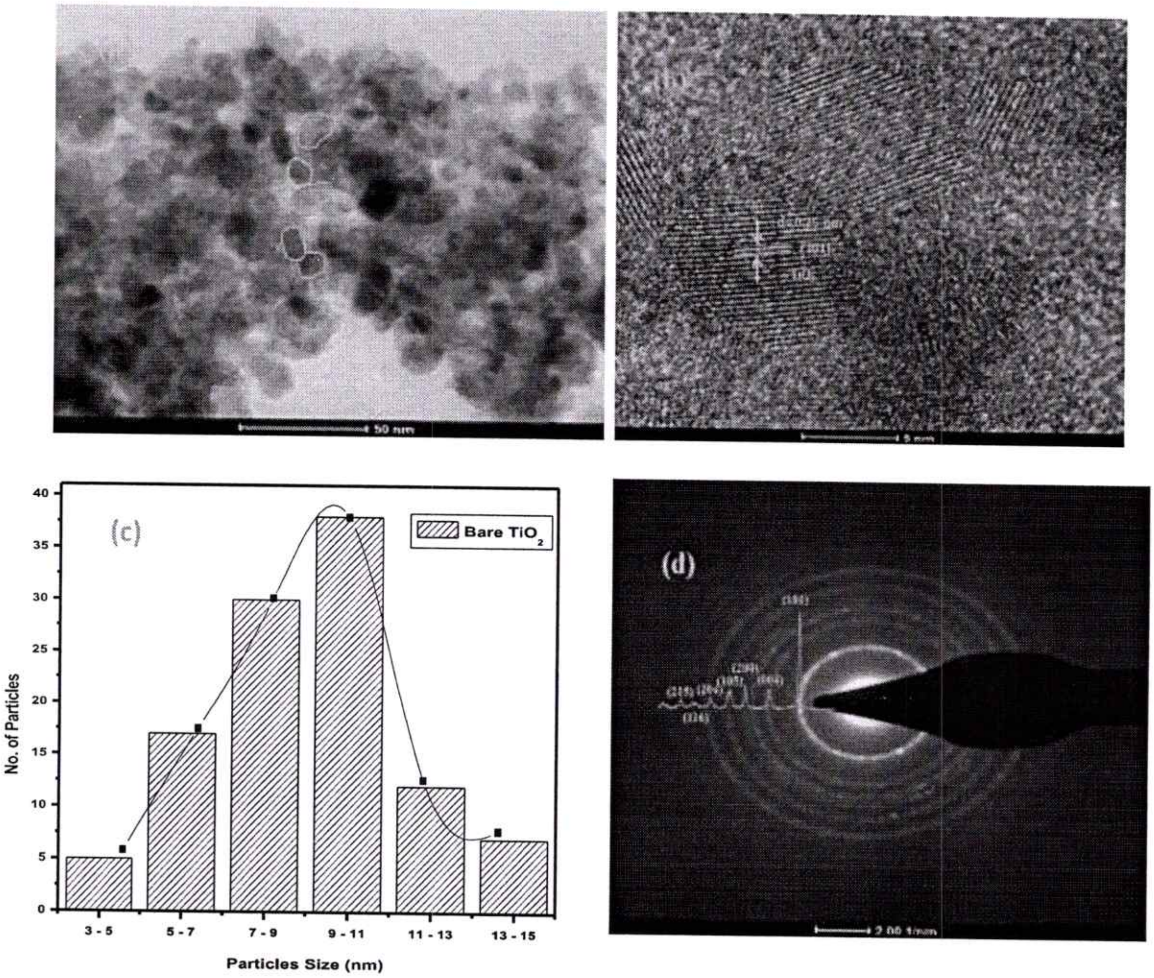


Figure 6 : (a, b, c, d) shows the TEM, High-resolution TEM (HR-TEM), Histogram of particle size and selected area electron diffraction (SAED) pattern for bare TiO$_2$

HR-TEM technique was used to analyze the surface morphology and particle structure of bare and P doped TiO$_2$ nanoparticles. The representative HR-TEM images of the bare TiO$_2$ are shown **Figure 6** (a) to (d) shows the TEM, high-resolution TEM (HR-TEM), histogram of particle size and selected area electron diffraction (SAED) pattern. These images confirm that the bare TiO$_2$ particles show a spherical-like structure with a size distribution from 9 to 11 nm. While morphological structure of P doped TiO$_2$ shown in **Figure 7** (a) to (d) confirm that the 5 mole % P doped TiO$_2$ nanoparticles are elongated-spherical in shape with an average size of 5-7 nm. The nanoparticles are clearly observed in all the images, which shown the high degree of crystallinity. The particle size of 5 mole % P doped TiO$_2$ nanoparticles are less than that of bare TiO$_2$ NPs, which is similar with the crystallite size obtained from XRD. Further observation by SAED **Figure 6** (d) and in **Figure 7** (d) confirmed that the nanoparticles are well crystalline in nature with tetragonal anatase structure.

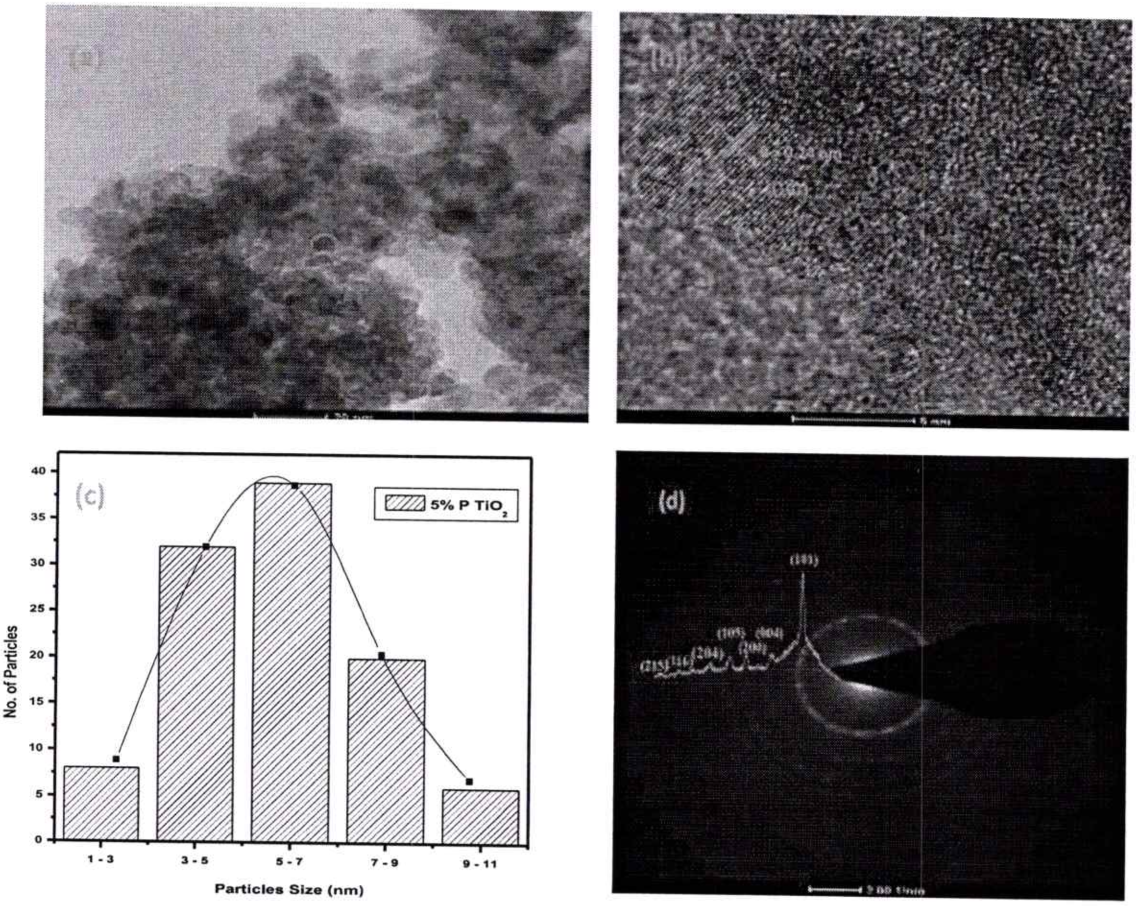


Figure 7 : (a, b, c, d) shows the TEM, High-resolution TEM (HR-TEM), Histogram of particle size and selected area electron diffraction (SAED) pattern for 5 mole% P doped TiO_2

3.6 UV–Visible diffuse reflectance spectroscopy

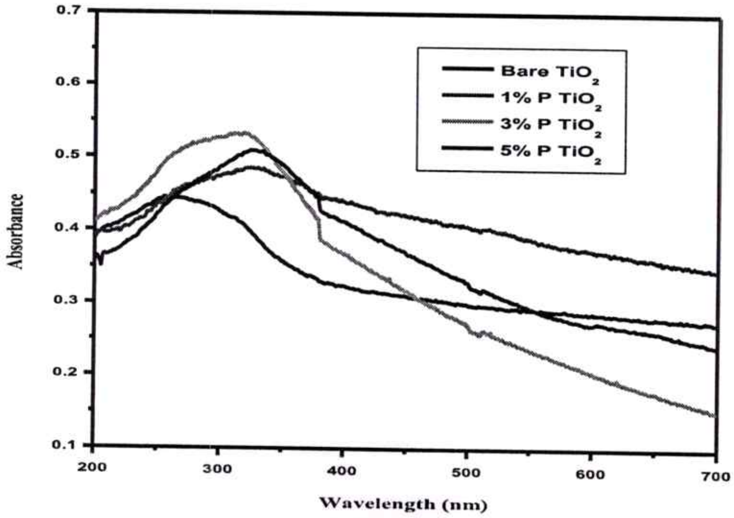


Figure 8: UV-Visible DRS (absorption mode) spectra of bare TiO_2 and 1, 3 and 5 mole % P doped TiO_2 NPs

UV-Visible diffused reflectance spectroscopy (DRS) was used for the investigation of the optical properties and band gap energies of the synthesized materials. **Figure 8** shows the UV-Visible DRS (absorption mode) spectra of bare TiO_2 NPs shows the optical absorption edge in the wavelength region between 250 to 390 nm [45], while compared to P doped TiO_2 (1, 3 and 5 mole % P) shows the shifting its absorption edge from UV to visible region, indicates doping of P in the TiO_2 lattice. As the mole% of P increases in the TiO_2, the visible absorption edge shifted towards higher absorbance as well as higher wavelength region; this is reflected through decrease in the optical band gap. The P-doped TiO_2 samples shown stronger absorption edge in the range of wavelengths from 400 to 550 nm compared to bare TiO_2 [46]. In their electronic structure calculations of phosphorus cation-doped anatase TiO_2 found the band gap narrowing because of the substitution of pentavalent phosphorus (P^{5+}) into Ti^{4+} sites [47].

The optical energy band gap of the P doped TiO_2 was determined by plotting the Tauc plot $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) and fixed from the intercept tangent to the x-axis [45] and presented in **Figure 9**.

The energy band gap decreases from 3.2 to 2.0 eV as the doping of mole % of P increases as 1, 3 and 5 mole %. The doping of phosphorous in the TiO_2 lattice, the band gap is lowered to 2.37 eV for 1 mole% P, further reduced to 2.25 eV for 3 mole% P and 2.0 eV for 5 mole% P doping in TiO_2. This absorption enhancement with decrease in band gap in the visible region can be assigned to the formation of dopant level nearer the valance band [48- 50]. The decrease in the optical energy band gap of the P doped TiO_2 NPs, leads to increase in optical absorption.

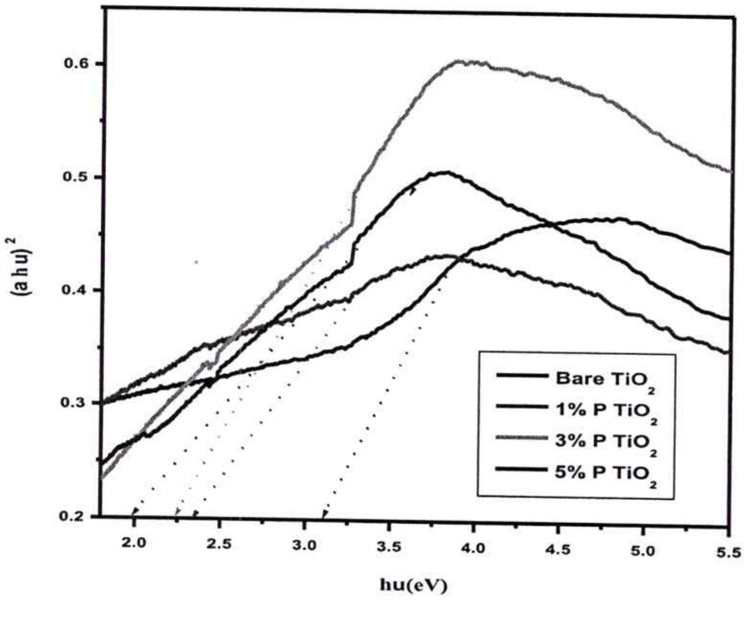


Figure 9: Tauc plot $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) of TiO_2 and P doped TiO_2 NPs with 1, 3, and 5 mole % P

4. Conclusion

The experimental results suggest that, the P doped TiO_2 influenced the structural, morphological, and optical properties significantly. UV-DRS studies investigate that the doping of P ion can directly shift band gap of semiconductors into the visible region. The energy band gap decreases from 3.2 to 2.0 eV as the doping of mole % of P increases as 1, 3 and 5 mole %. P doping can effectively decrease the recombination rate of photogenerated charges in TiO_2. FTIR spectra were investigated, as the mole% of P increases; these bands became broader and stronger than that for the bare TiO_2. The P doping is responsible for high adsorption capacity of the TiO_2 due to their large surface area. The absorption bands shown at 1040, 1095, and 1125 cm^{-1} is attributed to the doped materials, signifying the chemical environment of the P in the TiO_2. These bands are corresponding to P-O vibration. The broad peak at 1095 cm^{-1} is attributed to the ν3 vibration of the phosphate ions coordinated with TiO_2. The ν2 vibration of the phosphate in a bidentate state (associating at surface) is shown band at 1125 cm^{-1}, and the peak at 1040 cm^{-1} is related to Ti-O-P framework vibrations. It means that P perhaps would exist in the surface as bidentate phosphate and Ti-O-P bonds forming in the lattice. Morphology of bare and various mole % P doped TiO_2 analyzed by using FESEM images. It is apparent from these images that the P doped TiO_2 were included of non-spherical particles with an average diameter of 5 - 10 nm of its particle size. XRD data were investigate, no peak phase assigned to P was observed with doping concentration, the crystal structure of doped TiO_2 samples shows stability of anatase phase when compared with that of bare TiO_2 sample. EDAX studies revealed that the intensity of the P peak corresponding to emission lines at 2.0 keV(Kα1) increases with increasing P doping by comparing the EDAX spectra of the P doped samples with that of bare TiO_2. The presence of a 0.3, 0.4, 0.5, 0.6, 4.5 and 4.9 keV (Lα1) peaks are attributed to the Ti and O. HRTEM images were investigate the morphology of P doped TiO_2 nanoparticles are elongated-spherical in shape with an average size of 5-7 nm. The particle size of 5 mole % P doped TiO_2 nanoparticles are less than that of bare TiO_2 NPs, which is similar with the crystallite size obtained from XRD.

Acknowledgment

Author deeply acknowledges to C-MET, Pune, Principal, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad and Shri Chhatrapati Shivaji Mahavidyalaya, Omerga for providing the research facilities.

References

[1] Sturini M, Speltini A, Maraschi F, et al. Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight [J]. Applied Catalysis B: Environmental, 2012, 119: 32-39.

[2] Pfaff G, Reynders P. Angle-dependent optical effects deriving from submicron structures of films and pigments [J]. Chemical reviews, 1999, 99 (7): 1963-1982.

[3] Yuan S, Chen W, Hu S. Fabrication of TiO2 nanoparticles/surfactant polymer complex film on glassy carbon electrode and its application to sensing trace dopamine [J]. Materials Science & Engineering C, 2005, 25 (4): 479-485.

[4] Wu H B, Hng H H, Lou X W. Direct synthesis of anatase TiO_2 nanowires with enhanced photocatalytic activity [J]. Advanced Materials, 2012, 24 (19): 2567-2571.

[5] Peng Y, Le Z, Wen M, et al. Mesoporous single-crystal-like TiO2 mesocages threaded with carbon nanotubes for high-performance electrochemical energy storage [J]. Nano Energy, 2017, 35: 44-51.

[6] Zhao G, Pang H, Liu G, et al. Co-porphyrin/Carbon nitride hybrids for improved photocatalytic CO_2 reduction under visible light [J]. Applied Catalysis B: Environmental, 2016, 200: 141-149.

[7] Bian Z, Zhu J, Li H. Solvothermal alcoholysis synthesis of hierarchical TiO_2 with enhanced activity in environmental and energy photocatalysis [J]. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2016, 28: 72-86.

[8] Zhao, Zhao, Xiaoyan, et al. Effect of defects on photocatalytic activity of rutile TiO_2 nanorods [J]. Nano Research, 2015, 8 (12): 4061-4071.

[9] Zhu Y, Wang Y, Ling Q, et al. Enhancement of full-spectrum photocatalytic activity over $BiPO_4$ /Bi_2WO_6 composites [J]. Applied Catalysis B: Environmental, 2016, 200: 222-229.

[10] Xiao S, Zhu W, Liu P, et al. CNTs threaded (001) exposed TiO_2 with high activity in photocatalytic NO oxidation [J]. Nanoscale, 2015, 8 (5): 2899-2907.

[11] Zhang H, Wei J, Dong J, et al. Efficient Visible Light Driven Carbon Dioxide Reduction by a Single Atom Implanted Metal – Organic Framework [J]. Angewandte Chemie, 2016, 128 (46): 14522-14526.

[12] Zhu W, Liu P, Xiao S, et al. Microwave-assisted synthesis of Ag-doped MOFs-like organotitanium polymer with high activity in visible-light driven photocatalytic NO oxidization [J]. Applied Catalysis B: Environmental, 2015, 172: 46-51.

[13] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode [J]. Nature, 1972, 238 (5358): 37-38.

[14] Chen X, Mao S S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications [J]. Cheminform, 2007, 107 (7): 2891-2959.

[15] Wang Z, Lou X W. TiO_2 nanocages: fast synthesis, interior functionalization and improved lithium storage properties [J]. Advanced Materials, 2012, 24 (30): 4124-4129.

[16] Murphy A B, Barnes P R F, Randeniya L K, et al. Efficiency of solar water splitting using semiconductor electrodes [J]. International Journal of Hydrogen Energy, 2006, 31 (14): 1999-2017.

[17] Xu M, Da P, Wu H, et al. Controlled Sn-Doping in TiO_2 Nanowire Photoanodes with Enhanced Photoelectrochemical Conversion [J]. Nano Letters, 2012, 12 (3): 1503-1508.

[18] Wang Y, Zhang Y Y, Tang J, et al. Simultaneous etching and doping of TiO_2 nanowire arrays for enhanced photoelectrochemical performance [J]. Acs Nano, 2013, 7 (10): 9375-9383.

[19] Hu C C, Hsu T C, Kao L H. One-Step Cohydrothermal Synthesis of Nitrogen-Doped Titanium Oxide Nanotubes with Enhanced Visible Light Photocatalytic Activity [J]. International Journal of Photoenergy, 2012, 2012 (51): 1302-1312.

[20] Sun H, Zhou G, Liu S, et al. Visible light responsive titania photocatalysts codoped by nitrogen and metal (Fe, Ni, Ag, or Pt) for remediation of aqueous pollutants [J]. Chemical Engineering Journal, 2013, 231 (9): 18-25.

[21] Shin S H, Chun H H, Jo W K. Enhanced Photocatalytic Efficiency of N-F-Co Embedded Titania under Visible Light Exposure for Removal of Indoor-Level Pollutants [J]. Materials, 2014, 8 (1): 31-41.

[22] Hamadanian M, Jabbari V, Shamshiri M, et al. Preparation of novel hetero-nanostructures and high efficient visible light-active photocatalyst using incorporation of CNT as an electron-transfer channel into the support TiO_2 and PbS [J]. Journal of the Taiwan Institute of Chemical Engineers, 2013, 44 (5): 748-757.

[23] Ding S, Chen J S, Luan D, et al. Graphene-supported anatase TiO_2 nanosheets for fast lithium storage [J]. Chemical Communications, 2011, 47 (20): 5780-5782.

[24] Yan J, Wu G, Dai W, et al. Synthetic Design of Gold Nanoparticles on Anatase TiO_2 {001} for Enhanced Visible Light Harvesting [J]. Acs Sustainable Chem Eng, 2014, 2 (8): 1940-1946.

[25] Alcadipani R. Hydrothermal Synthesis of Nitrogen-Doped Titanium Dioxide and Evaluation of Its Visible Light Photocatalytic Activity [J]. International Journal of Photoenergy, 2012, 2012 (2): 2058-2069.

[26] Jia T, Fu F, Zhao J, et al. Sonochemical Synthesis, Characterization, and Photocatalytic Activity of N-Doped TiO_2 Nanocrystals with Mesoporous Structure [J]. Materials Technology, 2014, 2014 (6): 372-376.

[27] Fang J, Wang F, Qian K, et al. Bifunctional N-Doped Mesoporous TiO_2 Photocatalysts [J]. Journal of Physical Chemistry C, 2014, 112 (46): 18150-18156.

[28] Peres A, Ron A. N-TiO2 Photocatalysts highly active under visible irradiation for NO_X abatement and 2-propanol oxidation [J]. Catalysis Today, 2013, 206 (1): 19-25.

[29] Shin S W, Lee J Y, Ahn K S, et al. Visible Light Absorbing TiO_2 Nanotube Arrays by Sulfur Treatment for Photoelectrochemical Water Splitting [J]. Journal of Physical Chemistry C, 2015, 119 (24): 13375-13383.

[30] Ma X Z, Jin B, Wang H Y, et al. S-TiO_2 composite cathode materials for lithium/sulfur batteries [J]. Journal of Electroanalytical Chemistry, 2015, 736: 127-131.

[31] Han C, Pelaez M, Likodimos V, et al. Innovative visible light-activated sulfur doped TiO_2 films for water treatment [J]. Applied Catalysis B: Environmental, 2011, 107 (1-2): 77-87.

[32] Khan M, Gul S R, Li J, et al. Variations in the structural, electronic and optical properties of N-doped TiO_2 with increasing N doping concentration [J]. Modern Physics Letters B, 2015, 29 (8): 1550022.

[33] Liu Y, Wu Y, Zhou Y, et al. Direct Synthesis of Urchin-Like N-doped TiO_2 Microstructures with Enhanced Photocatalytic Properties [J]. Transactions of the Indian Ceramic Society, 2016, 75 (3): 155-160.

[34] Huang Z, Feng J, Pan W. Electronic Structure and Optical Properties of N-Doped Anatase TiO_2 by First-Principles Calculations [J]. Rare Metal Materials & Engineering, 2011, 40 (22): 475-477.

[35] Kuo C Y, Wu C H, Wu J T, et al. Synthesis and characterization of a phosphorus-doped TiO_2 immobilized bed for the photodegradation of bisphenol A under UV and sunlight irradiation [J]. Reaction Kinetics, Mechanisms and Catalysis, 2015, 114 (2): 753-766.

[36] Elghniji K, Soro J, Rossignol S, et al. A simple route for the preparation of P-modified TiO_2 : Effect of phosphorus on thermal stability and photocatalytic activity [J]. Journal of the Taiwan Institute of Chemical Engineers, 2012, 43 (1): 132-139.

[37] Pan X, Yang M Q, Fu X, et al. Defective TiO_2 with oxygen vacancies: synthesis, properties and photocatalytic applications [J]. Nanoscale, 2013, 5 (9): 3601-3614

[38] Li X, Song J, Liu Y, et al. Controlling oxygen vacancies and properties of ZnO [J]. Current Applied Physics, 2014, 14 (3): 521-527.

[39] L. Wang, Y. Yamauchi, Chemistry of Materials, 21 (2009) 3562.

[40] Lertpaitoonpan W, Ong S, Moorman T (2009) Effect of organic carbon and pH on soil sorption of sulfamethazine. Chemosphere 76:558– 564. https://doi.org/10.1016/j.chemosphere.2009.02.066

[41] Xia Y, Jiang Y, Li F (2014) Effect of calcined atmosphere on the photocatalytic activity of P-doped TiO_2. Appl Surf Sci 289:306–315. https://doi.org/10.1016/j.apsusc.2013.10.157

[42] Elghniji K, Soro J, Rossignol S, Ksibi M (2012) A simple route for the preparation of P-modified TiO_2: effect of phosphorus on thermal stability and photocatalytic activity. J Taiwan Inst Chem Eng 43: 132–139. https://doi.org/10.1016/j.jtice.2011.06.011

[43] Körösi L, Papp S, Bertóti I, Dékány I (2007) Surface and bulk composition, structure, and photocatalytic activity of phosphate-modified TiO_2. Chem Mater 19:4811–4819. https://doi.org/10.1021/cm070692r

[44] Yu J, Zhang L, Zheng Z, Zhao J (2003) Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity. Chem Mater 15:2280–2286. https://doi.org/10.1021/cm0340781

[45] G. Cheng, M. S. Akhtar, O.-B. Yang, F. J. Stadler, *ACS Appl. Mater. Interfaces* 2013, *5*, 6635-6642.

[46] Y. Zhou, Y. Liu, P. Liu, W. Zhang, M. Xing, J. Zhang, A facile approach to further improve the substitution of nitrogen into reduced TiO_2_x with an enhanced photocatalytic activity, Appl. Catal. B Environ. 170e171 (2015) 66e73, http:// dx.doi.org/10.1016/j.apcatb.2015.01.036.

[47] Zheng, R. Y.; Lin, L.; Xie, J. L.; Zhu, Y. X.; Xie, Y. C. J. Phys. Chem. C 2008, 112, 15502

[48] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669.

[49] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, J. Phys. Chem. Solids 63 (2002) 1909.

[50] J. Ben Naceur, R. Mechiakh, F. Bousbih, R. Chtourou, Appl. Surf. Sci. 257 (2011) 10699.

CHAPTER 4

Role of Data Science in Modern World for Better Lifestyle

Sandhya Jagtap

Department of Computer Science, Ramkrishna Paramhansa Mahavidyalaya,
Osmanabad, Maharshtra, India
Email:jagtapsandhya12@gmail.com

Abstract

Today's market is changing in incredible ways with an increased buzz around AI and machine learning. Data science assists these new technologies by figuring out solutions to problems by linking similar data for future use. Data Science is considered one of the best job fields of the 21st century. It is the combined study of mathematics, statistics and computer science (including domain and programming expertise); which is used to drawing out the insight of both structured and unstructured data. This topic tells what is mean by data science .also different roles of data science in our life. Data science technology provides us new facilities for better life style. Data science is being used everywhere. Institutions are opening their doors to data science. This topic covers various applications of data science in modern world. It can help people make better decisions, solve problems, and discover new insights.

Keywords: Data Science, Finance, E-Commerce, Healthcare sector, Travel industry, Sports

Introduction

Data is come across over the various sites of internet, also various app used in mobile such as what Sapp, Facebook, Instagram, Google pay, phone pay and many more. All these data resides on server side. The modern technology has enabled the creation and storage of information, data volumes has exploded .It estimated that 90 percent of data in world was created in the two years.

For example:-Facebook users upload 10 million photos every hour it is not exact value but much more.

The data stored by this technology can bring transformative benefits to organisms and societies around the world but only we interpret that data. On these concepts Data Science technics are come in.

Data Science combines multiple fields as mathematics, statistics, algorithms, scientific methods, artificial intelligence (AI), data analysis. Who practices the data science called as data scientists. Data Scientists collects all data from web, smartphones, customers, sensor, and other resources .on collected data, Data scientists apply method process, and different algorithms to analysis the data n extract knowledge from it also find certain patterns from it for future perdition. This provide a robust forecasting model to predict phone prices in European markets using Long Short-Term Memory (LSTM) neural network and Support Vector Regression (SVR) (Bakir et al., 2018).

Data science uses structured and unstructured data. Data science enables you to translate a business problem into a research project and then translate it back into a practical solution.

In computer field data is base of any innovation buts its values come from the information. Data scientist gain that value form data and act upon it.To understand data science technics we understood the other correlated field of data science such as Machine learning, Artificial intelligence, Deep learning.

1) **Machine learning:-** It is subset of Artificial Intelligence. It automates any machine without interaction of human being .It learns any machine on basis of data.
2) **Artificial Intelligence:-**It learn the any machine or software on the basis of data also by observation ,also by the image capturing technics and so on
3) **Deep Learning:-**It is subset of machine learning. It creates algorithms that operate as functions of brain. It also called as artificial neural networks.

Data science play important role in medical fields. Hospitals and insurance companies must demonstrate efficiency and the improved health of its customers to remain compliant with government policy changes and stay competitive in the free market. From medical devices and insurance claims, to scribbled doctors' prescriptions and social media sites, the data in healthcare is massive and messy. One of the promises of organizing and analyzing those data is the ability to predict the future, with the goal of early intervention preventing heart attacks or hip fractures from happening in the first place (Dembosky 2012).

Data Science is future of artificial Intelligence. Data Science helps us on the basis of past history data. The segmentation is based on customers' commercial activity and role within the site's social network. In this social network, customers profit from the transactions they make on affiliate websites (Ballestar et al., 2018).

For Example: I like reading books, I always purchase book online on amazon. Each time while purchasing the book I was confused because there are lots options of book on amazon. At that time amazon gives recommendation of product depend on my previous data which books I purchased .when I chose one of them again amazon give recommendation which one book mostly bought by other customers. So recommendation on the basis of previous history of customers is one of the examples of Data science.

Roll of Data Science in Different Field

1) In search engine:

Our search engines are Google, yahoo, safari, n so on. When I search certain topics on that engines they give top most visited links on my webpage .The technics behind it is web mining which is part of data science.

For example:-

When I search the data science for beginners on Google then Google server serves the no of application but starting few applications are top most visited by users for topic data science .This is by data science technics.

2) In travel field:

Now a days data science enter in this field best example for this is Driverless car, this concepts help to reduce accident which is increased now a days. In this car trained data is feed in algorithms .with help of data analysis technics car is to be instructed like what speed is maintain on highway on traffics road, on narrow road with the help of algorithms created with given data and data science technics car is trained how to drive on different situation without driver.

3) In E-Commerce:

Flipkart, AMEZON, Meesho, Myntra are e-commerce websites people will purchase items from that websites or app. At the time of purchasing anything the website give us recommendation on the basis of previous purchases history. Also give recommendation for most selling items and most trending items. This is because of technology of data science. WEB Mining in data science checks the history of all records in websites and gives conclusion in the form of recommendation what user will purchase.

4) In Finance:

In finance, data science play important role. Finance company always need strategic decisions in risk condition of company .Data science analytics tools help the company for predicting future on the basis of past history , records of company. It allows the companies to predict customer lifetime value and their stock market moves.

In stock market Data scientist always check past behavior of shares of any company and predict the future rating of that company ,that their shares Can moves up or down .If values are be up then how much rate company got profit .If share value be down then company faces loss problem in what percentage. Data is analyzed in such a way that it makes it possible to predict future stock prices over a set timetable.

5) In Target recommendation:

It is most important application of data science. Target recommendation means whatever user search on internet, they will see numerous post everywhere in the forms of ads.

Example: if we want to search learn data science on Google website, then web mining technics gives recommendation related topics of data science on various apps on mobile like Facebook, YouTube in the form of ads such as courses related data science, where it is needed.

6) In health care sector :-

All new technology of health care field is come under the concepts of data science. Data science used for diseases diagnosis, various scans reports, analysis of DNA and gens of patients and much more.

To diagnosis disease data science various technics are used .The demonstration of Diagnosing asthma and chronic obstructive pulmonary disease with machine learning (Spathis and Vlamos 2019).

Depend on patients history we have to take some decision before patients goes to next stage or to avoid future bad results of patients health so machine learning algothims helps to do preauthorization decisions (Araújo et al., 2016).

i) Medical image processing:

X-ray, CT scan, MRI scan show inner most part of body .By deep learning in data science it is possible to find microscopic scanned image.so defects present in the parts find easily .By deep learning algorithms machines can trained how the actual parts looks human body so defects presents are easily find by computer and generate the reports on it.

ii) Detecting tumors

iii) Genetics and Genomics

Genomics is study of DNA & GENS of organisms .Before Data Science, organisms spend much more time & money for analysis of DNA & GENS.But with Data Science tools it is possible to analyzes gens in short time with low cost. It also finds irregularity & defects in gens .it also find relation between genetics & person.

iv) Drugs discovers used in medicines

7) Sports:-

In sports Data scientists with the past history of team & players in it, predict how team will played what is future score of team .Also who will win the match, which player scored much run, each players scores they predict .All these future prediction is made on the basis of collected past history data .Data Science analysis the data in past history also find pattern of players playing games technics and gives prediction on that. Game theory provides a compelling guide for analyzing business decisions and strategies (Chatterjee and Samuelson 2001).

Conclusion

This topic tells scope and future of data science in the world. Each area is covered with technology of data science .Data Science will ability to take all area that have complex's challenges. There are lots of opportunities for data scientist in various fields. Data Science is interdisciplinary field which collect data, analysis data .After that used for various task.

References

Bakir H, Chniti G, Zaher H, 2018. E-Commerce Price Forecasting Using LSTM Neural Networks. International Journal of Machine Learning and Computing, 8, 169-174.

Ballestar MT, Grau-Carles P, Sainz J, 2018. Customer segmentation in e-commerce: Applications to the cashback business model. Journal of Business Research, 88, 407-414.

Dembosky A, 2012. Data Prescription for Better Healthcare. Financial Times, p. 19.

Cao L, 2017. Data science: challenges and directions. Commun. ACM 60(8), 59–68.

Craja P, Kim A, Lessmann S, 2020. Deep learning for detecting financial statement fraud. Decis. Support Syst. 139, 113421.

Araújo FHD, Santana AM, Neto PDAS, 2016. Using machine learning to support healthcare professionals in making preauthorisation decisions. Int. J. Med. Inform. 94, 1–7.

Chatterjee K, Samuelson W, 2001. Game Theory and Business Applications. Springer, Berlin.

Fang K, Jiang Y, Song M, 2016. Customer profitability forecasting using big data analytics: A case study of the insurance industry. Comput. Ind. Eng. 101, 554–564.

Spathis D, Vlamos P, 2019. Diagnosing asthma and chronic obstructive pulmonary disease with machine learning. Health Inform. J. 25(3), 811–827.

लोककवी वामनदादा कर्डकांच्या बुध्दगीतांचे सामाजिक महत्त्व

- प्रा. डॉ. शिवाजी संभाजी गायकवाड
मराठी विभाग प्रमुख
रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद
मो.नं. 8999483211
ईमेल : ssgaikwad20@gmail.com

लोककवी वामनदादा कर्डक म्हणजे आधुनिक युगातले महान कलावंत होते. सामाजिक परिवर्तनाच्या चळवळीतील चालतं बोलतं विद्यापीठ म्हणजे वामनदादा कर्डक होय. त्यांचा जन्म 15 ऑगस्ट 1922 देशवंडी ता. सिन्नर जि. नाशिक येथे झाला. मृत्यु 15 मे 2004 रोजी वयाच्या 81 व्या वर्षी झाला. वामनदादांच्या घरी 18 एकर शेती असली तरी जगणे हालाखीचे असायचे. शेतीचा हंगाम संपला की, त्यांच्या आई-वडीलांना मोलमजूरी करावी लागत असत. आषाढ श्रावणात तर पोटाची खूप आभाळ व्हायची. कधी तरवटयाची, कधी माठाची तर कधी भाजी विना नुसती भाकर खाऊनच दिवस काढावे लागत असत. वयाच्या 19-20 व्या वर्षी वामन दादांचे पत्नी अनुसयाशी विवाह झाला त्यांना मीरा नावाची एक मुलगीही झाली. पत्नीचे व वामनदादाचे घरी जमत नसल्याने फारकत घेऊन पत्नी माहेरी गेली, पुढे दोन वर्षाची मुलगी मीरा हीचेही आजारपणाने निधन झाले. आई सईबाई वडील तबाजी यांच्या सोबत पोटाची खळगी भरण्यासाठी मुंबईला आले शिवडीच्या बीडीडी चाळीत राहून त्यांना चिक्की विक्रीचा, आईसफ्रुटची विक्री केली. वखारीत कधीही कोळसा उचलला. तेथेच त्यांनी समता सौनिक दलात सामील झाले. त्या चाळीत रहात असताना एका व्यक्तीने वामनदादांना पत्र वाचून दाखवण्यासाठी विनंती केली. गरिबीमुळे शिक्षण घेता आले नसल्याने अक्षरांचा परिचय नव्हता तेंव्हा त्यांना खूप वाईट वाटले ते पत्र वाचून दाखवता आले नाही. त्यांना थोडे बहुत शिकावे वाटले. शेजारी राहणाज्या देहलवी नावाच्या मास्तरांकडून त्यांनी मुळाक्षरे, बाराखडी समजून घेतली तेथूनच त्यांना वाचनाची, लिहिण्याची आवड निर्माण झाली. समता सौनिक दलात काम करताना पहिल्यांदा ते 1943 साली डॉ. बाबासाहेबांना पाहिले आणि डॉ. आंबेडकरांचा विचार समाजापर्यंत पोहंचण्यासाठी प्रबोधनात्मक गीते लिहीत राहिले. पुढे 14 ऑक्टोंबर 1956 साली डॉ. बाबासाहेबांनी नागपूर येथे बौध्दधम्माची दीक्षा घेतली त्याचा साक्षीदार म्हणून वामनदादा जवळून हे पाहत होते, ऐकत होते आणि तेंव्हापासून त्यांना गौतम बुध्दाच्या विचारांची ओढ लागली, बुध्द त्यांच्या प्रतिभेप्रमाणे समजून घेत बुध्दगीतांची रचना केली त्यांच्या बुध्दगीतांनी समाजाचे प्रबोधन केले समाजाला नितीमूल्य शिकविले. अशिक्षित जनतेपर्यंत बुध्दाचा विचार समजून सांगण्यासाठी वामनदादांचीबुध्दगीते महत्वाची भूमिका बजावली. त्यांच्या बुध्दगीतांचे समाजात असणारे महत्त्व पुढील प्रमाणे विशद करता येईल

उद्देश :-

1) लोककवी वामनदादा कर्डकांच्या बुध्दगीतामागील प्रेरणा समजू न घेणे
2) गौतम बुध्दाच्या त्रिशरण पंचशीलाचे समाजातील महत्त्व समजावून सांगणे
3) भांडवलदारी देशाला युध्दापेक्षा बुध्दविचारांची किती गरज आहे हे वामनदादांच्या गीताद्वारे स्पट करणे
4) बोधगया येथील पिंपळवृक्षाचे महत्त्व स्पष्ट करणे.

लोककवी वामनदादा कर्डक यांनी 1973 साली 'वाटचाल' 1976 साली 'मोहळ' व 1977 साली 'हे गीत वामनाचे'

असे तीन गीत संग्रहाचे प्रकाशन केले 1996 साली 'माझ्या जीवनाचं गाणं' हे आत्मकथन प्रकाशित केले. याशिवाय 'सांगत्ये ऐका' या चित्रपटासाठी 'सांगा ह्या वेडीला' तर 'पंचारती' चित्रपटासाठी ' चल गं हरणे तुरुतुरु' हे गीत लिहून दिले. त्यांच्या विविध प्रकारच्या रचना बरोबरच बुध्दगीतांचेही लेखन केले आहे त्यांच्या बुध्दगीतांमधून प्रज्ञा, शील, समाधी, समता, बंधूता इत्यादी मानवी जीवनमूल्यांचे दर्शन घडते बुध्दविचार समजून सांगण्यासाठी त्या गीतांना स्वरचित चाली लावूनस्वत:च्या आवाजात गाऊन दाखविल्याने समाजाच्या अंत:करणापर्यंत बुध्दांचा विचार पोहंचविण्यात ते यशस्वी झाले. तो विचार बुध्दगीताद्वारे सांगण्यासाठी त्यांनी माध्यम म्हणून मराठीतील साधी, सोपी अनलंकृत भाषेची निवड केली, त्यामुळे वामनदादांची बुध्दगीते लोकांना मुखोद्गत झाली आहेत. ते नागपूरच्या धम्मदिक्षा सोहळयाचे व डॉ. आंबेडकरांनी उच्चारलेल्या पालीभाषेचे वर्णन करताना 'तो भारताचा वाली' या गीतात वामनदादा लिहितात, "तो भारताचा वाली, एकोणीशे छप्पन साली त्या बोधीवृक्षाखाली आम्ही पाहिला. दीक्षा घेता मंगल काली, बोल बोलताना पाली"[1] डॉ. बाबासाहेब आंबेडकरांनी दीक्षा घेताना गौतमबुध्दाच्या काळातील सर्वसामान्यांच्या जीवना बोलली जाणारी जी पाली भाषा होती. त्या प्राकृत भाषेतून त्रिशरण, पंचशीलेचा उच्चार केला होता. त्यामुळे पुन्हा एकदा बोधीवृक्षाखालील आधुनिक मौत्रेय बुध्द म्हणून लोकांनी डॉ. आंबेडकरांना डोळयात साठवून ठेवले आहे असे यथार्थ वर्णन वामन दादांनी वरील गीतांतून केले आहे पुढे 'नवा नूर' या गीतातून वामनदादा लिहितात, घडले हे छप्पन साली, क्रांतीची लाट आली, आली ती लाट आली, मुक्तीची वाट झाली, मायलेकरांची तेथे पून्हा भेट झाली. क्रांतीचे गीत गाया, ममता पेरीत जाया, लाभले कवीला नवे सूर, रंगला भूमीचा नूर"[2]

उक्त ओळीतून असे निदर्शनास येते की, या धम्मीदीक्षेच्या प्रसंगानेच कवी वामनदादाना बुध्दगीते लिहिण्याची खरी प्रेरणा मिळाली असे म्हणता येते. नवासूर लाभणे म्हणजे वामनदादाला बुध्दांची नवीन ओळख झाली आणि आपल्या मगदूराप्रमाणे बुध्दाला समजून घेत त्यांनी बुध्दगीते लिहीली आहेत श्रावस्तीची नगरवधू म्हणून प्रसिध्द असलेली आम्रपाली बुध्ददर्शनाने प्रभावीत होऊन तथागताला गुरु मानून धम्मदीक्षा घेऊन स्वतचा आणि समाजाचा उध्दार केली. त्या प्रसंगाचे वर्णन करताना पिंपळाच्या झाडाखाली आली आम्रपाली या गीतात ते लिहितात. "नाद नर्तनाचा सोडला म्हणाली, घडा पातकाचा फोडला म्हणाली, गुरु हाच आता जोडला म्हणाली, पिंपळाच्या झाडाखाली आली आम्रपाली"[3]

आम्रपालीच्या संपूर्ण व्यक्तीमत्वाचे दर्शन मोजक्या व सार्थ शब्दांत वामनदादांनीमांडल्याचे निदर्शनास येते. वरील ओळी वाचताना आम्रपालीच्या पूर्व व उत्तर कालीन जीवनाचा उलगडा होत जातो. याच मोहळ गीतसंग्रहात तुझीच कमाई या गीतात वामनदादा लिहितात "वाळून ज्यांची पाने गळाली, घालून पाणी अशा फुलवेळी, फुलवून गेली तूच ठाई ठाई, कुणाचेच काही इथे कष्ट नाही"[4]

बोधीवृक्षाची पाने वठलेली होती. परंतू त्याची मूळे हिरवी होती त्या वठलेल्या बुध्दधम्माला डॉ. बाबासाहेब आंबेडकरांनी पुन्हा एकदा धम्मदीक्षा घेऊन पूर्नजिवीत केले बुध्दधम्माला पुन्हा एकदा या भारतात नवी पालवी फुटली. बाबासाहेबांच्या कष्टामुळेच हा वृक्षआज बहरलेला आहे, याची वरील ओळीतून सत्यता पटते.

ते त्रिसरणाची वाणी या कवीतेत लिहितात, "त्रिसरणाची वीणा वाजे, पंचशिलांचे टाळ, भजन करारे भगवंताचे, आज सांज सकाळ, जीवन जळता संसारी, भजन हे तारी"[5] प्रापंचीक जीवन जगणाऱ्यांना वरील ओळीतून ते सल्ला देतात संसार दु:खमय आहे, प्रत्येक जीवाला सुख आणि शांती हवी असेल तर बुध्दांच्या त्रिसरणाची व पंचशीलतेची कास धरली पाहीजे असे निक्षून सांगताना दिसतात.

भारतदेशाला करोडो रुपयांचा घोटाळा करुन दारिद्रयात आणि संकटात टाकणाऱ्यांना बुध्दाच्या विचारांची किती गरज आहे, हे सांगताना बुध्दाच्या चरणी या गीतात वामनदादा लिहितात, "दारिद्रय आणि निराशा, कारण सर्वांच्या नाशा, कुणीही येईल पायी तुडवील आपुल्या भारत देशा, बडव्यांनो, धनदडव्यांनो, देशसंकटी बुडव्यांनो, अंतर्शुध्दी करुन जल्दी नष्ट करा काळी करणी"[6]

याच गीतात पुढे ते लिहितात, "नरभक्षक दारु गोळा, रशियाने केला गोळा सर्व जगाच्या संपत्तीवर अमेरिकेचा डोळा आज अशा संकटकाळी ना बुध्दावाचून वाली, ऐक वामन नमेल दुष्मन अग्निचे होईल पाणी"[7]

संपत्तीची अतिहाव भारत देशाला दारिद्रयात लोटण्यास कारणीभूत ठरते तेंव्हा अशा व्यक्तींना अंत:करण व मन शुध्द करण्याचा सल्ला वामनदादा देतात. अंत:करण व मने शुध्द करण्याचे सामथ्र्य बुध्द विचारात आहे असा त्यांचा ठाम विश्वास आहे. त्यासाठी बुध्दाची विपश्यना जीवनात उपयोगी पडते. महासत्ता होण्यासाठी रशिया व अमेरिका यांची स्पर्धा सुरु आहे एकमेकांना नष्ट करु पाहण्याची वृत्ती काही देशात निर्माण झाली आहे. अशा भांडवलदारी देशाने जगाला युध्दाच्या खाईत लोटण्यासाठी सज्ज आहेत, तेंव्हा एकमेकावर कुरघोडी करुन महासत्ता बनण्याची जी तृष्णा आहे, तिला नष्ट करण्यासाठी अशा

स्पर्धायुक्त जगाला बुध्दाच्या तत्त्वज्ञानाची गरज आहे. बुध्दाविचारानेच दुष्मनाची आग शांत होईल तेंव्हा युध्दापेक्षा जगाला बुध्दाची गरज आहे याची वरील ओळीतून सत्यता पटते.

बबन लोंढे यांनी वामनदादांच्या गीतांच्या संदर्भात लिहितात "त्यांच्या गीतांनी समाजप्रबोधन तर केलंच, पण सामाजिक परिवर्तनाची क्रांतिज्योत अखंड तेवत ठेवली. या ज्योतीनं अनेक ज्योती उजळल्या"[8] वामनदादांच्या गीतांनी हजारो कलावंत निर्माण केले आजच्या नवकलावंताकडे पाहिल्यास याची सत्यता पटते .

ज्या बोधीवृक्षाखाली सिध्दार्थ गौतमाला ज्ञानप्राप्ती झाली त्या वृक्षाचे अप्रूप वाटताना वामनदादा 'साऊली गोड तुझी' या गीतात लिहितात, "बोधीवृक्षा मला लागली ओढ तुझी साऊली गोड तुझी, साऊली गोड तुझी, तुझ्या छायेत आणि मायेच्या पंखाखाली, इथेच गौतमाला ज्ञानाची प्राप्ती झाली, तुझ्या तोडीला जगी नाही तोड दुजी"[9]

पिंपळवृक्ष हा सिध्दार्थाच्या ज्ञानप्राप्तीची प्रेरणा आहे म्हणूनच त्या वृक्षाशी कोणताही वृक्ष बरोबरी करु शकत नाही हे वामनदादांनी निक्षून सांगितले.

समारोप :-

लोककवी वामनदादा कर्डकांच्या गीतांनी गौतमबुध्द घरोघरी पोहंचण्यासाठी महत्वाचा वाटा उचलला आहे बुध्दाचे तत्त्वज्ञान व संदेश अशिक्षित माणसापर्यंत पोहंचविण्याचे मौलिक कार्य वामनदादांच्या गीतांनी केले आहे सामान्य माणसाच्या अंत:करणाचा ठाव घेणारी त्यांची प्रतिभा विलक्षण होती. तिला मराठी भाषेत तोड नाही. त्यांच्या वाणीत गोडवा होता. रसिकांना खिळवून ठेवण्याचे सामथ्र्य होते. त्याची गाणी म्हणजे कोंडलेल्या मनाचा हुंकार होता. त्यांचा हुंकार लय तत्त्वाचा अंदाज घेत मनाचे बांध फोडून रुवणारा होता वामनदादांची गीते प्रचारकी वाटत असली तरी त्यात समाजाचे मूर्तीमंत स्वरुप आहे. मानवी संघर्षाचे धागे उकलून दाखविले आहे. त्यांची गीते मानवी संघर्षाला सामोरे जातात वामनदादा स्वत:च्या गीताबद्दल म्हणतात, माझे गीत कवितेच्या कसोटीस उतरले किंवा नाही ही शंकाच आहे. जे सादर होत आहे त्यातही दोष आहेत. यात वीटा नाहीत. चिरेही नाहीत, ही मातीची ढेकळं जिथं बसतील तिथं बसवा ना तर माती आहेच. स्वत:च्या गीताबद्दल इतक्या प्रांजलपणे, तटस्थतेने भाष्य करणारा लोककवी वामनदादा मराठी कवीमध्ये विरळाच आहे असे म्हणावे लागेल. त्यांच्या बुध्दगीतांचा अभ्यास करताना आजच्या समाजाला बुध्दविचारांची किती गरज आहे ते दिसून येते

निष्कर्ष :-

1) डॉ. बाबासाहेब आंबेडकरांच्या धम्मदीक्षेमुळेचं वामनदादा कर्डक यांनी बुध्दगीतांचे लेखन केल्याचे निदर्शास येते.
2) संसारिक जीवन जगत असताना प्रत्येकाने त्रिशरण व पंचशीलेची कास धरली पाहिजे तरच प्रत्येक जीवाला सुख व शांती लाभू शकते असे वामनदादा म्हणताना दिसतात
3) भ्रष्टाचाराच्या माध्यमातून देशाला संकटात टाकणाज्या धनदडव्यांना देशाप्रती मन व अंतकरण शुध्द ठेवण्याचा सल्ला वामनदादा देताना दिसतात.
4) महासत्तेच्या तृष्णेने जगाला युध्दाच्या खाईत लेटणाज्या भांडवली देशाने युध्दापेक्षा बुध्दाचा स्वीकार केला तर जगात शांतता नांदेल असा वामनदादांना विश्वास आहे
5) बोधीवृक्ष हा सिध्दार्थाच्या ज्ञानप्राप्तीची खरी प्रेरणा आहे असे सांगताना त्या वृक्षाला जगात तोड नाही असा गौरव करतात.

संदर्भ सूची :-

1) वामन कर्डक 'मोहळ', आनंद प्रकाशन जयसिंगपूर, आठवी आवृत्ती, 7 नोव्हेंबर 2013, औरंगाबाद, पृष्ठ क्र. 24.
2) तत्रैव, पृ.क्र. 25.
3) तत्रैव, पृ.क्र. 21.
4) तत्रैव, पृ.क्र. 26.
5) तत्रैव, पृ.क्र. 28.
6) तत्रैव, पृ.क्र. 30.
7) तत्रैव, पृ.क्र. 30.
8) बबन लोंढे 'एका कवीचे जीवनगाणे', ग्रंथाली प्रकाशन, प्रथमावृत्ती, 4 ऑगस्ट 2012, मुंबई, पृष्ठ क्र. 06.
9) वामन कर्डक, 'मोहळ', उनि, पृ.क्र. 133.

◆ ◆ ◆ ◆ ◆

ISSN 2349-638x
Impact Factor 6.293

AAYUSHI INTERNATIONAL INTERDISCIPLINARY RESEARCH JOURNAL

PEER REVIEW & INDEXED JOURNAL

Email id : aiirjpramod@gmail.com
www.aiirjournal.com

SPECIAL ISSUE No. 65

Executive Editor
Dr. S.M. Maner
Principal
Tuljabhavani Mahavidyalaya,
Tuljapur, Dist. Osmanabad (M. S.)

Co-Editor
Prof.G.V.Baviskar
Head, Dept. of History
Tuljabhavani Mahavidyalaya,
Tuljapur, Dist. Osmanabad (M. S.)

Co-Editor
Dr. B.V.Gund
Head, Dept. of Pol.Sci.
Tuljabhavani Mahavidyalaya,
Tuljapur, Dist. Osmanabad (M. S.)

Co-Editor
Prof. B.J.Kukde
Head, Dept. of Sociology
Tuljabhavani Mahavidyalaya,
Tuljapur, Dist. Osmanabad (M.

Chief Editor
Prof. Pramod Tandale

भारतीय स्त्रियांच्या राजकीय स्थितीचा अभ्यास

प्रा. स्वाती प्रकाशराव बैनवाड
(राज्यशास्त्र विभाग)
रामकृष्ण परमहंस महाविद्यालय, उस्मानाबाद.

1) प्रस्तावना :-

भारतीय समाजव्यवस्थेत स्त्रियांची स्थिती काळानुरूप बदलत गेलेली आहे पूर्व वैदिक काळामध्ये स्त्रियांची स्थिती खूप मजबूत होती व त्यांना प्रतिष्ठा देखील प्राप्त होती परंतु कालांतराने त्यांच्या स्थितीत हळूहळू बदल होत गेला काळ बदलला तसे स्त्रियांचा दर्जा समाजव्यवस्थेमध्ये खालावला पूर्व वैदिक काळात शास्त्रार्थ पुरुषांना हरवणारी स्त्री कालांतराने केवळ घरातील चौकटीतच अडकून पडली पुरुषांची दासी झाली. पूर्व वैदिक कालखंडात स्त्रियांना संपूर्ण स्वातंत्र्य होते त्यात त्यांना स्वतःच्या अनुरूप जोडीदार निवडण्याचे देखील स्वातंत्र्य होते पूर्व वैदिक कालखंडात स्त्रियांमध्ये पडदा पद्धत नव्हती त्या पुनर्विवाह करू शकत होत्या त्यांना शिक्षणाचा व संध्या करण्याचा अधिकार होता पण नंतर उत्तर वैदिक कालखंडात मात्र बालविवाहाची पद्धत आली त्यामुळे स्त्रियांची शिक्षणाची सोय बंद झाली व पतीला दैवत्व प्राप्त झाले ही स्थिती हळूहळू खालावतच गेली या पुढील काळात वैदिक आधार जाऊन त्याची जागा मनुस्मृतीने घेतली मनुस्मृतीनुसार " स्त्रिया कधीच स्वतंत्र राहण्याच्या योग्य नाहीत लहानपणी वडिलांच्या नियंत्रणात तरुणपणी पती तर म्हातारपणी पुत्राच्या नियंत्रणात राहिली पाहिजे " व पुढे त्यांना संपत्तीच्या अधिकारातून देखील वंचित करण्यात आले.

मध्ययुगानंतरतर इस्लामिक राजवटीच्या स्थापनेनंतर हे नियम अधिकच कडक बनले पडदा पद्धत आली सती प्रथा आली, व बहुपत्नीत्व प्रतिष्ठेची बाब बनली तर स्त्रियांचे विवाह 5-8 वर्षातच लावले जाऊ लागले पुरुष प्रधान संस्कृती अजूनच बळकट बनली.

पूर्व वैदिक कालखंडातील तिचे प्रबळ स्थान मध्ययुगात दयनीय बनले तर आज आधुनिक कालखंडात तर ती स्वतःच्या अस्तित्वासाठी लढताना दिसून येत आहे सदर शोधनिबंधात भारतीय राजकारणातील स्त्रियांच्या स्थितीचा अभ्यास करण्याचा प्रयत्न करण्यात येणार आहे.

2) संशोधनाची उद्दिष्टे :-

i) स्त्रियांची सध्याची राजकीय स्थिती अभ्यासणे.

ii) राजकारणात काम करत असताना स्त्रियांच्या समोर उद्भवणाऱ्या समस्यांचा अभ्यास करणे.

3) संशोधन पद्धती :-

प्रस्तुत शोध निबंधातील माहिती दुय्यम साधन सामग्री द्वारे मिळवली आहे त्यामध्ये प्रामुख्याने संदर्भ, ग्रंथ, मासिक, ग्रंथ, विविध संकेत स्थळे यांचा अवलंब केला आहे.

4) भारतीय महिलांची राजकीय स्थिती :-

भारतीय राज्यघटनेने महिलांना पुरुषांच्याबरोबरीने स्थान दिली आहे असे असले तरी राजकारणात मात्र त्यांचे स्थान कमी प्रमाणात दिसून येते पुरुषप्रधान संस्कृतीचा तो दृश्य परिणाम आहे. स्वातंत्र्योत्तर कालखंडातील राजकारणातील त्यांचे स्थान हे स्वातंत्र्य चळवळीतील त्यांच्या सहभागीतेमुळे दिसून येते महात्मा गांधीजींच्या स्वातंत्र्य आंदोलनातील चळवळीतून महिलांचा सहभाग वाढला व त्या नव्या भूमिकेत दिसून आल्या.

19 व्या शतकात झालेली समाज सुधारणेची चळवळ व स्त्री शिक्षणाचा प्रसार यामुळे महिलांच्या स्थितीत सुधारणा होण्यास सुरुवात झाली परंतु ही स्थिती काही विशिष्ट गटा पुरतीच मर्यादित होती त्यात शहरी भागातील सुशिक्षित व उच्च जातींच्या स्त्रियांचा समावेश होता समाजातील उर्वरित ते यांचा हाच दृष्टिकोन होता की त्या केवळ कौटुंबिक जबाबदारी सांभाळू शकतात पुढे जाऊन मात्र काही स्त्रियांनी सुधारणा चळवळीत भाग घेतला सुरुवातीच्या कालखंडात एक लहानसा गट यात सहभागी झाला ज्यात सर्व धर्मातील उच्च जातीच्या स्त्रियांचा सहभाग होता व त्यात हिंदू धर्मातील स्त्रिया मोठ्या प्रमाणात सहभागी होत्या या सर्व स्त्रियांना या सहभागात त्यांच्या कुटुंबाने कधी उघड तर कधी गुप्त पद्धतीने पाठिंबा दिला. 19 व्या शतकाच्या प्रारंभी स्त्रियांमध्ये शिक्षणाचा प्रसार दिसून आला जो स्त्रियांच्या संघटनांमधूनदिसून आला ज्यात यापूर्वी कधीही नव्हता एवढ्या महिला त्यात सहभागी झालेल्या दिसून आल्या याच कालखंडात भारतीय महिला संघटना स्थापन झाली महिला चळवळीला ही संघटना समकक्ष ठरली.

इ. स. 1917 मध्ये पहिल्यांदा स्त्रियांना मताधिकार असावा ही मागणी पुढे आली 1917 मध्ये सरोजिनी नायडू यांनी पार्लमेंट कडे स्त्रियांच्या मताधिकाराची मागणी केली जो पुरुषांना आधीच प्राप्त होती या मागणीचा परिणाम म्हणजे स्त्रि पहिल्यांदा नागरिकत्वाचा दर्जा प्राप्त झाला.

इ. स. 1919 च्या मॉन्टेग्यू चेम्सफर्ड सुधारणा कायद्याने जवळजवळ दहा लाख महिलांना मतदानाचा अधिकार मि 1932 मध्ये त्यांना पहिल्यांदा मतदान करण्याची संधी मिळाली मथ्थू लक्ष्मी रेड्डी ह्या पहिल्यांदा मद्रास कायदे मंडळाव आलेल्या व त्याचबरोबर त्यांची निवड उपसभापती म्हणूनही करण्यात आली त्यांनी देवदासी प्रथेविरुद्ध पहिल्यांदा कायदा के या कुप्रथेपासून स्त्रियांना मुक्ती मिळवून दिली महिला चळवळीच्या मार्गदर्शक असणाऱ्या कमलादेवी चटोपाध्याय या देखील 19 मध्ये निवडून आल्या राधाबाई सुब्बरयान, रेणुकारॉय, अनु स्वामीनाथन या महिला केंद्रीय कायदे मंडळावर निवडून आल्या.

महात्मा गांधीजींनी स्त्रियांना स्वातंत्र्य आंदोलनात सहभागी होण्यासाठी जी हाक दिली ती भारतीय महिलांसाठी एक न युगाची सुरूवात होती त्यांना स्त्रियांच्या सहभागाचे महत्त्व माहीत होते. गांधीजींनी स्त्रियांची ताकद सत्याग्रहात दाखवून दि पुरुषांच्या तुलनेने खूप अधिक प्रमाणात होती त्यांच्यामध्ये अहिंसात्मक चळवळीमध्ये पुरुषांपेक्षा स्त्रियांचा अधिक फायदा कारण की सहनशीलता हा त्यांचा सर्वात मोठा गुण आहे त्या एकदा एखादी गोष्ट ठरविल्यानंतर ती पूर्ण होईपर्यंत मागे हटत नाही

1919 मध्ये रोलेट एक्ट विरुद्ध जी चळवळ उभारण्यात आली स्त्रिया मोठ्या प्रमाणात यात सहभागी झाल्या याच्या पु काळात 1930 मध्ये गांधीजींनी सविनय कायदेभंग अंतर्गत दांडी यात्रा काढली त्यात अनेक महिला सहभागी झाल्या विजयालक्ष्मी पंडित, कृष्णा सिंह, लक्ष्मी मेनन, सुशीला नायर, जयश्री रायजी, हंसा मेहता मनिबेन पटेल आणि म्हात्रे भगिनी समावेश होता. इतकेच नव्हे तर लीलावती मुंशी व सरोजिनी नायडू यांनी महिलांचे अनेक गट तयार केले व त्यांना मुंबईच्या भागात पाठवून मीठ तयार करण्यास सांगितले पुढे फक्त सहकारी म्हणून सहभागी होणाऱ्या स्त्रिया आता नेतृत्व देखील करू ला स्वदेशी चळवळ व सहकार चळवळ व सविनय कायदेभंग चळवळ यातून त्यांचा सहभाग अधोरेखित झाला.

1931 मध्ये सरोजिनी नायडू यांच्या अध्यक्षतेखाली मुंबई येथे एक सभा भरली ज्यात महत्वाचा मुद्दा हा होता की सर्व व्यक्तींना प्रौढ मताधिकाराचा अधिकार असावा व सर्वांना लिंगभेदावर राजकीय अधिकार असावेत 1931 कराची अधिवे पंडित नेहरूंच्या अध्यक्षतेखाली झाली. ज्यात नेहरूंनी स्त्री-पुरुषांचा समान मूलभूत अधिकार असतील ज्यात राजकीय अधिकारा समावेश ही असेल असे त्यांनी स्पष्ट केले. 1937 च्या निवडणुकीत महिलांचा मत अधिकाराचा विस्तार झाला 1937 च्या निवडणुकीत 42 महिला कायदे मंडळावर निवडून आल्या व पाच महिलांना वरिष्ठ सभागृहात नियुक्त करण्यात आले.

1942 चले जाव (छोडो भारत आंदोलन) आंदोलनातील वरिष्ठ नेते जेव्हा तुरुंगवासात होते व ही चळवळ नेतृत्वहीन झाली तेव्हा स्त्रियांनी हे आंदोलन पुढे नेले ज्यात सभा भरविणे सत्याग्रह घडवून आणणे असे उपक्रम करीत होत्या अरुणा असफ अली कल्पना जोशी, प्रीती वडेर, रुपावती जैन, दुर्गाबाईसुशिलादेवी, उषा मेहता यांचा 1942 च्या चळवळीत सहभाग होता 1943 मध्ये सुभाष चंद्र बोस यांनी महिलांसाठी एक सैन्य तुकडी बनविली ज्याचे नाव "झाशीची राणी रेजिमेंट" असे ठेवण्यात आले व त्याच्या प्रमुख लक्ष्मी सेहगल ह्या झाल्या.

त्यानंतर भारताला स्वातंत्र्याचे वेध लागले व जात महिलांचा सहभाग अजूनच जास्त वाढला संविधान सभेची स्थापना ऑक्टोबर 1947 मध्ये झाल्यानंतर सरोजिनी नायडू, दुर्गाबाईदेशमुख, रेणुका रॉय, आणि हंसा मेहता त्यात सहभागी झाल्या.

स्वातंत्र्यानंतरच्याकालखंडात स्त्रियांचा राजकारणातील सहभाग वाढला अनेक स्त्रिया राजकारणात सहभागी झाल्या पण ह सहभाग अत्यल्प आहे. 1993 मधील 73 व्या व 74 व्या घटनादुरुस्तीनेमहिलांना स्थानिक स्वराज्य संस्थेत 33 टक्के आरक्षण दि गेले स्त्रियांचा मतदानातील सहभाग वाढला आहे आणि बऱ्याच महिलांना राजकीय पक्षात देखील त्या महत्त्वाच्या पदावर आहे परंतु ही सहभागिता वाढलेली दिसत नाही भारतीय महिलांच्या लोकसभेतील सहभाग 14 % पेक्षा वाढलेला नाही पहिल्या लोकसभेत 22, 13 व्या लोकसभेत 42 महिला निवडून आल्या व ही टक्केवारी 9.2 % होती. तर 17 व्या लोकसभेत आतापर्यंतच्या इतिहासातील सर्वात जास्त म्हणजे 78 महिला प्रतिनिधी निवडून आले आहेत याची टक्केवारी 14 टक्के आहे 54 सदस्य असणाऱ्या या लोकसभेत केवळ 78 महिला आहेत एकूण 29 घटक राज्य पैकी सात घटक राज्य अशी आहेत तेथे एकही महिला उमेदवार निवडून आलेली नाही 48 % महिलांची लोकसंख्या असताना ही टक्केवारी 14 % आहे जी अत्यल्प असल्याचे दिसून येते.

लोकसभेतील महिला आरक्षणाचे विधेयक 1996 पासून सादर केले जात आहे, 1998 मध्ये जेव्हा हे विधेयक मांडले गेले तेव्हा लोकसभेत एवढा गोंधळ माजला व या आरक्षण विधेयकाची प्रत देखील फाडून फेकण्यात आली व आज 17 व्या लोकसभेत देखील हे विधेयक पास होण्याची वाट पाहणे एवढेच भारतीय महिला करीत आहेत.

5) निष्कर्ष :-

1. भारतीय राज्यघटनेने महिलांना पुरुषांच्या बरोबरीने समान [illegible] राजकारणात महिलांचे प्रमाण अत्यंत कमी असल्याचे दिसून येते.
2. समाज सुधारकांच्या कार्यामुळे महिलांच्या शिक्षणामध्ये वाढ होत गेली आहे परंतु ही वाढ [illegible] बाबतीत दिसून आली आहे मात्र ग्रामीण स्त्रिया मूळ आणि मूळ [illegible] आहेत.
3. सरोजिनी नायडू यांच्या प्रयत्नातून भारतीय महिलांना [illegible] अधिकार मिळाला.
4. स्वातंत्र्योत्तर कालखंडात [illegible] महिलांचा सहभाग अत्यल्प राहिला आहे.
5. 17 व्या लोकसभेत एकूण 29 घटक राज्यांपैकी सात घटक राज्यात एक ही महिला प्रतिनिधी निवडून आलेली नाही.
6. संसदेत 33 टक्के महिला आरक्षणाचे विधेयक अजूनही पारित होण्याच्या प्रतीक्षेत आहे.
7. स्त्रियांचा राजकारणातील सहभाग वाढावा यासाठी शासनाने लक्ष दिले पाहिजे.

6) सारांश :-

स्त्रियांची राजकारणात एक अढळ स्थान निर्माण करण्याची गरज आज निर्माण झाली आहे [illegible] एक ही महिला पंतप्रधान झाली नाही स्त्रियांना आरक्षण केवळ स्थानिक पातळीवर दिले गेले आहे [illegible] शकले नाही स्थानिक स्वराज्य संस्थेत हळूहळू बदल होताना दिसून येत आहे. [illegible] भारतीय राजकीय व्यवस्थेत स्त्रिया आपले महत्त्व स्थापित करताना दिसत आहेत [illegible] 17 व्या लोकसभेत महिला प्रतिनिधींची वाढती संख्या एक आशादायी चित्र निर्माण करत आहेत [illegible] राजकारणातील स्थिती सुधारण्यास मदत होताना दिसून येत आहे.

7) संदर्भग्रंथसूची :-

1) भागवत विद्युत "स्त्री - प्रश्नांची वाटचाल", प्रतिमा प्रकाशन, पुणे, प्रथमावृत्ती 8 मार्च 2004.
2) डॉ. सिंहल एस. सी., "समकालीन राजनीतिक मुद्दे", लक्ष्मीनारायण अग्रवाल, आग्रा, तृतीय आवृत्ती 2007.
3) Internet printout.

IMPACT FACTOR – 5.61 **LangLit** ISSN 2349-5189

An International Peer-Reviewed Open Access Journal

LangLit Latur (MS) Indi

AIPROAJ

SOCIAL REALISM IN THE RIOT

BHOVAL VIKAS GOVINDRAO,
Dept of English,
Ramkrishan Paramhans College,
Osmanabad.

ABSTRACT

Social Realism is a narrative technique. In every society, social problems have existed. Social problems like communal conflict, cultural issues, political interference, women discrimination, and corruptions. Artist is a product of the society in which he/ she grows up. It is natural for the author to present his experiences and social issues in his creative work. Shashi Tharoor is an Indian politician and he has spent his maximum time in politics that is on the ground level. In his novel Riot, he presented the Indian condition and the two communities' delicate relationship. The present paper focuses on the love-hate relationship between two communities (Hindu and Muslim)

Keywords: Communal Riots, Cultural Conflicts, Political Influence, Unity & Diversity, And Corruption.

Social Realism in Indian English literature refers to the portrayal of social, economic, and political realities in novels written in English by Indian authors. In the 1960s, Indian English literature began to move away from the dominant themes of colonialism and national identity and started to focus on the everyday lives and struggles of ordinary people. Many Indian English novels were written after the 1960s, therefore, depict social realities such as poverty, inequality, discrimination, and corruption, and address issues such as gender, caste, and class.

The following novels deal with themes of social issues *The God of Small Things* by Arundhati Roy, *The White Tiger* by Arvind Adiga, and *The Great Depression* by Amitav Ghosh. The above novels provide a glimpse into the lives and struggles of ordinary people in India and offer a commentary on the social and political realities of the country. They also highlight the complexities and contradictions of Indian society and the challenges faced by its people.

Shashi Tharoor is a notable Indian English novelist. He is a noted critic, public intellectual, columnist, and author of sixteen books. His notable works are The Great Indian Novel is a path-breaking satire.

The Riot, novel deals with one of the major problems of India, which is a Hindu-Muslim relation. In the novel various political, social, cultural, and religious problems are discussed. Politics plays a vital role to make the mind of the common person. The role of religion in the present century is essential but politicians have applied it as per their desires and for their benefit.

The novel moves around the relationship between Lakshman and his American friend Priscilla Hart, from US. She was killed in a riot that took place in Zalilgarh. The story was written in the interview form and the pages from the diaries of Priscilla Hart, Katharine Hart, Rudyard Hart, and from the journal of Lakshman.

Mr. and Mrs. Hart arrived at Air Port, Delhi; the airport was crowded as usual. They arrived in India to see where their daughter lived and what had happened to her. There is meeting with Shankar Das, project Director, HELP – US, Zalilgarh.

The condition of Zalilgarh's women and the roads are not posh. The people do not have a strong roof. Some pan stalls are along the roadside. The bodies of women are undernourished Miss. Priscilla Hart was here in Zalilgarh to bring change in the life of women. She talks to them but women used to ignore her. They serve men and had unprotected sex with their men she used the word, Abuser for the men who impregnate their wives after each year to allow misery with the rest. And rural women are said that it is God's desire. In the poem, she puts down the core Indian ladies' problem.

Hart wrote that Lakshman a District magistrate rich, soft sounds. He has arranged marriage and has a six-year-old daughter, Rekha. He guided about Hindu- Muslim relations in Zalilgarh as well as the mentality of both communities. British promoted divisions between Hindus and Muslims as a policy of "divide and rule". How the nationalist movement tried to involve everybody but the Muslim League broke away and called for a state of Pakistan. The country was partitioned in 1947 to give the Muslims a separate state. For the decades since the partition there have been small–scale problems in many parts of the country, riots pitting one group against the other, usually over the same religious procession or festival intruding on other religious group's space.

The Indian government invited a foreigner to invest money in the Indian market. Meanwhile, Mrs. Indira Gandhi was quite hostile to America and she proclaimed a state of emergency in mid – 1975 to destabilize her government. She banned the press and she locked her opponents. She had given dinner with American Ambassador Saxbe and she wanted to open up a door for American companies. Her younger son, Sanjay, was already talking to McDonald's about coming to India. Coke Company had been in India and Coke had limitless benefits in India. Mrs. Indira Gandhi adopted new policies for foreign investment.

Mehta, The head of the Coke in India, told to Rudyard Hart that India has passed a law called FERA, the Foreign Exchange Regulation Act, in 1973. Coke Company had to apply it seemed them as red tape runs in Indian veins means just excessive regulation or bureaucratic procedure. So Coke Company applied but the proposal was not sanctioned because of a bit of political hostility.

Some members of Parliament accused Coke of "*looting the Country and destroying the health of Indians". One firebrand socialist, George Fernandes, demanded to know, "What kind of a country is India, where you can get Coke in the cities but not clean drinking water in the villages?*" (Tharoor: 2001:31)

George Fernandis did not waste his time controlling all companies under his new ministry. IBM and Coke became his first victims. He demanded to be brought all companies under the ministry of Industries. But the chairman of Coke, Paul Austin said, *"If India wants Coke, they'll have to have on our terms."* (Ibid: 32) and the long pending application of Coke was rejected by the government. Coke was ordered to wind up in India. He tried to re-establish the Coke business in India. He invited it to please the Indian government but it was not possible for him.

Shashi Tharoor focuses on the political condition in India and how private companies try to get their work done using many tricks some time giving a heavy amount too.

Lakshman gave his views on the Indian social and political condition. As an administrator, he stated that there are five major sources of division in India – language, region, caste, class, and religion. There are thirty-five languages in India spoken by more than a million people each, and fifteen are spoken by more than ten million each. He denoted that have looked at the rupee note; one can see "ten rupees" written out in seventeen languages Hindi is supposed to be the national language, but half the country does not speak it. In the state of Lakshman, Tamil Nadu, one would not be answered, if he is asked for any information in Hindi. English would be welcomed. Language is one of the major factors that divide India. The government reorganized the state on linguistic lines, so most language groups have their own political entities to look towards to give expression to their linguistic identity. The next problem is class. In India, there is major two class one rich class and the poor class or the lower class. Another source of division is religion. *"Hinduism is great for encouraging social peace because everyone believes their suffering in this life is the result of misdeeds in a past one, and their miseries in this world will be addressed in the next if only they'd shut up and be good and accept things as they are, injustices included. So Hinduism is the best antidote to Marxism*". (Ibid: 43)

The religion breeds what the country call "communalism" – the sense of religious chauvinism that transforms itself into bigotry, and sometimes violence, against the followers of other faith. India had seen various kinds of clashes in history – Hindu – Muslim, Muslim – Sikh, Sikh – Hindu, and Hindu – Christian.

In India, many problems are created by religion, caste, and class but some are not inherent problems, but for their own benefit, these problems are created. The untouchable wants to undo three thousand years of discrimination. This type of demand is fair. Even to some extent the problems of Dalit people have been solved like giving quota in universities, reservation in a job, and eight–five seats in Parliament. Shashi Tharoor here denotes that every community in India enjoys its own life and still there is violence. Shashi Tharoor says that only Democracy will solve all problems of India.

Ram Charan Gupta, a local Hindu Chauvinist leader. He could not win the last election but he expected that he'll do better next time. When he was being interviewed he said that it was the glorious day of September, 15. The all leaders of his party launched the Ram Sila Poojan program.

Ram, the hero of the epic Ramayana, was born in Ayodhya in the treat-Yug, period of the Hindu calendar. It is the Ram Janmabhoomi, the birthplace of Ram. Pilgrims from all over India would come to worship Ram. But the Muslim king, Babar, not an Indian, a foreigner from central Asia, knocked it down. He built a big mosque, which was named after him, the Babri Masjid.

Ram Charan Gupta asked a question would Muslims be happy if some Hindu king had gone and built a temple to Ram in Macca? Here Ram Charan Gupta complained about Muslims. Before independence Hindus were yoked with Muslims, then British came, and things were no bitter. We thought after independence, everything would change. But nothing changed. The government used the name secularism and under secularism still, Hindus are being suppressed.

When many Muslims had migrated to Pakistan, nobody worshipped Babri Masjid, and a miracle occurred some devotees found that an idol of Ram had emerged spontaneously in the courtyard of the Mosque.

Indian government is atheist and communist. They do not believe even they forgot that English had left. It is English law they upheld not Indian justice, they said no. Neither Hindus nor Muslims could worship there. They refused to believe the idol hasemerged spontaneously; they claimed someone has put it there. So here Ram Charan Gupta asked question, *"Do we Hindus have no rights in our country."* (Ibid:53)

Ramcharan Gupta thought that since 1947 Indian Government has been doing injustice to Hindus. Muslim people stayed in India but their loyalty is to Pakistan. They are not native Indians. They are more loyal to a foreign religion. They are all converted from the Hindus faith of their ancestors, but they refuse to acknowledge conquerors from Arabia, Persia, or Samarkand. Let them go back to those places. Why did they stay here if they would assimilate into India?

Muslim people are too ambitious and Indian politicians are always in favour of Muslims. Here in the words of Ram Charan Gupta, *"The Muslims want more! And we had Muslim – loving rulers, like that brown Englishman Jawaharlal Nehru who was our first prime minister, to give it to them. Muslim men want four wives, whom they can divorce by chanting a phrase three times – so Nehru gives them the right to follow their own Personal Law instead of being subject to the civil code of the rest of the country. Muslims want to go abroad to worship at their Mecca, so the government pays for the ships and planes to take them there every year and the hotels and lodges for them to stay in on the way. I ask you, why should my tax money go to helping Muslims get closer to their foreign god?"* (Ibid: 55)

Even Muslims have their own educational institutions, with government subsidies.

Rajiv Gandhi, grandson of Nehru also worked only for Muslims. Here Shashi Tharoor gives the example of the Shah Banu case. The Muslim woman does not get alimony as their religion does not give permission. So Rajiv Gandhi had gone against the Supreme Court's decision and made changes in the constitution and Shah Banu did not get alimony. So only for vote Bank Rajiv Gandhi made changes in the law.

In an incident, a Hindu boy is murdered by two Muslim men so Ram Charan Gupta and other Hindu people visit the police station but the police have not taken it seriously, and later the file remains pending and police try to bring peace between the two communities. Police departments try to maintain law and order in society. But already a Hindu boy is murdered. So the police said that Ram Sila Poojan Program has awakened the fear of the minority community.

Professor Mohammad Sarwar, a professor at Delhi University, and wants to research a man called Syed Salar Masaud Ghazi, popularly known as Ghazi Miyan. Actually, he wants to dig out the truth which would bring social stability especially Hindu – Muslim peace. So he would come in Zalilgarh and some warriors, as well as saint from the Muslim community, would be the theme of his research. North India has an extraordinary tradition. They worshipps Muslim saints as well as hero Both Hindus and Muslim people had respect for a saint like Nizamuddin Aulia, Moinuddin Chisti, Shah Madar, and Shaikh Nasiruddin.

Professor Mohammad tried to bring peace and harmony between the two religions. He also stated that Hindu people deliberately wanted to change past and for their own benefit, some wrong past was presented. Mohammad Iqbal, the great Urdu poet who wrote "*Sare Jahan se achha, Hindustan hamara"* – better than all the world is our India. He wanted that Muslim homeland is India in a con federal India.

The main problem, according to professor Muhammed, is that our Hindu Chauvinists don't read much Iqbal these days.

Lakshman gave details about his job and Hindu – Muslim relations in India as well as Zalilgarh. An American girl Priscilla Hart, is killed in Hindu – Muslim riot. So Lakshman answers that she has nothing to do with the Hindu – Muslim nonsense Lakshman says that the Ram and Sita poojan program would be held so many Hindu people are going from the Muslim ghetto and the riot took place. Actually the government official wanted to bring a ban on the procession but except Bangal government, nobody brought Ban on the procession.

The riot broke in Utter Pradesh, Bihar, and in Madhya Pradesh. But Zalilgarh is classified in official files as "communally hypersensitive". The record shows that the first communal clash took place in 1921. Communal clashes mean just the suffering of both religious people and the reasons were such as attacks on religious processions, desecration of shrines, and illicit relationships between men and women of different communities. The two communities live separately but near each other in crowded shanty towns and any small spark could set ablaze a bloody confrontation.

Lakshman complained about the incompetence of the government and the inefficiency of the postal system and the unpredictability of the water supply.

In India, how the problem of status is discussed by Shashi Tharoor. A boy is taking the IAS exam but he has not cracked the exam, but he was in love with a girl from a Brahmin family and a boy from Naga Community. Her father did not allow her daughter to marry him. But when the boy made his place in the IAS Rank list, her father's objection melted away. From this incident money and social position was also the main matter. They are now married and her father was railed against an "accursed tribal" and now boasts of his "IAS son–in–law."

Lakshman is a good-natured person but he is conflicted about his work. On the one hand, he said, he can do good, as district magistrate he has real power, but on the other hand, he is frequently disillusioned with the cynicism he sees around him in government, especially the corruption. All his colleagues are busy making money as businessmen, and engineers. Indian Administration system is full of rules and regulations that government officials can make a fortune from the way they exercise their power to permit – the building of a factory, the grant of loan, and so on. So one can earn money but some loyal officer does not apply this way to earn money so they are transferred from one place to another.

Maulana Azad was a religious scholar, born in Mecca, educated in the Koran and the Hadith, fluent in Persian, Arabic, and Urdu, and an exemplar of Muslim learning and culture in India. Yet he confessed that "every fiber of my being revolted" against the thought of dividing India on communal lines. His principal rival for the allegiance of India's Muslims was Mohammed Ali Jinnah, the leader of the Muslim League, an Oxbridge – educated Lincoln's Inn lawyer who wore Savile Row suits, enjoyed his Scotch and cigars, ate pork, barely spoke Urdu, and married a non – Muslim. There was no question in the Maulana's mind as to who was the better Muslim; yet Jinnah claimed to speak for India's Muslims and to assert their claims to be a separate nation, while the Maulana worked in the secular. "I am a Muslman and proud of the fact," he said in that great speech. Shall I go on? Is your tape recorder working? "Islam's splendid traditions of thirteen hundred years are my inheritance". He was unwilling to lose even the smallest part of this inheritance. It was India's historic destiny that many human races and cultures and religions should flow to her and that many a caravan should rest here… one of the last of these caravans was that of the followers of Islam. Islam's treasury is the message of human equality. Full eleven centuries have passed by since then. Islam has now as great a claim on the soil of India as Hinduism.

Once, when Prof. Sarwar was in college, a fellow got into an argument with him and lost his temper. "You partitioned the country!" he yelled. Prof. Sarwar interrupted him. "If I'd partitioned the country, I wouldn't be here. I'd be in Pakistan," Prof. Sarwar said. "If you mean I'm a Muslim, I plead guilty to the charge of being Muslim. But do not charge others. Muslims didn't partition the country – the British did, the Muslim League did, and the congress party did. There are more Muslim in India today than in Pakistan.

As a Muslim, a person has to look different; perhaps a Muslim's forehead should bear the indentation of banging it on the floor five times a day in namaz; ladies should no doubt be in a burqa, shielded from infidel's eyes; Muslim boys should wear the marks of their circumcisions like a badge.

Prof. Sarwar wanted to say to him that he is a Muslim, but Prof. Sarwar would never allow any kind to define what kind of Muslim he is. There's prejudice in this country. Prof. Sarwar knows he has had a privileged upbringing, and an elite education, and he is now in a position of intellectual authority. He has been conscious of how important it is for him never to forget that isn't that way for millions of his fellow Muslims.

Prof. Sarwar loves this country. He loves it not just because He was born here, as his father and mother was, as their parents before they were, not just because he knows it, he has studied its history. He has traveled its geography, He has breathed its polluted air, and he has written words to its music. India shaped his life, his mind, his tastes, his friendships, and his passions. The fact that Prof. Sarwar bows his head towards the Kaaba five times a day – after years in college when He did not pray even three times a year – does not mean he is turning away from His roots.

Prof. Sarwar hears the Muslim Dagar brothers sing Hindu devotional songs, and then he attends a qawwali performance by one of our country's greatest exponents of this Urdu musical form, who happens to be a Hindu, Shankar Shambhu, and he is transported as he chants the long list of Muslim pirs to whom he pays devotional tribute.

Prof. Sarwar is determined to resist this minority complex that the Hindu chauvinists want to impose upon him and others like him. What makes him a minority? Is it a mathematical concept? Well, mathematically Muslims were always a minority in India, before Partition, even in the medieval Muslim period, he spent his life researching and teaching. But when the Great Mughals ruled on the throne of Delhi, were Muslims a "minority" then"? Mathematically no doubt, but no Indian Muslim thought of himself as a minority. Brahmins are only ten percent of the population of India today – do they see themselves as a mionority? No, minority hood is a state of mind. It is a sense of powerlessness, of being out of the mainstream. He told his fellow Muslims; no one can make you a minority without consent.

Prof. Sarwar had been in Pakistan once for an academic conference. Where a Pakistani scholar stood up and spoke about the importance, indeed the centrality, of Islam as Pakistan's national identity. Professor Mohammad Sarwar commented following words, "If the Turks cease to be Muslim, they are still Turks, if the Egyptians cease to be Muslim, they are still Egyptians but if Indian Muslims cease to be Muslims, what they are? They are Indian." (Ibid: 115)He was introduced as Mohammed Sarwar, an Indian. It indicates a sense of Indianness in the mind of every Indian.

The only possible idea of India is that of a nation greater than the sum of its parts. An India is, neither Hindu nor Muslim, but both. That is the only India that will allow them to continue to call themselves Indians.

Human beings are rather like electrical appliances that need to be charged regularly, and prayer is a way of plugging into that charge. Lakshman has believed Hindu but he does not have anything in common with these so-called Hindu fundamentalists. Actually it is odd to speak of "Hindu fundamentalism" because Hinduism is a religion without fundamentals, no organized church, no compulsory beliefs or rites of worship, no single sacred book. In many languages – French and Persian amongst them – the word for "Indian" is Hindu. Originally "Hindu" simply meant the people beyond the river Sindhu or Indus. For Priscilla "Hinduism" is the name others applied to the indigenous religion of India. Many Hindu simply call Sanatan Dharm, the eternal faith.

Muslim invaders may indeed have destroyed Hindu temples, putting Mosque in their place, but this did not – could not destroy the Indian dream. Faith is a matter of hearts and minds.

AUTOBIOGRAPHICAL ELEMENTS IN ALICE MUNRO'S *DEAR LIFE*: A SHORT STORY

MULLA SHAIKH SABA SULTANA IQBAL AHMED,
Assistant Professor,
Department of English,
Ramkrishna Paramhansa Mahavidyalaya,
Osmanabad.

ABSTRACT

The present paper focuses on the autobiographical elements in Alice Munro's short story. She is an enormous writer in Canadian literature. She has contributed a crucial role in the genre of short stories. She is called Anton Chekhov in the post-modern period. She tries to explore the life of her own generation in the two collections of stories. She attempts to express deep concern about each phase in the lives of women. She does not forget to focus their inner quest on patriarchal domination. An autobiographical element is a way to give an open space to express inner thoughts through ordinary events. Munro's most works are set in her native place Huron Country in Southwestern Ontario. She is the Nobel Prize winner of 2013 for her collection of stories. Dear Life is a collection of stories. The collection has comprised of fourteen stories based on Munro's native Canada. She has selected common people who undergo a major change and realize the significance of daily life. The collection is unified by the evaluation of love, sex, and death. The entitled story 'Dear Life' is a centerpiece in the present collection. The story is narrated by an unknown woman. She recounts various aspects and events of her childhood. She grows up in a rural area in Southwestern Ontario. She has an interest in literature as Munro used to spend her time with books.

Keywords: Autobiographical, Life, Family, Intense Consciousness, And Developed Relations

An autobiography is a subjective work of one's. An autobiographical element is a way to express one self's experiences. A writer writes an autobiography to bring out hidden feelings before the world. Writers are inspired by their own emotional life, their experiences, and their contact with society which connect them with their fictional characters and bring similarities with them. A writer is free to record only such events that are important to him. Autobiography sticks to the facts of his life which creates a picture of his experiences. An author selects events in his life that help him to develop his artistic personality. He is a center to bring the attention of readers. While incorporating his personality, it becomes significant to present society which helps to shape his personality.

"Autobiography is a biography written by the subject about himself or herself. It is to be distinguished from the memoir, in which the emphasis is not on the author's developing

self but on the people and events that the author has known or witnessed, and also from the private diary or journal, which is a day-to-day record of the events in one's life written for personal use and satisfaction, with little or no thought of publication." (Abrams: 2012:27)

An autobiography is an individual's experiences written by an author. It is a different form from the memoir. A memoir pretends to be a true story of an author. It is similar to the pseudo-autobiographical mode. It is often first-person narration. An autobiography does not emphasize on author's progress but focuses on the people and events that he knows. Diary and journal are two different forms that record day-to-day events of life for self-satisfaction and for personal interest.

"*Autobiographies are always written for a public audience. Indeed, autobiography is ideally understood by both its authors and its readers to be exemplary, as a reliable and true portrayal of a life from which others can learn*."(Cuddon: 2013: 60-61)

Autobiography is written often for the public interest. It is his/her own record of his or her life events. It helps readers to make familiar with the incidents and experiences of an author. It is formed in perfect order to trust easily. The records are reliable to trust and it seems a true portrayal of a life that readers understand and learn from it.

The first developed and influential autobiography *'Confessions'* is written by St. Augustine in the fourth century. Spiritual autobiography is a description of the author's struggles with God. He discovered his Christian identity and religious vocation. A memoir is slightly different from an autobiography. An author minutely focuses on memories, emotions, and feelings. Michel de Montaigne's *Essays* published in 1580 constitute great autobiographical mode. Rousseau's *Confession* and Goethe's *Dichtung und Wahrheit* are called secular autobiographies. John Bunyan's *Grace Abounding* to the Chief of Sinners (1666) follows Augustine's religious self-revelation focusing on a crisis and conversion. In the Romantic Period, William Wordsworth's *The Prelude* is a romantic autobiography published in verse form. It is a record of poet's childhood memories and middle-aged experiences. The subtitle of the poem '*The Growth of Poet's Mind'* gives a distinctive nature to the poem. The poem focuses on the struggle of poet to a mature poet.

A fictional autobiography is similar to an autobiography. The fictional characters write about their lives as first-person narrators. The novels by Charles Dickens's *David Copperfield* and Daniel Defoe's *Moll Flanders* focus on the internal and external experiences of characters. *Moll Flanders* is a fictional autobiography written in the eighteenth century by Daniel Defoe. It is a fictional story of a woman who was born in Newgate and lived as a prostitute for twelve years later she marries five times and last she married her brother after that she spent her life in the criminal field.

In American literature, there are a number of autobiographical writers but some are more eminent autobiographers. *The Autobiography* of Benjamin Franklin was written from 1771 to 1790. The work has its own significance as a historical document of his life. The work remains a popular and exact example of the genre. He emphasizes his remarkable career and becomes a successful writer in American literature. He divides an autobiography into four parts and gives detailed sequences of his life.

Fredrick Douglass is an American social reformer famous for his three autobiographical works. *'Narrative of the life of Fredrick Douglass, A American Slave* (1845)' is his first autobiography in which he tells about his experience as a slave and the abolition movement.

Sylvia Plath is an admired poet known for her confessional poetry in American Literature. *The Bell Jar* (1963) is her semi-autobiographical novel published before few years of her death. She gives a fictional name in the work to express her agony and dry relationship with her husband. Her character is an undergraduate student who neither feels motivated nor energized about the work. She struggles to keep aside all anxiety and bewilderment.

An autobiography is a way to keep alive an author in the reader's heart. It is a way to structure his life in accordance with his wishes. It is a document in which the author talks directly with readers. He makes familiar with the true life and upright strong desire for life. Every person has different experiences and hurdles but lastly, if he has a strong desire, to get success every great person's life story should be written so the autobiographies will show a path to a new generation. Every struggler has to go through depression, frustration and from the same situation; every great person once had gone. Autobiography boosts the new generation. Mahatma Gandhi has written an autobiography in Gujarati language and later translated it into English *My Experiences with Truth.*

ALICE MUNRO AND WORKS:

Alice Munro is a contemporary short story writer in Canadian literature. She was born in a farmer's family whose father was a fox farmer and whose mother was a teacher. At the age of her 13, her mother suffered from Parkinson disease and as the eldest child in the family, she spent most of the time working at home. Over the course of time, it helps her to understand the responsibility and purpose of life. She started to write in her early teens. She published her first story "*The Dimensions of Shadow*" in 1950. She has been influenced by a different style of writing. She is a writer of fourteen phenomenal collections of stories. Throughout her life, she constantly writes for different journals and publishers. She has broken down the traditional style of writing. Her stories move forward and backward in time. She has also tried to give a fictional touch to her life through her women characters. She begins her career as a short story writer despite she comes to know later that it is not possible for her to engage a long time in a novel. She engages herself initially in caring for her family to give time for her career. Her first collection of stories "*Dance of the Happy Shades* (1968)" becomes the turning point in her career to be a short story writer. The collection brings her prestige and respect in Canadian literature and wins Governor General Award. She has written her first painful autobiography 'The Peace of Utrecht' about her mother's death. Her success follows two interlinked collections of stories that move around the progress of central characters.

Munro's women characters acquire gender identity from childhood. It is a unique feature of her writing. First-person narration is a quality of her writing. In first-person narration, her characters recount personal experiences which talk directly to readers. Another remarkable characteristic of her stories is to pay attention to women's lives in patriarchal societies. Her thoughts reflect through her female characters and norms govern women's lives. She depicts women's secret desire to get free from socially structured life and their struggle against stereotyped life. She keeps the boundary between childhood and adolescence and their participation in the world of father and mother. Her girl narrators exist as an innocent and helpless child who is limited in the restricted world. They have limited knowledge of the world and demand safe space. The term innocence is applied to adults who try to protect the characteristics of innocent characters.

Her child narrator unfolds her inability to describe the events. She cannot analyze anything that happens in her life but describe everything in confusing circumstances. Munro designs women narrators to reveal the tension between the superficial and hidden reality and visible and invisible gender identity.

Munro's other collection of stories '*Who Do You Think You Are*' was awarded by Governor General Award. The book revolves around a protagonist, Rose. Munro has not bound stories by a time, place, or strict narrator. A central character wants to stress her identity. The character is called bildungsroman that grows up in a small town and goes to university to complete her education. In further stories, Rose tries to bridge her relationship with her stepmother. The book gives a complete glance at a central character from her childhood to be a successful person and attempt to maintain normal relations in the family.

'The Moons of Jupiter' has followed some different structures. The narrator introduces her paternal and maternal aunts and their approach toward the world. She shows her aunts are completely different from each other, as maternal aunts have enjoyed educated life whereas paternal aunts have lived vulgar life. Each story reflects Munro's attachment to the town place. *'The Progress of Love'* is an entitled story in the anthology. It is a story of three generations. The story tells about a young girl and her upbringing relation in a family.

'Dear Life' is an outstanding and last anthology of Munro. In the collection, she has divided stories into sections. She uses autobiographical elements in the present collection of stories. She gives a background of her experiences to give an autobiographical touch to her story. Her stories are combined with accidents and dangers, imagined and real, painted and radiant, and extraordinary lives of women. She often gives the essence of life in her timeless stories. The entitled story *Dear Life* is narrated by an unknown woman.

"I lived when I was young at the end of a long road, or a road that seemed long to me. Back behind me, as I walked home from primary school, and then from high school, was the real town with its activity and its sidewalks and its streetlights for after dark. Marking the end of town were two bridges over the Maitland River: one narrow iron bridge, where cars sometimes got into trouble over which one should pull off and wait for the other, and a wooden walkway which occasionally had a plank missing, so that you could look right down into the bright, hurrying water." (Munro: 2012:299)

As the story begins the unknown narrator grows up in Ontario is remarkably personal. She remembers her childhood days. She recounts her school days when she used to go just walking. She goes to town after completing her primary education for further study. She walked to town in streetlights to her home crossing two bridges over the Maitland River. A narrow bridge shows a small town and the congested life of a writer. Munro uses a majority of her life references to characterize regional life.

The narrator remembers her grandfather who imagined her father would have a good life. Her father has a paternal descent farm from where her father begins his new life. Her parents leave their communities behind and buy a plot of land at the edge of a road near a town. They did not have an idea to have a prosperous life by raising silver foxes and mink. Her father feels about himself well to have a new business rather than working on a farm. Her parents use their savings to begin their new business. They work together to build pens and shelters to remain animals in it. In those days narrator also worked with her father. Her mother always thinks differently that she and her husband would be different kinds of persons.

A narrator makes friendship with her classmates. But her mother has a problem with two girls with whom she does not want friendship of her daughter. Even she has an issue allowing her daughter to spend time with two girls. She forbids a narrator to enjoy some time with them. She knows their mothers are prostitutes who have died due to suffering from a sexual disease. The narrator harbors a grudge against her mother to deny her friendship.

> *"My mother had two miscarriages before she had me, so when I was born, in 1931, there must have been some satisfaction. But the times were getting less and less promising. The truth was that my father had got into the fur business just a little too late. The success he'd hoped for would have been more likely back in the mid-twenties, when furs were newly popular and people had money."* (Ibid: 307)

The narrator recalls that her mother suffered twice before her birth so her parents will be happy to have a daughter after the third time. The birth year 1931 gives stresses the writer's birth year which make reader conscious of Munro's life. Her parents run a fur business and raising minks and other animals and selling pelts. During the depression time, her father buys an old shed in town in order to send the narrator country school. Her father is the taxpaying property owner. Her father expects that his all financial issues will be solved. He anticipates that his new business will run smoothly. But he gets little late to get profit in new business. He wants to cover up his poor life to have a settled life.

> *"In those days, I had to help my father sometimes, because my brother wasn't old enough yet. I pumped fresh water, and I walked up and down the rows of pens, cleaning out the animals' drinking them. I enjoyed this. The importance of the work, and the frequent solitude were just what I liked. Later on, I had to stay in the house to help my mother, and I was full of resentment and quarrelsome remarks. "Talking back" it was called. I hurt her feelings, she said, and the outcome was that she would go to the barn to tell on me, to my father. Then he'd have to interrupt his work to give me a beating with his belt."* (Ibid:305-6)

In the initial days, the narrator helps her father in pens to do everything in a proper way because her brother is not old enough to help their father at the farm. Munro emphasizes her nature. She grows in solitude and it creates space to think of herself from a different point of view. It becomes the turning point of her life to dream of herself as a writer. She recalls everything like pumping water, and go down to pens, and cleaning out animals. Even she enjoys all the work to do with her father. She thinks that she is liable to work with her father or to spend her time with him. She knows only the importance to work in solitude. Afterward, she stays at home to help her mother in domestic work. She is full of hatred and argumentative condition with her mother. Her mother is hurt by narrator so she goes into pens to complain to her father in order to give her a beating with his belt. Munro recounts minute incidents of her childhood which are evergreen memories of her life.

"Something had come upon us that was even more unexpected and would become more devastating that the loss of income, though we didn't know it yet. It was the early onset of Parkinson's disease, which showed up when my mother was in her forties." (Ibid: 308)

The narrator sees her family once again face losses and this time her family does not overcome hurdles of financial problems. Her father pelts all foxes and afterward minks and does not get profit from them. As soon as she comes back home from school she goes to cook lunch for her father. She never expects her family will suffer from all sides. She sees the devastating condition of her family business. Her family has not overcome from the loss. Her family goes through the worst condition when they come to know her mother's severe disease. Her mother is diagnosed with Parkinson's disease at the age of forties and the symptoms gradually increased. In the course of time, all responsibilities come on her shoulder. And she realizes the responsibility of family and lives in her relationship.

The narrator's mother likes to tell several times about her life and about an old woman named Mrs. Netterfield. She does not believe in the wild stories of an old woman without her desire despite she has to listen her mother. The old woman is cruel that she allegedly chased a deliveryman from her property with a hatchet because there was a mistake in her grocery order.

Her mother further claims that Mrs. Netterfield snuck up to her house when she was a child and peered in the windows before scurrying away.

The narrator goes to Vancouver at her adult age and where she meets with her husband. She still maintains her contact with her hometown to subscribe newspaper. While reading one day she reads a poem written by Mrs. Netterfield's daughter. She discovers Mrs. Netterfield's family used to live where the narrator grows up.

"*I did not go home for my mother's last illness or for her funeral. I had two small children and nobody in Vancouver to leave them with. We could barely have afforded the trip, and my husband had contempt for formal behavior, but why blame it on him? I felt the same. We say of some things that they can't be forgiven, or that we will never forgive ourselves.*" (Ibid: 319)

Eventually, the narrator's mother died due to severe disease. She does not go to her mother's funeral. She knows the travel is also long from Vancouver. She cannot afford the costly travel. She has two daughters and nobody is friendly or relative to leave her daughters in their trust. She misses her mother and her talk. She does not have a good relationship with her husband. Her husband does not like too much attachment with in-laws family. He maintains formal behavior and attachment but simultaneously she reveals her dry relationship with her parents. They cannot forgive each other for whatever mistakes they have done.

In the present story, Munro openly talks about her childhood, her struggle for education, and her loveless relationship with her mother. She competes in any condition to overcome her poor conditions. She regrets not being closer to her mother. She knows that her mother had a lot to tell her. She is inspired by her mother's stories. She gets late to correct her mistakes. The story clearly reflects that she was unhappy with her husband. She shows that her childhood memories are powerful which she easily combines with her imagination to give artistic reflections. She gives a complete account of information on true human relations whether the parents-daughter, husband-wife, contact with society, or any else relations. She states in her stories her complicated relations. Taking into account Munro has tried the setting and characters in '*Dear Life'* personal establishments. She accepts whatever turns have taken her life. She positively molds herself with the conditions.

REFERENCES

1. Munro, Alice: '*Dear Life,*' Toronto; McClelland and Stewart, 2012
2. Thackery, Robert (ed): 'Alice *Munro, Writing Her Lives'* Toronto, Cloth International, 2005.
3. Yagoda, Ben. *About Town*: The New Yorker and World It Made. New York: De Capo, 2001.
4. Morris, Wright. *The Home Place*, 1948. Lincoln: U Nebraska P, 1972.
5. Ross, Catherine Sheldrick. *Alice Munro: A Double Life*. Toronto: 1992
6. Heble, Ajay. *The Tumble of Reason: Alice Munro's Discourse of Absence*. Toronto: University of Toronto Press,1994.
7. 7) Cudden, Revised by Habib M. R. A. *A Dictionary Of Literary Terms and Literary Theory*. Blackwail Publication: 2013
8. 8) Abrams and Harpham. *A Glossary of Literary Terms*. Tenth Edition. Cengage Learning Publication: 2012

J. Chem. Sci. (2022) 134:120
https://doi.org/10.1007/s12039-022-02116-3

REGULAR ARTICLE

Novel CAL-B catalyzed synthetic protocols for pyridodipyrimidines and mercapto oxadiazoles

ANUSAYA S CHAVAN[a], ARUN S KHARAT[b], MANISHA R BHOSLE[a],
SAMBHAJI T DHUMAL[a] and RAMRAO A MANE[a,*]
[a]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India
[b]Laboratory of Applied Microbiology, School of Life Sciences, Jawaharlal Nehru University,
New Delhi 110067, India
E-mail: manera2011@gmail.com

MS received 6 May 2022; revised 26 August 2022; accepted 2 November 2022

Abstract. CAL-B catalyzed novel synthetic routes have been developed for getting better to excellent yields of the pyridodipyrimidines and mercapto oxadiazoles. Here, for the first time, one pot cyclo condensation of barbituric acid, aromatic aldehydes, and ammonium acetate has been carried at room temperature in dichloromethane in the presence of biocatalyst, CAL-B and obtained 5-aryl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraones (**3a-k**). CAL-B catalyzed cyclo condensation of arylhydrazides and carbon disulphide has also been carried in ethanol for getting 5-(p-substituted phenyl)-1,3,4-oxadiazole-2-thiol (**6a-b**). Mercapto oxadiazoles (**6a-b**) are also separately allowed to react with substituted phenacyl bromides in the presence of trimethylamine and obtained 1-aryl-2-((5-substitutedphenyl-1,3,4-oxadiazol-2-yl)thio)ethanones (**8a-h**). The developed routes are efficient, clean, and cost-effective. Synthesized compounds; (**3a-k**), (**6a-b**), and (**8a-h)** are thoroughly characterized by their spectral data.

Keywords. CAL-B; pyridodipyrimidines; mercapto oxadiazoles; cyclocondensation.

1. Introduction

Nitrogen-containing heterocycles, *viz.* pyridopyrimidines and 1,3,4-oxadiazoles, have diverse biological activities and are found to be interesting area of research in heteroaromatic chemistry.[1] Literature survey reveals that pyrimidine ring-bearing molecules are found to display a vital role in the various biological processes. The pyridopyrimidine scaffold has widely occurred in many bioactive heterocycles of natural and synthetic origins, and this also plays a significant role in different drug discovery programs. Heterocycles with pyridopyrimidine moiety are found to have a broad range of biological, medicinal, and pharmacological properties, like antitumor,[2] antibacterial,[3,4] antifungal,[4] antiviral,[5] anti-oxidant,[6] dihydrofolate reductase inhibitory,[7] tyrosine kinase inhibitory,[8] calcium channel antagonist,[9] and fibroblast growth factor receptor 3 inhibitory[10] (Figure 1).

Mercapto oxadiazoles and 1,3,4-oxadiazoles are also nitrogen-containing heterocycles, generally utilized as pharmacophoric systems, due to their metabolic profile and ability to engage in hydrogen bonding interaction with receptors. Therefore mercapto oxadiazole and 1,3,4-oxadiazole scaffolds are well explored in agricultural, pharmaceutical, and industrial fields. Various substituted mercapto oxadiazoles possess significant anti-inflammatory, antibiotic, analgesic, anticonvulsant, hypoglycemic, and antitubercular activities.[11–13] The literature survey reveals that mercapto oxadiazoles, 1,3,4-oxadiazoles, and their amino derivatives are prominent antimicrobial agents.[14–16] These compounds are said to be more potent antibiotics compared to the standard antibiotics, penicillin G,[17] gentamicin, and ampicillin.[18] 1,3,4-Oxadiazole skeleton in association with various other heterocycles are displaying broad spectrum of biological activities like anti-inflammatory, antidiabetic, antitumor,[19]

---

*For correspondence

Supplementary Information: The online version contains supplementary material available at https://doi.org/10.1007/s12039-022-02116-3.

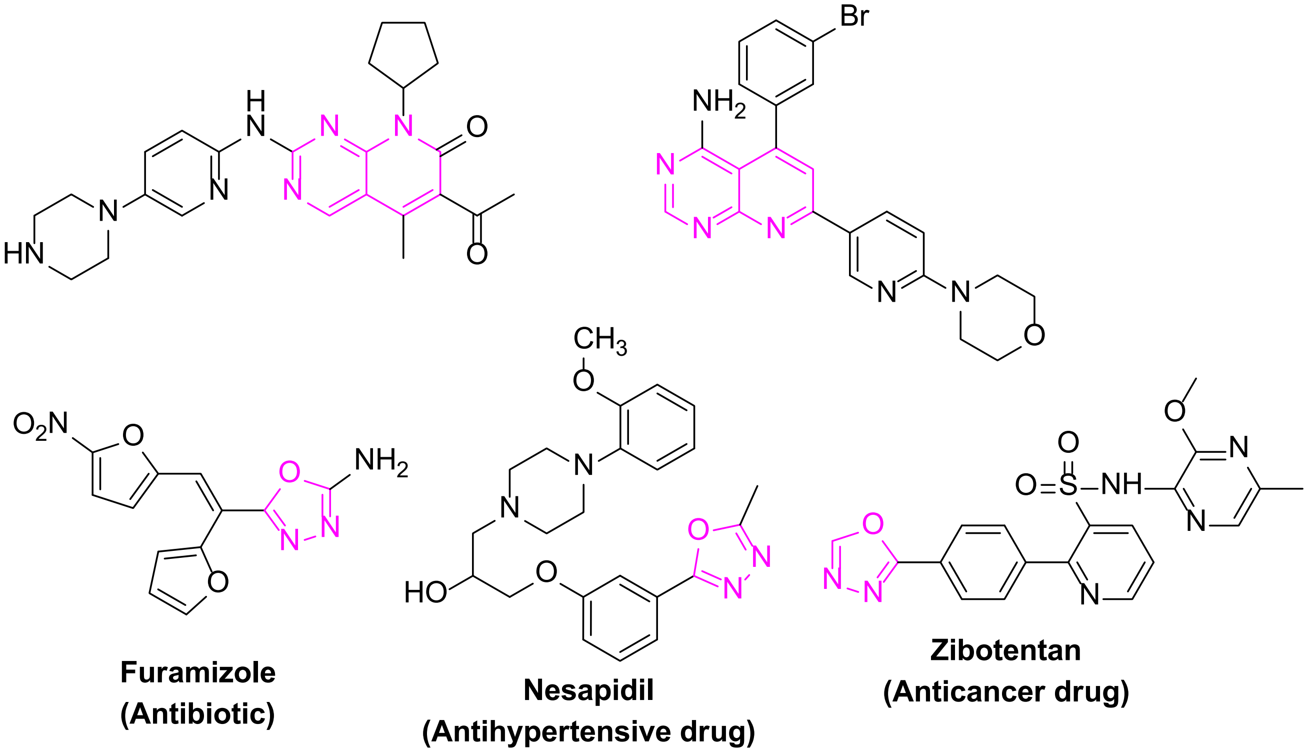


Figure 1. Drugs having pyrido[2,3-d]pyrimidine and 1,3,4-oxadiazole scaffolds in their skeleton.

antifungal,[20] hypotensive,[21] antitubercular,[22] corrosion inhibiting and tyrosinase inhibitory[23] (Figure 1).

Due to this wide range of pharmacological properties and biological activities, pyridodipyrimidines and mercapto oxadiazoles occupy a noteworthy place in the subject of medical research. These applications of pyridodipyrimidines and mercapto oxadiazoles have insisted that researchers synthesize therapeutically important newer pyridodipyrimidines and mercapto oxadiazoles. Researchers have reported one pot cyclocondensation of barbituric acid, aldehydes and ammonium acetate separately incorporating ultrasound irradiation,[24] catalyst-free condition,[25] SBA-15-supported sulfonic acid nanocatalyst,[26] ionic liquid $[\text{H-NMP}]^+$ $[\text{HSO}_4]^-$ under ultrasonic irradiation,[27] and β-cyclodextrin-ultrasonication,[28] for obtaining pyridodipyrimidines.

Classical methods for the preparation of the 1,3,4-oxadiazole-2(3*H*)-thiones include the cyclo condensation of acylhydrazides and carbon disulphide in ethanol in the presence of potassium hydroxide,[29] under the microwave.[30] It is also reported that the conversion of aromatic acyl hydrazides into 1,3,4-oxadiazoles is more convenient than aliphatic hydrazides, assisted separately by microwave,[31] DMF,[32] sodium dodecyl sulfate (SDS),[33] polymer-supported reagents/resin-bound reagents,[34] polymer-supported reagents separately under thermal and microwave condition,[35] tosylchloride and pyridine,[36] under microwave irradiation using $POCl_3$, and Al_2O_3,[37] and resin-bound acylhydrazines.[38]

These above-reported protocols are found to have certain limitations, such as tedious workup procedures, non-readily available catalysts, and require high energy. It seems from the above reports that there is no attention paid to the use of enzymes as catalysts while carrying the syntheses of pyridodipyrimidines and mercapto oxadiazoles.

Recently, biocatalysts/enzymes have been used to accelerate various organic transformations leading to biodynamic compounds, and they are functional proteins used currently as innocuous and cost-effective catalysts. Lipases are ubiquitous, naturally endowed catalysts with the ability to perform reactions in aqueous and organic solvents. They are well-explored as biocatalysts to catalyze the hydrolysis of water-soluble carboxylic esters, particularly triglycerides and phospholipids.[39] Among the lipases, Candida antartica lipase B (CAL-B) has been used as a biocatalyst in its pure form as well as immobilized CAL-B form to accelerate various organic reactions and biotransformations.[40–43] Recently, CAL-B has been well characterized and is structurally similar to several other lipases and has Serine, Histidine, and Aspartic catalytical triads with secondary alcoholic binding pocket. Usually, these active sites *viz.,* Serine, Histidine, Aspartic residues participate to display catalytic behaviors to accelerate the rates of organic/biotransformations.[44,45] Our group has used biocatalysts, Baker's yeast as a whole cell source of enzymes and lipase as an isolated pure enzyme for conducting various organic transformations.[46–49]

To overcome the limitations in the above-mentioned synthetic protocols, and considering the eco-friendly nature of biocatalysts, and in continuation of our earlier interest in developing greener protocols for the synthesis of different therapeutically important heterocycles, here we have decided to use a biocatalyst, CAL-B for the synthesis of pyridodipyrimidines and mercapto oxadiazoles.

2. Experimental

2.1 *General*

All the chemicals used were of laboratory grade. Lipase B Candida Antarctica immobilized on immobead 150 recombinant from yeast is procured from Sigma Aldrich. Melting points of all the synthesized compounds were determined in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded with a BrukerAvance 300 spectrometer operating at 400 MHz using DMSO-d_6 solvent and tetramethylsilane (TMS) as the internal standard, and chemical shift in δ ppm.^{13}C NMR spectra were recorded on BrukerAvance 75 MHz on Jeol. The purity of each compound was checked by Thin Layer Chromatography using silica-gel, $60F_{254}$ aluminum sheets as adsorbent, and visualization was accomplished by iodine/ultraviolet light.

2.2 *General procedure for the synthesis of 5-(substituted phenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,5H,7H)-tetraones (3a-k)*

A mixture of substituted aldehydes (0.94 mmol), barbituric acid (1.88 mmol), and ammonium acetate (1.2 mmol) was stirred in DCM (10 mL). CAL-B (200 mg) was added to this reaction mass, and the reaction mixture was further stirred at room temperature for 18 h. After completion of reaction, the reaction content was then stirred with ethanol (50 mL) + DMF (5 mL) and then filtered. The residue, CAL-B was then reused. The crude pyridodipyrimidines were obtained by removing the solvent from the filtrate by a rotatory evaporator. The crude products have been crystalized using ethanol. All the synthesized compounds are known, and their ^{1}H NMR, ^{13}C NMR, and HRMS spectral data and melting points are found to be in good agreement with those reported in the literature[28].

Scan copies of spectra of **3a** are provided as a representative of the series (**3a-k**).

2.2a *Spectral data of the compounds*: **5-Phenyl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3a):** Yield: 77%; M.p.: 284-286 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.95 (s, 1H, -CH), 6.98-7.16 (m, 5H, Ar-H), 7.95 (s, 2H, -2NH) and 9.96 (s, 3H, -3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.79, 91.01, 124.36, 126.70, 127.38, 144.83, 150.73, 162.34 and 163.96. HRMS: (ESI$^+$) Mode: Calculated 326.0889, Observed 326.3425.

5-(4-Hydroxyphenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3b): Yield: 65%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.87 (s, 1H, -CH), 6.95-7.64 (m, 4H, Ar-H), 7.98 (s, 2H, 2NH) and 10.04 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.89, 91.45, 124.67, 126.53, 127.47, 144.74, 150.65, 162.38 and 164.86. HRMS (ESI$^+$): (M+H)$^+$ Calculated 342.0838, Observed 342.0414.

5-(4-*N*,*N*-Dimethylaminophenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3c): Yield: 61%; M.p.: 288-289 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 3.19 (s, 6H, -2CH$_3$), 5.67 (s, 1H, -CH), 6.22-6.96 (m, 4H, Ar-H), 7.93 (s, 2H, 2NH) and 9.26 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.88, 42.97, 91.27, 124.87, 126.94, 127.54, 144.92, 150.81, 162.54 and 164.33. HRMS (ESI$^+$): (M+H)$^+$ Calculated 369.1311, Observed 369.1345.

5-(4-Chlorophenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3d): Yield: 73%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.87 (s, 1H, -CH), 7.02-7.36 (m, 4H, Ar-H), 7.92 (s, 2H, 2NH) and 9.98 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.97, 91.52, 124.54, 126.93, 127.56, 145.14, 150.93, 162.87 and 164.62. HRMS (ESI$^+$): (M+H)$^+$ Calculated 360.0499, Observed 360.0443.

5-(3-Bromophenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3e): Yield: 59%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.91 (s, 1H, -CH), 7.32-7.56 (m, 4H, Ar-H), 8.09 (s, 2H, 2NH) and 10.26 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 35.66, 91.23, 124.41, 126.83, 127.49, 144.90, 150.87, 162.49 and 164.26. HRMS (ESI$^+$): (M+H)$^+$ Calculated 403.9994, Observed 403.9456.

5-(4-Nitrophenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3f): Yield: 67%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.85 (s, 1H, -CH), 7.38-7.76 (m, 4H, Ar-H), 8.15 (s, 2H, 2NH) and 10.31 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 36.19, 91.14, 124.37, 126.76, 127.67, 144.88, 150.89, 162.55 and 164.18. HRMS (ESI$^+$): (M+H)$^+$ Calculated 371.0740, Observed 371.0625.

5-(4-Methoxyphenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3g): Yield: 64%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 3.92 (s, 3H, -OCH$_3$), 5.89 (s, 1H, -CH), 6.32-6 96 (m, 4H, Ar-H), 7.12 (s, 2H, 2NH) and 9.34 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 36.04, 59.09, 91.43, 124.49, 126.86, 127.49, 144.95, 150.84, 162.87 and 164.26. HRMS (ESI$^+$): (M+H)$^+$ Calculated 356.0995, Observed 356.0425.

5-(4-Tolyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3h): Yield: 72%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 2.43 (s, 3H, -CH$_3$), 5.87 (s, 1H, -CH), 6.38-7.02 (m, 4H, Ar-H), 7.65 (s, 2H, 2NH) and 9.45 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 23.67, 35.88, 91.28, 124.48, 126.89, 127.49, 144.98, 150.96, 162.74 and 163.78. HRMS (ESI$^+$): (M+H)$^+$ Calculated 340.1046, Observed 340.0854.

5-(4-Trifluromethyl-phenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3i): Yield: 71%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.91 (s, 1H, -CH), 7.18-7.36 (m, 4H, Ar-H), 8.09 (s, 2H, 2NH) and 10.26 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 36.22, 91.31, 124.36, 124.57, 126.82, 127.45, 144.92, 150.86, 162.57 and 164.22. HRMS (ESI$^+$): (M+H)$^+$ Calculated 394.0763, Observed 394.0531.

5-(4-Fluorophenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3j): Yield: 68%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.96 (s, 1H, -CH), 7.18-7.31 (m, 4H, Ar-H), 8.15 (s, 2H, 2NH) and 10.19 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 36.32, 91.21, 124.49, 126.88, 127.51, 145.09, 151.17, 162.74 and 164.36. HRMS (ESI$^+$): (M+H)$^+$ Calculated 344.0795, Observed 344.0642.

5-(4-Trifluromethoxyphenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (3k): Yield: 73%; M.p.: >300 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 5.94 (s, 1H, -CH), 7.18-7.44 (m, 4H, Ar-H), 7.95 (s, 2H, 2NH) and 9.96 (s, 3H, 3NH). ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 36.89, 91.45, 124.36, 126.98, 127.65, 130.46, 144.98, 150.78, 162.45 and 164.22. HRMS (ESI$^+$): (M+H)$^+$ Calculated 410.0712, Observed 410.0425.

2.3 *General procedure*

2.3a *Synthesis of 5-aryl-1,3,4-oxadiazole-2-thiols (6a-b)*: *P*-Substituted phenyl hydrazides (**4a-b**, 3.4 mmole) was dissolved in ethanol (10 mL). Then CAL-B (50 mg) and carbon disulphide (1.7 mmole) were added to the reaction mass. It was then stirred at room temperature. The reaction was monitored by thin layer chromatography. After 11 h of stirring at room temperature, the reaction mass was dissolved in ethyl acetate (25 mL) and filtered. The residue CAL-B was then reused. The solvent ethyl acetate was removed using rotatory evaporator, and the residual solid was crystallized using ethanol. All the synthesized compounds are known, and their ^{1}H NMR, ^{13}C NMR and HRMS spectral data and melting points are found to be in good agreement with those reported in the literature.[30]

2.4 *Synthesis of 1-aryl-2-((5-substitutedphenyl-1,3,4-oxadiazol-2-yl)thio)ethanones (8a-h)*

5-Aryl-1,3,4-oxadiazole-2-thiols (0.8 mmol) was dissolved in ethanol (10 mL), and then trimethylamine (1 mmol) was added to the reaction solution. The reaction mass was stirred for 15 min, and then 2-bromo-1-phenylethanones (0.8 mmol) were added to the reaction mass and refluxed at 80 °C. The reaction was monitored by thin-layer chromatography. After 6 h of reflux, the reaction mass was then poured on ice, neutralized with glacial acetic acid and filtered. The obtained solid was then crystalized using ethanol. All the synthesized compounds are known, and their ^{1}H NMR, ^{13}C NMR, and HRMS spectral data and melting points are found to be in good agreement with those reported in the literature.[50,51]

Scan copies of spectra of **6a** and **8b** are submitted as a representative of the series (**6a**-**b** and **8a**-**h**).

2.5 *Spectral data of compounds*

5-(*P*-Tolyl)-1,3,4-oxadiazole-2-thiol (6a) Yield: 81%; M.p.: 171-173 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 2.50 (s, 3H, CH$_3$), 7.37-7.39 (d, 2H, Ar-H), 7.82-8.84 (d, 2H, Ar-H) and no signal up to 12 for SH. ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 21.50, 21.61, 120.47, 126.38, 129.47, 129.91, 130.41, 142.59, 142.69, 161.11, and 177.95. HRMS (ESI$^+$): (M+H)$^+$ Calculated 193.0435, Observed 193.0441.

5-(*p*-Chlorophenyl)-1,3,4-oxadiazole-2-thiol (6b) Yield: 78%; M.p.: 211-213 °C

^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 7.46-7.48 (d, 2H, Ar-H), 7.93-8.97 (d, 2H, Ar-H) and no signal up to 12 for SH. ^{13}C NMR (DMSO-d_6, 75 MHz, δ ppm): 21.61, 120.47, 126.38, 129.47, 129.91, 130.41, 142.59, 142.69, 161.11, and 177.95. HRMS (ESI$^+$): (M+H)$^+$ Calculated 211.9811, Observed 211.9715.

1-(4-Methoxyphenyl)-2-((5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8b) Yield: 78%; M.p.: 155-157 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 2.42 (s, 3H, CH$_3$), 3.80 (s, 3H, OCH$_3$), 4.95 (s, 2H, -CO-CH$_2$-S), 7.10 (d, 2H, Ar-H) 7.31 (d, 2H, Ar-H) 7.82 (d, 2H, Ar-H) and 8.05 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm): 21.65, 41.61, 55.61, 114.15, 118.74, 120.77, 126.69, 127.95, 129.75, 130.97, 142.27, 163.57, 164.39, 166.11 and 190.67. HRMS (ESI$^+$): (M+H)$^+$ Calculated 341.0960, Observed 341.0965.

1-(4-Phenyl)-2-((5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8a) Yield: 85%; M.p.: 135-137 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 2.39 (s, 3H, CH$_3$), 4.93 (s, 2H, -CO-CH$_2$-S), 7.23 (d, 2H, Ar-H), 7.39 (d, 2H, Ar-H), 7.78 (d, 3H, Ar-H) and 8.01 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm): 21.45, 57.68, 115.27, 119.82, 122.74, 126.93, 128.74, 129.69, 131.27, 143.31, 164.63, 165.39, 166.29 and 190.73. HRMS (ESI$^+$): (M+H)$^+$ Calculated 311.0854, Observed 311.0865.

4-(2-((5-(*p*-Tolyl)-1,3,4-oxadiazol-2-yl)thio)acetyl)benzonitrile (8c) Yield: 87%; M.p.: 165-167 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 2.48 (s, 3H, CH$_3$), 4.93 (s, 2H, -CO-CH$_2$-S), 7.24 (d, 2H, Ar-H), 7.40 (d, 2H, Ar-H) 7.89 (d, 2H, Ar-H) and 8.21 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm):21.61, 57.38, 115.34, 119.31, 121.37, 127.75, 128.04, 129.59, 131.98, 144.73, 165.62, 166.39, 167.11 and 191.62. HRMS (ESI$^+$): (M+H)$^+$ Calculated 335.0728, Observed 335.0774.

1-(3-Methoxyphenyl)-2-((5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8d) Yield: 88%; M.p.: 145-147 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 2.44 (s, 3H, CH$_3$), 3.85 (s, 3H, OCH$_3$), 5.05 (s, 2H, -CO-CH$_2$-S), 7.11 (d, 2H, Ar-H), 7.38 (d, 2H, Ar-H), 7.85 (d, 2H, Ar-H) and 8.17 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm): 21.57, 42.11, 56.17, 115.19, 119.24, 121.35, 126.69, 127.95, 129.75, 130.97, 142.27, 163.62, 165.39, 167.21 and 191.61. HRMS (ESI$^+$): (M+H)$^+$ Calculated 341.0960, Observed 341.0965.

2-((5-(4-Chlorophenyl)-1,3,4-oxadiazol-2-yl)thio)-1-phenylethanone (8e) Yield: 78%; M.p.: 122-124 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 4.85 (s, 2H, -CO-CH$_2$-S), 7.11 (d, 2H, Ar-H), 7.38 (d, 2H, Ar-H), 7.77 (t, 1H, Ar-H), 7.85 (d, 2H, Ar-H) and 8.17 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm): 56.17, 115.19, 121.35, 126.69, 127.75, 129.85, 130.97, 142.27, 163.62, 165.39, 167.21 and 191.61. HRMS (ESI$^+$): (M+H)$^+$ Calculated 330.0230, Observed 330.0214.

1-(4-Mecaptophenyl)-2-((5-(*p*-chlorophenyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8f) Yield: 82%; M.p.: 133-137 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 5.25 (s, 2H, -CO-CH$_2$-S), 7.11 (d, 2H, Ar-H), 7.38 (d, 2H, Ar-H), 7.85 (d, 2H, Ar-H) and 8.17 (d, 2H, Ar-H). ^{13}C NMR (CDCl$_3$, 75 MHz, δ ppm): 54.17, 117.18, 119.24, 121.35, 126.69, 127.95, 129.75, 130.97, 142.27, 163.62, 165.39, 167.21 and 191.61. HRMS (ESI$^+$): (M+H)$^+$ Calculated 355.0182, Observed 355.0845.

1-(4-Methoxyphenyl)-2-((5-(*p*-chlorophenyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8g) Yield: 80%; M.p.: 112-114 °C

^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 3.83 (s, 3H, OCH$_3$), 5.15 (s, 2H, -CO-CH$_2$-S), 7.14 (d, 2H, Ar-H), 7.39 (d, 2H, Ar-H), 7.76 (d, 2H, Ar-H) and 7.87 (d, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 48.17, 58.12, 115.19, 119.24, 121.35, 126.69, 127.95, 130.97, 142.27, 163.62, 165.39, 167.21 and 191.61. HRMS (ESI$^+$): $(M+H)^+$ Calculated 360.0335, Observed 360.0235.

1-(3-Methoxyphenyl)-2-((5-(*p*-chlorophenyl)-1,3,4-oxadiazol-2-yl)thio)ethanone (8h) Yield: 71%; M.p.: 129-131 °C

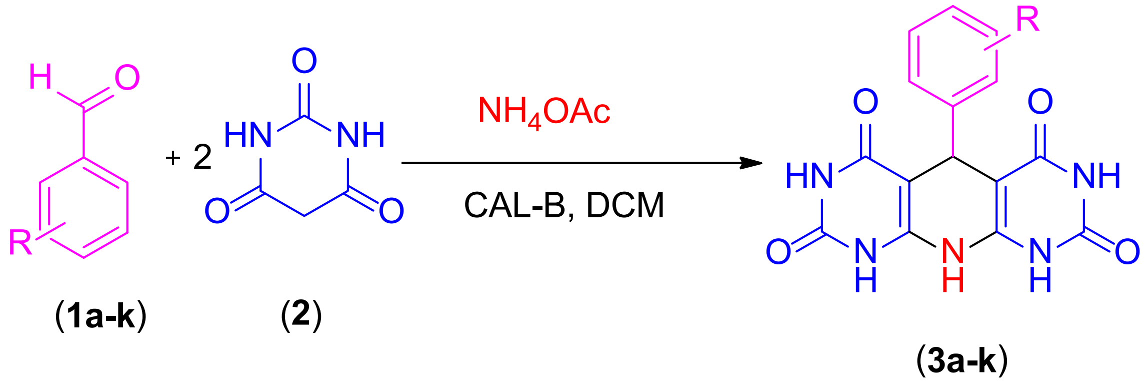
^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 3.91 (s, 3H, OCH_3), 5.09 (s, 2H, -CO-CH_2-S), 7.11 (d, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.76 (d, 1H, Ar-H), 7.78 (m, 1H, Ar-H) 7.82 (d, 2H, Ar-H), and 7.91 (d, 2H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 42.11, 55.27, 116.18, 117.23, 121.45, 125.29, 127.55, 129.64, 130.87, 142.57, 163.74, 165.48, 167.41 and 191.97. HRMS (ESI$^+$): $(M+H)^+$ Calculated 360.0335, Observed 360.0325.

3. Results and Discussion

The advantageous pharmacological properties of molecules containing pyridodipyrimidines and mercapto oxadiazoles prompted us to develop CAL-B-assisted efficient, environmentally benign methods for synthesizing pyridodipyrimidines and mercapto oxadiazoles. To optimize the reaction conditions, we initiated our studies by conducting one-pot cyclo condensation of benzaldehyde (**1**) (0.94 mmol), barbituric acid (**2**) (1.88 mmol), and ammonium acetate (1.2 mmol) as a model reaction in the presence of a biocatalyst, CAL-B by varying solvents, amount of catalyst and temperature (Scheme 1). It has been observed that when the reaction was performed in dichloromethane gave product (**3a**) with better yield (77%) as compared to other solvents (Table 1). Keeping dichloromethane as a solvent, we varied the amount of CAL-B, then we noticed that when 200 mg CAL-B was used under similar conditions, the yield of **3a** was better (Table 1, entry 4). To check the influence of temperature, we performed the model reaction under various temperatures (RT, 40. 45, and 50 °C) and noticed no considerable rise in the yield of **3a**. It was noticed that the reaction was efficiently catalyzed by CAL-B in dichloromethane at room temperature using 200 mg of CAL-B, leading to a better product yield (**3a**) within 18 h.

Similarly, we have also carried the synthesis of 5-(*p*-tolyl)-1,3,4-oxadiazole-2-thiol (**6a**), allowing cyclo condensation of *p*-tolyl hydrazide (**5a**) and carbon disulphide as a model reaction, (Scheme 2) varying the amount of CAL-B. By changing the amount of CAL-B, it was noted that there was no proportionate rise in the product yield. (**6a**) (Table 2, entries 1-3) We observed that when the transformation conducted in ethanol (10 mL) using lipase (50 mg) at room temperature gave a better yield of **6a** within 11 h. The cyclocondensations under reference were not found to be run satisfactorily in the absence of CAL-B (Table 1 entry 6 and Table 2 entry 4), indicating that the CAL-B is necessary for the cyclocondensations leading to substituted pyridodipyrimidines (**3a**) and substituted mercapto oxadiazoles (**6a**).

To evaluate the scope and applicability of these optimized catalytic protocols and in order to generalize the reaction conditions, we have performed separately i) cyclocondensation of different substituted benzaldehydes, barbituric acid, and ammonium acetate in DCM in the presence of CAL-B (Scheme 1) and ii) cyclo condensation of benzohydrazides, and carbon disulfide in ethanol (Scheme 2) and obtained titled substituted 5-aryl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraones (**3a-k**) and 5-phenyl-1,3,4-oxadiazole-2-thiols (**6a-b**), respectively with better to excellent yields.

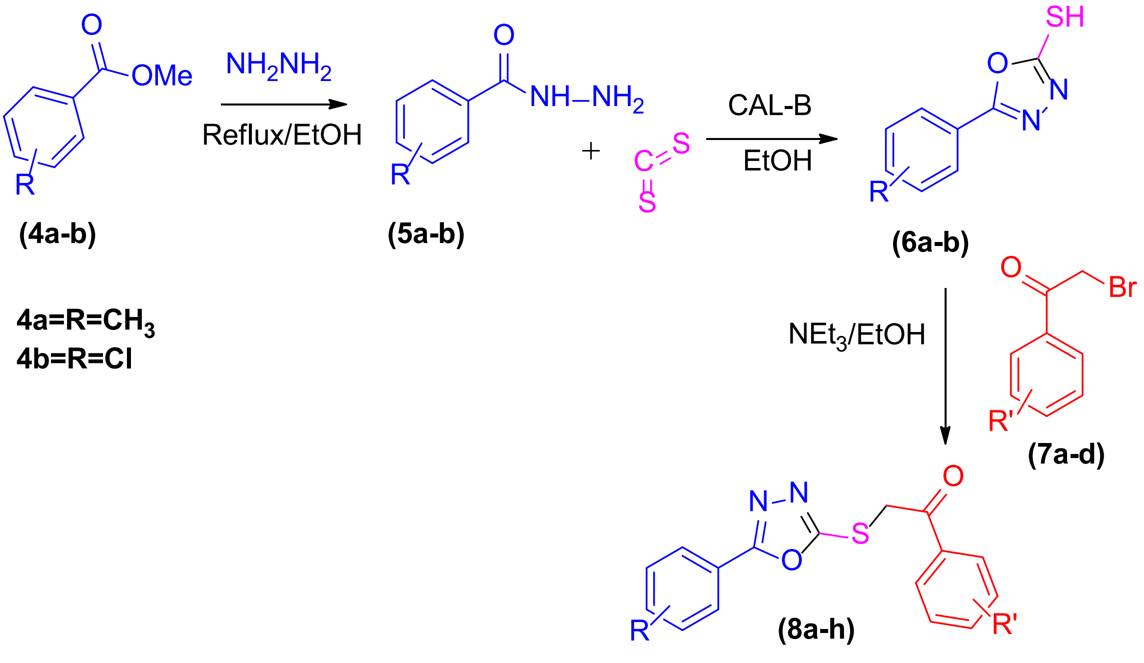


Scheme 1. Synthesis of 5-(substituted phenyl)-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraones (**3a-k**).

Table 1. Screening of reaction media, amount of catalyst, and temperature for the synthesis of 5-phenyl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraone (**3a**).

Entry	Solvent	CAL-B (mg)	Temp (^{o}C)	Time (h)	Yield (%)
1	**DCM**	200	RT	18	77
2	MeCN	200	RT	18	59
3	EtOH	200	RT	18	54
4	DCM	150	RT	18	62
5	DCM	250	RT	18	78
6	DCM	200	**RT**	18	77
7	DCM	200	40	18	79
8	DCM	200	45	18	80
9	DCM	0	RT	18	Trace

Reaction conditions: Benzaldehyde (0.94 mmol), barbituric acid (1.88 mmol), ammonium acetate (1.2 mmol), in Solvent (10 mL)



Scheme 2. Synthesis of 1-aryl-2-((5-substitutedphenyl-1,3,4-oxadiazol-2-yl)thio)ethanones (**8a-h**).

Table 2. Screening of amount of catalyst and temperature for the synthesis of 5-(*p*-Tolyl)-1,3,4-oxadiazole-2-thiol (**6a**).

Entry	Solvent	CAL-B (mg)	Temp (^{o}C)	Time (h)	Yield (%)
1	EtOH	25	RT	11	76
2	**EtOH**	**50**	**RT**	**11**	**85**
3	EtOH	75	RT	11	87
4	EtOH	0	RT	11	Trace

Reaction conditions: *p*-Tolyl hydrazide (3.4 mmole), carbon disulphide (1.7 mmole), ethanol (10 mL) at room temperature.

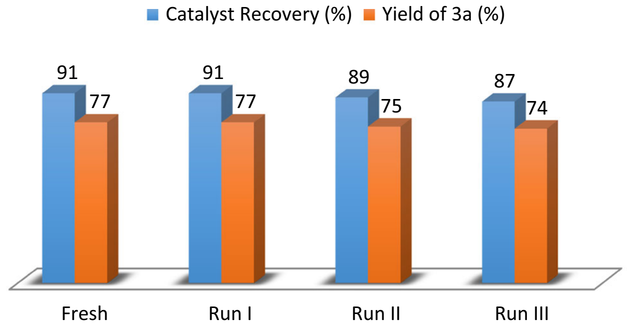


Figure 2. Recycling and reuse of CAL-B and its effect on yield of (**3a**).

Encouraged by these results, an effort was also made to obtain 1-aryl-2-((5-substituted phenyl-1,3,4-oxadiazol-2-yl)thio)ethanones (**8a-h**) with better yield by carrying condensation of 5-phenyl-1,3,4-oxadiazole-2-thiols (0.8 mol, **6a-b**) separately with substituted phenacyl bromides/2-bromo-1-phenylethanones (0.8 mol, **7a-d**) in the presence of triethylamine (1 mmol), in ethanol (10 mL).

3.1 *Recycling study of catalyst CAL-B*

The recycling study of the catalyst was done using the model reaction of benzaldehyde (**1**) (0.94 mmol), barbituric acid (**2**) (1.88 mmol), ammonium acetate (1.2 mmol), and CAL-B (200 mg) in DCM (10 mL) to afford **3a**. The reaction mixture was stirred at room temperature for 18 h. After completion of the reaction, the reaction content was then stirred with ethanol (50 mL) + DMF (5 mL) to dissolve the product. The reaction mass was filtered to separate the catalyst CAL-B which was then reused for the next three consecutive cycles for the synthesis of **3a**. The crude pyridodipyrimidines were obtained by removing the solvent from the filtrate. The catalyst was reused for subsequent cycles and was found to retain the catalytic activity up to the third cycle with over 74% conversion of the substrate to the product (Figure 2).

The synthesized 5-aryl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraones (**3a-k**), 5-phenyl-1,3,4-oxadiazole-2-thiols (**6a-b**) and 1-aryl-2-((5-substituted phenyl-1,3,4-oxadiazol-2-yl)thio)ethanones (**8a-h**) are thoroughly characterized with the help of their HRMS, ^{1}H NMR, and ^{13}C NMR. The melting points and spectral data are in good agreement with those reported in the literature.[28,30,50,51]

The enzymes having strong nucleophilic and electrophilic active amino residues and these may be interacting with carbonyl carbon of aldehydes, active methylene group of barbituric acid, acid hydrazide, and carbon disulphide, enhancing the electrophilic character of carbonyl carbon, carbon of carbon disulphide, and nucleophilic character of active methylene group of barbituric acid and the amino group of acid hydrazide, respectively. This fact might help accelerate the rates of reactions of these works. Our earlier reports have already elaborated on the details of these mechanistic pathways.[49]

4. Conclusions

For the first time, we have utilized CAL-B as an excellent biocatalyst for the synthesis of 5-aryl-9,10-dihydropyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1*H*,3*H*,5*H*,7*H*)-tetraones while carrying cyclo condensation of barbituric acid, aromatic aldehydes, and ammonium acetate in DCM. The cyclo condensation of acid hydrazides and carbon bisulfide has also been performed in the presence of CAL-B for getting 5-aryl-1,3,4-oxadiazole 2-thiols. The additional features of these protocols are easy workup, rapid rate of reactions, moderate to excellent yields, and reusability of biocatalyst CAL-B. Here we have also reported the condensation of 5-aryl-1,3,4-oxadiazole 2-thiols and phenacyl bromides in the presence of trimethylamine, and obtained biodynamic 1-aryl-2-((5-substituted phenyl-1,3,4-oxadiazol-2-yl)thio)ethanones.

Declarations

Conflict of interest The authors declare no conflict of interest.

Supplementary Information (SI)

The supplementary information related to this article is available at www.ias.ac.in/chemsci.

References

1. Mohsenimehr M, Mamaghani M, Shirini F, Sheykhan M and Azimian Moghaddam F 2014 One-pot synthesis of novel pyrido[2,3-d]pyrimidines using HAp-encapsulated-γ-Fe_2O_3 supported sulfonic acid nanocatalyst under solvent-free conditions *Chin. Chem. Lett.* **25** 1387
2. Kumar A, Ahmad I, Chhikara B S, Tiwari R, Mandal D and Parang K 2011 Synthesis of 3-phenylpyrazolopyrimidine-1,2,3-triazole conjugates and evaluation of their Src kinase inhibitory and anticancer activities *Bioorg. Med. Chem. Lett.* **21** 1342
3. Bakavoli M, Bagherzadeh G, Vaseghifar M, Shiri A, Pordel M, Mashreghi M, *et al.* 2010 Molecular iodine

promoted synthesis of new pyrazolo[3,4-d]pyrimidine derivatives as potential antibacterial agents *Eur. J. Med. Chem.* **45** 647

4. Holla B S, Mahalinga M, Karthikeyan M S, Akberali P M and Shetty N S 2006 Synthesis of some novel pyrazolo[3,4-d]pyrimidine derivatives as potential antimicrobial agents *Bioorg. Med. Chem.* **14** 2040
5. Chern J H, Shia K S, Hsu T A, Tai C L, Lee C C, Lee Y C, *et al.* 2004 Design, synthesis, and structure-activity relationships of pyrazolo[3,4-d]pyrimidines: a novel class of potent enterovirus inhibitors *Bioorg. Med. Chem. Lett.* **14** 2519
6. Rigueiroa F, Teixeiraa S, Salaheldinb A M, Oliveira-Camposb A M F, Rodriguesb L M, Peixotoc F and Oliveira M M 2008 *Biochim. Biophys. Acta.* **1777** S62
7. Bystryakova I D, Burova O A, Chelysheva G M, Zhilinkova S V, Smirnova N M and Safonova T S 1991 *Pharm. Chem. J.* **25** 874
8. Kammasud N, Boonyarat C, Sanphanya K, Utsintong M, Tsunoda S, Sakurai H, *et al.* 2009 5-Substituted pyrido[2,3-d]pyrimidine, an inhibitor against three receptor tyrosine kinases *Bioorg. Med. Chem. Lett.* **19** 745
9. Pastor A, Alajarin R, Vaquero J J, Alvarez-Builla J, Casa-Juana M F, Sunkel C, *et al.* 1994 Synthesis and Structure of New Pyrido[2,3-d]pyrimidine Derivatives with Calcium Channel Antagonist Activity *Tetrahedron* **50** 8085
10. Corre L L, Girard A L, Aubertin J, Radvanyi F, Benoist-Lasselin C, Jonquoy A, et al. 2010 Synthesis and biological evaluation of a triazole-based library of pyrido[2,3-*d*]pyrimidines as FGFR3 tyrosine kinase inhibitors *Org. Biomol. Chem.* **8** 2164
11. Bhandari S V, Bothara K G, Raut M K, Patil A A, Sarkate A P and Mokale V J 2008 Design, synthesis and evaluation of anti-inflammatory, analgesic and ulcerogenicity studies of novel S-substituted phenacyl-1,3,4-oxadiazole-2-thiol and Schiff bases of diclofenac acid as nonulcerogenic derivatives *Bioorg. Med. Chem.* **16** 1822
12. Suresh Kumar G V, Rajendraprasad Y, Mallikarjuna B P, Chandrashekar S M and Kistayya C 2010 Synthesis of some novel 2-substituted-5-[isopropylthiazole] clubbed 1,2,4-triazole and 1,3,4-oxadiazoles as potential antimicrobial and antitubercular agents *Eur. J. Med. Chem.* **45** 2063
13. Shingalapur R V, Hosamani K M, Keri R S and Hugar M H 2010 Derivatives of benzimidazole pharmacophore: synthesis, anticonvulsant, antidiabetic and DNA cleavage studies *Eur. J. Med. Chem.* **45** 1753
14. Salgin-Goksen U, Gokhan-Kelekci N, Gokfas O, Koysal Y, Kilic E, Isik S, *et al.* 2007 1-Acylthiosemicarbazides, 1,2,4-triazole-5(4H)-thiones, 1,3,4-thiadiazoles and hydrazones containing 5-methyl-2-benzoxazolinones: synthesis, analgesic-anti-inflammatory and antimicrobial activities *Bioorg. Med. Chem.* **15** 5738
15. Ahoya A C, Daouda B, Bouhfid R, Hancil A, Bousmina M, Zerzouf A, El Aouad R and Essassi E M 2011 *ARKIVOC* **ii** 217
16. Makaev F, Ribkovskaia Z, Pogrebnoi S, Boldescu V, Rusu G, Shvets N, *et al.* 2011 The structure-antituberculosis activity relationships study in a series of 5-aryl-2-thio-1,3,4-oxadiazole derivatives *Bioorg. Med. Chem.* **19** 6792
17. Shafiee A, Sayadi A, Roozbahani M H, Foroumadi A and Kamal F 2002 Synthesis and in vitro antimicrobial evaluation of 5-(1-methyl-5-nitro-2-imidazolyl)-4H-1,2,4-triazoles *Arch. Pharm. Pharm. Med. Chem.* **335** 495
18. Palaska E, Sahin G, Kelicen P, Durlu N T and Altinok G 2002 Synthesis and anti-inflammatory activity of 1-acylthiosemicarbazides, 1,3,4-oxadiazoles, 1,3,4-thiadiazoles and 1,2,4-triazole-3-thiones *Farmaco* **57** 101
19. Selvaraj K, Kulanthai K and Sadhasivam G 2017 Synthesis, characterization and biological evaluation of novel 2,5 substituted-1,3,4 oxadiazole derivatives *Saudi Pharm. J.* **25** 337
20. Zou X J, Lai L H, Jin G Y and Zhang Z X 2002 Synthesis, fungicidal activity, and 3D-QSAR of pyridazinone-substituted 1,3,4-oxadiazoles and 1,3,4-thiadiazoles *J. Agric. Food Chem.* **50** 3757
21. Tyagi M and Kumar A 2002 Synthesis of 2-[2'-Carbomyl-5'-(Heteroarylinomethylene)-1',3'4'-Thiadiazol-2' -Yl/Oxadiazol-2'-Yl)]-4,5-Dihydroimidazolines as Hypotensive Agents *Orient. J. Chem.* **18** 125
22. Dhumal S T, Deshmukh A R, Khedkar V M, Nawale L U, Bhosle M R, Sarkar D and Mane R A 2016 Synthesis and antitubercular activity of new 1,3,4-oxadiazoles bearing pyridyl and thiazolyl scaffolds *Bioorg. Med. Chem. Lett.* **26** 3646
23. Ghani U and Ullah N 2010 New potent inhibitors of tyrosinase: novel clues to binding of 1,3,4-thiadiazole-2(3H)-thiones, 1,3,4-oxadiazole-2(3H)-thiones, 4-amino-1,2,4-triazole-5(4H)-thiones, and substituted hydrazides to the dicopper active site *Bio. Med. Chem.* **18** 4042
24. Mosslemin M H and Nateghi M R 2010 Rapid and efficient synthesis of fused heterocyclic pyrimidines under ultrasonic irradiation *Ultrason. Sonochem.* **17** 162
25. Azizi N, Mobinkhaledi A, Amiri A K and Ghafuri H 2012 Catalyst-free synthesis of dihydropyridine from barbituric acid in water *Res. Chem. Intermed.* **38** 2271
26. Rostamizadeh S, Tahershamsi L and Zekri N 2015 An efficient, one-pot synthesis of pyrido[2,3-*d*:6,5-*d'*]dipyrimidines using SBA-15-supported sulfonic acid nanocatalyst under solvent-free conditions *J. Iran. Chem. Soc.* **12** 1381
27. Naeimi H, Didar A, Rashid Z and Zahraie Z 2017 Sonochemical synthesis of pyrido[2,3-d:6,5-d']-dipyrimidines catalyzed by $[\text{H-NMP}]^+[\text{HSO}_4]^-$ and their antimicrobial activity studies *J. Antib.* **70** 845
28. Jadhav C, Khillare L and Bhosle M R 2018 Efficient sonochemical protocol for the facile synthesis of dipyrimido-dihydropyridine and pyrimido[4,5-*d*]pyrimidines in aqueous β-cyclodextrin *Synth. Commun.* **48** 233
29. Xian-Li W, Chunfeng Z, Zhidan L, Chengshi W and Xincheng L 2011 Synthesis of Sulfur Ethers Containing 1,3,4-Oxadiazole and 1,3,4-Thiadiazole *Chin. J. Org. Chem.* **6** 824
30. Shahzad S A, Yar M, Khan Z A, Khan I U, Naqvi S A R, Mahmood N and Khan K M 2012 Microwave-assisted solvent free efficient synthesis of 1,3,4-

oxadiazole-2(3H)-thiones and their potent in vitro urease inhibition activity *Eur. J. Chem.* **3** 143

31. Joshi S and Karnik A V 2002 Facile Conversion of Acyldiithiocarbazinate Salts to 1,3,4-Oxadiazole Derivatives Under Microwave Irradiation *Synth. Commun.* **32** 111
32. Beigi M S, Aryan R, Yousofizadeh M and Khosravi S A 2013 A Combined Synthetic and DFT Study on the Catalyst-Free and Solvent-Assisted Synthesis of 1,3,4-Oxadiazole-2-thiol Derivatives *J. Chem.* **476358** 1
33. Yıldırım A 2015 Improved Protocol Toward 1,3,4-Oxadiazole-2(3H)-thiones and Scale-up Synthesis in the Presence of SDS as a Micelle Promoted Catalyst *Acta Chim. Slov.* **62** 473
34. Coppo F T, Evans K A, Graybill T L and Burton G 2004 Efficient one-pot preparation of 5-substituted-2-amino-1,3,4-oxadiazoles using resin-bound reagents *Tetrahedron Lett.* **45** 3257
35. Brain C T and Brunton S A 2001 Synthesis of 1,3,4-Oxadiazoles Using Polymer-supported Reagents *Synlett* **3** 382
36. Dolman S J, Gosselin F, O'Shea P D and Davies I W 2006 Superior Reactivity of Thiosemicarbazides in the Synthesis of 2-Amino-1,3,4-oxadiazoles *J. Org. Chem.* **71** 9548
37. Farshori N N, Rauf A, Siddiqui M A, Al-Sheddi E S and Al-Oqail M M 2017 A facile one-pot synthesis of novel 2,5-disubstituted-1,3,4-oxadiazoles under conventional and microwave conditions and evaluation of their *in vitro* antimicrobial activities *Arab. J. Chem.* **10** S2853
38. Liu Z, Zhao J and Huang X 2006 Solid-phase synthesis of 1,3,4-oxadiazoline-5-thione derivatives from resin-bound acylhydrazines *Bioorg. Med. Chem. Lett.* **16** 1828
39. Sharma S and Kanwar S S 2014 *Hindawi Publ. Corp. Sci. World J.* **625258** 15
40. Elliot S G, Andersen C, Tolborg S, Meier S, Sadaba I, Daugaard A E and Taarning E 2017 Synthesis of a novel polyester building block from pentoses by tin-containing silicates *RSC Adv.* **7** 985
41. Kundys A, Białecka-Florjańczyk E, Fabiszewska A and Małajowicz J 2018 *Candida antarctica* Lipase B as Catalyst for Cyclic Esters Synthesis, Their Polymerization and Degradation of Aliphatic Polyesters *J. Polym. Environ.* **26** 396
42. Yina D, Liub W, Wanga Z, Huanga X, Zhanga J and Huang D 2017 Enzyme-catalyzed direct three-component aza-Diels–Alder reaction using lipase from *Candida* sp. 99–125 *Chin. Chem. Lett.* **28** 153
43. Yuki O, Zhang Y, Ge J and Liu Z 2016 Epoxidation of Fatty Acids by Pluronic-Conjugated Lipase in Organic Media *Catal. Lett.* **146** 1073
44. Stauch B, Fisher S J and Cianci M 2015 Open and closed states of *Candida antarctica* lipase B: protonation and the mechanism of interfacial activation *J. Lipid Res.* **56** 2348
45. Uppenberg J, Trier Hansen M, Patkar S and Jones T A 1994 The sequence, crystal structure determination and refinement of two crystal forms of lipase B from Candida antarctica *Structure* **2** 293
46. Chavan A S, Kharat A S, Bhosle M R and Mane R A 2017 A convenient Baker yeast accelerated, one-pot synthesis of pentasubstituted thiopyridines *Synth. Commun.* **47** 1777
47. Chavan A S, Kharat A S, Bhosle M R and Mane R A 2018 Baker's yeast catalyzed one-pot synthesis of bioactive 2-[benzylidene (or pyrazol-4-ylmethylene) hydrazono]-1, 3-thiazolidin-4-one-5-yl-acetic acids *Heter. Commun.* **24** 103
48. Chavan A S, Kharat A S, Bhosle M R, Dhumal S T and Mane R A 2021 Water mediated and Baker's yeast accelerated novel synthetic protocols for tetrahydrobenzo[a]xanthene-11-ones and pyrazolo[3,4-b]quinolines *Synth. Commun.* **51** 1963
49. Chavan A S, Kharat A S, Bhosle M R, Dhumal S T and Mane R A 2021 CAL-B accelerated novel synthetic protocols for 3,3'-arylidenebis-4-hydroxycoumarins and dimethyl ((substituted phenyl) (phenylamino)methyl) phosphonates *Res. Chem. Intermed.* **47** 4497
50. Zhang L R, Liu Z J, Zhang H, Sun V, Luo V, Zhao V, *et al.* 2012 Synthesis, biological evaluation and molecular docking studies of novel 2-(1,3,4-oxadiazol-2-ylthio)-1-phenylethanone derivatives *Bioorg. Med. Chem.* **20** 3615
51. Kashtoh H, Hussain S, Khan A, Saad S M, Khan J A J, Khan K M, *et al.* 2014 Oxadiazoles and thiadiazoles: novel α-glucosidase inhibitors *Bioorg. Med. Chem.* **22** 5454

***Letters in Organic Chemistry*, xxxx, *xx*, x-x** **1**

RESEARCH ARTICLE

A Mild and Rapid Synthesis of 2-aryl Benzimidazoles by using SO_4^{2-}/ZrO_2-TiO_2 as a Heterogeneous Catalyst

Sushil V. Shelke[1], Sambhaji T. Dhumal[2], Tejshri R. Deshmukh[3] and Meghshyam K. Patil[1,*]

[1]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad- 413 501, MS, India; [2]Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad- 413 501, MS, India; [3]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad- 431 004, MS, India

ARTICLE HISTORY

Received: September 30, 2022
Revised: November 13, 2022
Accepted: November 15, 2022

DOI:
10.2174/1570178620666230103140744

Abstract: Herein, we have reported an efficient synthesis of 2-aryl benzimidazoles by reacting *o*-phenylenediamines and substituting aromatic aldehydes using SO_4^{2-}/ZrO_2-TiO_2 as a heterogeneous catalyst. This methodology is straightforward to obtain 2-aryl benzimidazoles with good to excellent yields. It has been performed in ethanol as a green solvent. The reported protocol has some advantages such as a safe and reusable heterogeneous catalyst, without any need for column chromatography to obtain desired products. The catalyst can be recovered for up to five catalytic cycles without significant loss in the catalytic activity.

Keywords: SO_4^{2-}/ZrO_2-TiO_2, 2-Aryl benzimidazoles, recyclable, heterogeneous catalyst, cyclocondensation, benign GERD.

1. INTRODUCTION

Heterocyclic compounds are an important part of many research sectors, including medicine, pharmaceuticals, organic chemistry, industrial chemistry, polymer chemistry, biochemistry, and many more. They are also found in a wide variety of vitamins, drugs, biomolecules, biologically active compounds, like antitumor, antifungal, antidiabetic, anti-HIV, antibiotic, herbicidal, antibacterial, anti-inflammatory, antidepressant, antitubercular, antimalarial, antimicrobial, antiviral, and insecticidal agents [1]. Indeed, more than 90% of novel drugs contain heterocycles in their molecular structure, proving heterocycles significant contribution to medicinal chemistry [2,3]. Over 75% of the top 200 branded drugs in the pharmaceutical business contain aromatic and aliphatic heterocyclic fragments in their molecular structures [4-6].

Benzimidazole skeleton is one of the most bioactive heterocycles having a variety of therapeutic properties. Therefore, benzimidazole and its derivatives are given much importance due to their therapeutic properties in medicinal chemistry research [7]. The structural resemblance of benzimidazoles with some naturally occurring moieties such as purines makes them easier to bind with enzymes or receptors of living entities [8]. Literature survey also reveals that benzimidazole and its derivatives are versatile scaffolds observed in various pharmaceutical agents and display a broad spectrum of biological activities such as antiviral [9], antifungals [10], antitumor [11], antihistaminic [12], antiulcer [13], antihelminthic [14], antihypertensive [15], anticoagulant [16], anti-inflammatory [17], antiparasitic [18], antioxidant, antitubercular [19], and antimicrobial [20-24].

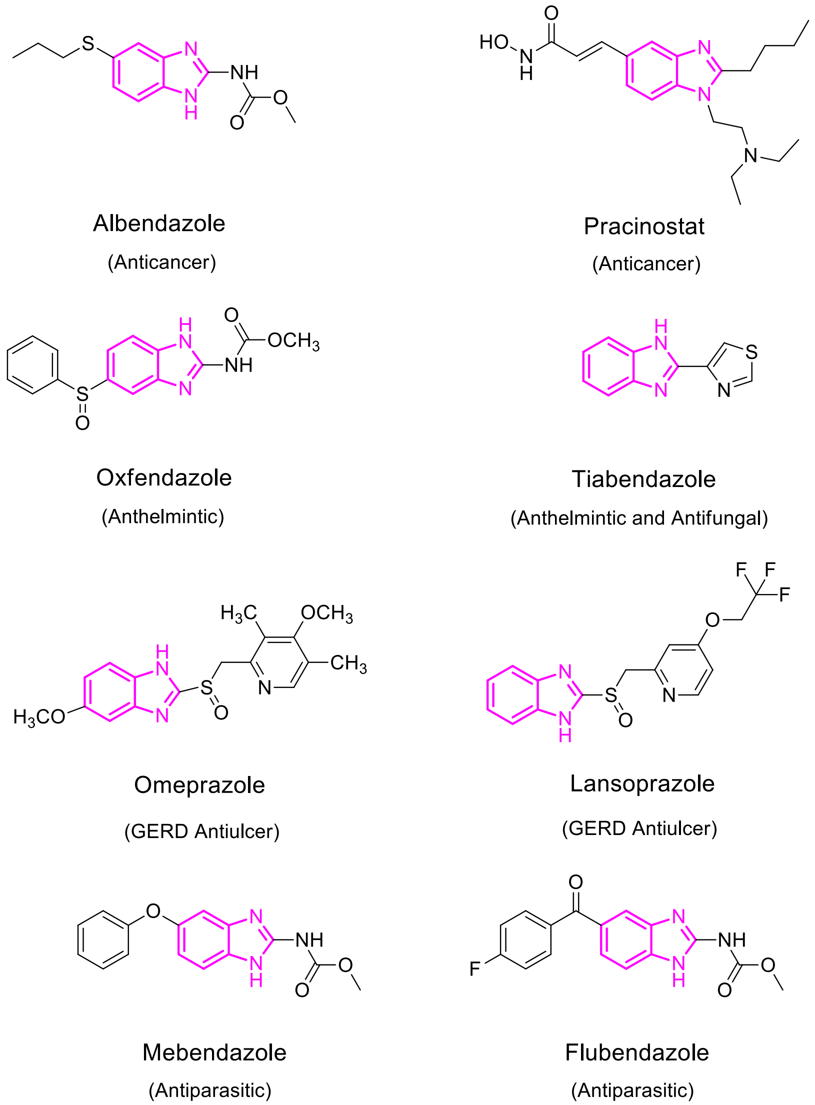
Many market approved drugs contain a benzimidazole skeleton in their structural motif, for example, Albendazole and Pracinostat as anticancer drugs, omeprazole, Ilarazole and lansoprazole act as GERD antiulcer drugs, oxfendazole and Tiabendazole as anthelmintic and antifungal drugs, Mebendazole and Flubendazole act as antiparasitic drugs, Adibenden as phoshodisterase inhibitor, Cloimozide as antisychotic drug, Lerisetron and Bilastine act as antihistaminic drugs Ridinalazole as an antibacterial drug, Mibefradil as an antihypertensive drug, and Samatasvir as an antiviral drug. Fig. (**1**) summarises some chemical structures of market-approved drugs incorporating benzimidazole skeleton.

Numerous synthetic approaches have been described in recent years as a result of environmental problems and the pharmacological importance of benzimidazole scaffolds. Among all the well-known methods, solid-phase condensation of *o*-phenylenediamine with aromatic aldehydes is generally preferred. There are several lacunas with the reported protocols like the need for catalysts and desiccants, higher reaction temperature, longer reaction time, and tedious workup procedure.

---

*Address correspondence to this author at the Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad-413 501, MS, India; meghshyam_patil@yahoo.com

1570-1786/xx $65.00+.00



Albendazole (Anticancer)

Pracinostat (Anticancer)

Oxfendazole (Anthelmintic)

Tiabendazole (Anthelmintic and Antifungal)

Omeprazole (GERD Antiulcer)

Lansoprazole (GERD Antiulcer)

Mebendazole (Antiparasitic)

Flubendazole (Antiparasitic)

Fig. (1). Some clinically used drugs bearing benzimidazolyl skeleton in their structural motif.

Considering these limitations with the already reported synthetic methodologies, there is still a need for creating acceptable synthetic methods as well as the synthesis of new catalysts with acidic strength and recyclability to be environmentally benign [25]. Heterogeneous solid acid catalysts offer various advantages over conventional liquid acids and Lewis acids. These advantages include recovery and recyclability of the catalyst, easy handling, simple work-up procedure, mild reaction conditions, and so on. Due to associated advantages, these catalysts have been thoroughly studied for organic synthesis and transformation reactions as well as industrial processes [26-28]. There is also a lot of opportunity to study catalysts for the synthesis of valuable medicinal compounds by creating eco-friendly methodologies. A literature survey reveals that the zirconium-based catalyst is highly efficient in organic synthesis [29-31]. By considering above mentioned advantages, zirconium based acid catalysed organic transformations and in continuation with our earlier research [32], here, we have decided to use SO_4^{2-}/ZrO_2-TiO_2 as a heterogeneous solid acid catalyst for the green synthesis of 2-aryl benzimidazoles [33, 34].

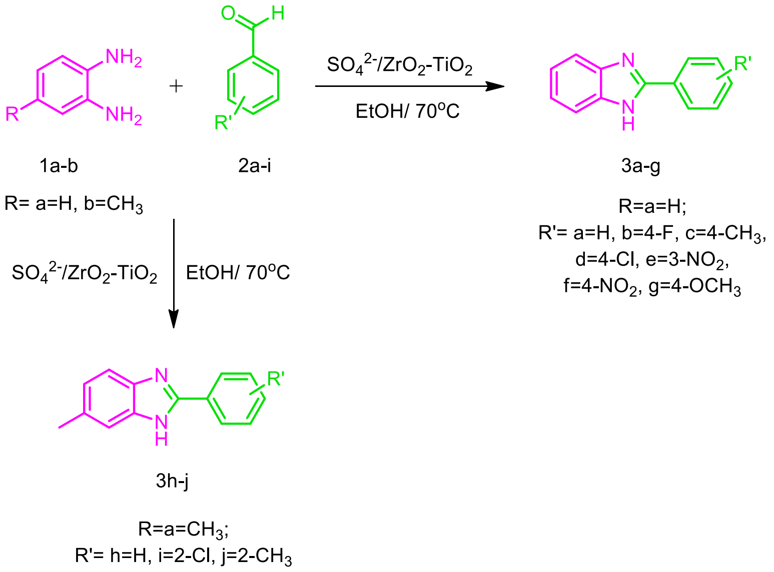
2. RESULTS AND DISCUSSION

The synthesis of 2-aryl benzimidazoles (**3a-j**) was carried out by reacting substituted aromatic aldehydes (**2a-j**) (0.001 mole) and *o*-phenylenediamines (**1a-b**) (0.001 mole) in the presence of SO_4^{2-}/ZrO_2-TiO_2 as a heterogeneous catalyst, stirred at 70°C for 2h with good to excellent yields and high purity products (Scheme **1**).

The structures of all the synthesized 2-aryl benzimidazoles are shown in Fig. (**2**).

The model reaction was carried out in the presence of *o*-phenylenediamine (**1a**) and benzaldehyde (**2a**) as shown below.

The optimization of the reaction was performed by varying the reaction parameters such as reaction time, solvents and temperature. It was observed that the 2-aryl benzimidazoles formation in ethanol solvent proceeds with an excellent yield at 70°C for 2 h (Table **1**, entry 3). Whereas, no reaction was observed in the presence of water as a solvent. (Table **1**, entry 1).



Scheme 1. Synthesis of 2-aryl benzimidazoles (**3a-j**) using SO_4^{2-}/ZrO_2-TiO_2 catalyst.

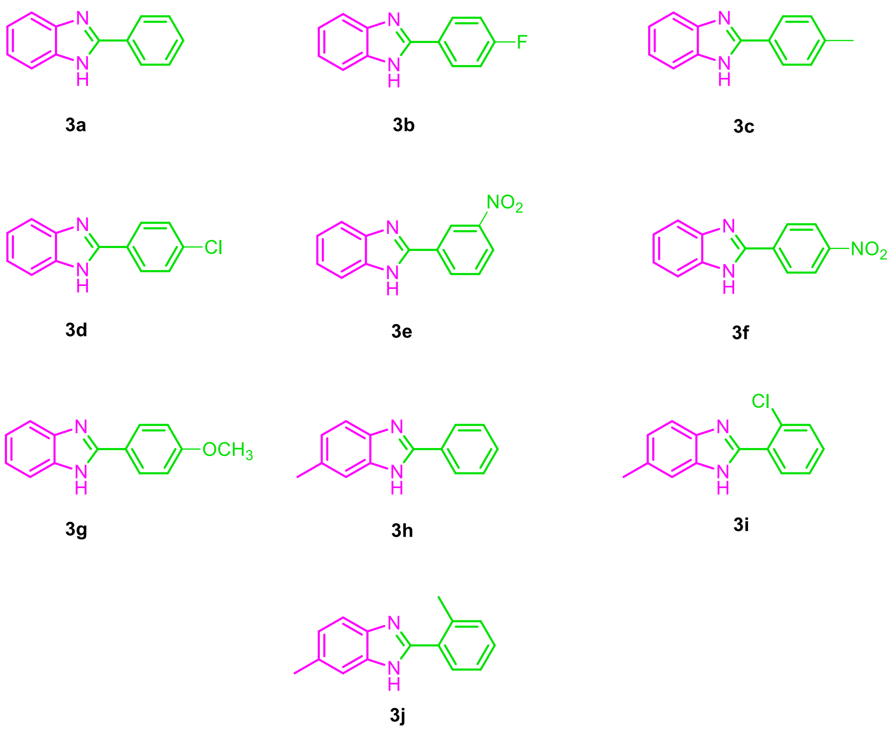


Fig. (2). Structures of all the synthesized 2-aryl benzimidazoles (**3a-j**).

Table 1. Screening of reaction condition with respect to solvent and catalyst loading 3a[a].

S. No.	Solvent	Catalyst	Yield[b] (%)
1	Water	SO_4^{2-}/ZrO_2-TiO_2	NR
2	Methanol	SO_4^{2-}/ZrO_2-TiO_2	78
3	Ethanol	SO_4^{2-}/ZrO_2-TiO_2	94
4	Dichloromethane	SO_4^{2-}/ZrO_2-TiO_2	58
5	Acetonitrile	SO_4^{2-}/ZrO_2-TiO_2	78
6	Dimethylformamide	SO_4^{2-}/ZrO_2-TiO_2	45
7	EtOH	No catalyst	02

Note: [a]**Reaction conditions**: *o*-pheneylenediamine (0.001 mole), benzaldehyde (0.001 mol), SO_4^{2-}/ZrO_2-TiO_2 in 10 mL EtOH, at 70°C for 2 h; [b]Isolated yields, NR: No Reaction.

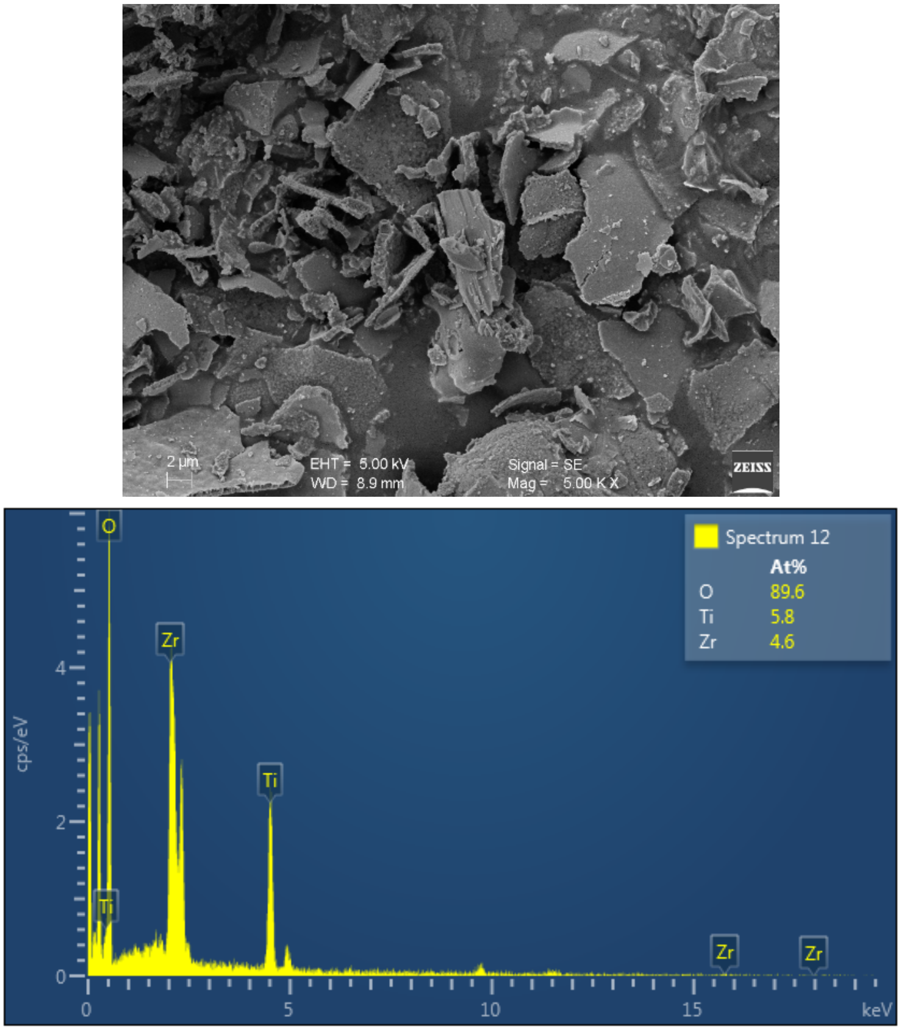
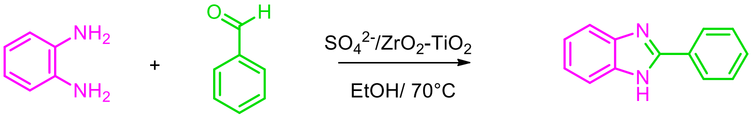


Fig. (3). SEM and EDX analysis of SO_4^{2-}/ TiO_2-ZrO_2 catalyst.



1a **2a** **3a**

Scheme 2. Model reaction for the optimization of solvent and catalyst.

3. CHARACTERIZATION OF SO_4^{2-}/ZRO_2-TIO_2

The detail characterization of the prepared heterogeneous catalyst SO_4^{2-}/ZrO_2-TiO_2 has been discussed in our previous reports [32]. XRD result shows the formation of tetragonal ZrO_2 and anatase TiO_2 in the prepared catalyst, which is confirmed by JCPDS data. FTIR spectra show the presence of peaks at 1348 cm^{-1}, 1440 cm^{-1} and 1180-1050 cm^{-1}, which may be associated with asymmetric and symmetric stretching frequency of the O = S = O and O – S – O groups. Further, the peaks in the range of 500 to 1100 cm^{-1} correspond to M-O stretching *i.e.* Ti-O and Zr-O stretching. The differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) of SO_4^{2-}/ TiO_2-ZrO_2 uncalcinated sample confirms the stability of the catalyst at a higher temperature. One of the major weight loss is observed in the range of 600°C to 800°C, which is due to the decomposition of sulfate groups. SEM and EDX results of the catalyst have been shown in Fig. (**3**). EDX results show the presence of Zr, Ti, and O in the catalyst. SEM image shows the agglomeration of nano-size particles in the form of plates with small cracks on the surface.

We have also investigated the recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the model reaction of *o*-

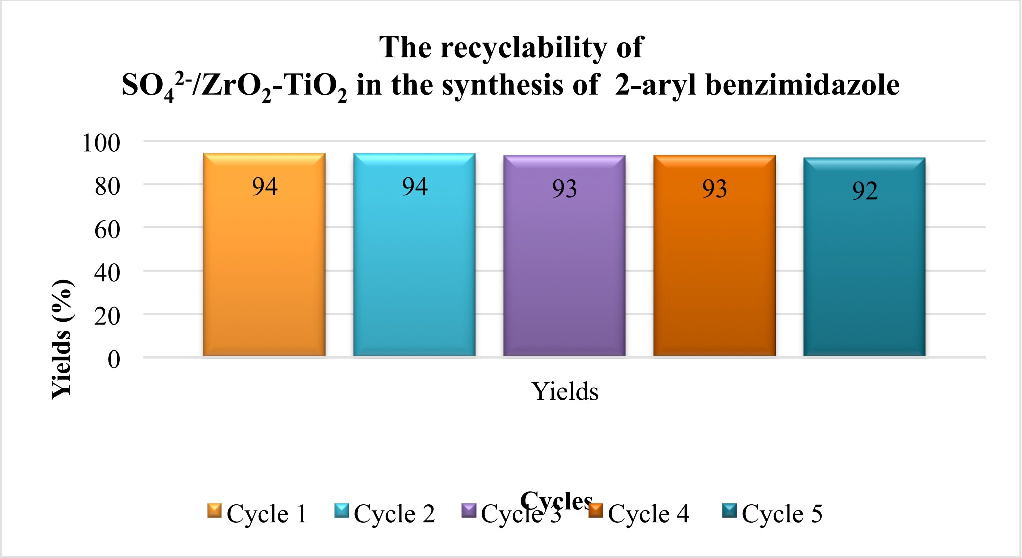
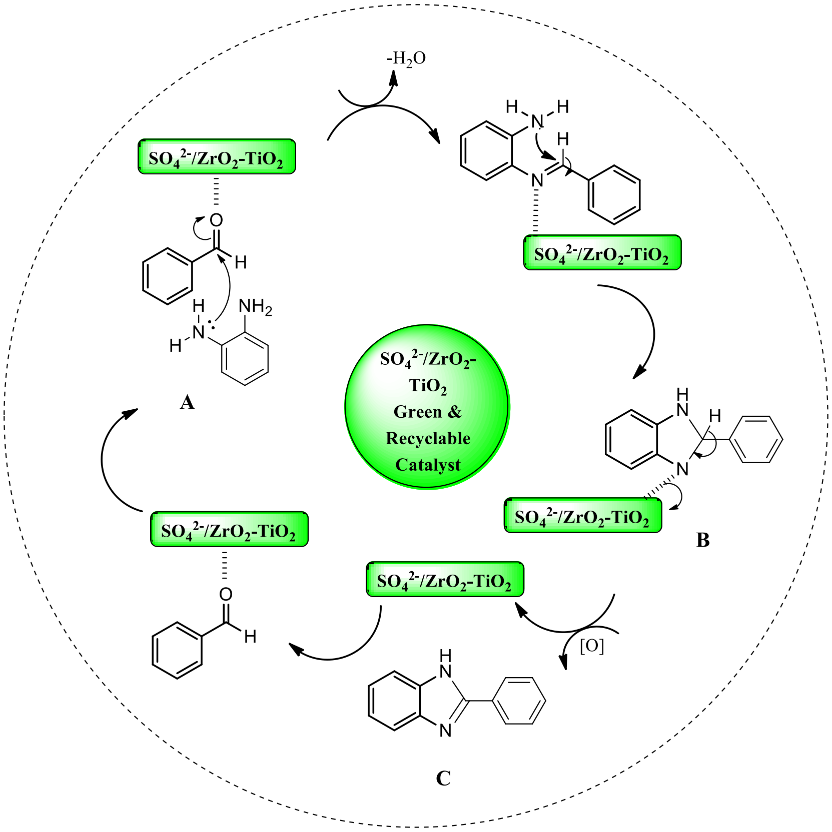


Fig. (4). The recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*)



Scheme 3. Plausible mechanism for the synthesis of 2-aryl benzimidazole derivative. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

phenylenediamine (**1**) and benzaldehyde (**2a**) in ethanol solvent at 70°C for 2 h and results were incorporated in Fig. (**4**) Scheme **2**.

The plausible mechanism for the 2-aryl benzimidazole synthesis [19] is depicted in Scheme **3**, which involves the protonation of the carbonyl group of benzaldehyde over SO_4^{2-}/ZrO_2-TiO_2 catalyst **A**, later it reacts with *o*-phenylenediamine involves the dehydration resulted into the formation of cyclic product **B**, which is readily oxidise in air to form desired product **C** that is 2-aryl benzimidazoles. Hydroxyl group and sulfate groups present on the surface of the catalyst act as Bronsted and Lewis acid sites and help to proceed with the acid-catalyzed reactions.

4. EXPERIMENTAL SECTION

4.1. General Procedure for the Preparation of SO_4^{2-}/ZrO_2-TiO_2 Catalyst

SO_4^{2-}/TiO_2-ZrO_2 solid acid catalyst has been synthesized by sol-gel method followed by impregnation method [32]. In a 500 ml beaker, the mixture of 50 mL ethyl alcohol, 2 mL conc. HCl and 0.5 mL acetic acid have been prepared and stirred for 30 min. To this mixture of the solution, 3.16 mL titanium isopropoxide and 3.35 mL zirconium propoxide were added as a precursor of Ti and Zr, respectively with constant stirring for 1 h. Resultant solution has been heated at 50°C. The gel was formed. The excess ethanol was evaporated and the gel was dried using an oven to form a white powder. For sulphate impregnation, 0.5 M H_2SO_4 solution has been prepared. About 15 mL H_2SO_4 solution was used per gram of the prepared powder. After this, the formed powder was added to the sulfuric acid solution and excess water has been evaporated into a sand bath. The obtained sulphate-impregnated powder was dried and crushed to get fine powder and finally calcined at 650°C for 4h.

4.2. General Experimental Procedure for the Synthesis of 2-aryl Benzimidazoles

Benzaldehyde (0.001 mole) and SO_4^{2-}/ZrO_2-TiO_2 catalyst (50 mg) were dissolved in EtOH (3 mL) at room temperature for 10 min. Then, *o*-phenylenediamine (0.001 mole) was added slowly to the reaction mass. The resultant mixture was heated for the stipulated time. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was diluted with ethyl acetate (10 mL) and catalyst was recovered by simple filtration. The crude product was purified by crystallization using ethanol to afford pure 2-aryl benzimidazoles. The melting points of the desired products were found to be in good agreement with the reported in the literature [35-40].

4.3. Spectral Analysis Data

4.3.1. 2-Phenyl-1H-benzo[d]imidazole (3a) [35-40]

The compound (**3a**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and benzaldehyde (**2a**) as pale white solid; yield 92%; mp 288-290°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.11-7.39 (m, 2H, Ar-H), 7.40-7.53 (m, 3H, Ar-H), 7.98 (d, 2H, Ar-H), 8.13 (d, 2H, Ar-H), 12.65 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 115.3, 122.5, 126.8, 129.1, 130.1, 135.2, 143.3, 151.8; HRMS (ESI^+) calcd. for $C_{13}H_{10}N_2$ $(M+H)^+$: 195.0922; found 195.0926.

4.3.2. 2-(4-Fluorophenyl)-1H-benzo[d]imidazole (3b)

The compound (**3b**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 4-fluorobenzaldehyde (**2b**) as off white solid; yield 88%; mp 250-252°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.12-7.16 (m, 2H, Ar-H), 7.24 (d, 2H, Ar-H), 7.52 (d, 2H, Ar-H), 8.15 (d, 2H, Ar-H), 12.77 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 116.2, 122.5, 122.7, 129.0, 129.1, 147.9, 149.3, 162.8; HRMS (ESI^+) calcd. for $C_{13}H_9FN_2$ $(M+H)^+$: 213.0828; found 213.0830 [35].

4.3.3. 2-(4-Tolyl)-1H-benzo[d]imidazole (3c)

The compound (**3c**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 4-methylbenzaldehyde (**2c**) as off white solid; yield 90%; mp 275-277°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.42 (s, 3H), 7.10-7.16 (m, 2H, Ar-H), 7.20 (d, 2H, Ar-H), 7.57 (d, 2H, Ar-H), 8.11 (d, 2H, Ar-H), 12.57 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.7, 116.7, 117.4, 124.8, 132.3, 133.2, 141.0, 150.2, 152.1; HRMS (ESI^+) calcd. for $C_{14}H_{12}N_2$ $(M+H)^+$: 209.1079; found 209.1081 [37].

4.3.4. 2-(4-Chlorophenyl)-1H-benzo[d]imidazole (3d)

The compound (**3d**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 4-chlorobenzaldehyde (**2d**) as off white solid; yield 89%; mp 291-293°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.10-7.15 (m, 2H, Ar-H), 7.20 (d, 2H, Ar-H), 7.48 (d, 2H, Ar-H), 8.10 (d, 2H, Ar-H), 12.72 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 116.7, 117.9, 124.8, 131.7, 132.3, 141.8, 150.4, 151.1; HRMS (ESI^+) calcd. for $C_{13}H_9ClN_2$ $(M+H)^+$: 229.0533; found 229.0535 [35].

4.3.5. 2-(3-Nitrophenyl)-1H-benzo[d]imidazole (3e)

The compound (**3e**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 3-nitrobenzaldehyde (**2e**) as pale yellowish solid; yield 91%; mp 207-209°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.16-7.17 (m, 2H, Ar-H), 7.55 (d, 2H, Ar-H), 7.67 (t,1H, Ar-H), 8.18 (d, 2H, Ar-H), 8.53 (d, 2H, Ar-H), 9.00 (s, 1H, Ar-H), 12.66 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 115.4, 121.3, 123.0, 124.2, 130.5, 132.0, 132.7, 139.0, 148.6, 149.4; HRMS (ESI^+) calcd. for $C_{13}H_9N_3O_2$ $(M+H)^+$: 240.0773; found 240.0775 [35].

4.3.6. 2-(4-Nitrophenyl)-1H-benzo[d]imidazole (3f)

The compound (**3f**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 4-nitrobenzaldehyde (**2f**) as pale yellowish solid; yield 93%; mp 226-228°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.18-7.20 (m, 2H, Ar-H), 7.57 (d, 2H, Ar-H), 8.30 (d, 2H, Ar-H), 8.38 (d, 2H, Ar-H), 13.05 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 123.3, 124.3, 127.6, 129.1, 136.1, 139.0, 148.1, 149.3; HRMS (ESI^+) calcd. for $C_{13}H_9N_3O_2$ $(M+H)^+$: 240.0773; found 240.0776 [35].

4.3.7. 2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (3g)

The compound (**3g**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-phenylenediamine (**1a**) and 4-methoxybenzaldehyde (**2g**) as off white solid; yield 90%; mp 225-227°C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.44 (s, 3H), 7.15-7.21 (m, 2H, Ar-H), 7.27 (d, 2H, Ar-H), 7.60 (d, 2H, Ar-H), 8.17 (d, 2H, Ar-H), 12.71 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.7, 117.2, 117.9, 124.5, 132.3, 132.9, 141.8, 150.1, 151.9; HRMS (ESI^+) calcd. for $C_{14}H_{12}N_2O$ $(M+H)^+$: 225.1028; found 225.1025 [37].

4.3.8. 6-Methyl-2-phenyl-1H-benzo[d]imidazole (3h)

The compound (**3h**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between 4-methyl-o-phenylenediamine (**1b**) and benzaldehyde (**2a**) as light yellow solid; yield 91%; mp 240-242°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.45 (s, 3H), 6.94-7.35 (m, 2H, Ar-H), 7.38-7.45 (m, 3H, Ar-H), 7.93 (d, 2H, Ar-H), 8.10 (d, 2H, Ar-H), 12.66 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.7, 114.5, 115.2, 123.9, 126.7, 128.9, 129.7, 130.3, 131.9, 131.9, 135.0, 137.7, 144.4, 151.5; HRMS (ESI$^+$) calcd. for $C_{14}H_{12}N_2$ $(M+H)^+$: 209.1079; found 209.1082 [40].

4.3.9. 2-(2-Chlorophenyl)-6-methyl-1H-benzo[d]imidazole (3i)

The compound (**3i**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between 4-methyl-o-phenylenediamine (**1b**) and 2-chlorobenzaldehyde (**2h**) as light yellow solid; yield 91%; mp 105-108°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.65 (s, 3H), 7.24-7.45 (m, 4H, Ar-H), 7.58-7.65 (m, 3H, Ar-H), 12.86 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.3, 115.3, 115.7, 126.0, 128.6, 129.8, 130.0, 131.2, 132.1, 133.2, 135.0, 135.8, 140.0, 152.7; HRMS (ESI$^+$) calcd. for $C_{14}H_{11}ClN_2$ $(M+H)^+$: 243.0689; found 243.0691 [40].

4.3.10. 2-(2-Tolyl)-6-methyl-1H-benzo[d]imidazole (3j)

The compound (**3j**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between 4-methyl-o-phenylenediamine (**1b**) and 2-methylbenzaldehyde (**2i**) as light yellow solid; yield 91%; mp 153-155°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.42 (s, 3H), 2.63 (s, 3H), 6.92-7.15 (m, 2H, Ar-H), 7.22-7.60 (m, 5H, Ar-H), 12.54 (s, 1H, broad N-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.2, 21.6, 55.7, 111.4, 114.4, 115.2, 115.6, 120.0, 125.6, 130.0, 131.7, 132.2, 133.1, 151.7, 153.0; HRMS (ESI$^+$) calcd. for $C_{15}H_{14}N_2O$ $(M+H)^+$: 223.1235; found 223.1237 [40].

CONCLUSION

In conclusion, we have developed a mild, efficient and environmentally benign synthetic protocol for the synthesis of 2-aryl benzimidazoles (**3a-j**) from substituted aromatic aldehydes and *o*-phenylenediamines using SO_4^{2-}/ZrO_2-TiO_2 as a heterogeneous and recyclable catalyst. The key feature of the proposed protocol involves simple reaction conditions, no side reaction, no kind of side products, and high yields of the final products. The present greener synthetic method is a better alternative to the conventional processes for the synthesis of 2-aryl benzimidazoles. The catalyst was recovered several times without loss of catalytic activity, which makes process cost-effective.

LIST OF ABBREVIATIONS

DSC = Differential Scanning Calorimetry

TGA = Thermogravimetric Analysis

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data that support the findings of this study are available within the article.

FUNDING

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

One of the authors SVS is thankful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad- 413501, MS, India for providing laboratory facility.

SUPPLEMENTARY MATERIAL

Experimental details can be found via the "Supplementary Content" section of this article's webpage.

REFERENCES

[1] Mulla, A.A. *Der Pharma Chem.,* **2017**, *9*(13), 141-147.

[2] Katritzky, A.R.; Ress, C.W.; Scriven, E.F.V. *Comprehensive Heterocyclic Chemistry II*; Pergamon: Oxford, U.K., **1996**.

[3] Balaban, A.T.; Oniciu, D.C.; Katritzky, A.R. *Chem. Rev.,* **2004**, *104*(5), 2777-2812. http://dx.doi.org/10.1021/cr0306790 PMID: 15137807

[4] Lai, Y.; Ma, L.; Huang, W.; Yu, X.; Zhang, Y.; Ji, H.; Tian, J. *Bioorg. Med. Chem. Lett.,* **2010**, *20*(24), 7349-7353. http://dx.doi.org/10.1016/j.bmcl.2010.10.056 PMID: 21055929

[5] Chauhan, K.; Sharma, M.; Saxena, J.; Singh, S.V.; Trivedi, P.; Srivastava, K.; Puri, S.K.; Saxena, J.K.; Chaturvedi, V.; Chauhan, P.M.S. *Eur. J. Med. Chem.,* **2013**, *62*, 693-704. http://dx.doi.org/10.1016/j.ejmech.2013.01.017 PMID: 23454512

[6] Makadia, P.; Shah, S.R.; Pingali, H.; Zaware, P.; Patel, D.; Pola, S.; Thube, B.; Priyadarshini, P.; Suthar, D.; Shah, M.; Giri, S.; Trivedi, C.; Jain, M.; Patel, P.; Bahekar, R. *Bioorg. Med. Chem.,* **2011**, *19*(2), 771-782. http://dx.doi.org/10.1016/j.bmc.2010.12.023 PMID: 21215640

[7] Bansal, Y.; Silakari, O. *Bioorg. Med. Chem.,* **2012**, *20*(21), 6208-6236. http://dx.doi.org/10.1016/j.bmc.2012.09.013 PMID: 23031649

[8] Sharma, P.; Thummuri, D.; Reddy, T.S.; Senwar, K.R.; Naidu, V.G.M.; Srinivasulu, G.; Bharghava, S.K.; Shankaraiah, N. *Eur. J. Med. Chem.,* **2016**, *122*, 584-600. http://dx.doi.org/10.1016/j.ejmech.2016.07.019 PMID: 27448916

[9] Emery, V.C.; Hassan-Walker, A.F. *Drugs,* **2002**, *62*(13), 1853-1858. http://dx.doi.org/10.2165/00003495-200262130-00002 PMID: 12215056

[10] Bossche, H.V.; Engelen, M.; Rochette, F. *J. Vet. Pharmacol. Ther.,* **2003**, *26*(1), 5-29. http://dx.doi.org/10.1046/j.1365-2885.2003.00456.x PMID: 12603774

[11] Kagechika, H. *Curr. Med. Chem.,* **2002**, *9*(5), 591-608. http://dx.doi.org/10.2174/0929867024606975 PMID: 11945126

[12] Al-Muhaimeed, H. *J. Int. Med. Res.,* **1997**, *25*(4), 175-181. http://dx.doi.org/10.1177/030006059702500401 PMID: 9283989

[13] Noor, A.; Qazi, N.G.; Nadeem, H.; Khan, A.; Paracha, R.Z.; Ali, F.; Saeed, A. *Chem. Cent. J.,* **2017**, *11*(1), 85. http://dx.doi.org/10.1186/s13065-017-0314-0 PMID: 29086868

[14] Dubey, A.K.; Sanyal, P.K. *Vet. J.,* **2010**, *5*(2), 63.

[15] Naik, P.; Murumkar, P.; Giridhar, R.; Yadav, M.R. *Bioorg. Med. Chem.,* **2010**, *18*(24), 8418-8456. http://dx.doi.org/10.1016/j.bmc.2010.10.043 PMID: 21071232

[16] Mederski, W.W.K.R.; Dorsch, D.; Anzali, S.; Gleitz, J.; Cezanne, B.; Tsaklakidis, C. *Bioorg. Med. Chem. Lett.,* **2004**, *14*(14), 3763-3769. http://dx.doi.org/10.1016/j.bmcl.2004.04.097 PMID: 15203158

[17] Mader, M.; de Dios, A.; Shih, C.; Bonjouklian, R.; Li, T.; White, W. *Bioorg. Med. Chem. Lett.,* **2008**, *18*(1), 179-183. http://dx.doi.org/10.1016/j.bmcl.2007.10.106 PMID: 18039577

[18] Alp, M.; Göker, H.; Brun, R.; Yıldız, S. *Eur. J. Med. Chem.,* **2009**, *44*(5), 2002-2008. http://dx.doi.org/10.1016/j.ejmech.2008.10.003 PMID: 19010569

[19] Hebade, M. J.; Dhumal, S. T.; Kamble, S. S.; Deshmukh, T. R.; Khedkar, V. M.; Hese, S. V.; Gacche, R. N.; Dawane, B. S. *Polycycl. Aromat. Compd.,* **2022**. http://dx.doi.org/10.1080/10406638.2022.2056210

[20] Lam, T.; Hilgers, M.T.; Cunningham, M.L.; Kwan, B.P.; Nelson, K.J.; Brown-Driver, V.; Ong, V.; Trzoss, M.; Hough, G.; Shaw, K.J.; Finn, J. *J. Med. Chem.,* **2014**, *57*(3), 651-668. http://dx.doi.org/10.1021/jm401204g PMID: 24428639

[21] Desai, N.C.; Shihory, N.R.; Kotadiya, G.M. *Chin. Chem. Lett.,* **2014**, *25*(2), 305-307. http://dx.doi.org/10.1016/j.cclet.2013.11.026

[22] Seenaiah, D.; Reddy, P.R.; Reddy, G.M.; Padmaja, A.; Padmavathi, V.; Siva krishna, N. *Eur. J. Med. Chem.,* **2014**, *77*, 1-7. http://dx.doi.org/10.1016/j.ejmech.2014.02.050 PMID: 24607584

[23] Kazimierczuk, Z.; Andrzejewska, M.; Kaustova, J.; Klimešova, V. *Eur. J. Med. Chem.,* **2005**, *40*(2), 203-208. http://dx.doi.org/10.1016/j.ejmech.2004.10.004 PMID: 15694655

[24] Stanley, S.A.; Grant, S.S.; Kawate, T.; Iwase, N.; Shimizu, M.; Wivagg, C.; Silvis, M.; Kazyanskaya, E.; Aquadro, J.; Golas, A.; Fitzgerald, M.; Dai, H.Q.; Zhang, L.X.; Hung, D.R. *Chem. Biol.,* **2012**, *7*(8), 1377-1384.

[25] Hebade, M.J.; Deshmukh, T.R.; Dhumal, S.T. *Synth. Commun.,* **2021**, *51*(16), 2510-2520. http://dx.doi.org/10.1080/00397911.2021.1939060

[26] Patil, M.K.; Prasad, A.N.; Reddy, B.M. *Curr. Org. Chem.,* **2011**, *15*(23), 3961-3985. http://dx.doi.org/10.2174/138527211798072430

[27] Reddy, B.M.; Patil, M.K. *Chem. Rev.,* **2009**, *109*(6), 2185-2208. http://dx.doi.org/10.1021/cr900008m PMID: 19408954

[28] Gupta, P.; Paul, S. *Catal. Today,* **2014**, *236*, 153-170. http://dx.doi.org/10.1016/j.cattod.2014.04.010

[29] Peng, L.; Zhao, Y.; Yang, T.; Tong, Z.; Tang, Z.; Orita, A.; Qiu, R. *Top. Curr. Chem. (Cham),* **2022**, *380*(5), 41. http://dx.doi.org/10.1007/s41061-022-00396-4 PMID: 35951161

[30] Mo, L.P.; Zhang, Z.H. *Curr. Org. Chem.,* **2011**, *15*(22), 3800-3823. http://dx.doi.org/10.2174/138527211797884520

[31] Zhang, Z.H.; Li, T.S. *Curr. Org. Chem.,* **2009**, *13*(1), 1-30. http://dx.doi.org/10.2174/138527209787193783

[32] Shelke, S.V.; Dhumal, S.T.; Karale, A.Y.; Deshmukh, T.R.; Patil, M.K. *Synth. Commun.,* **2022**, *52*(4), 597-607. http://dx.doi.org/10.1080/00397911.2022.2039711

[33] Patil, M.K.; Prasad, A.N.; Reddy, B.M. *Curr. Org. Chem.,* **2011**, *15*(23), 3961-3985. http://dx.doi.org/10.2174/138527211798072430

[34] Reddy, B.; Patil, M. *Curr. Org. Chem.,* **2008**, *12*(2), 118-140. http://dx.doi.org/10.2174/138527208783330019

[35] Saha, D.; Saha, A.; Ranu, B.C. *Green Chem.,* **2009**, *11*(5), 733-737. http://dx.doi.org/10.1039/b823543k

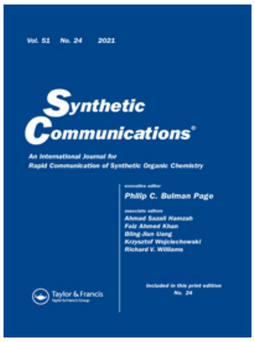
[36] Du, L.H.; Wang, Y.G. *Synthesis,* **2007**, *1*(5), 675-678.

[37] Gogoi, P.; Konwar, D. *Tetrahedron Lett.,* **2006**, *47*(1), 79-82. http://dx.doi.org/10.1016/j.tetlet.2005.10.134

[38] Srivastava, R.G.; Venkataramani, P.S. *Synth. Commun.,* **1988**, *18*(13), 1537-1544. http://dx.doi.org/10.1080/00397918808081311

[39] Itoh, T.; Nagata, K.; Ishikawa, H.; Ohsawa, A. *Heterocycles,* **2004**, *63*(12), 2769-2783. http://dx.doi.org/10.3987/COM-04-10215

[40] Li, J.; Bénard, S.; Neuville, L.; Zhu, J. *Org. Lett.,* **2012**, *14*(23), 5980-5983. http://dx.doi.org/10.1021/ol3028847 PMID: 23151245



Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

A facile synthesis of quinoxalines by using $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and recyclable heterogeneous catalyst

Sushil V. Shelke, Sambhaji T. Dhumal, Akshay Y. Karale, Tejshri R. Deshmukh & Meghshyam K. Patil

To cite this article: Sushil V. Shelke, Sambhaji T. Dhumal, Akshay Y. Karale, Tejshri R. Deshmukh & Meghshyam K. Patil (2022): A facile synthesis of quinoxalines by using $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and recyclable heterogeneous catalyst, Synthetic Communications, DOI: 10.1080/00397911.2022.2039711

To link to this article: https://doi.org/10.1080/00397911.2022.2039711

SYNTHETIC COMMUNICATIONS®
https://doi.org/10.1080/00397911.2022.2039711

A facile synthesis of quinoxalines by using $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and recyclable heterogeneous catalyst

Sushil V. Shelke[a], Sambhaji T. Dhumal[b], Akshay Y. Karale[a],
Tejshri R. Deshmukh[c], and Meghshyam K. Patil[a]

[a]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad, India; [b]Department of Chemistry, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad, India; [c]Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India

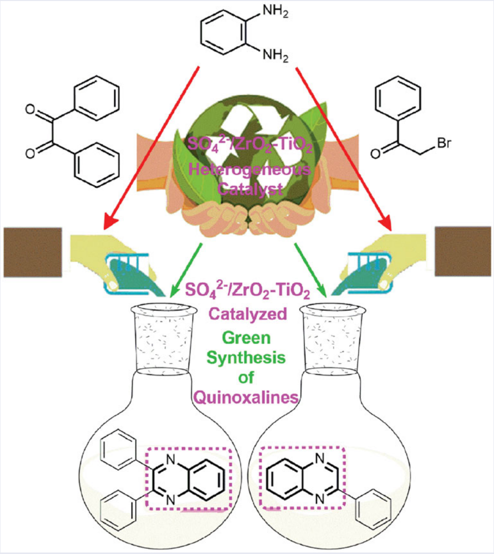
ABSTRACT

Quinoxaline derivatives have been synthesized in good to excellent yields by the cyclocondensation reaction of *o*-pheneylenediamine with substituted phenacyl bromides/benzil in the presence of $SO_4^{2-}/ZrO_2\text{-}TiO_2$ as an efficient and heterogeneous catalyst. The catalyst can be recovered up to five catalytic cycles without significant loss in catalytic activity. The reported $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst has been thoroughly characterized by using infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and powder X-ray diffraction (XRD). Here, we have used ethanol as a green solvent in this cyclocondensation. This new method has several advantages, such as excellent yields, short reaction time, non-toxic, and easily recoverable catalyst.

ARTICLE HISTORY
Received 29 November 2021

KEYWORDS
$SO_4^{2-}/ZrO_2\text{-}TiO_2$; quinoxalines; recyclable; heterogeneous catalyst; cyclocondensation

GRAPHICAL ABSTRACT



CONTACT Meghshyam K. Patil ✉ meghshyam_patil@yahoo.com Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Sub-campus, Osmanabad 413501, India.

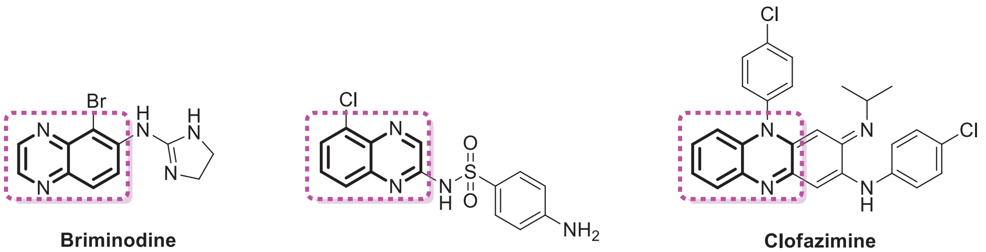
Supplemental data for this article can be accessed on the publisher's website.

Introduction

Quinoxalines are one of the important classes of nitrogen-containing heterocycles.[1] They are rarely occurred in nature and mostly synthesized by using various synthetic approaches.[2] In a quest to develop sustainable and greener synthetic strategies for quinoxalines, most of the researchers have been developing different greener synthetic approaches that involve recyclable catalysts, mild reactants, and reaction conditions.[3] Over the last few years, quinoxalines have grabbed more attention by researchers as they display a broad range of pharmaceutical as well as biological applications.[4] Various derivatives of quinoxalines have revealed a wide variety of bioactivities, such as antitubercular,[5] anti-inflammatory, antioxidant,[6] antifungal, anticancer, anti-HIV,[7] and antiprotozoan,[8] etc. Most of the clinically used drugs also possess quinoxalinyl moiety in their structural scaffold as an active pharmacophoric unit. Some of them are summarized in Figure 1.

In recent years, focusing on several environmental issues and considering the pharmacological importance of quinoxaline scaffolds there are numerous synthetic methods have been reported. Some of them are the condensation of *o*-phenylenediamine with 1,2-dicarbonyl compounds,[9] oxidation trapping of α-hydroxy ketones,[10] and 1,2-diazenylbutens.[11] Following are the various synthetic protocols involved for the synthesis of quinoxalines, such as heteropoly acid,[12] cellulose sulfuric acid,[13] hypervalent iodine (III) in PEG-400,[14] polyaniline-sulfate salt,[15] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,[16] PVPPOTf,[17] and $Ga(ClO_4)_3$.[18]

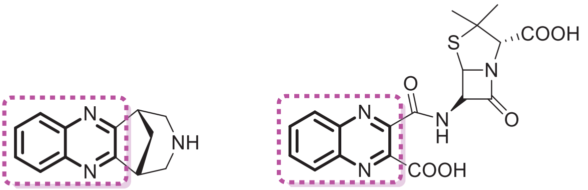
Among the aforementioned protocols, condensation of *o*-phenylenediamine with phenacyl bromides in the solid phase is highly preferred. This method has involved the use of a catalyst-free approach[19] as well as by using transition metal catalysts[20] and various heterogeneous catalysts like $HClO_4$-SiO_2,[21] silica-supported dodecatungstophosphoric acid,[1] TMSCl,[22] *β*-cyclodextrin,[23] silica-supported phosphomolybdic acid,[24] miceller SDS,[25] T3PDMSO or T3P,[26] *N*-Bromosuccinimide,[27] and ionic liquid.[28]



Briminodine

Chloroquinoxaline sulphonamide

Clofazimine



Varencline

Quinacillin

Figure 1. Some clinically used drugs bearing quinoxalinyl moiety.

Among the reported synthetic protocols, there are many synthetic approaches that having some limitations or lacunas, such as the use of $HClO_4$-SiO_2 catalyst is hazardous in nature than its potential application, the reaction catalyzed by TMSCl required higher temperature with low yield, the *β*-cyclodextrin, and miceller SDS catalyzed reactions were required longer time. Considering these lacunas/limitations with reported synthetic methods and used catalysts, still, there is a need for designing appropriate synthetic methods with the development of new catalysts having acidic strength and recyclability to be environmentally benign.

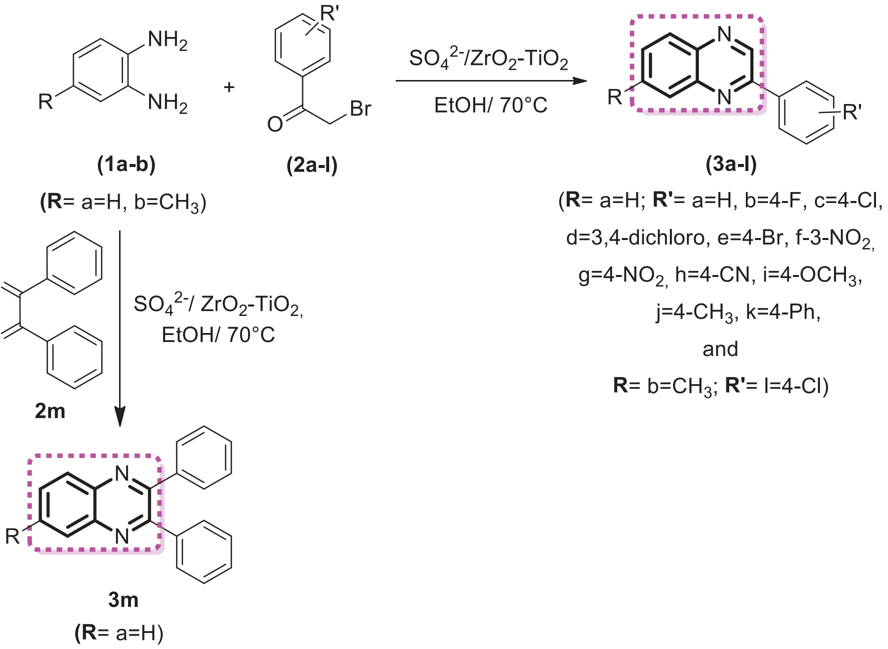
Results and discussion

The synthesis of quinoxalines was carried out by reacting substituted phenacyl bromides/benzil (**2a–m**) (0.001 mol) and *o*-pheneylenediamine (**1a–b**) (0.001 mol) in the presence of SO_4^{2-}/ZrO_2-TiO_2 as a catalyst. Further, the reaction mass was stirred at 70 °C for 50–80 min. afforded quinoxalines (**3a–m**) with excellent yields and high purity. This reaction is outlined in Scheme 1.

The structures of all the synthesized quinoxalines (**3a–m**) are shown in Figure 2.

The model reaction was carried out in presence of *o*-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as shown in Scheme 2.

The optimization of the reaction was performed by varying the reaction parameters, such as reaction time, solvent, and temperature. It was observed that the quinoxaline formation in ethanol solvent proceeds with an excellent yield at 70 °C for 50 min (Table 1, entry 3). Whereas, no reaction was observed in presence of water as a solvent (Table 1, entry 1).



Scheme 1. Synthesis of quinoxalines (**3a–m**) using SO_4^{2-}/ZrO_2-TiO_2 catalyst.

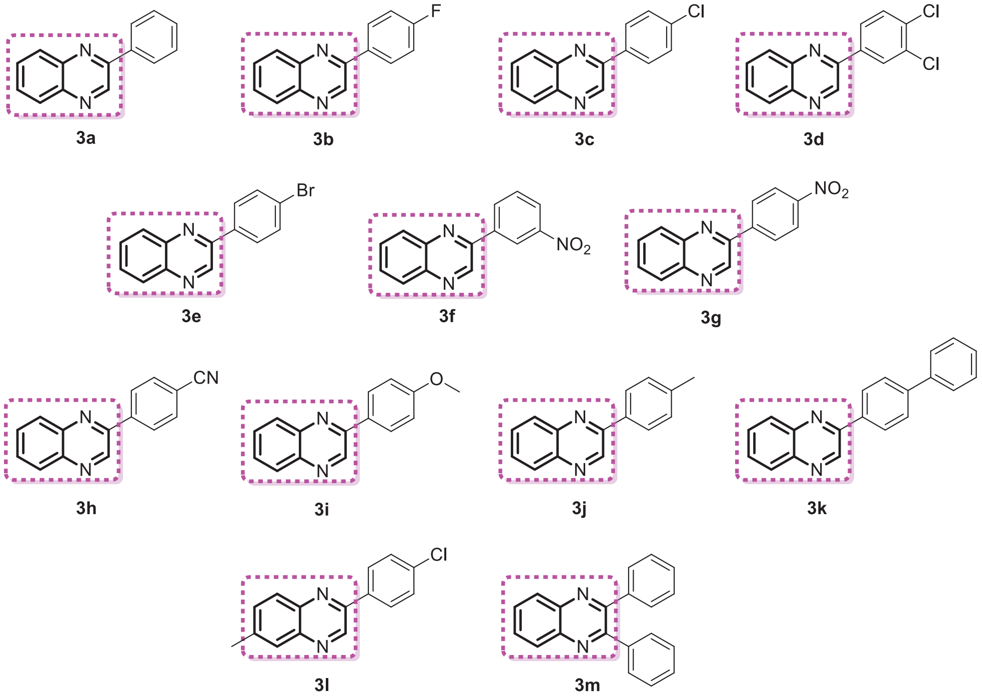
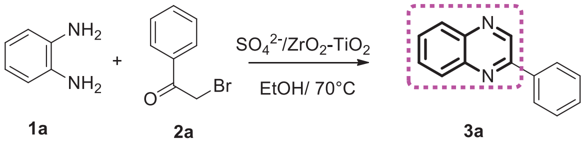


Figure 2. Structures of all the synthesized quinoxalines (**3a–m**).



Scheme 2. Model reaction for the optimization of solvent and catalyst.

Table 1. Screening of reaction condition with respect to solvent and catalyst loading **3a**.[a]

Sr. No.	Solvent	Catalyst	Yield[b] (%)
1	Water	SO_4^{2-}/ZrO_2-TiO_2	NR
2	Methanol	SO_4^{2-}/ZrO_2-TiO_2	82
3	Ethanol	SO_4^{2-}/ZrO_2-TiO_2	94
4	Dichloromethane	SO_4^{2-}/ZrO_2-TiO_2	65
5	Acetonitrile	SO_4^{2-}/ZrO_2-TiO_2	75
6	Dimethylformamide	SO_4^{2-}/ZrO_2-TiO_2	64
7	1,4-Dioxane	SO_4^{2-}/ZrO_2-TiO_2	58
8	Dimethylformamide	SO_4^{2-}/ZrO_2-TiO_2	65
9	EtOH	No catalyst	03

NR: no reaction.

[a] Reaction conditions: Phenacyl bromide (0.001 mol), *o*-phenylenediamine (0.001 mol), 20 SO_4^{2-}/ZrO_2-TiO_2 in 10 ml EtOH, at 70 °C for 50 min.

[b] Isolated yields.

Characterization of SO_4^{2-}/ZrO_2-TiO_2 catalyst

XRD pattern of sulfated TiO_2-ZrO_2 solid acid catalyst is shown in Figure 3. The diffraction pattern confirms the presence of the anatase phase of TiO_2 (JCPDS-211272), and the tetragonal and monoclinic structure of ZrO_2 (JCPDS-897710 and JCPDS-371484).

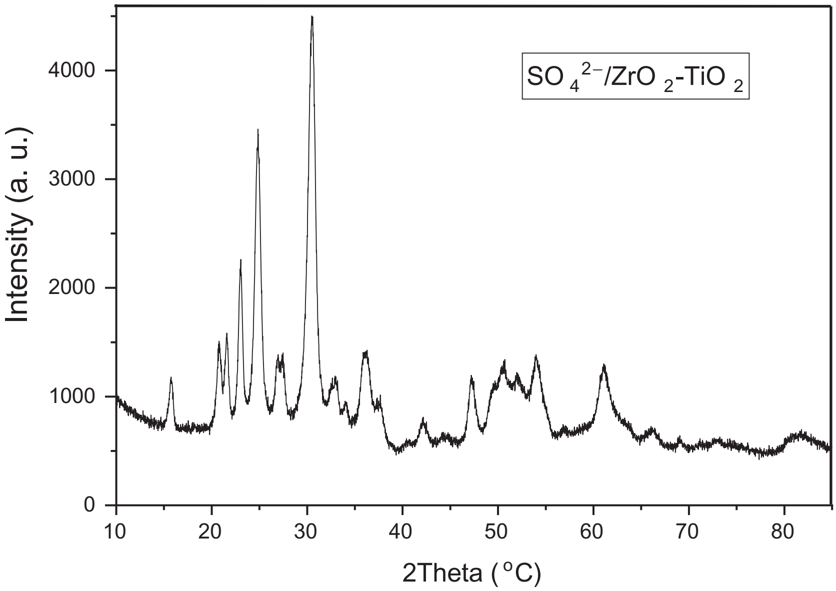


Figure 3. X-ray diffraction pattern of as prepared SO_4^{2-}/ZrO_2-TiO_2 catalyst.

In Figure 3, diffraction peaks are observed due to anatase TiO_2 at 24.83, 36.15, 37.67, 47.20, 53.98, 61.08, and 68.94°, which corresponds to the crystal planes (101), (103), (004), (200), (105), (204), and (116), respectively.[29] However, diffraction peaks are detected due to tetragonal ZrO_2 at the 27.47, 30.49, 32.91, 33.97, 50.57, 59.11, and 75.06° that corresponds to the reflections of crystal planes (−111), (101), (111), (110), (112), (211), and (220), respectively.[30,31]

Figure 4 shows the FT-IR spectra of sulfated TiO_2-ZrO_2 solid acid catalyst. The peaks at 1348, 1440 cm^{-1}, and in the region 1180–1050 cm^{-1}, can be attributed to the asymmetric and symmetric stretching frequency of the O = S = O and O–S–O groups.[32–34] The peaks at lower frequency in the range 500–1100 cm^{-1} are due to M–O stretching, which confirms the presence of metal oxides. Whereas, the peak observed at 1625 cm^{-1} was refers to the bending modes of the –OH groups of water molecules present in the sample.

Figure 5 shows the differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) of sulfated TiO_2-ZrO_2 uncalcinated sample. The TGA measurements agreed fairly well with those expected decompositions of uncalcinated sulfated metal oxide samples. The weight loss events below 600 °C were corresponds to the removal of adsorbed water and the dehydroxylation process. However, the major weight loss in the temperature range is about 600–800 °C, which refers to the decomposition of sulfate groups. Differential scanning calorimetry has shown the endothermic peaks that correspond to the removal of adsorbed water, dihydroxylation process, and decomposition of sulfate groups.

We have also investigated the recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the model reaction of *o*-phenylenediamine (**1**) and phenacyl bromide (**2a**) in ethanol solvent at 70 °C for 50 min. and observed results were incorporated in Figure 6.

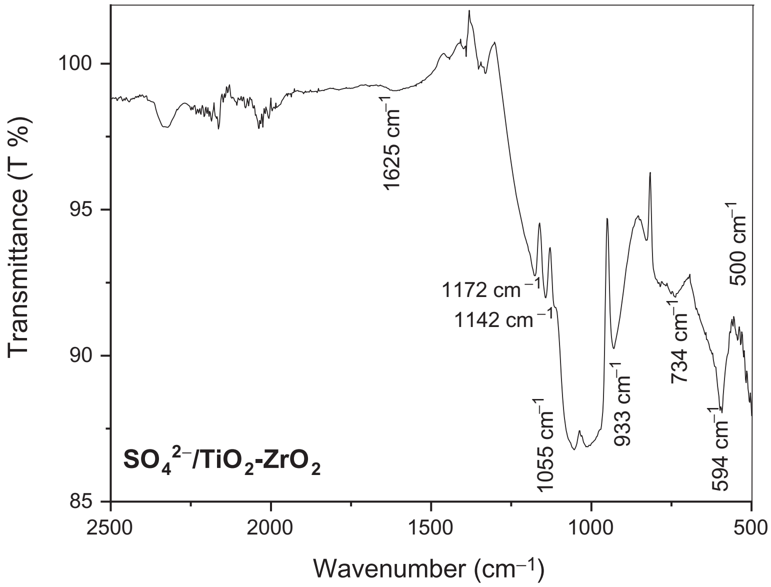


Figure 4. FT-IR spectra of as prepared $SO_4^{2-}/TiO_2\text{-}ZrO_2$ catalyst.

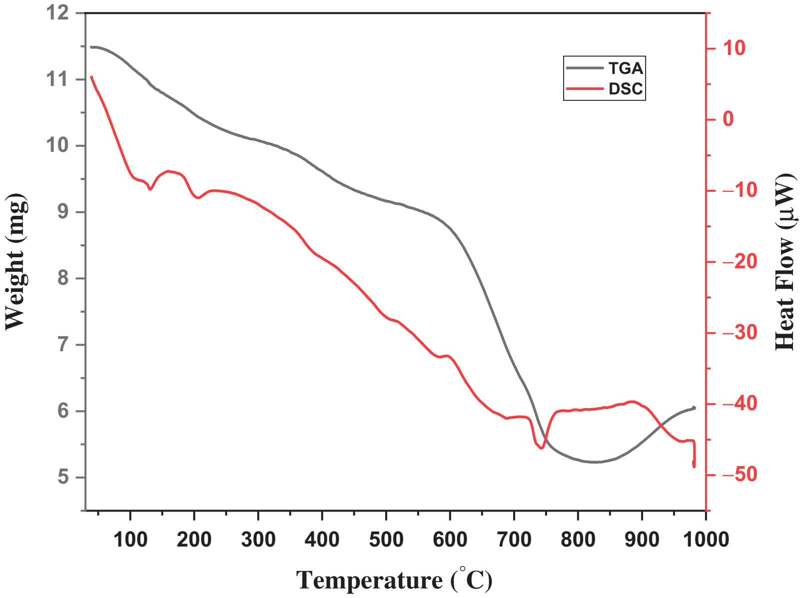


Figure 5. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) pattern of uncalcinated sulfated $TiO_2\text{-}ZrO_2$ sample.

The plausible mechanism for the quinaxolines synthesis was depicted in Scheme 3, which involves the protonation of the carbonyl group of phenacyl bromide over $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst (**A**). Later on, it reacts with *o*-pheneylenediamine that involves dehydration and dehalogenation simultaneously resulting in the formation of cyclic product **B**, which is readily oxidized in air to form desired product **C**.

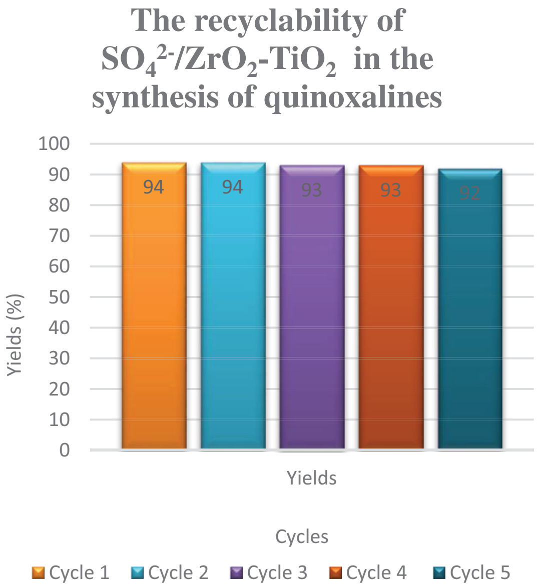


Figure 6. The recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the synthesis of quinoxalines.

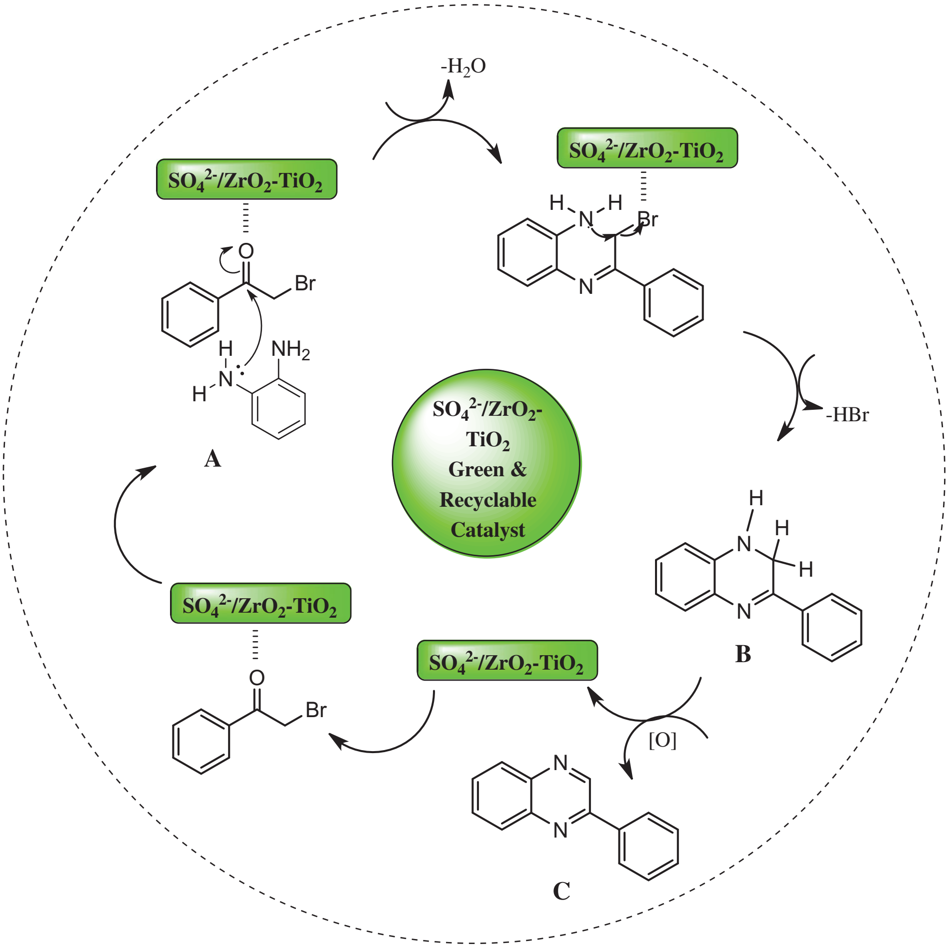
Conclusion

In conclusion, we have developed a mild, efficient, and environmentally benign synthetic protocol for the synthesis of quinoxalines (**3a–m**) from substituted phenacyl bromides/benzil and *o*-pheneylenediamines using SO_4^{2-}/ZrO_2-TiO_2 catalyst. The key feature of the current protocol involves simple reaction conditions, no side reaction with the formation of the desired product in high yield. The present method is an alternative to the conventional processes for the synthesis of quinoxalines. The catalyst could be recovered several times without loss of catalytic activity, which makes the process cost-effective.

Experimental

General procedure for the preparation of SO_4^{2-}/ZrO_2-TiO_2 catalyst

SO_4^{2-}/TiO_2-ZrO_2 solid acid catalyst has been synthesized by sol-gel synthetic method followed by impregnation method. Initially the solution of 50 mL ethyl alcohol, 2 mL conc. HCl and 0.5 mL acetic acid were stirred for 30 min. To this solution, titanium isopropoxide (3.16 mL) and zirconium propoxide (3.35 mL) were added dropwise with constant stirring for 1 h. The solution has been treated at 50 °C for a gel formation and the ethanol has been evaporated. The formed gel has been dried in an oven to form a powder. The formed powder has been used for sulfate impregnation. Here, we have used the 15 mL 0.5 M H_2SO_4 per gram of powder. After this, the formed powder has been added to the H_2SO_4 solution. The water has been evaporated by heating on the sand bath. The formed sulfonated powder has been calcined at 650 °C for 4 h.



Scheme 3. Plausible mechanism for the synthesis of quinoxaline derivatives.

General experimental procedure for synthesis of quinoxalines

Phenacyl bromides/benzil (**2a–m**) (0.001 mol) and $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyst (50 mg) were dissolved in EtOH (3 mL) at room temperature for 10 min. Then *o*-phenylenediamine (**1a–b**) (0.001 mol) was added slowly to the reaction mass. The resultant mixture was heated for a stipulated time. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was recovered by simple filtration. The crude product was purified by crystallization using ethanol to afford the pure quinoxalines (**3a–m**). The melting points of the desired products were found to be in good agreement with those reported in the literature.[35–41]

2-(Phenyl)quinoxaline (3a)

The compound (**3a**) was obtained by $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyzed reaction in between o-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as bright yellow solid; yield 94%; mp 73–75 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48–7.77 (m, 5H, Ar-H), 8.06–8.14 (m, 4H, Ar-H), 9.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 126.42, 128.15, 129.43, 131.32, 135.22, 141.62, 142.15, 143.12, 150.34; HRMS (ESI^+) calcd. for $C_{14}H_{10}N_2$ $(M+H)^+$: 207.0923; found 207.0926.

2,3-Diphenylquinoxaline (3m)

The compound (**3m**) was obtained by $SO_4^{2-}/ZrO_2\text{-}TiO_2$ catalyzed reaction in between o-pheneylenediamine (**1a**) and benzil (**2m**) as white solid; yield 91%; mp 123–125 °C; 7.32–7.54 (m, 5H, Ar-H), 7.74–7.80 (m, 2H, Ar-H), 8.18–8.20 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 128.28, 128.81, 129.21, 129.83, 129.97, 139.06, 141.23, 153.48; HRMS (ESI^+) calcd. for $C_{20}H_{14}N_2$ $(M+H)^+$: 283.1235; found 283.1238.

Disclosure statement

The authors declare no conflict of interest.

ORCID

Sambhaji T. Dhumal http://orcid.org/0000-0003-3018-6179
Tejshri R. Deshmukh http://orcid.org/0000-0002-1818-0316

References

[1] Hebade, M. J.; Deshmukh, T. R.; Dhumal, S. T. Silica Supported Dodecatungstophosphoric Acid (DTP/SiO_2): an Efficient and Recyclable Heterogeneous Catalyst for Rapid Synthesis of Quinoxalines. *Synth. Commun.* **2021**, *51*, 2510–2520. DOI: 10.1080/00397911.2021.1939060.

[2] Dietrich, B.; Diederichsen, U. Synthesis of Cyclopeptidic Analogues of Triostin a with Quinoxalines or Nucleobases as Chromophores. *Eur. J. Org. Chem.* **2005**, *2005*, 147–153. DOI: 10.1002/ejoc.200400548.

[3] Nageswar, Y. V. D.; Reddy, H. V.; Ramesh, K.; Murthy, S. N. ChemInform Abstract: Recent Developments in the Synthesis of Quinoxaline Derivatives by Green Synthetic Approaches. *Org. Prep. Proc. Int.* **2013**, *45*, 1–27. DOI: 10.1080/00304948.2013.743419.

[4] Pereira, J. A.; Pessoa, A. M.; Cordeiro, M. N. D. S.; Fernandes, R.; Prudencio, C.; Noronha, J. P.; Vieira, M. Quinoxaline, Its Derivatives and Applications: A State of the Art Review. *Eur. J. Med. Chem.* **2015**, *97*, 664–672. DOI: 10.1016/j.ejmech.2014.06.058.

[5] Seitz, L. E.; Suling, W. J.; Reynolds, R. C. J. Synthesis and Antimycobacterial Activity of Pyrazine and Quinoxaline Derivatives. *J. Med. Chem.* **2002**, *45*, 5604–5606. DOI: 10.1021/jm020310n.

[6] Cheng, G.; Sa, W.; Cao, C.; Guo, L.; Hao, H.; Liu, Z.; Wang, X.; Yuan, Z. Quinoxaline 1,4-di-N-Oxides: Biological Activities and Mechanisms of Actions. *Front. Pharmacol.* **2016**, *7*, 64. DOI: 10.3389/fphar.2016.00064.

[7] Loriga, M.; Piras, S.; Sanna, P.; Paglietti, G. Quinoxaline Chemistry, Part 7, 2-[Aminobenzoates]- and 2-[Aminobenzoylglutamate]-Quinoxalines as Classical Antifolate Agents. Synthesis and Evaluation of *In Vitro* Anticancer, Anti-HIV and Antifungal Activity. *Farmaco* **1997**, *52*, 157–166.

[8] Hui, X.; Desrivot, J.; Bories, C.; Loiseau, P. M.; Franck, X.; Hocquemiller, R.; Figadere, B. Synthesis and Antiprotozoal Activity of Some New Synthetic Substituted Quinoxalines. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 815–820. DOI: 10.1016/j.bmcl.2005.11.025.

[9] More, S. V.; Sastry, M. N. V.; Yao, C. F. Cerium (IV) Ammonium Nitrate (CAN) as a Catalyst in Tap Water: A Simple, Proficient and Green Approach for the Synthesis of Quinoxalines. *Green Chem* **2006**, *8*, 91–95. DOI: 10.1039/B510677J.

[10] Robinson, R. S.; Taylor, R. J. K. Quinoxaline Synthesis from α-Hydroxy Ketones via a Tandem Oxidation Process Using Catalysed Aerobic Oxidation. *Synlett* **2005**, *2005*, 1003–1005. DOI: 10.1055/s-2005-864830.

[11] Aparicio, D.; Attanasi, O. A.; Filippone, P.; Ignacio, R.; Lillini, S.; Mantellini, F.; Palacios, F.; de Los Santos, J. M. Straightforward Access to Pyrazines, Piperazinones, and Quinoxalines by Reactions of 1,2-Diaza-1,3-Butadienes with 1,2-Diamines under Solution, Solvent-Free, or Solid-Phase Conditions. *J. Org. Chem.* **2006**, *71*, 5897–5905. DOI: 10.1021/jo060450v.

[12] Huang, T. K.; Shi, L.; Wang, R.; Guo, X. Z.; Lu, X. X. Keggin Type Heteropolyacids-Catalyzed Synthesis of Quinoxaline Derivatives in Water. *Chinese Chem. Lett.* **2009**, *20*, 161–164. DOI: 10.1016/j.cclet.2008.10.048.

[13] Shaabani, A.; Rezayan, A. H.; Behnam, M.; Heidary, M. Green Chemistry Approaches for the Synthesis of Quinoxaline Derivatives: Comparison of Ethanol and Water in the Presence of the Reusable Catalyst Cellulose Sulfuric Acid. *C. R. Chim.* **2009**, *12*, 1249–1252. DOI: 10.1016/j.crci.2009.01.006.

[14] Lin, P. Y.; Hou, R. S.; Wang, H. M.; Kang, L. J.; Chen, L. C. Hypervalent Iodine(III) Sulfonate Mediated Synthesis of Quinoxalines in Liquid PEG-400. *J. Chinese Chem. Soc.* **2009**, *56*, 683–687. DOI: 10.1002/jccs.200900102.

[15] Srinivas, C.; Kumar, C. N. S. S. P.; Rao, V. J.; Palaniappan, S. Efficient, Convenient and Reusable Polyaniline-Sulfate Salt Catalyst for the Synthesis of Quinoxaline Derivatives. *J. Mol. Catal. A Chem.* **2007**, *265*, 227–230. DOI: 10.1016/j.molcata.2006.10.018.

[16] Hasaninejad, A.; Zare, A.; Mohammadizadeh, M. R.; Karami, Z. Synthesis of Quinoxaline Derivatives *via* Condensation of Aryl-1,2-Diamines with 1,2-Diketones Using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as an Efficient, Mild and Reusable Catalyst. *JICS.* **2009**, *6*, 153–158. DOI: 10.1007/BF03246514.

[17] Khaksar, S.; Tajbakhsh, M.; Gholami, M.; Rostamnezhad, F. A Highly Efficient Procedure for the Synthesis of Quinoxaline Derivatives Using Polyvinylpolypyrrolidone Supported Triflic Acid Catalyst (PVPP·OTf). *Chinese Chem. Lett.* **2014**, *25*, 1287–1290. DOI: 10.1016/j.cclet.2014.04.008.

[18] Pan, F.; Chen, T. M.; Cao, J. J.; Zou, J. P.; Zhang, W. $Ga(ClO_4)_3$-Catalyzed Synthesis of Quinoxalines by Cycloaddition of α-Hydroxyketones and *o*-Phenylenediamines. *Tetrahedron Lett.* **2012**, *53*, 2508–2510. DOI: 10.1016/j.tetlet.2012.02.113.

[19] Kumar, K.; Mudshinge, S. R.; Goyal, S.; Gangar, M.; Nair, V. A. A Catalyst Free, One Pot Approach for the Synthesis of Quinoxaline Derivatives via Oxidative Cyclisation of 1,2-Diamines and Phenacyl Bromides. *Tetrahedron Lett.* **2015**, *56*, 1266–1271. DOI: 10.1016/j.tetlet.2015.01.138.

[20] Bhunia, S.; Ghosh, P.; Patra, S. R. Gold Catalyzed Oxidative Alkyne Functionalization by N–O/S–O/C–O Bond Oxidants. *Adv. Synth. Catal.* **2020**, *362*, 3664–3708. DOI: 10.1002/adsc.202000274.

[21] Das, B.; Venkateswarlu, K.; Suneel, K.; Majhi, A. An Efficient and Convenient Protocol for the Synthesis of Quinoxalines and Dihydropyrazines via Cyclization-Oxidation Processes Using $HClO_4\cdot SiO_2$ as a Heterogeneous Recyclable Catalyst. *Tetrahedron Lett.* **2007**, *48*, 5371–5374. DOI: 10.1016/j.tetlet.2007.06.036.

[22] Wan, J. P.; Gan, S. F.; Wu, J. M.; Pan, Y. Water Mediated Chemoselective Synthesis of 1,2-Disubstituted Benzimidazoles Using *o*-Phenylenediamine and the Extended Synthesis of Quinoxalines. *Green Chem.* **2009**, *11*, 1633–1637. DOI: 10.1039/b914286j.

[23] Madhav, B.; Murthy, S. N.; Reddy, V. P.; Rao, K. R.; Nageswar, Y. V. D. Biomimetic Synthesis of Quinoxalines in Water. *Tetrahedron Lett.* **2009**, *50*, 6025–6028. DOI: 10.1016/j.tetlet.2009.08.033.

[24] Tejeswararao, D. Synthesis of Quinoxaline Using Silica Supported Phosphomolybdic Acid as Reusable Heterogeneous Catalyst. *Asian J. Chem.* **2016**, *28*, 2353–2356. DOI: 10.14233/ajchem.2016.19533.

[25] Ghosh, P.; Mandal, A. Sodium Dodecyl Sulfate in Water: Greener Approach for the Synthesis of Quinoxaline Derivatives. *Green. Chem. Lett. Rev.* **2013**, *6*, 45–54. DOI: 10.1080/17518253.2012.703245.

[26] Harsha, K. B.; Rangappa, K. S. One-Step Approach for the Synthesis of Functionalized Quinoxalines Mediated by T3P-DMSO or T3P via a Tandem Oxidation-Condensation or Condensation Reaction. *RSC Adv.* **2016**, *6*, 57154–57162. DOI: 10.1039/C6RA03078E.

[27] Pardeshi, S. D.; Sathe, P. A.; Vadagaonkar, K. S.; Chaskar, A. C. One-Pot Protocol for the Synthesis of Imidazoles and Quinoxalines Using N-Bromosuccinimide. *Adv. Synth. Catal.* **2017**, *359*, 4217–4226. DOI: 10.1002/adsc.201700900.

[28] Meshram, H. M.; Ramesh, P.; Kumar, G. S.; Reddy, B. C. One-Pot Synthesis of Quinoxaline-2-Carboxylate Derivatives Using Ionic Liquid as Reusable Reaction Media. *Tetrahedron Lett.* **2010**, *51*, 4313–4316. DOI: 10.1016/j.tetlet.2010.05.099.

[29] Barkul, R. P.; Sutar, R. S.; Patil, M. K.; Delekar, S. D. Photocatalytic Degradation of Organic Pollutants by Using Nanocrystalline Boron-Doped TiO_2 Catalysts. *ChemistrySelect* **2021**, *6*, 3360–3369. DOI: 10.1002/slct.202003910.

[30] Sutar, R. S.; Barkul, R. P.; Patil, M. K. Visible Light Assisted Photocatalytic Degradation of Methylene Blue Dye and Mixture of Dyes Using ZrO_2-TiO_2 Nanocomposites. *Cnano* **2021**, *17*, 120–129. DOI: 10.2174/1573413716999200605154956.

[31] Manoharan, D.; Loganathan, A.; Kurapati, V.; Nesamony, V. J. Unique Sharp Photoluminescence of Size-Controlled Sonochemically Synthesized Zirconia Nanoparticles. *Ultrason. Sonochem.* **2015**, *23*, 174–184. DOI: 10.1016/j.ultsonch.2014.10.004.

[32] Li, X.; Nagaoka, K.; Lercher, J. A. Labile Sulfates as Key Components in Active Sulfated Zirconia for *n*-Butane Isomerization at Low Temperatures. *J. Catal.* **2004**, *227*, 130–137. DOI: 10.1016/j.jcat.2004.07.003.

[33] Ghafuri, H.; Rashidizadeh, A.; Ghorbani, B.; Talebi, M. Nano Magnetic Sulfated Zirconia (Fe_3O_4@ZrO_2/SO_4^{2-}): an Efficient Solid Acid Catalyst for the Green Synthesis of α-Aminonitriles and Imines. *New J. Chem.* **2015**, *39*, 4821–4829. DOI: 10.1039/C5NJ00314H.

[34] Nasseri, M. A.; Alavi, S. A.; Kazemnejadi, M.; Allahresani, A. The $CuFe_2O_4$@SiO_2@ZrO_2/SO_4^{2-}/Cu Nanoparticles: An Efficient Magnetically Recyclable Multifunctional Lewis/Brønsted Acid Nanocatalyst for the Ligand- and Pd-Free Sonogashira Cross-Coupling Reaction in Water. *RSC Adv.* **2019**, *9*, 20749–20759. DOI: 10.1039/C9RA03406D.

[35] Harsha, K. B.; Rangappa, S.; Preetham, H. D.; Swaroop, T. R.; Gilandoust, M.; Rakesh, K. S.; Rangappa, K. S. An Easy and Efficient Method for the Synthesis of Quinoxalines Using Recyclable and Heterogeneous Nanomagnetic-Supported Acid Catalyst under Solvent-Free Condition. *ChemistrySelect* **2018**, *3*, 5228–5232. DOI: 10.1002/slct.201800053.

[36] Lian, M.; Li, Q.; Zhu, Y.; Yin, G.; Wu, A. Logic Design and Synthesis of Quinoxalines via the Integration of Iodination/Oxidation/Cyclization Sequences from Ketones and 1,2-Diamines. *Tetrahedron* **2012**, *68*, 9598–9605. DOI: 10.1016/j.tet.2012.09.056.

[37] Jadhav, S. A.; Sarkate, A. P.; Shioorkar, M. G.; Shinde, D. B. Expeditious One Pot Multicomponent Microwave Assisted Green Synthesis of Substituted 2-Phenyl Quinoxaline and 7-Bromo-3-(4-Ethylphenyl)Pyrido[2,3-*b*]Pyrazine in Water-PEG and Water-Ethanol. *Synth. Commun.* **2017**, *47*, 1661–1667. DOI: 10.1080/00397911.2017.1337153.

[38] Nagarapu, L.; Palem, J. D.; Reddy, A. R. K.; Bantu, R. A Facile and Efficient Synthesis of Quinoxalines from Phenacyl Bromides and Ortho Phenylenediamine Promoted by Zirconium Tungstate. *Org. Chem. Curr. Res.* **2014**, *S4*, 1–5. DOI: 10.4172/2161-0401.S4-4001.

[39] Tanwar, B.; Purohit, P.; Raju, B. N.; Kumar, D.; Kommi, D. N.; Chakraborti, A. K. An "All-Water" Strategy for Regiocontrolled Synthesis of 2-Aryl Quinoxalines. *RSC Adv.* **2015**, *5*, 11873–11883. DOI: 10.1039/C4RA16568C.

[40] Khalafy, J.; Habashi, B. P.; Marjani, A. P.; Moghadam, P. N. The Synthesis of 2 Arylquinoxaline Derivatives. *Curr. Chem. Lett.* **2012**, *1*, 139–146. DOI: 10.5267/j.ccl.2012.5.002.

[41] Yang, J.; Zhu, H.; Huang, Y.; Huang, W.; Wang, W. Design and Synthesis of Extended Quinoxaline Derivatives and Their Charge Transport Properties. *RSC Adv.* **2016**, *6*, 100067–100071. DOI: 10.1039/C6RA22677A.

International Journal of Advance and Applied Research
www.ijaar.co.in
ISSN – 2347-7075 Impact Factor – 7.328
Peer Reviewed Bi-Monthly
Vol.10 No.1 September – October 2022

USE OF FACEBOOK SITES BY LIS PROFESSIONALS IN MARATHWADA: A CASE STUDY

Dr.Madansing D. Golwal[1]**&Mr. Badrinath D. Dhakne**[2]
[1]Librarian, RamkrishnaParamhansaMahavidyalaya, Osmanabad.
[2]Librarian, Dr. BabasahebAmbedkarMahavidyalaya, Aundh, Pune.
Corresponding Author - Dr.Madansing D. Golwal
Email-mgolwal4@gmail.com

DOI - 10.5281/zenodo.7204415

Abstract:

Current research focuses on examining how much, why and how LIS Professionals use Facebook, one of the most popular social networking site, and understanding its impact on education and social interaction. The aim of this study is to examine the purposes of Facebook use in Library and Information Science (LIS) Professionals sample and explore time investment of the professionals to Facebook social network site. The study was focus on to explore social networking site (SNS), Facebook to work as an effective tool for imparting information or knowledge and prove helpful in making awareness among LIS Professionals in Marathwada. Data was collected by means of a questionnaire that was circulated among the LIS Professionals randomly. Present article reports the survey of social networking site, Facebook in making awareness among LIS Professionals. Analysis will help the LIS professionals in deriving the benefits of SNS, Facebook.

Keywords: *Facebook, LIS Professionals, College Librarian, Social Networking Sites, Marathwada, Maharashtra and Internet.*

Introduction:

SNS such as such as Friendster, CyWorld, and MySpace allow individuals to present themselves, articulate their social networks, and establish or maintain connections with others. These sites can be oriented towards work-related contexts (e.g., LinkedIn.com), romantic relationship initiation (the original goal of Friendster.com), connecting those with shared interests such as music or politics (e.g., MySpace.com), or the college student population (the original incarnation of Facebook.com). Participants may use the sites to interact with people they already know offline or to meet new people. The online social network application analyzed in this article, Facebook, enables its users to present themselves in an online profile, accumulate ‘‘friends’’ who can post comments on each other’s pages, and view each other’s profiles. Facebook members can also join virtual groups based on common interests, see what classes they have in common, and learn each other’s’ hobbies, interests, musical tastes, and romantic relationship status through the profiles.

Facebook constitutes a rich site for researchers interested in the affordances of social networks due to its heavy usage patterns and technological capacities that bridge online and offline connections. We believe that Facebook represents an understudied offline to online trend in that it originally primarily served a geographically-bound community (the campus). When data were collected for this study, membership was restricted to people with a specific host institution email address, further tying offline networks to online membership. In this sense, the original incarnation of Facebook was similar to the wired Toronto neighborhood studied by Hampton and Wellman (e.g., Hampton, 2002; Hampton & Wellman, 2003), who suggest that information technology may enhance place-based community and facilitate the generation of social capital.1 Previous research suggests that Facebook users engage in ‘‘searching’’ for people with whom they have an offline connection more than they ‘‘browse’’ for complete strangers to meet (Lampe, Ellison, &Steinfield, 2006).

An Overview of Facebook:

Created in 2004, by 2022 Facebook was reported to have more than 2.934 billion registered members (July, 2022) generating 1.6 billion page views each day. The site is tightly integrated into the daily media practices of its users: The typical user spends about 20 minutes a day on the site, and two-thirds of users log in at least once a day (Cassidy, 2006; Needham and Company, 2007). Capitalizing on its success among college students, Facebook launched a high school version in early September 2005. In 2006, the company introduced communities for commercial organizations; as of November 2006, almost 22,000 organizations had Facebook directories (Smith, 2006). In 2006, Facebook was used at over 2,000 United States colleges and was the seventh most popular site on the World Wide Web with respect to total page views (Cassidy, 2006).

Much of the existing academic research on Facebook has focused on identity presentation and privacy concerns. Looking at the amount of information Facebook participants provide about themselves, the relatively open nature of the information, and the lack of privacy controls enacted by the users, Gross and Acquisti (2005) argue that users may be putting themselves at risk both offline (e.g., stalking) and online (e.g., identify theft). Other recent Facebook research examines student perceptions of instructor presence and self disclosure (Hewitt and Forte, 2006), temporal patterns of use (Golder, Wilkinson, and Huberman, 2007), and the relationship between profile structure and friendship articulation (Lampe, Ellison, and Steinfield, 2007).

In contrast to popular press coverage which has primarily focused on negative outcomes of Facebook use stemming from users' misconceptions about the nature of their online audience, we are interested in situations in which the intended audience for the profile (such as well-meaning peers and friends) and the actual audience are aligned. We use Facebook as a research context in order to determine whether offline social capital can be generated by online tools. The results of our study show that Facebook use among college-age respondents was significantly associated with measures of social capital.

LIS Professionals in Marathwada:

Generally all the people who are engaged with library and information science subject either as a Librarian or Lecturer or Research Scholar or Technical Assistant or Student are called LIS Professionals. But In LIS Professionals we have taken here the Assistant Librarian, Deputy Librarian who was working in Marathwada Region.

The name Marathwada identifies one of the five regions in Maharashtra state of India. The region coincides with the Aurangabad Division. There are 8 districts in Marathwada region i.e. Aurangabad, Jalna, Beed, Parbhani, Naned, Latur, Hingoli and Osmanabad. Marathwada is one of six administrative division India's Maharashtra state. Aurangabad division coincides almost perfectly with the Marathwada region of Maharashtra.

Eight questions were asked to them and we have received answers of all of them. We have taken five social networking sites – Facebook, Google+, Twitter, What's Up, YouTube and Yahoo to conduct our study and to reveal LIS Professional's view about them as whether these sites are helpful in making awareness among them or not.

Problem Statement:

There are many studies conducted to find out the impact of social networks on young generation. But the present work is conducted among the LIS Professionals to explore how social networking site Facebook proves helpful in generating awareness.

Review of Literature:

Online social network tools may be of particular utility for individuals who otherwise have difficulties forming and maintaining both strong and weak ties. Some research has shown, for example, that the Internet might help individuals with low psychological well-being due to few ties to friends and neighbors (Bargh and McKenna, 2004). Some forms of computer-mediated communication can lower barriers to interaction and encourage more self-disclosure (Bargh, McKenna, & Fitzsimons, 2002; Tidwell & Walther, 2002); hence, these tools may enable connections and interactions that would not otherwise occur. For this reason, we explore whether the relationship between Facebook use and social capital is different for individuals with varying degrees of self-esteem (Rosenberg, 1989) and satisfaction with life (Diener, Suh, and Oishi, 1997; Pavot and Diener, 1993), two well-known and validated measures of subjective well-being. This leads to the two following pairs of hypotheses:

Social media, social networking, online communication words used parallely. Zakaria et al (2010) believes that social media applications have already being accepted by young generations as a platform to socialize, collaborate and learn in an informal and flexible manner although their level of involvement and contribution varies significantly. Al-Daihani's study (2010) explores that the majority of MLIS students are aware of social software applications and they make moderate use of blogs, communication tools and social networking sites. Sheens study among students of the Pakistan reveals that the use of social networking site indicates popularity of facebook.com among these youth more often. The survey of Pew Internet (2010) says that Facebook is the most commonly used social network among adults. Subramanian, et al (2008) reported the findings of study conducted to understand the role of SNS in college student's lives. The figure and statistics shows how Facebook has a very influential role in the lives of young adults. In present paper the investigator has the aim of exploring how LIS Professionals integrated Facebook as a tool helpful in generating awareness.

Objectives of the Study:

- To find out the role of social networking site, Facebook in creating awareness among LIS Professionals in Marathwada.
- To explore LIS Professionals view about its uses and services.
- To identify potential contribution of Facebook to fill the gaps among LIS Professionals.
- To identify the methods of data collection and analysis.
- To explore how to retrieve the relevant information with the use of Facebook by LIS Professionals.
- To help LIS Professionals to generate a user driven environment and updates user with changing environment.
- To reveal Problems in the use Facebook.

Limitations:

The study is limited to LIS Professionals as we want to reveal uses of Facebook in developing awareness about current happenings, professional information, job opportunities and educational development.

Methodology:

The study was based on survey as were administered among LIS Professionals in Marathwada working as Librarian of randomly. The collected data were analyzed using statistical tools.

Data Analysis and Interpretation:

The data is analyzed in view to the objectives mentioned in the study as follows:

1. **Gender wise Analysis:**

Table No 1: Gender Wise Analysis of Respondents

Sr. No	Gender	Respondents	Percentage
1	Male	125	68%
2	Female	59	32%
	Total	**184**	**100%**

The result of this study shows that out of 184 respondents 125 (68%) were male and 59 (32%) were female.

2. **Most Used SNS:**

Table No 2: Most Used Social Networking Sites

Sr. No	SNS	Respondents	Percentage
1	What's Up	164	89%
2	Facebook	107	57%
3	You Tube	53	29%
4	Yahoo	49	27%
5	Twitter	28	15%
6	Other	11	6%

It is clear from the above table that What's Up was the most often used Social networking site among LIS Professionals with 164 (89%)%, Facebook was the second most used SNS with 107 (57%) respondents respectively. You Tube recite in third position having 53 (29%), Yahoo was in fourth position with 49 (27%), Twitter was in sixth position with 28 (15%) and other for exe, LinkedIn, Ning, Grouply, Blog, Flicker, Photo bucket, Net log, with 11 (6%) of respondents respectively.Respondents may select more than one checkbox, so percentages may add up to more than 100%.

3. Frequency of Using Facebook:

Table No 3. Frequency of use of Facebook

Sr. No	Frequency	Respondents	Percentage
1	Daily	112	61%
2	Sometime	62	34%
3	Rarely	10	5%
	Total	**184**	**100%**

It is observed in the study the out of 184 respondents 112 (61%) of LIS Professionals were use Facebook every day, 62(34%) used it sometimes, and 10 (5%) rarely used of Facebook respectively.

4. Purpose of Using Facebook:

Table No 4: Purpose of Using Facebook

Sr. No	Purpose	Respondents	Percentage
1	To get interact professionally	122	66%
2	To keep abreast of the latest news & commentaries	110	60%
3	To participating in discussions	87	47%
4	To Express Creativity	82	45%
5	Other	11	6%

It is revealed from the above table that 122 (66%) LIS Professionals were use Facebook to interact professionally, 110 (60%) to use keep abreast of latest news and commentaries, 87(47%) of users to use to participating in discussions of the LIS field, 82 (45%) used to Express Creativity and 11 (6%) used to other for example to connect LIS Professionals all over the World somebody have says it's very best platform in LIS field, for time pass, To build a strong library network across world with new people and distant friends. Respondents may select more than one checkbox, so percentages may add up to more than 100%.

5. Satisfaction Level of Using Facebook:

Table No 5: Satisfaction Leval of use of Facebook in Making Awareness

Sr. No	Satisfaction View	No of Respondents	Percentage
1	Agree	126	69%
2	Disagree	15	23%
3	Neutral	43	8%
	Total	**184**	**100%**

It is founded that the out of 184 respondents the 126 (69%) LIS Professionals were agree that Facebook proved helpful in making awareness, 43 (8%) have the neutral opinion and 15 (23%) were disagree with it.

6. Facebook work as a Platform:

Table No 6: Facebook works as a platform to interact beyond barriers of location & Nationality

Sr. No	Satisfaction View	Respondents	Percentage
1	Agree	142	78%
2	Disagree	8	4%
3	Neutral	34	18%
	Total	**184**	**100%**

In response to the above question it is founded that 142 (78%) LIS Professionals were of the view that Facebook actual works as a platform to interact beyond barrier, 35 (18%) were neutral and 8(4%) were disagree with it.

7. Satisfaction of Facebook Users:

Table No 7: Satisfaction of Facebook User

Sr. No	Satisfaction View	Respondents	Percentage
1	Satisfied	108	58%
2	Not Satisfied	16	9%
3	Neutral	60	33%
	Total	**184**	**100%**

The result of the study shows that majority of the respondents were satisfied in the use of Facebook with 108(58%), 16 (9%) were neutral and 60 (33%) were not satisfied with it.

8. Problems in Using Facebook:

Table No 8: Problems in Using Facebook

Sr. No	Problems	Respondents	Percentage
1	Lack of time	123	67%
2	Lack of technical support	56	30%
3	No privacy ensured	85	46%
4	It is not useful for education	33	18%
5	It has no role in making awareness	20	11%
6	Other	3	2%

Various problems have been mentioned by the respondents among them 123 (67%) LIS Professionals were of the view that they lacks time to use Facebook, 85 (46%) thought that no privacy secured in the use of Facebook, 33(18%) have the opinion that it was not useful for educational purpose, 56 (30%) were suffer from technical problem and 20 (11%) were founded that it plays nor role in making awareness and 3(2%) LIS professionals founded that other problems of using Facebook for example No Permission to use Facebook on duty, it gives information transfer to both parties. Respondents may select more than one checkbox, so percentages may add up to more than 100%.

Conclusion:

It is observed that most LIS Professionals are connected to each other by Facebook to share experiences, views and participated in creating awareness. It has become one of the largest platforms in the world for sharing real time information. Facebook allows users to interact and collaborate with each other in a social media dialogue as creators of user generated content in a virtual community, in contrast to websites where users are limited to the passive viewing of content that was created for them. The conducted study is an attempt to give an overview of social networking site Facebook and its possible uses for LIS Professionals and to assess how much real transformation this technology can deliver, while deflating reaffirmation and singling out the real value of these innovations.

References:

1. Bargh, J., and McKenna, K. (2004). The Internet and social life. Annual Review of Psychology, 55(1), 573–590.
2. Cassidy, J. (2006). Me media. The New Yorker, 50–59.
3. DATAREPORTAL (2022). Facebook Statistics and Trends. https://datareportal.com/essential-facebook-stats accessed on 15th September, 2022.
4. Diener, E., Suh, E., and Oishi, S. (1997). Recent findings on subjective well-being. Indian Journal of Clinical Psychology, 24(1), 25–41.
5. Gaikwad, M. N. Use Of Social Networking Sites Among Undergraduate Students Of Arts And Commerce College, Madha, Dist. Solapur, Maharastra.
6. Golder, S. A., Wilkinson, D., and Huberman, B. A. (2007). Rhythms of social interaction: Messaging within a massive online network. In C. Steinfield, B. Pentland, M. Ackerman, & N. Contractor (Eds.), Communities and Technologies 2007: Proceedings of the Third International Conference on Communities and Technologies London: Springer.
7. Gross, R., and Acquisti, A. (2005). Information revelation and privacy in online social networks. Paper presented at the WPES’05, Alexandria, Virginia.
8. Hampton, K. (2002). Place-based and IT mediated ‘‘community.’’ Planning Theory and Practice, 3(2), 228–231.
9. Hampton, K., and Wellman, B. (2003). Neighboring in Netville: How the Internet supports community and social capital in a wired suburb. City & Community, 2(4), 277–311.
10. Hewitt, A., and Forte, A. (2006). Crossing boundaries: Identity management and student / faculty relationships on the Facebook. Paper presented at CSCW, Banff, Alberta, Canada
11. Lampe, C., Ellison, N., and Steinfield, C. (2006). A Facebook in the crowd: Social searching vs.

social browsing. Proceedings of the 2006 20th Anniversary Conference on Computer Supported Cooperative Work (pp.167–170). New York: ACM Press.

12. Lampe, C., Ellison, N., and Steinfield, C. (2007). A familiar Facebook: Profile elements as signals in an online social network. Proceedings of the SIGCHI Conference on Human Factors in Computing Systems (pp.435–444). New York: ACM Press.
13. Pavot, W., and Diener, E. (1993). Review of the satisfaction with life scale. Psychological Assessment, 5(2), 164–172.
14. Rosenberg, M. (1989). Society and the Adolescent Self-Image (Rev.ed.). Middletown, CT: Wesleyan University Press.
15. Smith, J. (2006). Updated lists of all companies and regions on Facebook. Retrieved March 19,2012 from http://www.insidefacebook.com/2006/11/15
16. Stutzman, F. (2006). An evaluation of identity-sharing behavior in social network communities. Paper presented at the iDMAa and IMS Code Conference, Oxford, Ohio.
17. Subrahmanyam, K., Reich, S.M., Waechter, N, and Espinoza, G. (2008) Online and Offline social networks: use of social networking sits. Sites by emerging adults. Journal of applied Development Psychology, 29(6) 420-433.
18. Tidwell, L. C. and Walther, J. B. (2002). Computer-mediated communication effects on disclosure, impressions, and interpersonal evaluations: Getting to know one another a bit at a time. Human Communication Research, 28(3), 317–348.
19. Zakaria, M.H. Watson, J. and Edwards, S.L. (2010) Investigating the use of web 2.0 technology by Malaysian students. Multicultural Education and Technology journal, 4(1), 12-29.

International Journal of Advance and Applied Research
www.ijaar.co.in
ISSN – 2347-7075 **Impact Factor – 7.328**
Peer Reviewed **Bi-Monthly**
Vol.10 No.1 **September – October 2022**

CONTENT ANALYSIS OF RAYAT SHIKSHAN SANSTHA'S AUTONOMOUS COLLEGES LIBRARY WEBSITE

Badrinath D. Dhakne[1] & Madansing D. Golwal[2]
[1]Librarian, Dr. Babasaheb Ambedkar College, Aundh, Pune
[2]Librarian, Ramkrishna Paramhansa Mahavidyalaya, Osmanabad
Corresponding Author - Badrinath D. Dhakne
Email- bddhakne@gmail.com

DOI - 10.5281/zenodo.7203948

Abstract:

Library website is online public image of the library. The present study is carried out evaluation of the content available on library websites of the Rayat Shikshan Sanstha, Satara's Autonomous Colleges. Data was collected from the library websites and evaluated through defined checklists. Checklist are defined under the parameters i.e., general information, library services and website features. The purpose of present study is to find out the scope for improvement of the library website.

Keywords: *Content Analysis, Library, Websites, Autonomous College, Rayat Shikshan Sanstha,*

Introduction:

Covid 19 pandemic has changed the paradigm of learning system from classroom to online learning. Teacher, students and researchers are more familiar with the information and communication technology. Library stockholders are expecting the online services. College Library websites are playing the important role in providing online library services. It is public image of the library, where the information of collection, services, facilities, infrastructure are displayed. Library website provides the online services like, remote access to resources, reference service, ask a librarian etc. Content on the website is displayed in different forms. Website can be evaluated based on content displayed on the website.

Rayat Shikshan Sansth's Satara:

Rayat shikshan Sanstha is a leading educational institution in Asia established in 1919 by the Padmabhushan Karmaveer Bhaurao Patil and his legendary wife Sou. Laxmibai Patil. It's headquarter is located at the Satara (MH) in India. The vision of this Institution is " Education to all the classes of society, especially to the downtrodden, economically and socially backward sections of society" with the slogan "Education through self-help" (Rayat Shikshan Sanstha, n.d.). Rayat Shikshan Sanstha provides the education from primary to Ph.D. through 675 schools and colleges. More than 4,44,000 are studying in this Institution. The institution has 23 senior colleges which provides the bachelor and above degree education, out of the total colleges, 5 colleges has got the autonomous status from the concern authority. Present study is carried out the analysis of the content available on these autonomous college’s library websites.

Literature Review:

Ambika & Ganesan, (2021) carried out the study the content analysis of 13 central university library websites with 29 check lists , they observed need of more effort to develop the library website. They also recommended website development the training for library professionals. **Hugar (2019)** has analyse the content on engineering college library websites in goa. He evaluated the 5 engineering college library websites. He suggests the library website should be focus on services rather than providing the administrative information. **Kuri & Maranna, (2018)** presented in their conference paper “Content Analysis of Central University Library Websites of South India” . Study of 7library websites of central universities located at Andhra Pradesh, Telangana, Kerala, and Tamil Nādu. has been carried out. They concluded, most of the library has Rich e-collection, OPAC, Circulation, online database access has provided by the central university library. **Verma & Devi (2015)**carried out the content analysis study of the library webpage of the Central Universities of the North Eastern States in India. They found the basic information and services are provided on the university library websites. **Mohammed et al. (2014)** has done the content analysis of the university library websites in Nigeria. They are found that, there is enormous scope to develop the library websites. They also suggest the librarian should fully participate in developing the library website. Library website should focus on information need of the users.

Objectives of the Study:

- To analyse contents of the library websites of the Rayat Shikshan Sanstha’s Autonomous Colleges.
- To determine library resources, services available on the website.
- To suggest measures for the improvement the library websites.
- Ranking the library website of the colleges

Scope of the Study:

- This study is limited to the library websites of autonomous status colleges of the Rayat Shikshan Sanstha, Satara only.
- Study is limited to content available on the library websites in August-September 2022.

Methodology:

Data has been collected from the observation of the library websites. The websites have been evaluated by the checklist made before the observation. Content is evaluated based on three parameters. i.e. 1. General information 2. Library services 3. Special features. These parameters are defined based on previous library website evaluation studies. Data also collected from the librarian of colleges for more detail of information.

Autonomous Colleges of the Rayat Shikshan Sanstha:

The following colleges of the Rayat Shikshan Sanstha, Satara are Autonomous Colleges (Rayat Shikshan Sanstha, n.d.).

Sr. No.	**College**	**Abbreviation**	**Library Website**
01	Sadguru Gadage Maharaj College, Karad	SGMK	https://sgm.edu.in/sgmkplibrary/
02	Dhananjayrao Gadgil College of Commerce, Satara	DGCS	
03	Yashwantrao Chanvan Institute of Science, Satara	YCIS	http://ycisslibrary.weebly.com/
04	Karmaveer Bhaurao Patil College, Vashi	KBPV	https://www.kbpcollegevashi.edu.in/Department/Deptindex.aspx?page=a&ItemID=qe&nDeptID=ma
05	Chhatrapati Shivaji College, Satara	CSCS	https://csclibrary.weebly.com/
06	Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur	KBPP	https://www.kbppandharpurlibrary.in/

Table No. 1. Autonomous College Library Websites

There are 6 colleges of the Rayat Shikshan Sanatha, which got the autonomous status from the concern authority. Out of the total 6 colleges, 5 has the library website, Dhananjayrao Gadgil College of Commerce, Satara has not posted the library website on the web, therefore the analysis has been carried out of the 5 colleges in this study.

Content Analysis:

General Information:

This evaluation parameter finds the general information displayed on the library website.

Sr. No.	**Information**	**SGMK**	**YCIS**	**KBPV**	**CSCS**	**KBPP**	**Percentage**
1	About Library	Y	Y	Y	Y	Y	100%
2	Vision Mission Statement	Y	Y	Y	Y	N	80%
3	Library Hours	Y	Y	N	Y	Y	80%
4	Code of Conduct/ Rules & Regulation/ Library Policy	N	Y	Y	Y	Y	80%
5	Collection	Y	Y	Y	Y	Y	100%
6	Membership	Y	N	N	Y	N	40%
7	Services	Y	Y	Y	Y	Y	100%
8	Infrastructure	Y	N	N	N	N	20%
9	Library Staff	Y	Y	N	Y	Y	80%
10	Advisory Committee	Y	N	Y	Y	Y	80%
11	Library Sections	Y	N	N	N	N	20%
12	New Arrivals	Y	Y	N	N	N	40%
13	Statistics	N	N	N	N	N	0%
14	Library News /Events /Announcements	Y	N	N	Y	Y	60%
15	Contact Information	Y	N	N	Y	Y	60%
	Total Score	**13**	**8**	**6**	**11**	**9**	

Y= Yes, N=No

Table 2. General Information available on the library websites

It is observed in Table No. 2, all (100%) libraries displayed the information regarding library, collection and services on the website. Vision mission statement, library hours, code of conduct, library staff, advisory committee are displayed by the (80%) college libraries on their websites. Number of 3 (60%) libraries has provided the content of library events and contact information, whereas 2 (40%) libraries have displayed the new arrivals and membership details. Only SGMK colleges website shows the content of infrastructure, library sections and infrastructure. No library displayed the statistics on website.

SGMK Library has displayed 13 checklists of the content on the website, CSCS has provided 11 contents on their website. KBPP, YCIS, KBPV has displayed on website 9, 8 and 6 checklist contents respectively.

Library Services:

Sr. No.	Information	SGMK	YCIS	KBPV	CSCS	KBPP	Percentage
1	OPAC	Y	Y	Y	Y	Y	100%
2	Institutional Repository	Y	Y	N	Y	Y	80%
3	Link to Open Access Journals/Books/Databases	Y	Y	Y	Y	Y	100%
4	N List	Y	Y	Y	Y	Y	100%
5	Federated Search	N	N	N	N	N	0%
6	Ask a Librarian /Reference Service	N	Y	N	N	N	20%
7	Syllabus	Y	Y	N	Y	Y	80%
8	Question Papers	Y	Y	N	Y	Y	80%
9	FAQs	N	N	N	N	N	0%
10	Photo/ Video Gallery	Y	Y	N	Y	Y	80%
11	Plagiarism policy	N	N	N	N	N	0%
12	Book Suggestions	Y	N	N	N	N	20%
13	News Paper Clipping	Y	N	N	N	N	20%
	Total Score out of 13	9	8	3	7	7	

Y= Yes, N=No

Table 2. Library Services on the library websites

Table No.3 provides the information of the library services provided on website by the autonomous college libraries. All (100%) Libraries provide OPAC, links of the library open access e resources and link to NLIST on their website. Access to institutional repository, syllabus, question papers, photo gallery is provided on the website by the 80% libraries. Ask a librarian facility provided by the YCIS only. Online Book suggestion and newspaper clipping are provided on SGMK Library website only. Whereas, no library provides federated search, FAQ, plagiarism policy.

It is observed that, all libraries tried to provide most of the basic library services on their website, whereas advanced library services like, federated search, plagiarism check service are not provided through website.

Features of Library Website:

Sr. No.	Information	SGMK	YCIS	KBPV	CSCS	KBPP	Percentage
1	Continuously update	Y	Y	Y	Y	Y	100%
2	Navigation	Y	N	N	N	N	20%
3	Downloads Forms	N	N	N	N	N	0%
4	Links of Social Networking	Y	N	N	N	N	20%
5	Feedback	Y	Y	N	N	N	40%
6	Website Visit Counter	Y	N	N	Y	N	40%
7	Copyright statement	N	N	N	N	N	0%
8	Google Map Location	Y	N	N	N	N	20%
9	Sitemap	N	N	N	N	N	0%
	Total Score	6	2	1	2	1	

Y= Yes, N=No

Table 4. Features of library websites

Table No. 4 shows the features of the library websites. It is observed that all library websites are continuously updated. SGMK library displayed the navigation, link to social networking sites, location of the library on map. Feedback and website visitor counter (hit counter) are provided by the 40% libraries on their website. No library website displayed the copyright statement, sitemap and facility to download the forms.

It is found that, SGMK library has tried to develop the easy access to the website through multiple features. YCIS, KBPV, CSCS, KBPP libraries have not given more attentions toward the features of the library for easy access to its multiple webpages and services.

Ranking:

Rank	**Name of the College**	**General Information (15)**	**Library services (13)**	**Website Features (9)**	**Score (37)**	**Percentage**
1	SGMK	13	9	6	28	75.67%
2	CSCS	11	7	2	20	54.05 %
3	YCIS	8	8	2	18	48.64 %
4	KBPP	9	7	1	17	45.94 %
5	KBPV	6	3	1	10	27.27 %

Table 5. Ranking of library websites

The content analysis is carried out based on three parameters i.e., general information, library services, websites features. These parameters made with the 37 check list points.Ranking has been carried out based on the parameters and content provided on the websites. It is observed that Sadaguru Gadage Maharaj College Karad (SGMK) has got the first position with the 27 (75.67%) points.

Chhatrapati Shivaji College Satara (CSCS) provided 20 (54.05%) points at second position, Yashvantrao Chavan Institute of Satara (18 points, 48.64%), Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur (17 points, 45.94 %) and Karmaveer Bhaurao Patil College, Vashi (10 points , 27.27 %) got the third, forth and fifth position respectively.

Conclusion:

Library website is the online gateway to the library. After the covid 19 pandemic role of library has been changed. The present study found that, most of the library provides access to the institutional repository through the library website. All libraries have given the links to the open access resources on the webpages. General information of the library provided by the most of libraries. Ask a librarian, reference service, federated search, plagiarism policy/service, forms for downloads, library statistics should be provided on the library websites.

References:

1. Ambika, C. A., & Ganesan, P. (2021). CENTRAL UNIVERSITY LIBRARY WEBSITES IN INDIA: WEB CONTENT ANALYSIS. *Library Philosophy and Practice (e-Journal)*, 16.
2. Arandhara, R. (n.d.). *Content Analysis of Library websites of four selected Universities of Assam: A Comparative Study*. 15.
3. Dhakne, B., Golwal, M., & Sonwane, S. (2012). *Web Portals of DLIS in Maharashtra: Website Evaluation of Department of Library & Information Science, Maharashtra*.
4. Haridasan, D. S., & Uwesh, M. (2014). CONTENT ANALYSIS OF CENTRAL UNIVERSITY LIBRARY WEBSITES IN INDIA: A STUDY. *Journal of Information Management*, *1*(2), 59–71.
5. Hugar, J. (2019). Content Analysis of Engineering College Library Websites in Goa. *SSRN Electronic Journal*. https://doi.org/10.2139/ssrn.3620064
6. Kuri, R., & Maranna, O. (2018). *Content Analysis of Central University Library Websites of South India* (B. T. Sampath kumar, T. Keshava, R. Govanakoppa, & T. A. Mohan, Eds.; pp. 98–102). The Registrar, Tumakuru University. http://eprints.rclis.org/32865/
7. Mohammed, A., Garba, A., & Umar, H. (2014). University Library Websites in Nigeria: An Analysis of Content. *Information and Knowledge Management*, *4*(3), 16.
8. Rahman, A., & Batcha, M. S. (2020). *Content Analysis of Library Websites of Select Colleges of Delhi University: A Study*. *40*(4), 6.
9. Rayat Shikshan Sanstha. (n.d.). *Rayat Shikshan Sanstha*. Colleges. Retrieved September 28, 2022, from http://rayatshikshan.edu/Content.aspx?ID=910&PID=906
10. Sahoo, S., & Panda, K. C. (n.d.). *Web Content Analysis of Indian Institute of Technology (IIT) Library Websites: An Evaluative Study*. 18.
11. Savitha, K. S. (2016). CONTENT ANALYSIS OF DEEMED UNIVERSITY LIBRARY WEBSITES OF KARNATAKA STATE: A STUDY Savitha K S. *International Journal of Digital Library Services*, *6*(1).
12. Gaikwad, M. N., &Dhakne, B. D. Designing Dynamic Library Website by Using Wordpress Open Source Content Management System: A Study.

13. Vasishta, S. (2013). Dissemination of electronic journals: A content analysis of the library websites of technical university libraries in North India. *The Electronic Library*, *31*(3), 278–289. https://doi.org/10.1108/EL-03-2011-0038
14. Verma, D. M. K., & Devi, K. (2015). Content Analysis of Central Universities Library Websites of North Eastern States of India: A Survey. *Journal of Research in Librarianship*, *2*(5), 48–59.
15. Yoon, A., & Schultz, T. (2017). Research Data Management Services in Academic Libraries in the US: A Content Analysis of Libraries' Websites. *College & Research Libraries*, *78*(7). https://doi.org/10.5860/crl.78.7.920
16.

Volume : 2 (2022)
Special Issue :1 (November)

LIBRARY SCHOLAR
International Peer-Reviewed Journal of Library Science

ISSN
2583-2549

WEEDING POLICY IN COLLEGE LIBRARY OF OSMANABAD

Dr.Madansing D. Golwal
Librarian,
Ramkrishna Paramhansa Mahavidyalaya
Osmanabad, Maharashtra
E-mail: mgolwal4@gmail.com

Abstract: *This paper is a case study of College Library of Ramkrishna Paramhansa Mahavidyalaya,, Osmanabad. The developments and changes in the ICT havechanged the user's expectations from the academic libraries in different ways.The college libraries not only provides stimulus toreading by procuring materials for study and research, by introducing open access system, by providing long hours of open, by organizing the library resources in a systematic way, but also feeds the intellect of the student, encourage the researches of the faculty and thus serve the teaching and research needs of the faculty. The automated library can provide extended services to the users of the library. The paper describes in detail aboutthe weeding policy &stock verification process using SLIM21 Library Automation Software and to identify the status of library.*

Keywords: *College Library, Library Automation, ICT, Library Automation Software, SLIM21, Weeding PolicyandStock Verification.*

---

1. Introduction:

Libraries play vital role in the educational, industrial and technological progress of a country. Progress of the nation depends upon advance knowledge gained by educationists, technologists, engineers and scientists of the country. Hence the role of libraries in Universities and then educational institutions is to active a free flow of information from the point of generation to the point of utilization of information efficiently and effectively. The present educational policy emphasizes on self-study, experiments, field study and research rather than classroom study. Therefore, library has to play vital role in the higher education to meet user requirements. Optimum use of resources is possible through networks only.

2. Development Of Library Automation:

Library automation began in the late 1970s in a few special libraries and has now reached most of the university libraries. It has yet to take off in college libraries in India owing to various problems. Many studies on library automation have been undertaken in the West, but few have been undertaken in IndiaThe automation of libraries and information centers in India started in middle 19th century till the concept of automation was entered on the use of computers for housekeeping operations and information services by individual libraries. There are certain factors responsible for the automation of the libraries. Information explosions, increased user's demand, labour intensive nature of work, changing concepts of documents.

3. A Profile:

Ramkrishna Paramhansa Mahavidyalaya, Osmanabad is the first college established on 01st June, 1959 by Shri Swami Vivekanand Shikshan Sanstha, Kolhapur, one of the established institutions in Maharashtra founded by Shikshan Maharshi Dr. Bapuji Salunkhe with a motto-Dissemination of Education for Knowledge, Science and Culture. Osmanabad is the district in Marathwada Region which is drought prone and economically backward and here only investment is Education. The College is affiliated to Dr. Babasaheb Ambedkar Marathwada University, Aurangabad and has been included under 2(F) and 12B category of the UGC. The college is reaccredited in the 3rd cycle with 'B+'grade by NAAC with CGPA 2.60. The UGC has identified the college as "The College with Potential for Excellence" (Phase – II).

The College has following full-fledged facilities -

- Library with 94,437books
- 41 Journals + 16 Newspapers
- N-LIST E-resources
- BAMU Remote Access
- Computer Lab with 10 computers
- Magzster Subscription
- Ladies Hostel
- Gymkhana

4. College Library: An Overview:

The library is the lung of every educational institute, which breathes knowledge and information into the minds of the students. The has well-equipped Library and Information Centre with an elaborate collection of books, e-books, CD-ROMs, journals, e-journals, project reports, audio-visual materials and other resources to serve its users.The Library Advisory Committee considers the development proposals of the library and budget allocations and policy decisions. It also provides directions for a structured and balanced growth of the library and to provide improved facilities and innovative services. Allocation and utilization of funds and introduction of developmental programs and requirements of the users are addressed and approved by the Library Advisory Committee.The scope of the study is the College Library in all respects such as in-house operation its automation, information services etc., since the computerization started in end of year 2012 the study will bring out its strength and weakness that will help the library to improve the system to user's satisfaction.

4.1 Collection development:

The Library and Information Centre came into existence in the year 1959. The main Library is equipped with a 94437 No. of national and international books, journals in the field of Arts, Commerce and Science Faculty including Personality Developments, Human Right, English, Research Methodology, and General reading, etc. and also with the modern and latest technology to cope up with latest development toprovide quality and quick services to its users.

4.2 LibraryCollection Statistics :

Sr. No	Year	No. of Books	Expenditure(Rs.)	No. of Journals	Expenditure (Rs.)
1	2016 – 2017	904	233604/-	85	233504/-
2	2017 – 2018	3485	298529/-	52	298529/-
3	2018 – 2019	340	97675/-	33	193250/-
4	2019 – 2020	290	80620/-	29	174250/-
5	2020 – 2021	330	97143/-	24	126400/-
6	2021 – 2022	335	91634/-	19	71250/-

Table No.1 Statistics of the year 2016 - 2022

4.3 Library Staff:

LC's Library and Information Centre has good team of qualified Professional Staff.

4.4 Library Services:

ASPC's Library and Information Centre is providing the following services to its users.

- Circulation
- Reference Service
- Current Awareness Service
- Selective Dissemination Service
- Reprographic Service
- Audio-Visual service
- News Paper Clipping Service
- WEB OPAC (Online Public Access Catalogue)
- Interlibrary Loan

4.5 Automation of College Library:

The term "Automation" describes the way in which a machine is programmed to do a job that a person might normally do. Automation is often used to assist with jobs, which must be repeated over and over again.

"Library Automation" is a process of using computer- based system to do house -Keeping operations. Such as acquisition, circulation, classification, cataloguing, stock verification, etc. Ramkrishna Paramhansa Mahavidyalaya, Osmanabad is one of the Best College of its kind in Marathwada Region to have a computerized Library Services. Computerization started since January, 2014 with the System for Library Information and Management (SLIM21) is state-of-the-art integrated library management software designed and developed by the INFLIBNET Centre based is used. Currently updated version 3.7.0 is being used. SLIM21 is multi-user, multi-tasking integrated library management software working either on a single machine or in a client-server multi-platform environment and built a complete database of over 94,437 books. Further we have Online Services provided to our users through UGC & INFLIBNET N-LIST program with INTER LIBRARY LAN SYSTEM consisting of 7 terminals connected to, the library and information center Server storing our database. The Online Public Access Catalog (OPAC) is used to carry out online searches of library database by Author, Title; Keywords and Accession Numbers, which enables users to provide goodreference service to staff and students.

4.6 Weeding Policy :

The development of collections of books, serials, and other sources of information as detailed in this policy plays a fundamental role in the Library's mission. Weeding is the process of identifying items to be withdrawn from a library collection. Weeding is an essential component of good library collection management because it is one of the tools for assuring that at any given time a library will contain the best and most relevant information. It is carried out with the library's mission and collection development policy in mind. Weeding is an essential, continuing library practice in which materials are removed permanently from the Library's collections. Book withdrawal is an important aspect of collection development.The following criteria were used to identify items to be withdrawn from the collection of the Library:

4.6.1 Physical Condition :

Items on the open shelves need to be sturdy enough to withstand repeated reading, circulation, and routine handling. Books in damaged condition can be considered for withdrawal, repair/binding, or replacement

4.6.2 Demand for the Information:

Past circulation is the best indicator of future circulation, items that have circulated little or none in the past five years are good candidates for withdrawal decision.

4.6.3 Relevance of Information :

Library wants to provide information relevant to the needs of Hampton University's faculty, staff, and students. However, the needs of both current and future faculty, staff, and students must be considered.

4.6.4 Currency of Information:

Library wants to provide current information. Items containing superseded information should generally be withdrawn. This is particularly true for items containing medical and scientific information.

4.6.5 Disposition of Withdrawn Materials:

All materials withdrawn from the collection should be stamped as "discarded" or "withdrawn. The Librarian in agreement with the library committee will make the final decisions regarding the disposition of materials withdrawn from the collection. Recommended disposition of discarded materials are donated to other Jesuit institutions.

4.7 Stock Verification:

Stock verification is one of the important functions of any enterprise. The term stock verification is also known as stock taking, physical verification or checking, stock inspection, inventory taking, etc.

Library automation plays an important role in integration of various library processes and help to reduce or avoid the human error. Access to library holdings available to users led to loss, damage and misplacement of books. To maintain the balance between various subjects and to take adequate precautionary measures it is necessary to do periodical inventory, accounting of library collection regularly. The systematic check of library holdings for finding out missing items is called as stock verification. It is also referred as stock taking, physical verification of stock inspection.Libraries adopt various methods to carry out the stock verification.

4.7.1 Frequency of Stock Verification:

As per provisions contained in rule 116 Sub- Para (V to VII) of general financial rules, 1963(3rd). The decision in this regards is dependent upon the size of library holdings and thestrength of the library qualified staff posted in the library.

Rule116. Sub-Para (V): “Complete annual physical verification of books should be done every year in the case of libraries having not mere than 20,000 volumes &not fewer than two library qualified staff. If in case there is only one qualified staff the verification may be done as per sub-para (VI)”.

Rule 116. Sub Para (VI): “Complete physical verification at intervals of not more than 3 yrsshould be done in case of libraries having more than 20,000 books but not more than 50,000 Volumes.”

Rules 116 Sub-Para (VII): “Sample verification at intervals of not more than 5 years shouldbe done in case of libraries having more than 50,000 volumes. If such a sample verificationreveals unusual or un reasonable shortages, complete verification shall be done”.

4.7.2 Permissible loss in Stock Verification:

As per provisions contained in rule 116 Sub – Para (II) Loss three volume per thousandvolumes issued consulted in year may be taken as a reasonable provided such loss cannot beattributed to dishonesty or negligence on the past of librarian. Loss of book of valueexceeding Rs 200/- and book of special nature and rarity shall invariably be invested &consequential action taken. All such losses will have been written off only by competentauthority.

4.7.3 Automated Stock Verification in Our College Library:

College has excellent updated fully computerized library which support the teaching learning & Research programme. Our library is fully automated with SLIM21 library management software. Barcode technology is one such technology being implemented in the libraries for its faster transactions. Barcodes are also widely used in the libraries for stock verification and circulation of documents

Computerized Stocks taking of these books are done by using IA21 ZEBRA stocks taking devisewith available manpower; it helps to reduce human error. Software in this devise is set such away that duplicate number will not enter into the stock. All our library staff takeouts books from the shelves,all the books arrange according to classification number. One person scan the barcode whichis pasted on book title page (Accession No.) & shelf number with the help of IA21 ZEBRA stocktalking devise. After the scanning get over all the cater data is transfer into computer andmissing accession no list is prepared and this list has to be prepared thoroughly withfollowing records.

5. Conclusion:

The library is the lung of every educational institute, which breathes knowledge and information into the minds of the students. The stock verification helps to know the present status of the holdings of the library. Stock verification using modern technologies is important which improve the efficiency and accuracy of the system. It helps to find out the anomalies in the library management accurately. The present paper explained the weeding policy and stock verification by using of IA21 ZEBRA Device for library stock verifications. The use of the applications proved that the stock verification is systematic and fault free andthe reports generated by the system is accurate without human interaction.

References :

- BansodeSadanad Y. (2008). A Survey of Library Automation in College Libraries Goa State, India. *Library Philosophy and Practice* 12(3), 15-23.
- Devrajan, G.(1996) *Library Computerization in India*, New Delhi: EssEss Publication.
- GolwalMadansing D.and Dr. Madhukar D. Garad (2015). Redefining the Role of LIS Professionals in Environment. Online International Interdisciplinary Research Journal 3 (6) p.234 – 238. ISSN: 2249 – 9598.

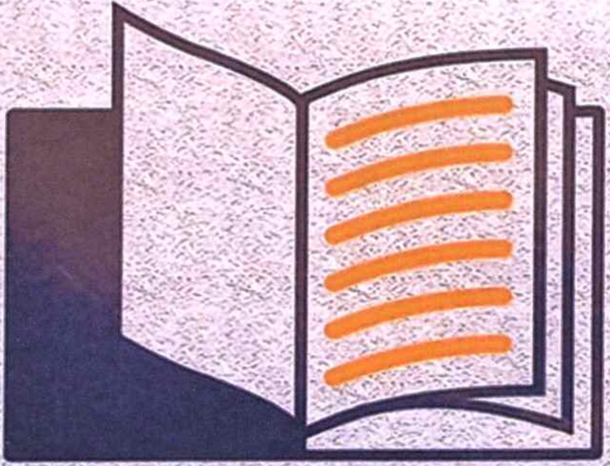
- Gupta, O.P. (1992). *Development of university libraries in India after independence*. New Delhi: Concept Publishing Company.
- Kimber, Richard T. (1968) *Automation in Libraries*, Oxford: Pergamun Press.
- Kumar, P.S.G. (1987) *Computerization of Indian Libraries*, Delhi: B.R. Publishing Corporation.
- Madansing D. Golwal (2012). Library Collection Development with reference to the Digital Era in Electronic International Interdisciplinary Research Journal [EIIRJ] 1 (1) pp.34 - 39.
- Mr. Sharad G. Yandayat and Dr.Madansing D. Golwal (2018). Best Practices in SantDnyaneshwar Library, Law College Osmanabad: A Study. Online International Interdisciplinary Research Journal 8 (2) p. 89 – 96.
- Mulla K. R., Shivkumar A. S. and Chandrashekar M. (2004). Automation of HKBK College of Engineering Library and Information Centre: A Case Study. *Digital Resources and Services in Libraries.* 1(2), 123-132.
- Ranganathan, S.R. (1965). Academic library system: Fourth plan period, Library Science with a slant *Documentation* 2(4), 293-347.
- Rice, James (1984) *Introduction to Library Automation*, Littleton: Libraries Unlimited, 1984.
- Stanley, J. Swihart and Beryl F. Hefley (1973) *Computer Systems in the Library: A Handbook for managers and designer*, Los Angeles: Melivile Publication.

MAH/MUL/03051/2012
ISSN-2319 9318

Vidyawarta®

Peer Reviewed International Multilingual Research Journal

Issue-43, Vol-03, July to Sept. 2022



Editor
Dr.Bapu G. Gholap

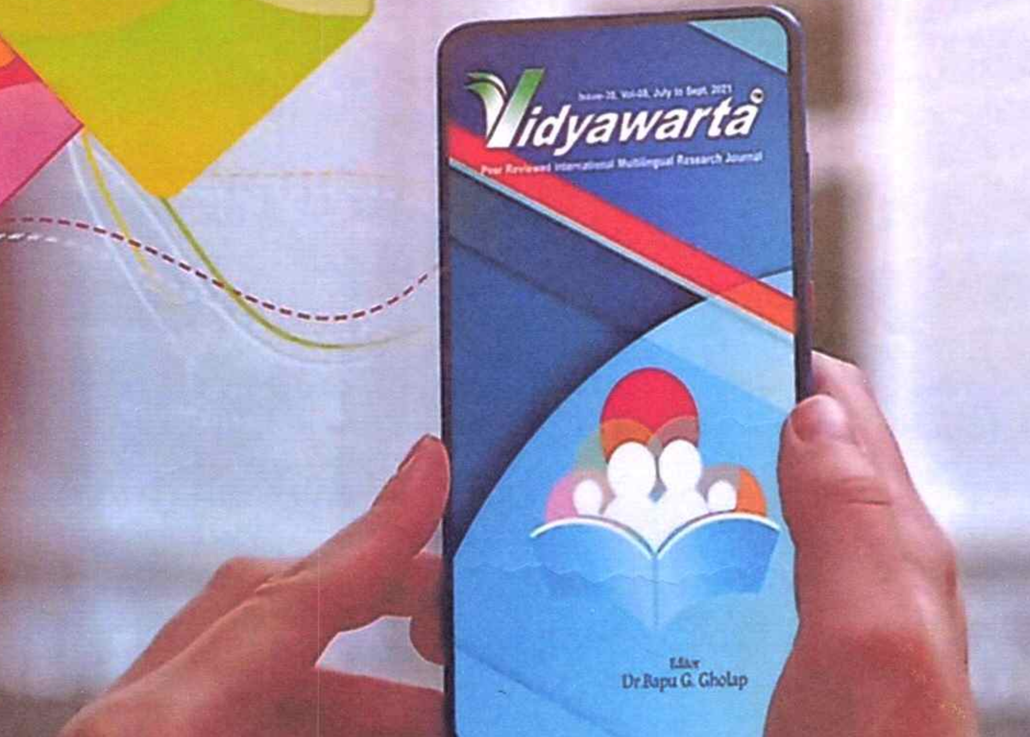
Publisher & Owner
Archana Rajendra Ghodke
Harshwardhan Publication Pvt.Ltd.
At.Post.Limbaganesh, Tq.Dist.Beed
Pin-431126 (Maharashtra)
vidyawarta@gamil.com
Edit By
Dr. Gholap Bapu Ganpat
Parli Vaijnath, Dist.Beed 431 515

Indexed

ISSN-2319 9318

IMPACT 8.014 IIJIF FACTOR

₹ 400/-



23

The Stud[redacted]f English Language and [redacted]iterature.

Bilure Suhasini Ramchandra
Ph.D. sch[redacted]at school of Language and [redacted]erature, PAHSUS

****

Abstract

The study and learning of English languageand English literature looks to establish substantialquestions and of the significant benefits of doingSo Why should the pupils or the benitors of English.language needs learning English literatura at thesame time? the final question remains the samewhat is the is bose its foundation, and what are theroots of the learning subject? what are theirrelationships enhance? what, why and how are [illegible] up to know that?

Keywords: English language English literature

Introduction

As we know. English Studies may contain ofEnglish Linguistic, English teaching and learning andEnglish Literature. All the three studies are theimportant steps to [illegible] skills and [redacted]iques inunderstanding English espe[redacted]or those who wantsto enhance their knowledge indepth and mastery of English.So an acceptable degree of mastery of English is needed. to study English literature for example. The higher one'sEnglish [illegible]'s and his sense of English's [illegible] hence more sensitive is one's [illegible] and critical awareness about English [illegible] ides that this article states that English language and English literature are in [illegible] with each other and one need [illegible]

However, the study of English literature is broaderthan just English, it is about nearly all literary works came up.that is the English speakers of certain country, academic, religious, working and cultural backgrounds andPolitical leaning and many a times express Variousaspects of their lives in written English. The mainobjective of studying their literary works are tosupplement our knowledge and understanding of highvalues of morality and wisdom they contain so toknow what an English literary is about and the message. It wants to conveyrequires know how" that comprise English skilland strategies. However, this paper asserts thatthe study of English literature can occur withthe presence between how, what, why balance. Thearguments are explaining with the following Sections.

Language and Literature inseparable Mates

There are various definitions of language someare simple, complex or some are deep.- Language is a set of (finite or infinite) of sentences,each: finite in length and constructed out of a finite setof elements" (1 957, P. 1 3) - chomsky'

Language is defined as a system of conventionalspoken or written symbols used by people in a sharedculture to. communicate with eachother

- Merriam Webster Dictionary

The way of cultural thinking both reflects and affectson language. In comparison, Oxford dictionarydefines language as 'the method of humancommunication.either spoken or written consisting ofthe use of words in a structured and conventionalway" from that of chomsky to the more recent definition of language, the essenceremains the same. Language contains rules andelements

takes both spoken or written form, reflects thespeakers culture and thinking and it is significantlyused to communicate ideas.

Literature's meaning in fact not less meaningfulthan language According to widdowson, literaturehas various meaning depending on the context thatthe speakers refers to. [illegible] the literary writtenlike fiction or literatu[illegible] major of studyLiterature referrin[illegible] writing defined as theachiev[illegible] beauty and morality. It isunder[illegible] creative and imaginative writing(1 [illegible], Literature as writing having excellenc[illegible] or expression and expressing ideas of [illegible] or universal interest illustrate[illegible] Webster, and Oxford terms [illegible] especially those conside[illegible] ingartistic merit. Literatur[illegible] acteristics like aesthetic, imaginat[illegible] pressive, Valuableexcellence and univers[illegible] Therefore, in delivering incharac[illegible] a tool-language isunavo[illegible] becomesthe only choice [illegible]

T[illegible] of language and literatur[illegible] been set their relations are consequ[illegible] in the modern digital world dictionar[illegible] as literature is the messag[illegible] art-Phone. Those two rela[illegible] bound and would not be [illegible] s.There is a facts that the[illegible] as [illegible] ate for a learner needs toSt[illegible] th language and literature.

In kind[illegible] primary and secondary schools [illegible] not a compulsory, it is a m[illegible] the students get exposu[illegible], Creative and imagina[illegible] ing [illegible] not a major study. literary [illegible] like poems, dramas, stories are well to[illegible] zed and played. Inour childh[illegible] stories are our lullabie[illegible] eams and dreams are ou[illegible] existence on the elemen[illegible] se[illegible] stages. One or two children[illegible] s are told by ourgrandmothers. grandfa[illegible] others. or fath[illegible] unclearly memorized. In high[illegible] from the simplest farmto[illegible] learning material for stu[illegible] de[illegible] literary work from [illegible] are available forlearning. Plays that commonly use more simplelanguage can be one of the discussion topics in alanguage in a classroom. It can be the purpose ofexpressing students informal language in whichstudents can adopt and adapt the expressions andlater on use it in a particular countries. Novels whichare of more complicated language style contents andtopics can be used advanced language classroom inorder to give more complex language known to thestudents. In that it is expected students language experiences which canaffect their language competence. All the abovepractices are indeed early or yet subtle introduction toliterature This simply shows that literature has a greatimpact on our early stage of life, and it is carried onand either huge or little impact on the present life.

Language and literature, are the two sides of acoin that used each other. To learn English literaturesuch as needs mastering English and to masterEnglish needs studying English literature why becauseEnglish language serves as a tool in Studying Englishliterature without which the study is impossible.

Similarly, the mastery of English can be enhancedand perfected by studying English literature. As themain objective of reading literary works are gainknowledge and understanding and to empoweroneself as well as improves one's skill in usingEnglish. ex-:A frequent reading of English novels.Essays, short stories develops and strengthens one'slanguage sense, as to how the dialogues betweencharacters . the setting description and thepsychological mood of the characters are written justlike the content reading of English history worksfamiliarizes one's with her chronologies arecomposed in English. Another imp is the awarenessof close relationship between text and context [illegible]ish skill residing from intense reading of [illegible]shliterary work between text and context.

The study of English literature can only occurwith the prese[illegible] -why-what balance why thepeopl[illegible] to l[illegible] English literature? if there is no[illegible] s the people will not study the English lit[illegible]

what benefits E[illegible] literature gives to reader? manyliterary w[illegible] y and wisdom lessons in m[illegible] and different times. Any lit[illegible] rks [illegible] that functions to enrich [illegible] nowledge and ourunderstanding and [illegible] ourselves are needed.There is an ass[illegible] that any literary work willcertainly give [illegible] The peoplelearns the P[illegible] from particular sources and t[illegible] up [illegible] city to give a value to any[illegible] rther the value mentioned in the given [illegible] ven by any one who reads and respond [illegible] own purpose, experience an[illegible]

In spite of that a[illegible] ature isconcerned there is la[illegible] nd [illegible] ue, whorules the world see[illegible] su[illegible] and is to be theone with Englis[illegible] first language. Now a days, itis very dif[illegible] English second or th dthe [illegible] ooks [illegible] me. This mean[illegible] guage mastery that may resu[illegible] tud[illegible] English literature is a precondit[illegible] ain[illegible]

If we don't know [illegible] all about English literarywork we [illegible] and capture themes [illegible] ges. [illegible] of society lives from which [illegible] works spring up That is En[illegible] al. [illegible] ple ofcertain country acad[illegible] rkin[illegible] ious, andcultural background [illegible] rning and sometimes express [illegible] their lives in writtenEnglish. [illegible] analyze through heint[illegible] text a[illegible] ontext in [illegible] est [illegible] and synthesize.meanings a[illegible] cia[illegible] the work, the inheritancerel[illegible] thes[illegible] to consequently provi[illegible] Besides this literary wor[illegible] critical analysis comb[illegible] ry history. Indeed it is enrichment beyond literature as a text.

Further, the study of English literature takesliterature as it's object of study. Literature itselfcontains many aspects that are supposed to be learnt such as knowledge, attitude, skills and responses -Brumfit (2001). In knowledge it includes the Englishliterary traditions generes, western culture, localcontext and analysis of literary texts in detail. Inaddition to that, the attitude towards

English literature should cover the tolerance, respectand understanding on cultural, imaginative andintellectual differences. As well as literary criticism asthe result of critical thinking and creativeinterpretation, is among the skills needed in learningEnglish Literature literary criticism seems to be acorrection or positive-negative appreciation as well asLiterary criticism is in fact a Contribution and anenhancement to the world of literature. It shows thathow a literary work has much deeper and extendedmeaning through the people's point of view andreaction and thus leads us to find wisdom in ourlives.

The strategies, techniques and methods used inthe study of English literature need to adjust toindividual purposes of studies. A close reading of aliterary work through language analysis might be agood start. In order to know how relate andinvestigate a literary work. learners have tounderstand the background of the writer, the societyin which the work is made and the authorspersonal experiences. They also need what kind ofapproach that need to be applied to analyze a literaryWork,

Now a days we are living in post modem

era.methods. Strategies and techniques used inlearning English literature are also influenced by it.The awakening of post modernism, feminism, postcolonialism have given to the more universal andflexible approches to studying English Literatur The Past [illegible] era gives more freedom andself values [illegible] (Widdowson 1993 P.87) Inshort of literary [illegible] understand literature has approaches [illegible] several various values and giving [illegible] truth [illegible] in literary works

[illegible] the language study, farm [illegible] has been regarded single to [illegible] and appropriate method as the [illegible] the study of literature to be in [illegible] interpretation and also [illegible] are not the passive agents [illegible] encouraged to initiate any [illegible] on their own intrest research [illegible] empower themselves so they [illegible] from literature which with the [illegible] lives.

Co[illegible]

[illegible] required in learning any subject [illegible] how. The aspects of [illegible] importance and [illegible] learning, the know-what [illegible] of the subject of learning [illegible] explains the way in which [illegible] should be conducted.

[illegible] reasons that there [illegible] to know how why, [illegible] learning English [illegible] the whole body of [illegible] system. The system is [illegible] interrelationship between [illegible] what, how, are build up [illegible] throughobservations

[illegible] study of English [illegible] to develop moral [illegible] work in order to [illegible]. The syllabus should be [illegible] learners todiscover [illegible] should be suit tothe

[illegible] strategies and [illegible] to the content and [illegible] learners to achieve the

Brumflt, C. (2001). Individual Freedom in LanguageTeaching: Helping Learners to Develop a Dialect of Their Own, New York: Oxford UniversityPress.

Carter. A. (1986) "Linguistic Models, Language andLiterariness." in R.Carter & G.J.Brumfit (ed)Literature and Language Teaching. Cambridge:Cambridge University Press. pp. 1 10-132. InRadhika O'Sullivan. (1991). Literature in theLanguage Classroom. The English Teacher.Vol. XX

IstaMaharsi,(2016)The Study of English LiteratureResearchGate .

Chomsky, N. (1957) Syntactic Structures, Tondon:Mouton

Eagleton, T. (1983), Literary Theory, Oxford: BlackwellFowler, R. (1 986), Linguistic Criticism, New York.Oxford University Press.

Merriam Webster Dictionary. Retrieved on II February2013. http://www.merriam webster.com/dictionary/language

Richards, J. C. and Theodore S. Rodgers (2001).Approaches and Methods in Language Teaching, 2 Edition, United Kingdom: CambridgeUniversity Press.vol .xx

Widdowson, P. (1999). Literature. London: Rouledge.