Sustainable Chemical Insight in Biological Exploration

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Published by:
Lincoln University College, Malaysia

www.lucp.net

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Published by:

Lincoln University College, Malaysia
www.lucp.net

Published on: 3rd July, 2024

Published by:

Lincoln University College
Wisma Lincoln
No. 12-18, Off Jalan, Perbandaran SS 6/12
47301 Petaling Jaya
Selangor Darul Ehsan
Malaysia
Tel.: +603-7806 3478
Fax: +603-7806 3479
Toll Free: 1-300-880-111
E-mail: lucp@lincoln.edu.my
Web.: www.lucp.net

ISBN: 978-967-2819-31-8

eISBN: 978-967-2819-32-5

Price : 175 MYR

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Dr. Hari Shankar Biswas earned his B.Sc. in Chemistry with Honours in 2005 from R.K.M.V.C. College. Dr. Biswas received his M.Sc. in 2008 from Presidency College, Kolkata. He completed his Ph.D. in Material Science in 2015 at the Saha Institute of Nuclear Physics, University of Calcutta. From 2008 to 2010, he worked as a school teacher at Keshub Academy in Kolkata. After that he joined Surendranath College, Kolkata, as an Assistant Professor in Chemistry. His research area focuses on Carbon Thin Films, Graphene, and Graphene Oxide-based Nanocomposites, with applications in environmental, biological, and technological fields. Dr. Biswas has authored 14 book chapters and over 30 papers in international journals. He holds life memberships in the Indian Science Congress Association and the Indian Chemical Society and is affiliated with the Royal Society of Chemistry. Additionally, he serves as a book editor and reviewer for esteemed international publishers and journals. He is the Editorial Board member of reputed International Journal and is a member of Rotary International. His editorial work includes titles such as Emerging Concepts in Chemical and Biological Science, Modern Approaches in Chemical and Biological Sciences, and Advances in Science Education published by Lincoln University College, Malaysia.

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Prof. Dr. Sandeep Poddar, presently the Deputy Vice Chancellor (Research & Innovation) of Lincoln University College, Malaysia. He also served as Senior Research Director and Executive Editor(Publications), Lincoln University College, Adjunct Faculty (Honorary), Bharat Center Canada. He has graduated from University of Calcutta in 1993 with Honours in Zoology, he has obtained Post Graduate Diploma in Dietetics from All India Institute of Hygiene and Public Health 1995, Master of Science in Zoology with specialization in Biochemical Genetics from Dayalbagh Educational Institute 1998 with distinction. In addition to this he also obtained Master of Business Administration (MBA) from Lincoln University College in 2021. He has completed Ph.D. in Zoology from Vivekananda Institute of Medical Sciences on Cytotoxicity in 2004. After completing Ph.D. he pursued Post Doctoral Research in different projects on Hemoglobinopathies and Oral Cancer mutation. He is serving as reviewer of several International Journals. He has published several research papers, organized international conferences, and edited books in Malaysia, Australia and India. Dr. Sandeep is founder Assistant Secretary of Dr. Tarak Nath Podder Memorial Foundation, Kolkata, India.

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Prof. Dr. Amiya Bhaumik is the Founder and Former Vice-Chancellor of Lincoln University College. He is purely from the field of education. Dr. Bhaumik is Executive Vice President of the International Education Consulting Group, St. Louis, USA since 1999. Dr. Amiya Bhaumik was Research Fellow of UNESCO, Paris. During this tenure, Dr. Bhaumik has traveled extensively to Europe, Africa, Asia and Latin America. He has served as Professor of Business Administration in University of Lucknow, India and in University of Malaya and many other places. Dr. Amiya Bhaumik is a very dynamic personality. He has authored numerous book chapters and has huge number of publication in many national and international journals. He has also edited several books.

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Dr. Murari Lal Gaur
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Foreword

In an era where interdisciplinary research is not just beneficial but also vital, exploring sustainable chemical processes within biological environments has become a key area of investigation. This book, entitled *"Sustainable Chemical Insight in Biological Exploration"*, is a timely and significant contribution to this evolving field, offering a comprehensive review that bridges the complexity of biological systems with the precision of chemistry, all with a focus on sustainability.

This book explores the mechanism by which sustainable chemical methods can be effectively incorporated into biological research and practice, addressing the intricate balance required to develop these solutions. The authors bring a wealth of experience and cutting-edge research with practical applications that emphasizes the profound impact of sustainable chemistry on biology.

This book is an essential resource for scientists, researchers, and students dedicated to expanding the boundaries in the biological sciences. It highlights both the scientific advancements and the shifts in mindset that is required to embrace a truly sustainable approach in biological research.

In reading this book, you will embark on a journey through the latest developments in sustainable chemistry and its applications in biology. You will gain a deeper understanding of the interconnectedness of our actions and their impact on the environment, and it will inspire you to contribute to a future where scientific advancement and sustainability are seamlessly integrated.

I am grateful to Lincoln University College, Malaysia for recognising the importance of this work and helping to make this edited volume available. This book *"Sustainable Chemical Insight in Biological Exploration"* offers a vital perspective on the intersection of chemistry and biology, emphasizing the importance of sustainability in scientific progress. This book not only informs but also inspires its readers to embrace innovative, sustainable solutions in their research. It stands as a endevour to inspire future development where science and sustainability go hand in hand.

Dr. Murari Lal Gaur
Vice Chancellor
Dr. C V Raman University, Vaishali Bihar, India

Preface

In a time where the intersection of chemistry and biology is rapidly evolving, the pursuit of sustainability has become a cornerstone of scientific research. This book *"Sustainable Chemical Insight in Biological Exploration"* embarks on a journey through the intricate relationship between chemical innovation and biological systems, emphasizing the importance of environmentally conscious approaches. The book explores into sustainable chemical practices that drive advancements in biological exploration, offering a comprehensive view of the principles of green chemistry integrated into biological research. By fostering a deeper understanding of these intersections, this book aims to inspire researchers, educators, and students to embrace sustainable methodologies that not only advance scientific knowledge but also contribute to the preservation of our planet.

Some species pollinators of order Hymeoptera have played an important role to cause pollination in most abundant spice plant like coriander in India. There activity in the coriander field is very important to facilitate the production of seeds as per demand. A detail study done by Biswanath Bhowmik explores some information related to the interaction between coriander plant and *Apis* bees.

Nanomaterials (NMs) possess unique properties due to their nanoscale dimensions and high surface areas, impacting fields from physics to biotechnology. The 2nd article explores the synthesis of NMs, focusing on eco-friendly and cost-effective bio-assisted methods. This chapter studies the living organisms, biomolecules, and plant extracts in the synthesis of nanomaterials. Innovative methods are emerging that are shaping the future of nanotechnology.

Another study entitled “Fish Species Diversity of the Lower Stretch of River Damodar with References to Pollution Effect” documents the fish diversity in the Damodar River confluence area, highlighting the impact of anthropogenic changes, such as flow diversion. The investigation identified 28 fish species, including brackish water species influenced by tidal changes. With favorable water quality and evidence of spawning and migration, the findings underscore the significance of the confluence for both fish conservation and aquatic habitat health.

Ants are essential for ecosystems, but some invasive species can harm crops, pollinate, and destroy pollen grains. Author Damayanti Bakra discusses the distribution of invasive ant species across various locations in and around the Indian Sunderbans. Invasive species disrupt native species, leading to habitat loss, competition, hybridization, fragmentation, and foraging behavior. It was found that seven invasive species are threatening the Indian Sunderbans, which is the world's largest mangrove ecosystem.

A total of 11 types of organisms belonging to 8 orders were found in the pitfall catches in a litter rich habitat. In his research, Sobhana Palit (Paul) discusses the diversity of soil arthropod fauna in pitfall catches in habitats rich in litter. The main dominant fauna in all the pitfall samples was spider (order Araneae). The other main orders included Collembola, Hymenoptera and Orthoptera. However different types of plantations did not exert any effect on the soil faunal composition of the area under study.

The paper entitled “Synthesis, Characterization and Biological activity of Schiff Base Metal (II) Binuclear Complexes with Alkali metal salt of *o*-Nitrophenol” by Chandan Kumar explores the synthesis of binuclear complexes derived from the Schiff base of 1,2-phenylenediamine and 2-hydroxy-1-naphthaldehyde. The structure and bonding of the heterobinuclear complexes has been discussed based on analytical, spectral and magnetic results. The complexes are non-electrolytic, square planar geometry and have dative bonding between transition metal chelate and alkali metal. The antimicrobial activity against *E. coli, S. aureus, and C. albicans* demonstrate significant results.

In the face of rapid urbanization and industrial growth, effective waste management has become crucial. This chapter, “Innovations in Waste Management: A Review,” examines recent advancements in recycling, waste-to-energy conversion, landfill management, and hazardous waste handling. Highlighting innovative technologies and strategies, it addresses the environmental and economic impacts of waste. Overcoming ongoing challenges requires a unified effort to ensure sustainable and efficient waste management for a healthier planet.

Solvent polarity plays a pivotal role in the Sonogashira coupling reaction, influencing both reaction rates and selectivity. “Effects of Solvent Polarity in the Sonogashira Coupling: A Brief Overview” chapter explores different solvents and their impact on the efficiency of coupling reactions, highlighting key experimental findings. Understanding these effects aids in optimizing reaction conditions for improved yields and product purity in organic synthesis.

Human serum proteins such as albumin and transferrin can act as carriers for flavonoid ligands, transporting them to target sites. Anamika Basu and coauthors explored the binding affinity between mango pulp flavonoids and human serum albumin through molecular interaction studies. Their in-silico molecular docking analysis revealed that, alongside hydrogen bonds, non-covalent interactions like Pi-alkyl, Pi-Pi T-shaped, and Van der Waals interactions significantly contribute to the binding process.

The Jhora fishery, a traditional practice in Darjeeling utilizing Himalayan stream systems, exemplifies sustainable fish farming. Author Priyankar Sanphui explores its evolution, current status, and the need for effective management to address challenges such as water pollution and climate change. By integrating data from various sources and local insights, the study highlights Jhora fishery’s role in biodiversity, food security, and local economies, advocating for policies to ensure its continued sustainability.

Apurba Biswas in his chapter offers a thorough overview of metal-organic frameworks (MOFs), highlighting their synthesis methods, including solvothermal, microwave-assisted, and emerging techniques like ionothermal and microfluidic synthesis. It explores the use of various solvents and the role of aromatic ligands and metal ions, emphasizing advancements in environmentally friendly MOF production.

In his paper, Rupankar Paira explores the transformational effect of rhodium chemistry on the activation of carbon-hydrogen bonds in aza-heterocycles with five-membered rings. By examining recent advancements and applications, particularly in pyridine and oxazole derivatives, the paper aims to inspire further research and collaboration, showcasing chemistry's potential to address future challenges.

Recently, there has been a paradigm shift towards ‘greener’ processes/products, with emphasis being placed on sustainability. Therefore, this book “*Sustainable Chemical Insight in Biological Exploration”* will serve as a vital resource that bridges the gap between sustainable chemistry and biological research. By integrating innovative approaches and progressive methodologies, this book aims to inspire future scientific advancements that prioritize sustainability while advancing our understanding of complex biological systems. As we delve into the chapters ahead, This compilation is expected to initiate new ideas and contribute to a more sustainable and enlightened scientific community.

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Content Pages

doi: 10.31674/book.2024scibe.001

Diversified Ecological Roles of Insect Pollinators in the Fruits of *Coriandrum sativum* L. (Rajasthan Coriander-41) from Nadia District, West Bengal, India

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Abstract

The present research is based on entomophily, which is a type of pollination through insects like bees, butterflies, moths and beetles in the fruits of *Coriandrum sativum* L. (Rajasthan Coriander-41) studied in Nadia district, West Bengal, from January 2020 to January 2022. The study reveals a total of seven species of insects belonging to five families and three orders, all of which were collected from eight blocks of Nadia Districts, West Bengal. The maximum number of species identified were from the Hymenoptera Order and the most abundant species was *Apis cerana*. The peak behavioural activity was recorded between 10-11 AM. The effect of bagging flowers on pollination was observed and the observation was found to be remarkably greater (p<0.001) in normal pollinated flowering plants than in closed flowering plants, respectively, by 136% and 23%. Germinability of seeds increased by open-pollinated flowers at 78%.

Keywords: *Insect Pollinator; Coriandrum sativum L.; Germination*

Introduction:

The global data reveals that 75% of staple important food crops were directly or indirectly dependent on animal pollination, which includes fruits, vegetables, coffee, cocoa and almonds (Millard *et al*., 2021). The value of Crop pollination is USD 195–387 billion per year (Porto *et al.,* 2020). The most efficient pollination produces increased and improved seed and crop production. Irshad and Stephen (2014) revealed that most food grains, vegetables, edible seed oil crops, dates and nuts were mostly based on insect pollination.

The spice *Coriandrum sativum* L. belongs to the family Apiaceae. The origin of this spice was in the Mediterranean region. This spice was economically grown in the equatorial vast croplands of, India (Madhya Pradesh), Morocco, Russia, Ukraine Romania, Mexico, and Argentina. Specially mentioned that India, is the largest spice growing country in the whole world (Priyadarshi & Borse, 2014) and coriander is one of them. This special spice belongs to the family Umbelliferae/Apiaceae. This hairless, branched, slender, glabrous, aromatic, erect annual and perennial herb has an ancient history of being a delicious herb. It was an effective source of aromatic compounds with affluent essential oils and lots of biologically active components; it holds antibacterial and antifungal properties (Mandal & Mandal, 2015). This seed is generally used as a dietary product, which might cure property-borne diseases. Msaada *et al*. (2007) opined that the essential oils from this spice undergo significant changes during ontogenesis, that might affect the aroma property of the plant. Coriander flowers draw insects, like Diptera, Coleoptera and Hymenoptera, for pollination. Among these, bees are dominant, which act as important pollinators. Khalid, Tamin and Mohammed (2008) studied *Apis* species with respect to bee pollination. The present study intended to reveal the diversified ecological roles of entomophilous insects in the fruits of coriander herbs from Nadia District, West Bengal at different times of the day, as there was no such information on the entomophilous insects' pollinators of *Coriandrum sativum* L. (Rajasthan Coriander-41), within or outside the southern part of West Bengal. The present observation also indicated the role of the pollinators with respect to the pollination ability that intends to increase the seed yield of the crop.

Methodology

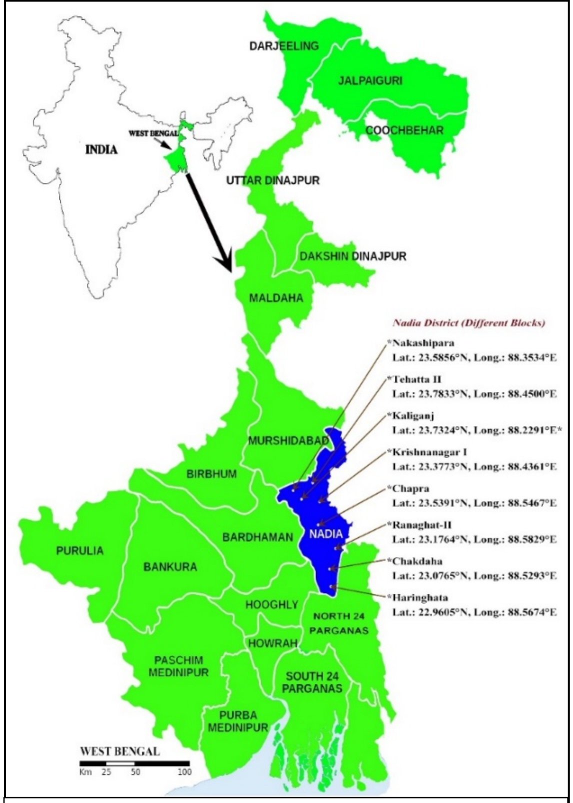

Figure 1: Map Showing the various locations of Nadia of West Bengal

The study and survey area

The observation and survey study were conducted at Nakashipara Block (23.5856˚N; 88.3534˚E) of district Nadia in the southern part of West Bengal state from January 2020 to January 2022. A triplicate study was conducted on each 1,200-square-foot plot. 'Sindhu variety', a local cultivate, was grown at the recommended spacing of 30 cm × 10 cm. The total time periods between 6 a.m. and 5 p.m. when insects visited the crop blooms, were preserved by sweeping the insect trap net (Arora, 1990). Mean weather reports like temperature (17^{o}C–23^{o}C) and relative humidity (50–65%) were studied every day for 4 consecutive months during the crop flower bloom. The statistical data analysis was done on the basis of the Shannon-Weiner diversity index for different orders of insect species (Belavadi & Ganeshaiah, 2013). *A. mellifera* and other species remained more or less the same throughout the day, with the H value remaining constant throughout the day, as similarly reported by Belavadi (2019).

Effectiveness and efficiency Index

The maximum perennial and abundant insect visitors were studied for Pollinator Performance: Effectiveness and efficiency Index (Vithanage, 1990; Sihag & Rathi, 1994).

Examination of qualitative and quantitative variables in crop yield

In the first-year study, flowering of the crop started in the mid-week of December 2020 and in next year, bloom was in the mid-week of January 2022. To activate hermaphroditism and air pollination (preventing insect pollination), unopened floral flowers were randomly selected and insect mesh nets were enclosed. The study area covered six quadrates with 81 square meters and approximately 300 plants.

In vitro pollen viability analysis

The pollen spores were grown in a simulated sucrose solution to assess *In vitro* pollen viability and study germinating viability (Belavadi & Ganeshaiah, 2013). In different concentrations of sucrose solution, the number of pollen grains is known. Approximately 20 pollen spores were taken and placed on a groove slide. The amount of sucrose solution required for germination was pre-decided. The sucrose solution at the measurement was taken at 2%, 5%, 8%, 10%, 15%, 20%, 25%, 30%, 40% and 50%. The test repeated 18 times to get the optimum concentration for use. Test results were recorded and real pictures were captured under *Primo Vert*, 40 x inverted phase contrast microscope, Carl Zeiss.

Estimation of Grain Propagation

The result of seed propagation was measured by controlling seeds, from the two sets of pollination conditions on a poly petridish, blotting paper (double layered). Grains have been pre-soaked in distilled water for 10 hours for maximum result. The grains were split open into two parts before planting. Propagation was noted in about 1-3 weeks.

Results and Discussion

The umbel of coriander was noticed to hold 6–9 pedicels, each containing approximately 22 flowers. Each pedicel consists of three sections, like the gynandrous, the staminate and the pistilate. One thing is important: the number of staminate parts is always higher than the pistilate ones and the gynandrous parts of flowers. During the inflorescence stage, the young male part and corolla curve the male reproductive part of a flower (Stamens) remains vertically above the female part of a flower (stigma) when the

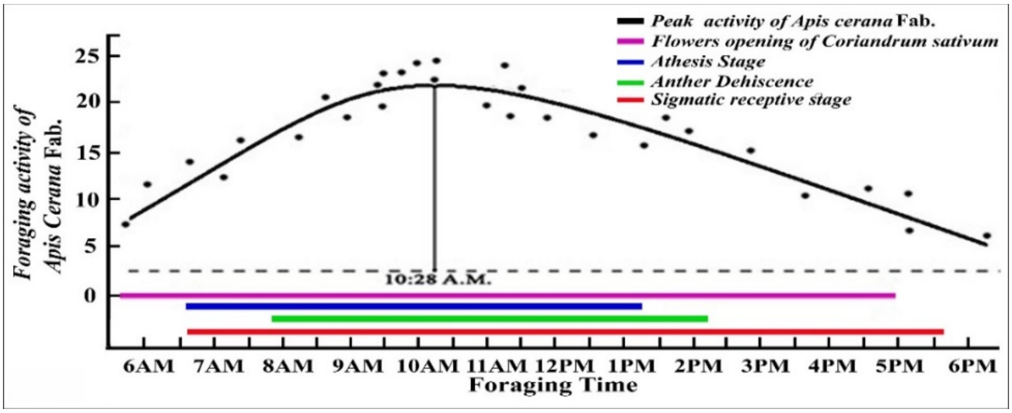

Figure 2: Inflorescence (Anthesis) and stigma activity of *Coriandrum sativum* L*.* (Rajasthan Coriander-41) and wandering activity of *Apis cerana* in Nadia, West Bengal

fertilizing dust is purely released and spreads fully, becoming distended after the pollen grains are discharged. It was also noticed that the fertilizing dust release starts in the late morning (from 9 a.m. to 1:30 p.m.), while the ability (receptivity) of stigma to support viable and compatible pollen to generate stigma activates in the afternoon (after 2 p.m. to 3 p.m.), with a non-occupying the same area in part among them. Therefore, they are hardly self-compatible, and the flower has to rely on the pollinators to accomplish cross pollination. Ultimately, pollinators gain the right set of circumstances for both pollen and nectar as a reward (Fig. 2).

Divergence, abundance, Pollinator Performance and Effectiveness of insect visitors in Coriandrum sativum L. (Rajasthan Coriander-41)

There are 7 insect species under 3 orders like Hymenoptera, Diptera and Coleoptera were visited on the plant *Coriandrum sativum* L. The order Hymenoptera and Diptera shared (3 species), followed by Coleoptera (1 species). Among Hymenoptera, *Apis dorsata, Apis cerana indica* and *Apis mellifera,* were both pollen and nectar acquirer, whereas 3 dipteran species like *Orthellia coerulifrons, Eristalinus arvorum* and *Chrysomya megacephala* were both nectar acquirer and normal visitors although at the same time, *Oenopia sp.* the Coleopteran was normal visitors (Table 2).

Table 2: *The pollen abundance with respect to insect visitors on the flower of Coriandrum sativum in Nadia, West Bengal*

Name of the Insect species	**Family of the species**	**Type of Forage**	**Diversity Index Calculated by Shannon-Wiener**	**Mean scale of pollen**		**Hourly study of ratio of flower and insects**	**Index showing pollination efficiency**
				Coriander Pollen	**Foreign Pollen**		

A. cerana Fab.	Apidae	PN	$H' = -\sum P_i(LnP_i) = -(-1.085) = 1.185$	839	28	150:28	4494(839× 150)/28 =4494
Apis dorsata Fab.	Apidae	PN		810	47	150:34	3573
Apis mellifera	Apidae	PN		729	18	150:32	3417
Orthellia coerulifrons	Muscidae	N	$H' = -\sum P_i(LnP_i) = -(-1.080) = 1.080$	-	-	-	-
Eristalinus arvorum	Syrphidae	N		196	13	150:19	1547
Chrysomya megacephala	Calliphoridae	NV		-	-	-	-
Oenopia sp.	Coccinellidae	NV	NIL	-	-	-	-
**** PN indicates Pollen and nectar; NF indicates: Nectar foragers & NV indicates Normal Visitors***				***** Method followed by Vithanage (1990), Sihag & Rathi (1994)***			

The result from Fig. 3 shows evidence of activity during the daytime, but their highest achievement times were different. Hymenopterans and Dipterans show top performance at 10.05 am and 11.10 am, accordingly. The abundance of the maximum of Hymenopterans approx. (65.6%) followed by Dipterans (29.7%) and Coleopterans (4.6%) (Fig. 4).

After the observation and analysis of three honeybee species, Apis cerana was the most frequent (28.8%), followed by *A. dorsata* (22.4 %) and *A. mellifera* (15.2 %). Normal Foraging activity of *A. cerana* was 9.5 bees/ 81 square meter /10 min, followed by A. mellifera with 7.5 bees/81 square meter/10 min and *A. dorsata* with 2.5 bees/81 square meter /10 min. The bees consumed more time for nectar acquire (~ 14 seconds) than collection of pollen grain (~ 12 seconds). During the nectar acquisition process, the honey collector bees descend to the border of the flower clutch and perform rapid movements. For the acquisition of pollen dust, pollinators delve into the core of the cluster, performing a circular maneuver. The pollen dust acquirers comprised 60–75% of the total pollinators visiting the flower, with the rest being the nectar collectors. The Shannon-Weiner index for Hymenoptera, H' was 1.185 & 1.080 for the order Diptera (Table2). The higher diversity index of Hymenoptera specifies an equal and liberal distribution for the species of the mentioned orders. At this time, the collected mean number of pollen particles from the body bristles of the Hymenoptera and Diptera insects was figured out in Table 3. Among these, the pollination efficiency index in species *A. cerana recorded as first and* second by (*A. mellifera, A. dorsata)* and the lowest by *Eristalinus arvorum*. *Apes cerana* was founded as the best effective pollinator of *Coriandrum sativum* L. (Rajasthan Coriander-41) followed by *Apes mellifera* and *A. dorsata.*

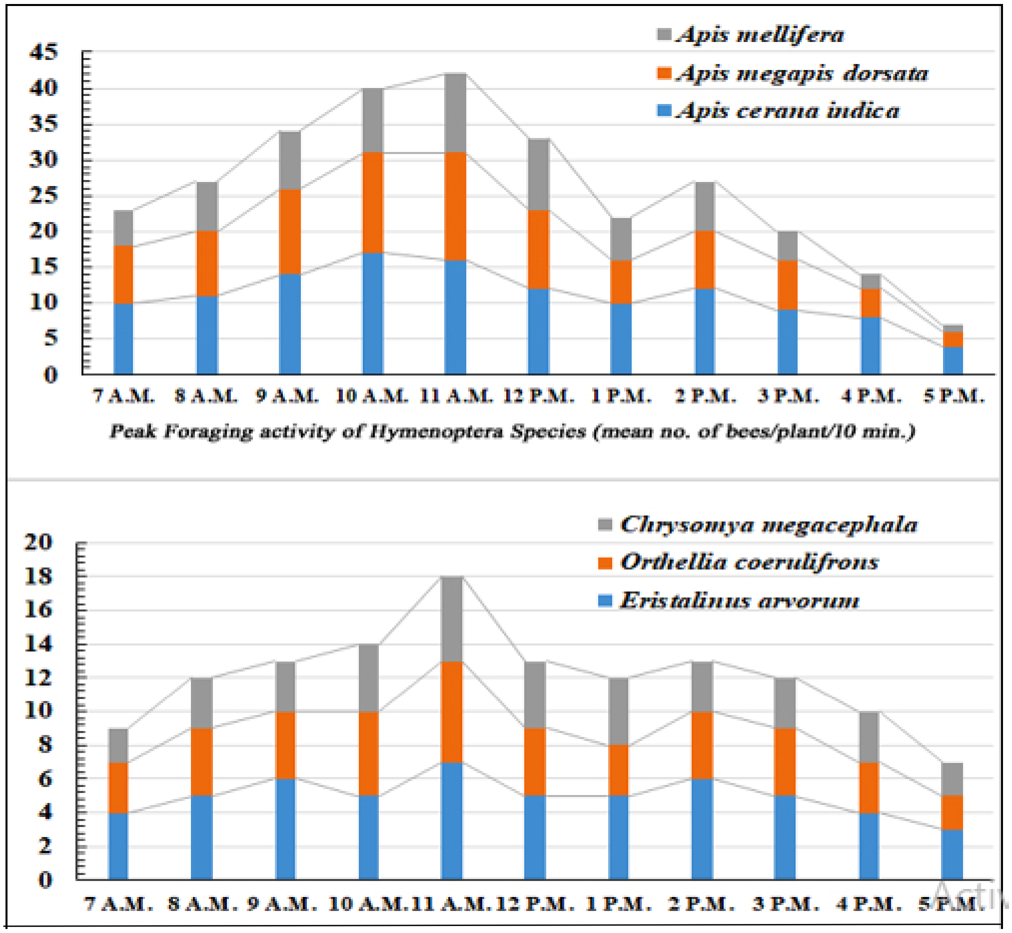

Figure 3: Peak Foraging activity. (A) Hymenoptera, (B) Dipterans, in Nadia, West Bengal

Grainy stuff (Pollen) efficacy

The quality of pollen grain is assessed in accordance with its efficacy and healthiness. The artificial germination test was the most effective test method to evaluate pollen efficacy (Belavadi & Ganeshaiah 2013). The release of pollen grains from open flowers during 9:00 a.m. to 12:30 p.m. was collected at an hourly interval between 9.00 a.m. and 1.00 p.m. in *C. sativum*. Also, pollen was accumulated from the hairy part of *Apes cerana* that give out peak bromizing activity which similar to the time of pollen indehiscence. For the development of pollen balls, the typical application of sugar fluid necessary per tube was 15–18 percent. Pollen from the insect body and an open pollinated flower. This technique was evaluated for the development of pollen channels in the required sugar fluid solution after 2.5, 4.5, 6.5, and 8.5 hours of study. In both cases, the feasibility differed from 70% to 80%. It is clear from this that both bee-collected pollen and flower-collected pollen had the same viability.

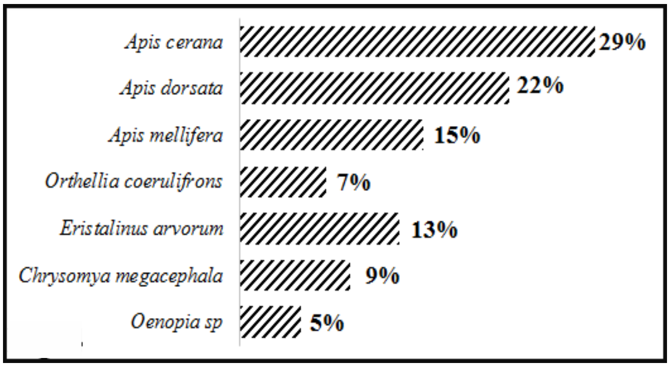

Figure 4: Relative abundance of various insect visitors on flower of Coriandrum sativum in Nadia, West Bengal

Influence of pollinators over seed and crop productivity of Coriandrum sativum

The data of seed productivity gathered (average 20/umbels), the result expressed that fruit (seed) set was 12% under insects' omission, and the data shows that it was 28.5% in unbagged pollination (136% of increase exception). The reports regarding the dominance of coriander flower visitors, except for the report from Chaudhary and Singh (2011), indicate that the Italian honeybee, *A. mellifera*, was the most dominant species, followed by *E. halteatus* and unidentified Hymenopteran species. In other crops, like onions, the observed Berger-Parker index was 0.288 (Karuppaiah, Soumia & Wagh, 2018). However, the result of increased seed yield in open pollination over the standard was 93.6%. The study revealed that the mean number of seeds was 12 and 36 per umbel, and the mean weight of 100 seeds was 2.2 gm and 2.6 gm, respectively, although in standard and natural conditions, respectively. The height of flowering peduncle was 24.9% increase in the breadth of seed was 56% in natural pollination increase (Table 3). The present study indicates that the results are validating with the outcomes observed by Kumar and Jaiswal (2012) in the case of pollinators, whose seed yield increased in *Coriandrum sativum.*

Table 3: *The influence of insect pollination on crop productivity constant of C. sativum (Rajasthan Coriander-41) in Nadia, West Bengal*

Constant	Standard (Closed inflorescence)	Free pollination	Growth in Percentage	Fischer *t*-test
Hight of flowering branch (cm)	9.98	11.8	17.9	13.8
Fruit & seed (%) production	12.06	28.51	136.22	56
Weight of 100 matured seeds in (gm)	2.2	2.6	24	11.70
Diameter of Seed (mm)	0.30	0.50	56.1	58.40
Productibility of seed (%)	47.5	85.0	78.94	71.34
Significant values are calculated against controlled and open pollination by using Fischer t-test at 18 DF and found significant at p< 0.001 in all cases.				

Germination of seed

The ability of seed germination observed from pollinated flowers under control (where the intervention of insects was excluded) and open pollinated flowers was examined. The result showed that the geitonogamy by insects improved and grow the seed productibility by 79% where unbagged flower pollination was done rather than bagged flowers (Table 3). Although the coriander plant is partially self-fertile, bees are beneficial to it. *A. cerana* indica played an important role as a pollinator of the crop, along with *A. mellifera*, *A. dorsata* and these resulted in grow the seed productivity as well as seed germinability.

Conclusion

The following observations led us to the inference that the floral visitors reported and observed were the pollinators of the aforesaid crop plants : 1) The time of visit by these visitors corresponds with the duration of pollen transfer onto the hairy stigma, 2) The visitors in a flower were seen to be profusely smeared with yellow pollen grains on the dorsal surface of their head, thorax, legs and antennae, 3) While moving within a flower, they come into contact with the dehisced anthers and the stigma. On the basis of the above observations, *Apis sp.* was found to be the most active and efficient pollinator of all four crop plants. Out of the three species of honey bees, *Apis mellifera* was found to have the highest pollination efficiency index, whereas the non-Apis bees were found to have a very low pollination efficiency index, though it was presumed that probably these non-Apis bees enhanced the foraging capability of Apis bees. Although coriander is partially self-fertile, bees proved beneficial to it, as *A. cerana* indica played an important role as a potent pollinator of the crop along with *A. mellifera* and *A. dorsata* which resulted in an increase in seed yield and germinability. Hence, the conservation and augmentation of these species’ diversity are necessary for crop plant pollination and seed production.

Acknowledgement

Dr. Indramohan Mandal, Principal, Sree Chaitanya College, West Bengal, India is acknowledged for encouragement.

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doi: 10.31674/book.2024cibe.002

Natural Sources and Bio-assisted Synthesis of Nano Particles: A Short Review

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Abstract:

Nanoamaterials (NMs) are unique chemical compounds characterized by exceptionally high surface areas and external dimensions in the nanoscale range, specifically between 1 and 100 nm. There are different types of nanomaterials, such as inorganic-based nanomaterials, organic-framed NMs, carbon-framed NMs, and composite-framed NMs. The extensive study of nanomaterials spans a vast area of research, including nanotechnology, nanoengineering, and nanoscience. Nanomaterials play a crucial role in various scientific fields, influencing disciplines such as physics, chemistry, microbiology, materials science, biotechnology, biochemistry, and microelectronics. Therefore, there is an urgent need for researchers to focus on synthesizing nanomaterials. Numerous methods for synthesizing nanomaterials have been established, utilizing various substances such as metals, semiconductors, ceramic-based materials, metal oxides, and polymeric materials. The specific synthetic procedures and the origin of the materials are key factors in determining the physicochemical, structural, and morphological characteristics of NMs. Among these methods, biosynthesis—also known as green synthesis or bio-assisted methods—stands out as the most eco-friendly, less toxic, and cost-effective approach. This review aims to provide an overview of the synthesis of nanomaterials using bio-assisted methods. It discusses different types of bio-assisted methods, including (i) living organisms-assisted biosynthesis, (ii) biomolecules (as templates)-assisted biosynthesis, and (iii) plant extracts-assisted biosynthesis of NMs.

Keywords: *Biological Assisted Method; Biomolecules; Enzyme; Green Method; Microorganism; Plant Phytochemicals*

Introduction:

Nanotechnology emerged in the 1980s (Bayda *et al.,* 2019). At the beginning of the 2000s, the commercial and transformative applications of nanomaterials were projected by nanotechnology (Roco, 2011). Today, research in science and technology is highly dependent on nanomaterials (Kostoff, Koytcheff & Lau, 2007). Thus, nanotechnology and nanoscience encompass a broad range of research areas. According to the National Nanotechnology Initiative in the US, nanotechnology involves handling matter with particles sized between 1 and 100 nanometers, with at least one dimension within this range. With the significant reduction of particle size to the nanoscale, statistical mechanical effects and quantum mechanical effects become pronounced, greatly altering the electronic properties of solids. This impacts a wide range of scientific and technological fields (Anthon, Seth & Thakral, 2017). The term "nano," which means "dwarf," comes from the Latin word "nanus" or its ancient Greek etymon "nanos" (Boholm, 2016). Nanomaterials have been utilized in technological development due to their extraordinary properties and enhanced performance compared to their bulk counterparts. Nanotechnology is a multifaceted field, and the application of nanomaterials spans almost all branches of science, including physical science, chemical science, materials science, solid-state science, and biological science (Khan, Saeed & Khan, 2019). Due to their unique features and characteristics, nanomaterials have extensive industrial applications. These include the biomedical industry, food processing industry, biotechnology, environmental remediation, construction, agriculture, communication, defense, security, renewable energy, electronics, and energy storage. The unique nature of nanomaterials is attributed to their excess surface energy, spatial confinement, and higher degree of perfection. The high surface area-to-volume ratio, exceptional penetrability, and quantization of electronic states in nanomaterials make them fundamentally different from their bulk counterparts. Nanoscience focuses on the arrangement of atoms at the nanoscale, while nanotechnology deals with the production and application of various nanomaterials across different fields. Various types of nanomaterials are available, differing in shape and size. Table 1 presents nanoparticles of various shapes. Based on dimensionality (with dimensions less than 100 nm), nanomaterials can be classified as zero-dimensional (e.g., nanoparticles), one-dimensional (e.g., nanorods and nanotubes), two-dimensional (e.g., nanofilms and nanolayers), and three-dimensional (e.g., hollow spheres and quantum dots formed by interacting with two or more nanoparticles).

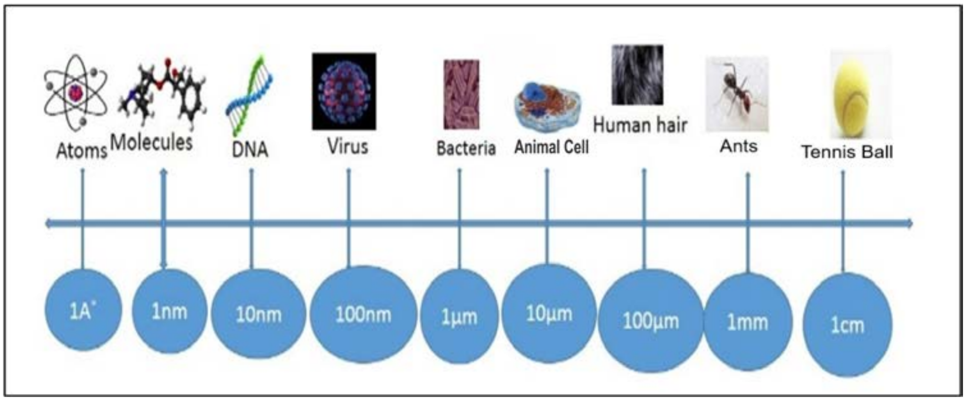

Figure 1: Various Sizes of Nano Materials *(Ealia & Saravanakumar, 2019 and Eaton et al., 2017)*

Nanomaterials are also categorized by morphology, composition, properties, and size into metal nanomaterials, ceramic nanomaterials, lipid-based nanomaterials, polymeric nanomaterials, semiconductor-based nanomaterials, and carbon-based nanomaterials.

Additionally, nanomaterials can be classified as single-phase solids, multi-phase solids, or multilayer solids depending on their phase composition. Due to their vast applications and significant impact on human well-being, researchers are dedicating substantial efforts to the synthesis of novel nanomaterials. Among the various synthesis methods, the most environmentally friendly is the green method, or biological synthesis. This method is non-toxic and environmentally benign, using microbial enzymes or plant phytochemicals. Although substantial progress has been made, there remains considerable scope for further research in this field. Table 1 describes different NMs with various shapes and examples.

Table 1: *Shapes of Different Kinds of Nanoparticles*

Types	Shapes	Materials
0D (amorphous or Crystalline)	Sphere	Carbon, Fullerene
1D (needle like)	Nanorod, nanowire, nanotube	Carbon, Metal oxide, Metal
polygonal of two dimensionality	Square, Triangle, disc, pentagon, hexagon, nano ring	Au, Ag, Pt, Pd, PLA, triacrylate, resin, poly(pyrrole), PEG-diacrylate
polyhedral of three dimensionality	Tetrahedron, cube, icosahedron, decahedron, octahedron, hollow nanocage, bundles of nanowires, nanotubes and multinanolayers.	Au, Ag, Pt, Pd, PLA, poly(pyrrole), PEG-diacrylate
Branched	Monopod, bipod, tripod, tetrapod, octopod, star shaped	Au, CdS, CdSe, CdTe, ZnO, MnS.
Complex	Snowflake, cone, flower, tree, thorn, hemisphere, urchin, worm, filamentous particle, biconcave discoid, dendrite, necklace, chain	Gold, Silver, Cu, Co, Platinum, Iron, Ruthenium, alloys and oxides of Si, metals, Si

Source: Ealia & Saravanakumar, 2019 and Eaton et al., 2017

Discussion

Different kinds of naturally occurring nanoparticles

Despite the various processes that can improve the synthesis of NMs, nature itself is an eminent nanotechnologist, providing a variety of naturally occurring nanoparticles through various processes, including volcanic eruptions, surface water, marine water, iceberg sedimentation, umber, ores, mineral wells, and particulate matter. For example, silicon dioxide (SiO_2) nanoparticles from volcanic eruptions are well documented. Iron oxide (Fe_3O_4) nanoparticles are found in iceberg sediments, and manganese oxide (MnO_2) nanoparticles are present in umber. Calcium carbonate ($CaCO_3$), silicates (SiO_2), and alumina (Al_2O_3) are just a few of the nanoparticles found in natural surface water. Additionally, silver, gold, carbon, and sulphur nanoparticles can be found in saltwater, mineral wells, ores, and particulate matter. Metal titanates ($FeTiO_3$) are obtained from ilmenite sand, alumina (Al_2O_3) nanoparticles from bauxite, TiO_2 nanoparticles from natural ilmenite, and iron oxide nanoparticles (Fe_3O_4) from ironstone. Carbon can be easily collected from ordinary organic biomass in the form of waste, whereas the sources of the previously described nanoparticles are often specialized inorganic wastes, minerals, and sediments. Researchers are continually seeking environmentally friendly alternatives to synthetic polymers. Chitin, a natural polymer found in crustacean shells, insect exoskeletons, and fungal cell walls, provides structural support. Like cellulose, chitin consists of nanoscale structural elements that can be extracted as nanofibers and nanocrystals using various top-down methods aimed at breaking down the natural structure. However, regarding the material properties of nanoscale components, chitin has largely been overtaken by cellulose. As the most abundant natural polymer on the planet, cellulose has received significant attention as a carbon source. It is biodegradable and can be derived from renewable resources such as wood, cotton, bamboo, and microorganisms. Cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) can be obtained from various cellulose materials like spruce dissolving pulp (SDP), bleached eucalyptus pulp (BEP), and cotton-based qualitative filter paper (QFP). Table 2 lists the names and different sources of nanoparticles. Table 2 describes different sources of naturally occurring NMs

Table 2: *Names and Sources of Different types of Natural NMs*

Name of some NMs	Natural Sources
Silica (SiO_2) nanoparticles	Volcanic eruptions
Iron oxide (Fe_3O_4) nanoparticles	Iceberg sediments
Manganese oxide (MnO_2) nanoparticles	Umber
Calcium carbonate ($CaCO_3$), Silicates (SiO_2)	Natural surface water
Silver (Ag), Gold (Au), Carbon (C), and Sulphur (S) nanoparticles	Saltwater, Mineral wells, Ore deposits, and particulate
Metal Titanates ($FeTiO_3$); TiO_2 nanoparticles	Ilmenite sand
Alumina (Al_2O_3) nanoparticles	Bauxite; Natural surface water
Iron oxide nanoparticles (Fe_3O_4)	Ironstone
Carbon	Organic biomass
Chitin	Crustacean shells, Insect exoskeletons, and Fungal cell walls
Cellulose Nano fibrils (CNFs) and Cellulose Nano crystals (CNCs)	Spruce dissolving pulp (SDP), Bleached eucalyptus pulp (BEP), and Cotton based qualitative filter paper (QFP)

Source: Frattini et al., 2021; Jin & Spontak, 2023; Malakar et al., 2021

Incidental Nanomaterials by nature

From the anthropogenic activities incidental nano particles (NPs) are produced. This is the unintended creation of NPs. The common sources of NPs generated incidentally are automobile exhaust, mining waste, industrial waste, corrosion processes, combustion from domestic work, heating of solid fuel, smelting, welding gases and cooking.

Fullerene, an incidental nano particle, is generated from burning candles and biomass. Figure 2 represents some sources of Incidental Nanomaterials.

Some sources of Incidental Nano materials

Figure 2: Incidental Nanomaterials ***(****Frattini et al., 2021; Jin & Spontak, 2023; Malakar et al., 2021)*

These types of accidental nanoparticles are carbon-based, such as carbon soot particles from combustion processes, metal-based nanoparticles from metal oxides, or plastic-based nanoparticles (nanoplastics) from the degradation of plastic materials. In our daily lives, nanoparticles can be found in various places and are absorbed in very small amounts through daily activities. Nanoparticles may be present in health products, household items like utensils, and furniture like drawers. Despite their widespread presence, many are unaware of their existence as they cannot be properly detected without specific conditions and specialized equipment.

It is essential to pay proper attention to the life cycles of both natural and synthetic nanoparticles. For health implications, we must protect our environment from the biogeochemical impacts of nanoparticles on various natural resources. The widespread presence of nanomaterials in drinking water, air, and agricultural soils is alarming. Understanding the potential toxicity of nanoparticles in the environment is crucial for predicting the long-term effects, including impacts on ecosystems and human health. The toxicological implications of the occurrence and exposure of natural, accidental, and artificial nanoparticles remain unclear.

Green synthesis of nano materials

Biological synthesis of nanomaterials, also known as the green method, utilizes microbial enzymes or plant phytochemicals. Enzymes extracted from microorganisms such as bacteria, fungi, algae, and phytochemicals from plant tissues like leaves, stems, roots, and flowers act as reducing agents, capping agents, and stabilizing agents for nanomaterials. Since no harmful chemicals are used in biological synthesis, the produced nanomaterials are eco-friendly and economically viable, as plants and microbes are readily available. This method offers more advantages compared to physical and chemical synthesis methods used for nanomaterials. Moreover, modifying the size, shape, and properties of nanomaterials is easier through adjustments in the cultural medium of microorganisms, such as temperature, pH, and nutrient media. Various biosynthetic nanomaterials are illustrated in Figure 3.

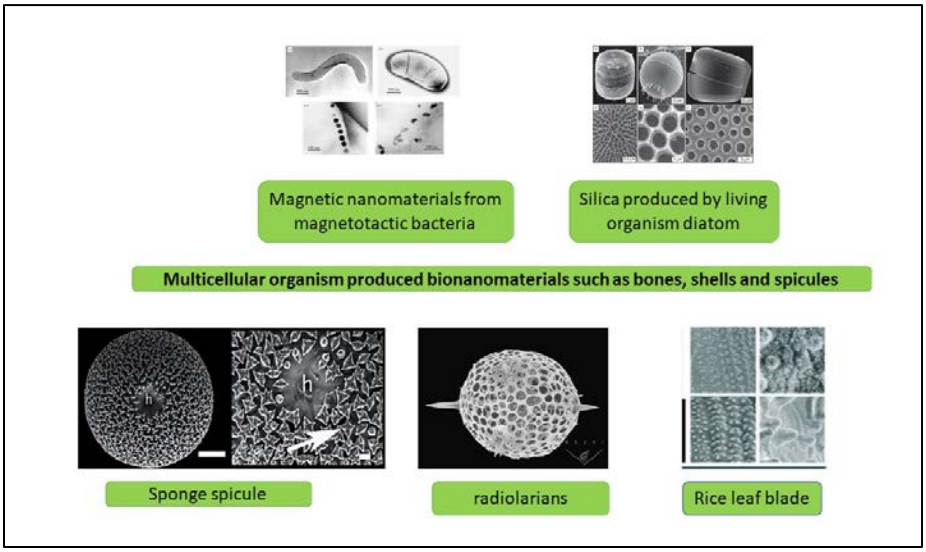

Figure 3: The Different Biosynthetic Nanomaterials (*Kuppusamy et al., 2016)*

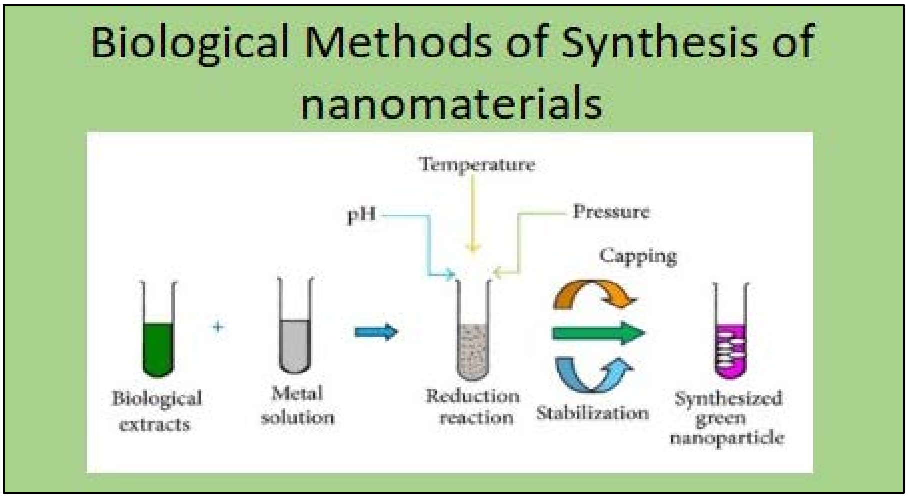

Figure 4: Schematic Representation of Synthesis Nano Materials (*Iravani, 2011*)

Biological methods can be classified into three categories:(i) Biological synthesis of nanomaterials using microorganisms (ii) Biological synthesis of nanomaterials using biomolecules as the templates (iii) Biological synthesis of nanomaterials using plant extracts. Figure 4 represents the schematic representation of biological synthesis of nano materials.

(i) Biogenic synthesis using microorganisms:

Microorganisms capture target metal ions from their environment either extracellularly or intracellularly and then convert these ions into elemental states through enzymes generated by cellular activities. In the intracellular method, metal ions are transported into microbial cells to form nanoparticles (NPs) in the presence of enzymes. Extracellular synthesis of NPs involves trapping metal ions on the surface of cells and reducing them in the presence of enzymes (Zhang *et al.,* 2011). Various anionic functional groups present in bacteria, proteins, enzymes, and reducing sugars in bacterial biomass aid in reducing interacting metal ions. The fungal-assisted green method for NP synthesis offers several advantages, including higher bioaccumulation, economic viability, and scalability due to simple downstream processing and biomass handling. In intracellular processes, aqueous solutions of silver ions are reduced to silver nanoparticles (Ag NPs) upon exposure to fungal biomass. Microscopic investigations have revealed that NP synthesis occurs at the surface of fungal mycelia, mediated by enzymes secreted from the fungal cell wall. In some cases, NMs are produced extracellularly in fungi through NADH-dependent enzyme-catalyzed reactions. Yeasts, eukaryotic microorganisms, and actinomycetes are involved in the biogenic synthesis of NPs. Carboxyl, hydroxyl, and amide groups on the cell surface of yeast may play a role in synthesizing various NMs. Actinomycetes possess numerous enzymes capable of reducing gold salt to gold

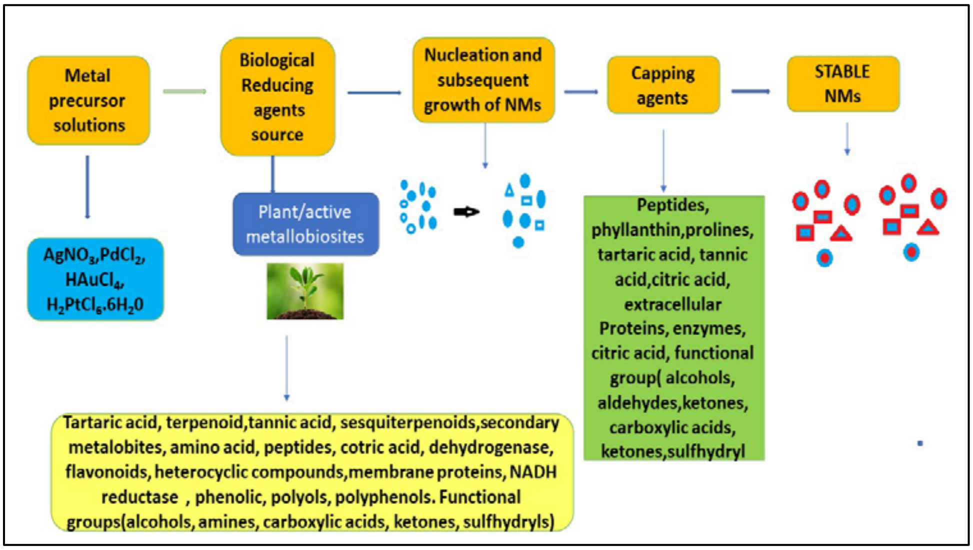

Figure 5: Phytosynthesis of NMs (*Akhtar, Panwar & Yun, 2013*)

nanoparticles. For the synthesis of NMs of noble metals, metal oxides, or bimetallic alloys, plant extracts or plant biomass have been utilized. Biogenetic synthesis of NMs using plants is highly cost-effective, environmentally friendly, rapid, and non-toxic compared to other biosynthesis methods. Many metalloproteins in plants can serve as both reducing agents and capping agents in the synthesis of nanomaterials. Figure 5 illustrates the schematic phytosynthesis of metal nanoparticles. Phytosynthesis of nanoparticles exhibits a higher rate compared to other biosynthetic routes. Some nanoparticles are stabilized by peptides and terpenoids present within the latex of plants (Vellora *et al.,* 2013).

The following tables, Table 3, Table 4, Table 5 and Table 6 represent the types of nanomaterials synthesized from bacteria, fungi, east and actinomycetes

Table 3: *Nanomaterials Synthesized from Microorganisms*

Bacteria	Nanoparticle	Size (nm)	Morphology
Aeromonas sp. SH10	Silver	6.4	—
Bacillus cereus	Silver	20–40	Spherical
Bacillus megatherium D01	Gold	1.9 ± 0.8	Spherical
Bacillus subtilis 168	Gold	5–25	Octahedral
Bacillus subtilis	Silver	5–50	Spherical and triangular
Clostridium thermoaceticum	Cadmium sulfide	—	Amorphous
Corynebacterium sp. SH09	Silver	10–15	—
Desulfobacteraceae	Zinc sulfide	2–5	Spherical
Desulfovibrio desulfuricans	Palladium and selenium	—	—
Desulfovibrio vulgaris	Gold, uranium, and chromium	—	—
Desulfovibrio magneticus strain RS-1	Magnetite	Up to 30	Crystalline
Enterobacter cloacae	Silver and selenium	—	—
Escherichia coli	Cadmium sulfide	2–5	Wurtzite crystal
Escherichia coli	Silver	8-9	Spherical
Escherichia coli DH5	Silver	10–100	Spherical
Escherichia coli DH5	Gold	25 ± 8	Spherical, triangular, and quasi-hexagonal
Escherichia coli MC4100	Gold	Less than 10 to 50	Spherical, triangular, hexagonal, and rod shape
Geobacillus sp.	Gold	5–50	Quasi-hexagonal
Geovibrio ferrireducens	Gold	—	—
Klebsiella aerogenes	Cadmium sulfide	20–200	Crystalline
Klebsiella pneumonia	Silver	28.2–122 (average size of 52.2)	Spherical
Lactobacillus strains	Gold	20–50 and above 100	Crystalline, hexagonal, triangular, and cluster
Lactobacillus strains	Silver	15–500	Crystalline, hexagonal, triangular, and cluster
Lactobacillus strains	Silver-gold alloys	100–300	Crystalline and cluster
Lactobacillus strains	Titanium	40–60	Spherical

Lactobacillus casei subsp. *casei*	Silver	25–50	Spherical
Magnetospirillum magnetotacticum	Magnetite	—	Cluster (folded-chain and flux-closure ring)
Nocardiopsis sp. MBRC-1	Silver	~45	Spherical
Plectonema boryanum UTEX 485	Gold	10–25 and ~1–10 and 10 to 6000	Cubic and octahedral Platelet
Pseudomonas aeruginosa	Gold	15–30	—
Pseudomonas aeruginosa	Lanthanum	—	Crystalline and needle-like
Pseudomonas fluorescens	Gold	50–70	Spherical
Pseudomonas putida NCIM 2650	Silver	~70	Spherical
Pseudomonas stutzeri AG259	Silver	35–46 and up to 200	Hexagonal, equilateral triangle, crystalline silver, and monoclinic silver sulfide acanthite
Rhodobacter sphaeroides	Zinc sulfide	Average diameter of 8	Spherical
Rhodopseudomonas capsulate	Gold	10–20	Nanoplate and spherical
Rhodopseudomonas palustris	Cadmium sulfide	8.01 ± 0.25	Crystalline, face-centered cubic
Serratia nematodiphila	Silver	10–31	spherical, and crystalline
Shewanella algae	Platinum	5	Elemental
Shewanella algae strain BRY	Gold	Various sizes changed with pH	—
Shewanella putrefaciens (Gs-15)	Magnetite	10–50	Fine-grained crystal
Thermoanaerobacter ethanolicus TOR-39	Magnetite, cobalt, nickel, and chromium	—	Octahedral

Table 3 describes various NPs with different morphologies with different sizes and examples.

Table 4: *Different nanomaterials synthesis from Fungi*

Fungi	**Types of nanomaterials**	**Size(nm)**
Verticillium.	Silver NPs	25±12
Aspergillus Terreus	Ag NPs	
Pleurotus ostreatus, Aspergillus avus, Bryophilous Rhizoctoni, etc.	Ag NPs	
Candida albicans	Au NPs	20–40 nm
Fusarium oxysporum(from agro based rice husk)	Nanocrystalline silica	2–6 nm
various fungal species. (Fusarium oxysporum)	Magnetite NMs TiO_2 NMs ZrO NMs	20–50nm 6–13 nm 7-8nm

Table 4 represents different kinds of fungi extracted nano materials with different characteristics with examples.

Table 5: *Various Nanomaterials Extracted from Yeast and Actinomycetes*

Yeast & actinomycetes	Types of nanomaterials	Size(nm)
Silver tolerant yeast strain MKY3.	silver NPs	2–5 nm
Hanensula anomala	AuNPs	**14nm**
Yarrowia lipolytica NCIM 3589	AuNPs	**9-23nm**
Candida glabrata and Rhodosporidium	Cd and PbS NPs	**2nm-5nm**
Candida albicans	Au NPs	**20-40nm**
Thermomonospora sp	Au NPs	8–40 nm
Rhodococcus sp.	Au NPs	**5-15nm**

Table 5 describes different nano materials extracted from Yeast and Actinomycetes and their examples

ii) Biomolecules as templates to design nanoparticles

Different biomolecular templates such as DNA, viruses' nucleic acids, membranes and diatoms have been used in the synthesis of NPs. DNA has strong attraction towards transition metal ions and before attached with transition metal ions crosslinked hydrogel could be made as in DNA macromolecules in the synthesis of AuNPs. First Au(III) has reduced to Au metals which eventually converted to metal clusters which form AuNPs on the chain of DNA (Zinchenko *et al.,* 2014). Kundu *et al*. reported the synthesis of different kinds of NPs e.g. stable wire-like clusters of Ag NPs (17±3 nm and inter-particle gap of ~1.7 ±0.2 nm) and their assemblies were using DNA templates and or organic scaffolds (Majumdar *et al*., 2013; Kundu, 2013; Kundu & Liang, 2008; Kundu & Nithiyanantham, 2014; Anantharaj *et al*., 2014; Nithiyanantham *et al*., 2015; Ede *et al*., 2015; Nithiyanantham *et al*., 2014a; Kundu *et al*., 2009; Kundu, Lee & Liang, 2009; Kundu & Liang, 2008a; Kundu & Jayachandran, 2013; Nithiyanantham *et al*. 2014b; Ede *et al*., 2014). They are used as ultrasensitive SERS substrates (Ghorbani, 2013) as well as good catalysts in the reduction of aromatic nitro compounds (Kundu, 2013). Au nanoclusters (10–40 nm) and long nanostructures (diameter: 40–70 nm) exhibit the resistivity like the pure metals when synthesized by electroless, photolytic, DNA-mediated metho (Kundu, Maheshwari & Saraf, 2008). In solar cell applications ZnO NPs with different morphologies (wire-like, ~150±15 nm; flake like, ~80±10 nm; flower like, ~350±50 nm) were reported by using DNA bio template (Nithiyanantham *et al.,* 2014c). Organosols of Os NPs and b-MnO_2 NPs were synthesized by using DNA as supports through the homogenous reduction route and these NPs have shown catalytic activity in hydrogenation and oxidative polymerization of pyrrole and in hydrogenation. Self-assembled $NiWO_4$, $ZnWO_4$ and $MnWO_4$ NPs having different shapes have been reported to synthesized using DNA scaffolds. DNA can be used as reducing and capping agent for the synthesis of electrically conductive nanowires of Au, Pd and CdS and used in functional nanodevices, miniaturized computers, sensors and optoelectronic applications (Kundu & Liang, 2008b). Table 6 represents the synthesis of self-assembled nano clusters by using DNA as bio template or scaffold. Biological membrane can also be used as templates for the synthesis of NPs as it has ultra fine pores. Au NPs were reported to be synthesized from Au(III) solution at 80^0C on the rubber membrane V (*Hevea brasiliensis* trees) which was used as preservative (Santos *et al*, 2019). Viruses having hollow center in their structure could be used as the template for the synthesis of uniform size and morphology of NPs (Pokorski & Steinmetz, 2011). Polycrystalline AgNPs (20 to 25 nm) were reported to be synthesized by extracts from Diatoms (e.g. as Amphora-46) and $AgNO_3$ solution in the presence of a pigment fucoxanthin which reduces Ag ions in the presence of light (Jena *et al*., 2014).

Table 6: *Representation of Various Self-Assembled Nanomaterials with Different Characteristics*

Various Self assembled nano clustures	**Shape of nano clustures**	**particle diameter, ϕ_p**	**chain diameter ϕ_c**	**wire diameter (ϕ_w)**	**chain length (L)**	**Applications**
Ag NPs	Wire like	17 ± 3 nm, (IPD = 1.7 ±0.2 nm)	-	-		As ultrasensitive surface enhanced Raman spectroscopy Substrate
Os NPs	Wire like Honeycomb like	2 ±0.5 nm 1.5 ±0.2 nm,	-	290 ±20 nm 400 nm		Catalysis and surface enhanced Raman spectroscopy
Os NPs (organosol)	Wire like Aggregated wires	2.6 ±0.2 nm, 1.2 ± 0.2 nm,	-	-	0.54 ±0.03 µm 8–10 micron	
ZnO NPs	Wire-like Flower-like Flake-like	150 ±15 nm 350 ±50 nm 80 nm ±10 nm	-	-	1–2 µm	Catalysis and dyesensitized solar cells
b-MnO_2 NPs	Wire-like Flake-like	35 ± 5 nm 25 ±5 nm	-	-	1.9 ±0.2 mm, 275 ±25 nm	Catalysis and supercapacitor
TiO_2 NPs	Wire like cluster (large) Wire like cluster (small)	15 ± 5 nm 10 ±2 nm,	180 ± 20 nm 40 ±5 nm	-	-	Supercapacitor and dye sensitized solar cells
$NiWO_4$ NPs	Chain like (small) Chain like (large)	20 ± 5 nm 26 ± 4 nm	175 ±15 nm 245 ±15 nm,	-	2 ± 0.2 mm 3.4 ± 0.2 mm,	Catalysis and supercapacitor
$ZnWO_4$ NPs	Aggregated, chain like	75 - 5 nm	~75 ±15 nm	-	L = ~3 mm	High performance supercapacitor and catalysis

$MnWO_4$ NPs	Wire-like Flake-like Rice-like	75 - 15 nm 25 - 5 nm	-	-	L $\geqslant$700 nm 90-180 nm 90 -10 nm	Magnetic, catalysis and supercapacitor studies

Table 6 represents various self-assembled nanoclusters with different shapes, diameters (chain and wire), chain length and their applications.

iii) Plant extracts for nanoparticles synthesis

Synthesis of NPs like noble metals, metal oxides, bi-metallic alloys, etc. (Iravani, 2011) are carried out by the bio synthesis method using plant extract. It is one of the most important environmentally friendly, non-toxic very quick and effective method. Various plant bio metabolites have been reported to be used as reducing agents and capping agents in this biosynthesis of NPs. Photosynthesis of NPs is given in Figure 5 (Akhtar, Panwar & Yun, 2013). Table 7 represents the various plant extracted NPs.

Table 7: *Various Plant Extracted Nanomaterials*

Plant Extracts	**Types of nanomaterials**	**Size(nm)**
lemongrass leaf extract	gold nanotriangles	
leaf extract of plants *(Tamarindus indica, Aloe vera, Emblica officinalis)*	Au NPs.	
various parts of different plants	Pd NPs and Pt NPs	
Azadirachta Indica (leaf extracts), *Emblica officinalis*(fruit extract)	Ag NPs	
Aloe vera, *Capsicum annuum* and *Helianthus annuus* (leaf extract)	Ag NPs	
Aloe vera.	In2O3 NPs	5–50 nm
Sedum alfredii (Zn-hyperaccumulator)	Wurtzite ZnO NPs	53.7 nm
Medicago sativa (alfalfa) Plant	Iron oxide NPs	
Glutathione (an antioxidant tripeptide in plants)	Au NPs(aggregate)	
Curcumin	shape-selective AgNPs	

Table 7 describes different types of nano materials varying in size extracted from various parts of the plants.

Conclusion

Nanomaterials can be synthesized through physical, chemical, and biological methods. However, bio-assisted techniques are also considered a green approach to synthesizing eco-friendly and economically viable nanoparticles. The bio-inspired technique causes much less environmental damage compared to other methods since toxic chemicals are not used. By simply modifying the culture medium, nanoparticles with different morphologies can be synthesized. Microorganisms, biomolecules, and plant extracts are utilized in biological synthesis.

Acknowledgment

The author is grateful for the kind support and encouragement from Netaji Nagar Day College, West Bengal, India to complete the present review.

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doi: 10.31674/book.2024scibe.003

Fish Species Diversity of the Lower Stretch of River Damodar with References to Pollution Effect

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Abstract:

Documentation of Icthyofauna reveals the present status of fish diversity and also indicates the effect of anthropogenic activities. Flow diversion is a serious problem of Damodar River in the lower valley, because the original pathway is totally dried up and in place of it a man-made channel has been drawn which represents the river at present. This channel joins river Hooghly at Attannogate. Investigation was done from Tarakeshwarup to Attannogate to reveal the existing fish faunal diversity of this confluence area. The present study reveals that the confluence stretches of Damodar River houses 65 fish species belonging to 13 Orders,24 Families and 49 Genera. The study indicates that 12 fish species recorded are brackish water fish.These brackish species entered due to tidal influences and are considered as transient species.The process of migration was revealed at this region,where those transient species were recorded to migrate upstream up to Tarakeshwar area. At Tarakeshwar spawns of these fishes were recorded during the post-monsoon season. At Tarakeshwar and Attannogate WQI is below 30, which indicates favourable aquatic habitat for fishes. Moreover, *Clupisoma garua,Gonialosa manmina,Septipinna phasa*had very high value catch data annually from Attannogate region which is a positive sign to the favorable aquatic condition.The physiochemical water quality parameters have been recorded during the study period and result indicated that water of Damodar river at the confluence was suitable for irrigation and also suitable habitat for fish conservation.

Keywords: *River; Pollution; Icthyofauna; Water Quality*

Introduction:

The Damodar River is a main tributary of River Hooghly and one of the most important among all other east flowing rivers. It flows through an undulating topography at its origin passes through hilly areas of Chotonagpur plateau created several falls and gorges on its way. The river originates from the hills of Chotonagpur in Jharkhand drains through undulating upper and middle valley and ultimately joins River Hooghly at Attannogate near Kolkata. The narrow upper valley flows through Gorge and rushing stream carries silt and mud with it which is deposited in the lower valley and as a result the depth of the riverbed rises, which leads to frequent flood. The river houses a good number of food fishes in the past (Sarkar & Banerjee,2012) but this research reveals the ichthyofaunal diversity of the lowervalley in the context of increasing water pollution. So, it is utmost necessary to identify and create proper documentation of fish species of lower Damodar River in order to develop an estuarine fish species diversityinformation system.

Methodology

Collection of Fish species: The present study was conducted during August 2020 to December 2023 and fishes were collected from eight collection sites including 1.Tarakeshwar,2.Santhoshpur,3.Bikunthapur,4.Deulpara,5.Attannogate,6.Garchumuk,7.Silampur, 8.Madaribar with the help of local fishermen using different type of nets, namely Cast net, Dragnet, Gill net, and Bharjal. Photographs were immediately taken in the field before preservation for further study. The fish landing stations at Attannogate were also studied during all the seasons. The fish species were identified by studying Morphometric and Meristic characters following reference Books and Journals, Day(1878), Jayaram(2010), Talwar and Jhingran(1991) Fricke *et al*. (2020), Das *et al*., (2004), Nelson, Grande and Wilson (2016). The heavy metal content limits in water and fish tissue (Muscle) were studied by using AAS(Atomic Absorption Spectro Photometer). The hydrological parameters of water were analyzed following standard methods APHA 1998.

Observation Table

Table 1: *Hydrology of 1. Tarakeshwar (a.Sanhoshpur, b.Bikunthapur,c.Deulpara) 2.Attannogate (a.Garchumuk,b.Silampur, c.Madaribar) at lower stretch of Damodar River during the study period*

Month	**Temperature of Water**		**pH**		**Salinity(PSUMin Max**		**DO(mg/l)**		**Transperency (cm)**		**Alkalinity (%)**	
	Min	**Max**	**Min**	**Max**			**Min**	**Max**	**Min**	**Max**	**Min**	**Max**
August	25.8	25.94	8.02	8.05	18.9	18.96	7.12	7.16	11	12.2	24.8	23.88
September	22.2	24.68	7.45	7.66	15.2	15.4	7.4	7.5	15	18.6	26	29.2
October	18.8	19.96	7.09	8	14.5	14.76	8.20	8.9	14	16.6	25.10	26.2
November	12.64	16	7.15	7.18	12	12.5	7.56	7.58	15	18.4	13.9	16
December	12.5	33.94	7.19	8	12.01	12.5	7.23	8	18.8	19.82	18.2	19.6
January	10.2	10.66	7	7.2	16.8	16.92	8	8.2	12	16.2	14.8	15.88
February	11.4	11.88	7.8	7.9	24.3	24.56	6.5	7	16.8	16.82	16.98	23.5
March	14.64	14.08	6.9	7	24.0	24.02	8	8.5	14	16.2	18.2	16.6
April	17.9	18.56	7	7.2	24.8	24.88	6.3	7	13	17.2	17	18.8
May	38.2	39.5	7.8	8	20.6	20.82	5.9	6	14.9	18.6	21.88	23.8

	8	8										8
June	37.70	38.12	7.9	8.2	24.5	24.8	8	8.4	8.5	9.01	14.8	16.6
July	**33.62**	**33.67**	**7.5**	**7.6**	**23.8**	**25.9**	**4.9**	**5**	**4.6**	**9.01**	**24**	**28.8**

Table 2: *Shows the Fish Species Diversity Indices During the Study Period*

S1	SPECIES RICHNESS	86	45	86	74
	MARGALEF INDEX	12.14253527	16.92261999	12.895674	12.84569
	SHANNON WIENER INDEX	5.08533234	5.08712858	5.846921	5.846971
S2	SPECIES RICHNESS	86	89	86	86
	MARGALEF INDEX	11.01297207	11.3027427	12.846325	12.7894587
	SHANNON WIENER INDEX	4.065523099	4.069572743	4.2189	4.3569
S3	SPECIES RICHNESS	86	87	86	86
	MARGALEF INDEX	11.06163392	19.25700165	16.89468	16.52398
	SHANNON WIENER INDEX	4.010821485	4.122511875	4.128459	4.15789
S4	SPECIES RICHNESS	86	89	89	89
	MARGALEF INDEX	11.15253527	16.67261999	16.28745	16.3258
	SHANNON WIENER INDEX	4.08533234	4.08712858	4.5892	4.6897
S5	SPECIES RICHNESS	89	89	82	82
	MARGALEF INDEX	11.01297207	11.3027427	11.5487	11.3659
	SHANNON WIENER INDEX	4.2569299	4.254672743	4.58762	4.02546
S6	SPECIES RICHNESS	89	87	89	89
	MARGALEF INDEX	11.06163392	19.25700165	15.32466	15.24879
	SHANNON WIENER INDEX	4.010821485	4.122511875	4.125846	4.236589
S7	SPECIES RICHNESS	89	89	89	89
	MARGALEF INDEX	12.01297207	12.3027427	12.35698	12.45698
	SHANNON WIENER INDEX	4.235689213	4.069572743	4.25789	4.650245
S8	SPECIES RICHNESS	89	89	89	89
	MARGALEF INDEX	10.01297207	10.3027427	10.56987	10.23659
	SHANNON WIENER INDEX	4.123895213	4.123533865	4.12587	4.25689

Table 3*: Shows the List of Fishes from the lower stretch of Damodar River in the Lower Stretch from Tarakeshwar to Attannogate*

Sl. No	**Class**	**Family**	**Sub Family**	**Order**	**Name of the Fish**	**Status**
1.	Actinopterygii	Cyprinidae		Cypriniformes	*Amblypharyngodon mola*	LC
2.	Actinopterygii	Cyprinidae		Cypriniformes	*Aspidoporia jaya*	LC
3.	Actinopterygii	Cyprinidae		Cypriniformes	*Chagunius chagunio*	LC
4.	Actinopterygii	Cyprinidae		Cypriniformes	*Cirrhinus reba*	LC
5.	Actinopterygii	Cyprinidae		Cypriniformes	*Laubuka laubuca*	NT
6.	Actinopterygii	Cyprinidae		Cypriniformes	*Pangusius pangusia*	LC
7.	Actinopterygii	Cyprinidae		Cypriniformes	*Puntius sophore*	LC
8.	Actinopterygii	Cyprinidae	Danionidae	Cypriniformes	*Salmostoma bacaila*	LC
9.	Actinopterygii	Cyprinidae	Danionidae	Cypriniformes	*Salmostoma phulo*	LC
10.	Actinopterygii	Cyprinidae	Danionidae	Cypriniformes	*Securiculagora*	LC

11.	Actinopterygii	Cyprinidae	Danionidae	Cypriniformes	*Danio aequipinnatus*	LC
12.	Actinopterygii	Cobitidae		Cypriniformes	*Lepidocephalichthys guntea*	LC
13.	Actinopterygii	Cyprinidae	Barbinae	Cypriniformes	*Pethia conchonius*	LC
14.	Actinopterygii	Latidae		Perciformes	*Lates calcarifer*	LC
15.	Actinopterygii	Ambessidae		Perciformes	*Ambassis kopsii*	NE
16	Actinopterygii	Ambessidae		Perciformes	*Chanda nama*	LC
17.	Actinopterygii	Ambessidae		Perciformes	*Parambassis baculis*	LC
18.	Actinopterygii	Ambessidae		Perciformes	*Parambassis ranga*	LC
19.	Actinopterygii	Badidae		Anabantiformes	*Badis badis*	LC
20.	Actinopterygii	Nandidae		Anabantiformes	*Nandus nandus*	LC
21.	Actinopterygii	Osphronemidae		Anabantiformes	*Trichogaster fasciata*	LC
22.	Actinopterygii	Osphronemidae		Anabantiformes	*Trichogaster lalius*	LC
23.	Actinopterygii	Osphronemidae		Anabantiformes	*Trichogaster chuna*	LC
24.	Actinopterygii	Channidae		Anabantiformes	*Channa orientalis*	VU
25.	Actinopterygii	Channidae		Anabantiformes	*Channa punctata*	LC
26.	Actinopterygii	Channidae		Anabantiformes	*Channa striatus*	LC
27.	Actinopterygii	Belonidae		Beloniformes	*Xenentodon cancila*	LC
28.	Actinopterygii	Anguillidae		Anguilliformes	*Anguilla bengalensis*	LC
29.	Actinopterygii	Anguillidae		Anguilliformes	*Anguilla bicolor*	NT
30.	Actinopterygii	Clupeidae		Clupeiformes	*Corica soborna*	LC
31.	Actinopterygii	Clupeidae		Clupeiformes	*Gonialosa manmina*	LC
32.	Actinopterygii	Clupeidae		Clupeiformes	*Gudusia chapra*	LC
33.	Actinopterygii	Clupeidae		Clupeiformes	*Nematalosa galatheae*	LC
34.	Actinopterygii	Clupeidae		Clupeiformes	*Tenualosa ilisha*	LC
35.	Actinopterygii	Pristigasteridae		Clupeiformes	*Llisha elongate*	LC
36.	Actinopterygii	Engraulidae		Clupeiformes	*Setipinna phasa*	LC
37.	Actinopterygii	Engraulidae		Clupeiformes	*Setipinna tenuifilis*	DD
38.	Actinopterygii	Siluridae		Siluriformes	*Wallago attu*	VU
39.	Actinopterygii	Siluridae		Siluriformes	*Ompok pabo*	NT
40.	Actinopterygii	Siluridae		Siluriformes	*Ompok bimaculatus*	NT
41.	Actinopterygii	Siluridae		Siluriformes	*Mystus cavasius*	LC
42.	Actinopterygii	Bagridae		Siluriformes	*Mystus bleekeri*	LC
43.	Actinopterygii	Bagridae		Siluriformes	*Mystus tengra*	LC
44.	Actinopterygii	Bagridae		Siluriformes	*Ailia coila*	NT
45.	Actinopterygii	Bagridae		Siluriformes	*Silonia silondia*	LC
46.	Actinopterygii	Pangasilidae		Siluriformes	*Pangasius pangasius*	LC
47.	Actinopterygii	Synodontidae		Aulopiformes	*Harpadon nehereus*	NT
48.	Actinopterygii	Mugilidae		Mugiliformes	*Planiliza macrolepis*	LC
49.	Actinopterygii	Mugilidae		Mugiliformes	*Chelon parsia*	LC
50.	Actinopterygii	Mugilidae		Mugiliformes	*Rhinomugil corsula*	LC
51.	Actinopterygii	Mugilidae		Mugiliformes	*Valamugil buchanani*	LC
52.	Actinopterygii	Oxudercidae	Oxudercinae	Gobiliformes	*Apocryptes bato*	LC
53.	Actinopterygii	Oxudercidae		Gobiliformes	*Apocryptodon madurensis*	LC
54.	Actinopterygii	Oxudercidae		Gobiliformes	*Glossogobius giuris giuris*	LC
55.	Actinopterygii	Oxudercidae		Gobiliformes	*Parapocryptes serperaster*	LC
56.	Actinopterygii	Oxudercidae		Gobiliformes	*Parapocryptes batoides*	LC
57.	Actinopterygii	Oxudercidae		Gobiliformes	*Periophthalmus kalolo*	LC
58.	Actinopterygii	Mastacembelidae		Synbranchiformes	*Macrognathus pancalus*	LC
59.	Actinopterygii	Mastacembelidae		Synbranchiformes	*Mastacembelus armatus*	LC
60.	Actinopterygii	Synbranchidae		Synbranchiformes	*Monopterus cuchia*	LC
61.	Actinopterygii	Notopteridae		Osteoglossiformes	*Notopterus notopterus*	LC
62.	Actinopterygii	Soleidae		Pleuronectiformes	*Synaptura albomaculata*	NE
63.	Actinopterygii	Cynoglossidae	Cynoglossinae	Pleuronectiformes	*Cynoglossus macrostomus*	VU
64.	Actinopterygii	Cynoglossidae	Cynoglossinae	Pleuronectiformes	*Cynoglossus lingua*	LC

65.	Actinopterygii	Cynoglossidae	Cynoglossinae	Pleuronectiformes	*Cynoglossus arel*	LC

LC:Least concerned category; NT: Nearly Threatened; NE: Not Evaluated ; VC: vulnerable category; DD : Data deficit ; ED: Endangered species. (IUCN, 2021)

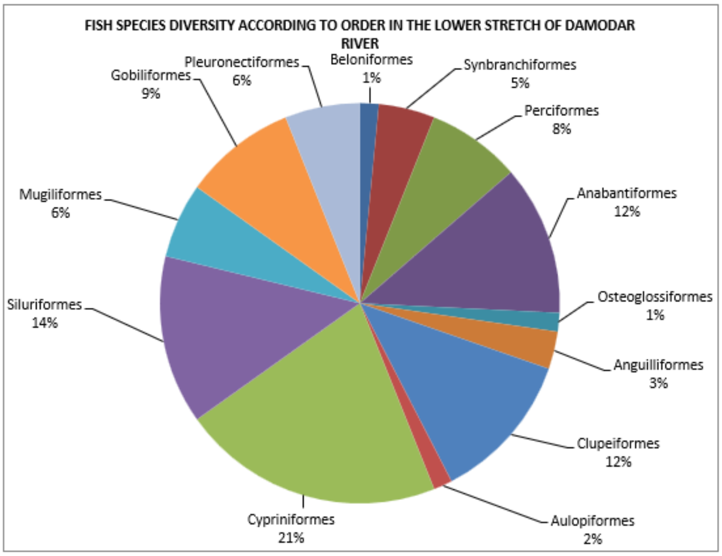
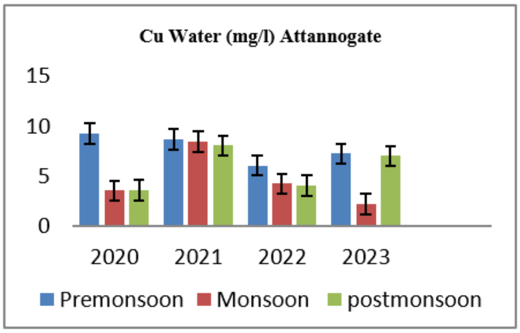


Figure 1: Damodar River Fish Diversity According to Orders



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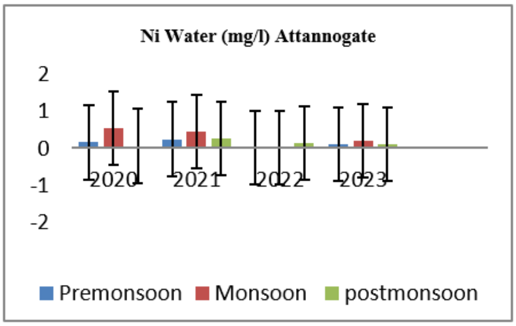

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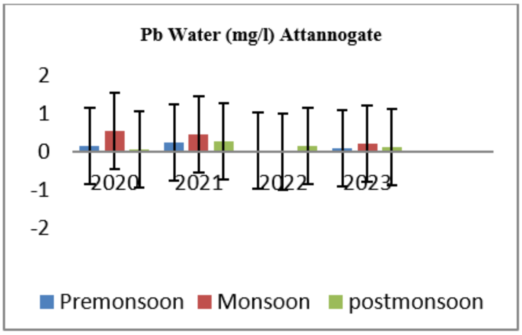

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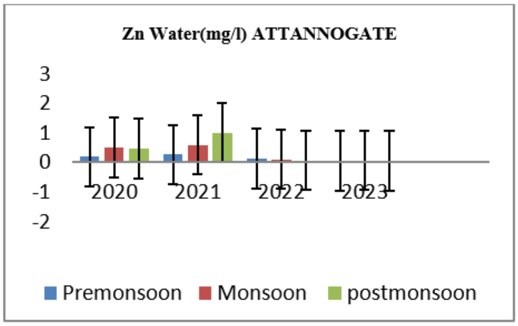

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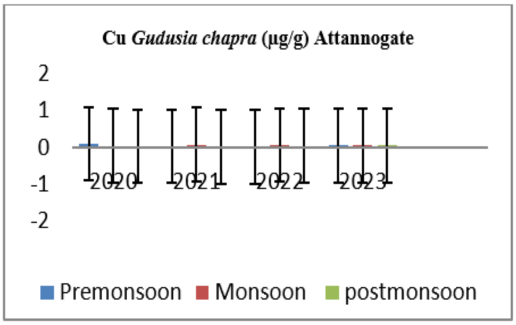

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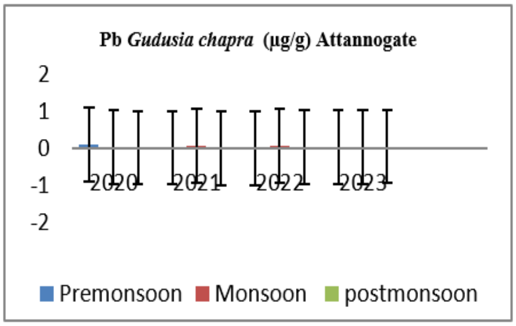

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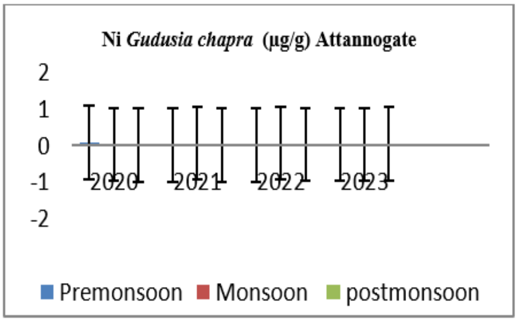

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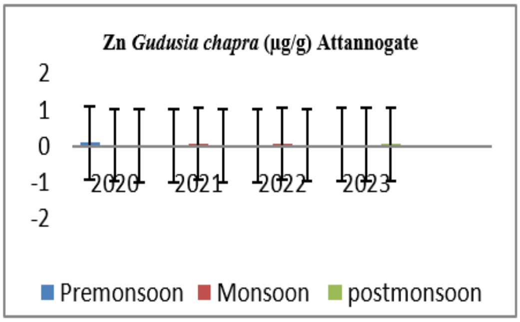


Figure 9

Figure 6 – 9: Shows the metal content in Gudusiachapra atAttannogate

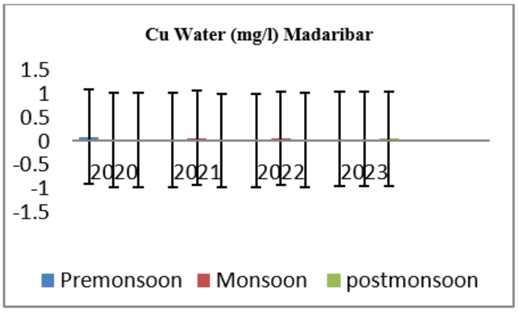
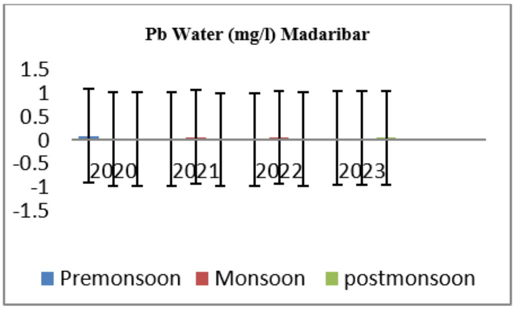


Figure10



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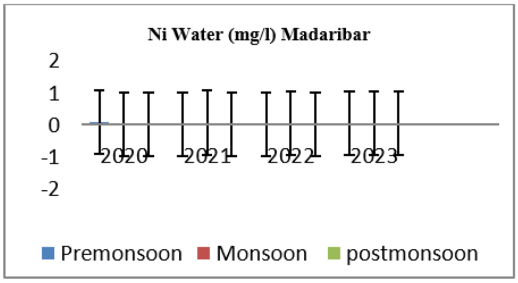

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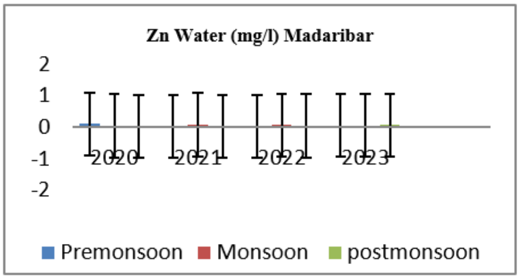
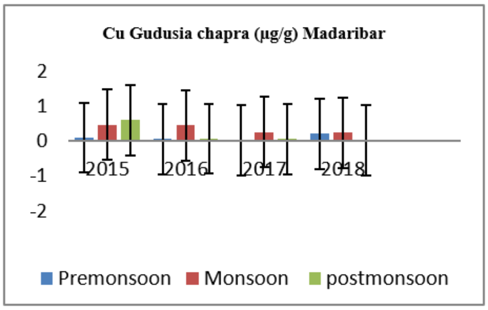


Figure 13

Figure 10 – 13: Shows the metal content in Water at Madaribar



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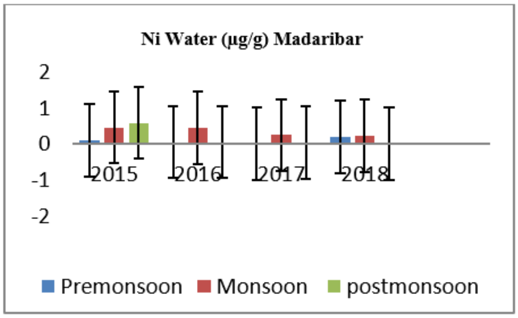

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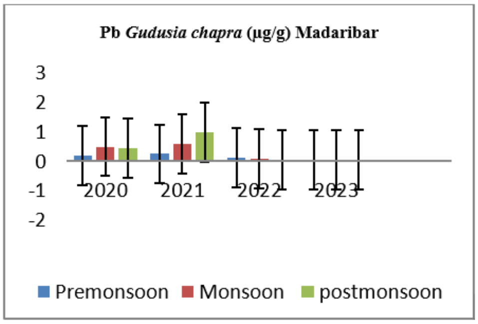

Figure 15

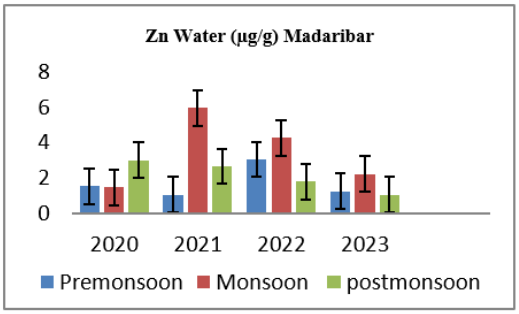

Figure 17

Figure 14 – 17: Shows the Metal Content in Gudusia chapra at Madaribar

Figure 2 – 17: Shows the Metals Content of Water and Gudusia chapra fish at Attannogate

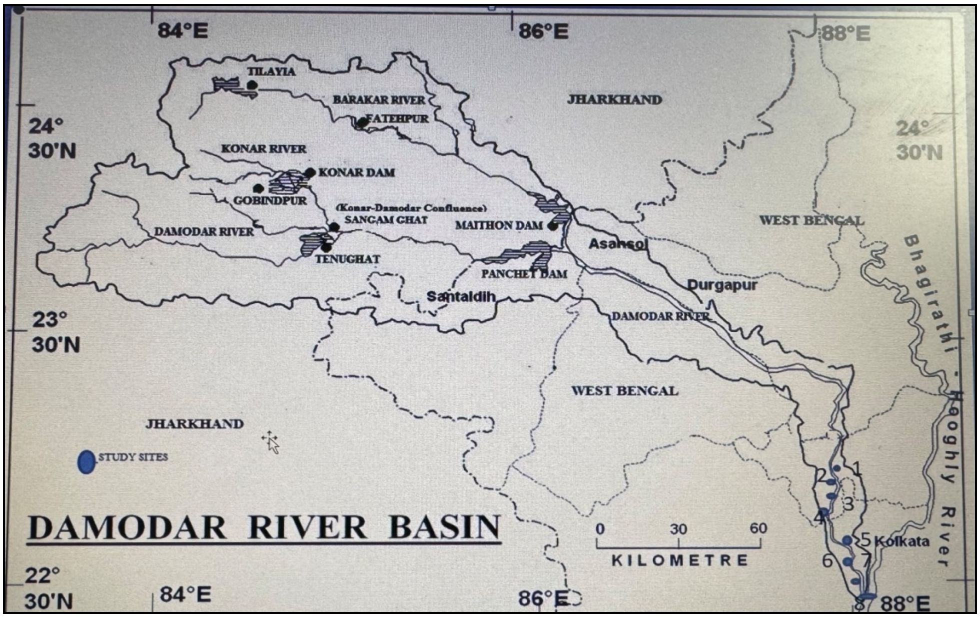

Figure 18: Map showing the study sites

Results and Discussion

The fishes studied from the lower stretch of the Damodar Riverbelong to 24 families,13 Orders, 49 Genera and 65 Species (Table 3). Among these fishes the most dominant species belongs to the Order Cypriniformes(21%), followed by Siluriformes(14%),then Clupeiformes, and Anabantiformes (12%), followed by, Gobiliformes (9%), Perciformes (8%), Pleuronectiformes and Mugiliformes(6%), Synbranchiformes (5%) Anguliformes(3%) Aulopiformes(2%) and the least Osteoglossiformes and Beloniformes(1%) (Figure 2). The present study reveals that the area of Damodar River beyond lock gate specially, Attannogate andGarchumuk houses a good number of estuarine fish species like *Harpadon nehereus, Chelon parsia,Valamugil buchanani, Apocryptes bato, Apocryptodon madurensis, Setipinna phasa,Gonialosa manmina, Gudusia chapra. Synaptura albomaculata, Cynoglossus macrostomus, Cynoglossus lingua, Cynoglossus arel*, which also shows restricted distribution in the area. Records from fish landing stations revealed that those fish were transported not only to local market but also to Bihar and Orissa fish market. The statistical analysis of the fish collection data reveals that the Highest Species richness 89 was found during the year 2021 in S2, S4 showed Highest Species richness 89 during the years 2021,2022,2023 and S7 and S8 showed Highest Species richness 89 during the all the study years (Table 2). This similarly in species richness (Table 2) in those study sites may be due to the similar aquatic conditions in all those study sites also may be due to similar nutrient available (Habit *et al*.,2006; Das *et al*., 2004). The Shannon diversity index indicates the relative abundance of the fish species, it shows almost similar pattern throughout study period(Table 2).Shelke(2023);Nelson, Grande and Wilson(2016); Chatla and Padmavathi (2021) revealed that the water quality of a river had immense effect on the diversity and distribution of ichthyofaunal status of the river.The present study indicates that the hydrological data(Table 1.) of the study sites varies within narrow range and that might be the cause of similar pattern of Shannon diversity index (Table 2) analysed for this study.

According to Khobragade and (2016) the food security of the society in terms of fishery can be established with the help of proper research information and regular survey of the ichthyofaunal diversity of the river confluence zone. Not only that, but it will also serve the conservation of the fish resource of the river system as well. Malik *et al*. (2021) revealed the fish faunal diversity of River Ganga in the upper basin might be the cause of seasonal nutrient variation, but the present study showed no such variation. During the present study the ichthyo species composition shows a larger number of estuarine fishes than the freshwater fishes in comparison to the study of Sarkar and Banerjee, 2012.

The toxic metals in river water are the major source of heavy metal contamination in aquatic vertebrates Elinge *et al*. (2019). The fish *Gudusia chapra* was selected for metal analysis as this fish was collected from all collection sites and found to be the most abundant species and a good food fish. The study of Heavy metals in river water (Figure 1-4 and Figure11-14) and the muscle tissue (Figure 7-10 and Figure 15-18) shows that the level of the metals was within acceptable limit according to(WHO, 2008; CPCB, 2011). The result reveals that concentration of heavy metals in muscle of *Gudusia chapra* sampled from all stations does not exceed the acceptable level for food sources for human consumption (WHO, 2008).

Conclusion

The present study indicates that Damodar River confluence area where Damodar joins the Hooghly River shows a high salinity in average during all the seasons because of the influence of high tide from Bay of Bengal through the Hooghly River. The species composition shows a larger number of estuarine fishes than the freshwater fishes. The salinity of the water at Garchumuk and Silampur was higher than the average freshwater salinity. The increased salinity and inflow from lock gate might have increased the estuarine species diversity. The fingerlings of some estuarine fish species were found at Santhoshpur, Bikunthapur, Deulpara,Garchumuk, Silampur and Madaribar as well during the post monsoon season. Thus, a detailed long-term investigation of the lower Damodar River fish diversity is required to protect and conserve the available fish species by taking effective measures. This will serve the fish-eating population of us well as the neighbor state as well.

Acknowledgement

The author is thankful to the Principal Sree Chaitanya College, West Bengal, India for providing funds for the present work and extending Laboratory facility.

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Distribution of Invasive Ant Species across Various Locations in and around the Indian Sunderbans

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Abstract

Ants, a keystone species of the order Hymenoptera, play a crucial role in ecosystems, serving essential functions like pollination, tillage and aeration of the soil, and suppressing insect populations of various crops. However, some species that harm crops, contribute to pests, destroy pollen grains, and threaten biodiversity. Invasive ant species are among the supreme threats to ecosystems. These species disrupt native species, leading to habitat loss, competition, hybridization, fragmentation, and foraging behavior. High densities of invasive species can have devastating effects on indigenous communities and ecosystems, disrupting community structure and disrupting ecosystem functions by replacing native species. The Sunderbans, the largest mangrove ecosystem in the world, are under threat from various invasive ant species. This article described the status of invasive ant species in different study sites of the Indian Sunderbans. The invasive species of ants were collected from different locations of Sunderbans during pre-monsoon and post monsoon seasons using honey bait, pitfall trap methods and hand collection techniques. A total of 7 invasive species, comprising 22.847% of total abundance, were distributed in the Sunderbans. Those were *Paratrechina longicornis*, *Tapinoma melanocephalum*, *Monomorium floricola*, *Technomyrmex albipes*, *Solenopsis geminata*, *Trichomyrmex destructor* and *Anoplolepis gracilipes*. *Paratrechina longicornis* had the highest abundance (13.8%). Invasive species pose a serious threat to the native species of agricultural lands of Sagar Island. Early detection of invasion and rapid management are significant for controlling these species.

Keywords: *Ants; Invasive; Keystone Species; Sunderbans*

Introduction

Invasive species are among the most serious threats to native communities and biodiversity (Mack *et al*., 2000; Rodriguez, 2006; Gentili *et al*., 2021). It has been well documented that the invasion caused massive and rapid losses of community structure and biodiversity (Charles & Dukes 2007; Kehoe *et al*., 2020; Zina *et al*., 2020; Farahat *et al*., 2021). Invasive species have ecological implications such as predation, hybridization, and competition with native species, which alter ecosystem processes due to biodiversity loss and pest infestation (Bruno *et al*., 2005; Crooks, 2002; Grosholz, 2002; Mack *et al*., 2000; Peh, 2010). Generalist non-native species may effectively become the ecologically dominant species, leading to trophic popularization (Kehoe *et al.*, 2020). Invasive species may out-compete native species, causing disruptions to ecological processes and communities (Peh, 2010). Certain alien species' direct and indirect influences can be so widespread and strong that they can reorganize entire communication networks and trigger abrupt changes in bio networks (Maron *et al*., 2006; Linders *et al*., 2019). Invasive species naturally have an impact on native species through resource competition, predation, and habitat deterioration (King & Tschinkel, 2008).

Among invasive species, ants are a particularly prominent group. More than 200 exotic species were recorded (Suarez *et al*., 2010), 19 are recognized as very invasive by listed by the IUCN Invasive Species Specialist Group (IUCN SSC Invasive Species Specialist Group 2012) and five are even on the IUCN ‘‘100 of the world’s worst invasive species’’ list (Lowe *et al*., 2000). Invasive ants are often highly aggressive, dominant competitors that displace many native species, through either direct or indirect competition, i.e. interference or exploitation competition (Holway, 2005; Rowles & O’Dowd, 2007; Carpintero, Reyes-Lo´pez & Arias de Reyna, 2005). Invasive ant species create major risks to local biodiversity, particularly native ants in some areas (Holway *et al*., 2002). Invasive ants can colonize human-modified habitats, such as urban environments. (Gibb & Hochuli, 2002), ability to nest in human structure (Schultz & McGlynn, 2000) and are easily spread by humans. Invasive ants can monopolize existing resources in an ecosystem and can get rid of existing native species (Eyer *et al*., 2018).

This research aims to determine the invasive ant diversity and function in Indian Sunderbans.

Methodology

Study Area

The Sunderbans, located between 21°31′00″ N and 22°30′00″ N latitude and 88°10′00″ E and 89°51′00″ E longitude, are among the world's largest mangrove forests. It was designated as a Sundarbans Biosphere Reserve (1989), a National Park (1984), and a World Heritage Site (1985). The Ganges, Brahmaputra, and Meghna Rivers confluence in the Bay of Bengal and create the delta that contains the mangrove region known as the Sundarbans. A total of five locations were selected for ant sampling, which is spread across the districts of North and South 24-Parganas in the state of West Bengal. Specimens were collected from five different sites of the Sunderbans.

Site 1: Sagar Island (21°43'01''N/88°03'27''E). Sagar Island is the westernmost island of the Ganges- Brahmaputra delta of West Bengal.

Site 2: Bakkhali (21°34'59''N/88°16'16''E).Bakkhaliis located in the South 24 Parganas district of West Bengal, India, which is a coastal region.

Site 3: Patharpratima (21°47'15''N/88°21'46''E). Patharpratima, the most remote block in South 24 Parganas district, comprises thirteen islands criss-crossed by numerous tidal rivers.

Site 4: Gosaba (22°7'51''N/88°50'10''E), is situated in the south 24 Parganas district and central region of the Sundarbans.

Site 5: Hingalganj (22°21'1''N/88°59'8''E), is located in the eastern Sundarbans which is located in the north 24 Parganas district.

Ant sampling

Ant sampling was conducted in 2019 during the pre and post monsoon seasons using honey bait, pitfall trap methods and hand collection. A cotton ball moistened with 20% honey and 80% water solution on transparent plastic plates was placed in each subplot. After 60 min, visual counts of all ants at the baits were completed and identifications were recorded to morphospecies. The ants were also collected using pitfall traps made of plastic cups and filled with water and detergent. After 24 hours, ants were collected and categorized in a laboratory for counting and analysis. Hand collections of ants using forceps were also carried out.

Identification

The identification of insects was conducted at the Central Entomological Laboratory, Zoological Survey of India, Kolkata. Morphological identification was performed using existing literature such as Bolton (1994) and Bingham (1903) and various keys available on antwiki.org.

Identification was carried out using Leica EZ4 stereo zoom microscope.

Results

A total of 2880 ants were sampled of which invasive species were 658 or 22.847% of the overall ant population. Among the 64 ant species encountered, seven are commonly classified as invasive species (as per Global Invasive Species Database: https://www.iucngisd.org/gisd/). Those were *Paratrechina longicornis*, *Tapinoma melanocephalum*, *Monomorium floricola*, *Technomyrmex albipes*, *Solenopsis geminata*, *Trichomyrmex destructor*, and *Anoplolepis gracilipes*. The *Paratrechina longicornis* of subfamily Formicinae had the highest abundance (13.8%), followed by *Tapinoma melanocephalum* (3.9%*)*, *Monomorium floricola* (3%),*Technomyrmex albipes* (1.2%),*Solenopsis geminate* (0.5%), *Trichomyrmex destructor* (0.2%) and *Anoplolepis gracilepis* (0.07%).

In Sagar Island (Site-1), during the pre-monsoon, the abundance of *Paratrechina longicornis* was 4.87%, followed by *Trichomyrmex destructor* (1.8%), *Tapinoma melanocephalum* (0.75%), and *Solenopsis geminata*(0.37%). In post-monsoon collections, the abundance of *Technomyrmex albipes* (20.8%) became the highest, followed by *Tapinoma melanocephalum* (2.38%) and *Paratrechina longicornis* (1.78%).

In Bokkhali (Site-2), the ant species *P. longicornis* (5.7%), *M. floricola* (4.4%), *T. melanocephalum* (1.333%), and *S. geminata* (0.444%) were the most abundant during the premonsoon. In the postmonsoon period, *T. melanocephalum* (4.4%), *M. floricola* (15.66%), and *P. longicornis* (25.7%).

In Patharpratima (Site-3) during pre-monsoon, *P. longicornis* (8.6%), *T. melanocephalum*(2.4%), *S. geminata* (0.4%) were abundant while during post-monsoon, *Paratrechina longicornis*(5.7%)and *Tapinoma melanocephalum* (0.598%).

Gosaba (Site-4) has *Paratrechin*a (16%) and *Tapinoma* (10%) during pre-monsoon, *Paratrechin*a (15%), *Tapinoma* (11.67%) and *Solenopsis* (4.01%) during post-monsoon, and Hingalganj (Site-5) has *Paratrechina* (22.29%), *Anoplolepis* (0.6%), and *Solenopsis* (4%) (Table 1).

While comparing the abundance of native ant species, viz., *Camponotus compressus*, *Monomorium indicum, and Crematogaster rogenhoferi,* it is found that the abundance of *Camponotus compressus* (11.86%) was much higher than *Paratrechina longicornis*(10%) during pre-monsoon. But after monsoon, abundance of *Paratrechina longicornis* was higher (17.7%) than *Camponotus compressus* (6.9%). In the post-monsoon season, the abundance of *Monomorium floricola* (5.4%) was near that of *Monomorium indicum* (6.7%), *Crematogaster rogenhoferi* (4%), and *Tapinoma melanocephalum* (4.1%) (Figure1).

***Table 1**: Relative Abundance of Invasive Ants during Pre-Monsoon and Post Monsoon Seasons in Different Locations of Indian Sunderbans*

Location	**Sagar**		**Bokkhali**		**Patharpratima**		**Gosaba**		**Hingalganj**	
Ant species	Pre monsoon	Post monsoon	Pre monsoon	Post monsoon	Pre monsoon	Post monsoon	Pre monsoon	Post monsoon	Pre monsoon	Post monsoon
Paratrechina longicornis	9.3	1.785	5.77	25.7	8.6	5.98	16	14.598		22.29
Trichomyrmex destructor	1.865		0.888							
Tapinoma melanocephalum	0.75	2.38	1.333	4.4	2.459	0.598	10.5	11.678	0.3	
Monomorium. floricola			4.4	15.66						
Solenopsis geminata	0.373		0.444		0.4			4.01		0.3
Technomyrmex albipes		20.8								
Anoplolepis gracilipes										0.6

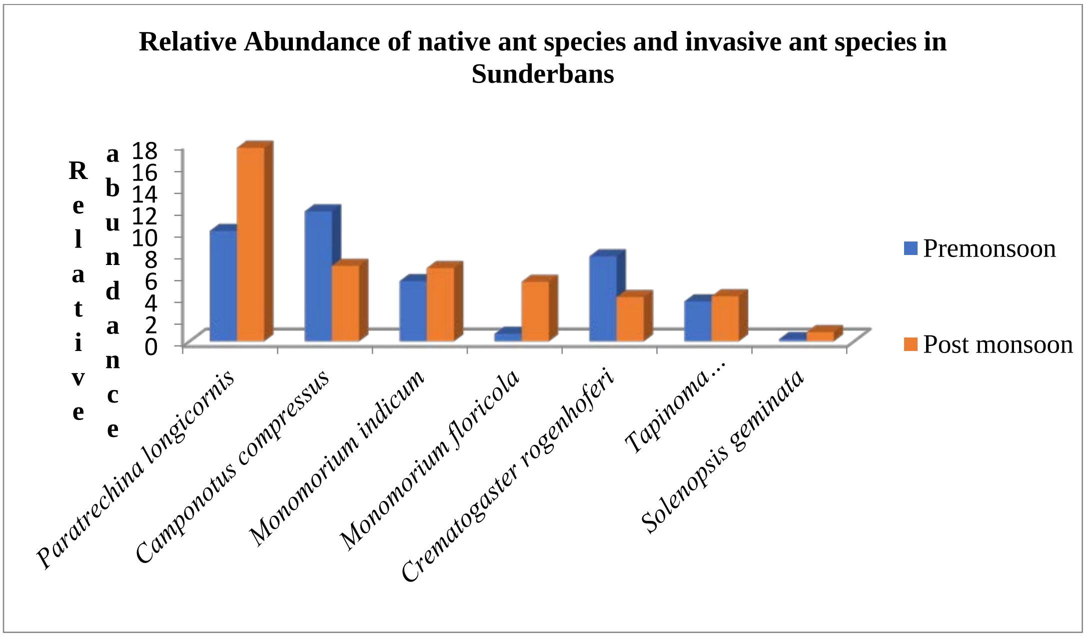

Figure 1: Relative Abundance of Native Ants and Invasive Ant Species During Pre-Monsoon and Post Monsoon Seasons in Sunderbans

Discussion

The abundance of ant species in a particular area is greatly affected by environmental changes, and ants respond to environmental disturbances or soil disruptions as they serve as their habitats (Andersen, 2019). In the present study, total seven invasive ant species were recorded during pre-monsoon and post monsoon seasons i.e. *Anoplolepis gracilipes, Paratrechina longicornis*, and *Solenopsis geminata*, *Tapinoma melanocephalum*, *Trichomyrmex destructo*r, *Technomyrmex albipes* and *Monomorium floricola*. The ant species *Paratrechina longicornis, Tapinoma melanocephalum* and *Solenopsis geminate* were found in all study sites, whereas *Trichomyrmex destructo*r found from Site-1 and Site-2*, Technomyrmex albipes* only in Site-1*, Monomorium floricola* only in Site-2 and *A. gracilipes* was only found in the Site-5. Abundance of invasive ant species, including *Paratrechina longicornis*, *Trichomyrmex destructor*, *Tapinoma melanocephalum*, and *Solenopsis geminata*, in Sagar Island, Bokkhali, Patharpratima, Gosaba, and Hingalganj, varies during the pre-monsoon and post-monsoon periods. Figure 1 showing that invasive antscompetewith native ant species and become dominant during post monsoon season**.** Another finding, Site-1 (Sagar Island) consists of a higher population of invasive ant species than other sites. Whereas Site-3, Site-4 and Site-5 are located near Reserve Forest and with low human disturbances have very few invasive ants.

While comparing the ant functional groups in Indian Sunderbans, it is found that *Paratrechina longicornis*, popularly known as crazy ants, are opportunistic omnivores that can adapt to various environments by feeding on insects, seeds, honeydew, fruits, and plant exudates. *Trichomyrmex destructor* is a tropical climate specialist and known to consume seeds and was viewed as a potential competitor for seed resources. Another most significant household ant species in the tropics is the ghost ant, *Tapinoma melanocephalum* (Lee & Robinson, 2001). *Tapinoma melanocephalum* is an opportunist and typical pest in residential areas in Malaysia (Lee 2002). The tropical fire ant, *Solenopsis geminata* is hot climate specialist, this species can well adapt in habitat such as settlement area, forest edge, and agriculture area (Ness & Bronstein 2004) and also regarded as an environmental and commercial pest that significantly affects the ecological balances of ecosystems (Risch & Carroll 1982; Plentovich, Hebshi & Conant 2009), and it is one of the most harmful and widespread introduced species (Holway *et al.*, 2002).

Conclusion

Invasive ants are easily dispersed by humans. They have a rapid adaptation mechanism and great competitive capacity, which has a negative impact on the survival of local ants. Studies of invasive ant diversity of Sunderbans will provide valuable insights into the health and functioning of mangrove forest ecosystems. Since early management actions are more practical and successful, early detection of invasive species, pests, and pathogens is essential for preventing damage. Therefore, their role in novel habitats should be addressed, and the factors that encourage their occurrence that have a severe impact on native species should be explored. These factors and processes are essential to control the expansion of invasive ant species, enhance their management, and conserve native species in the future.

Acknowledgement

The author expresses her sincere gratitude her supervisors, Dr**.** Sheela S., Scientist-E, Zoological Survey of India, Kolkata and Dr. Silanjan Bhattacharyya**,** Professor, Department of Zoology, West Bengal State University, for their guidance, support, and encouragement. The author is also grateful to the Department of Science & Technology and Biotechnology, Govt. of West Bengal for financial support.

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doi: 10.31674/book.2024scibe.005

Study of Diversity of Soil Arthropod Fauna in Pitfall Catches in a Litter Rich Habitat

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Abstract:

The abundance, richness and composition of invertebrate orders were examined in pitfall catches in a litter rich habitat beside Sree Chaitanya College, Habra, North 24 Parganas, West Bengal. A total of 11 types of organisms belonging to 8 orders were found. The main dominant fauna in all the pitfall samples was spider (order Araneae). The other main orders included Collembola, Hymenoptera and Orthoptera. The other groups contributed to the community in small numbers among the fauna during both the years of study. However, different types of plantations did not exert any effect on the soil faunal composition of the area under study.

Keywords: *Pitfall; Soil Fauna; Spiders*

Introduction

The soil fauna is an important part of terrestrial ecosystems. The soil fauna may be characterised by the degree of presence in the soil. The extent of biodiversity in soil is extremely large. The soil food webs are linked to above ground systems, on the other hand. Soil fauna is one of the major drivers of plant litter decomposition (Peng *et al*., 2023) and is diverse in litter rich habitats. However, the role of soil fauna on litter decomposition is poorly understood, despite the fact that it could influence decomposition by modification of the activities of microorganisms. Soil animals such as litter feeding macrofauna interact with leaf litter composition and modify effects exerted by litter species diversity (Schadler & Brandi, 2005). Soil communities exert strong influences on the processing of organic matter and nutrients. Soil faunal activity improves soil physico-chemical properties (Barrios, 2007; Kumar & Singh, 2016). Soil food web diversity impacts on ecosystem processes (Sunderland *et al.,*1995; Kardol *et al.,* 2016). Soil fauna also play a role in the regulation of plant litter decomposition and nutrient release. Research suggests that litter decomposition is primarily controlled by climate, litter quality and also decomposers present therein (Mori *et al.,*2020). Leaf litter provides habitat as well as food resources for soil organisms. In natural ecosystems, plants occur in mixtures; therefore, litter mixtures are also of different quality in different ecosystems (Grossman, Cavender-Bares & Hobbie, 2020). Recent studies suggest that the quality of litter is species specific and litter quality would surpass climate in controlling decomposition rates across biomes globally (Cassart *et al*., 2020; Hoeber *et al*., 2020). The aim of this study was to investigate the diversity of soil macrofauna as well as to find out whether the soil communities differ under different tree species. The pitfall trapping is the most efficient sampling strategy for detecting diversity of soil fauna and one of the most widely used methods for collecting soil arthropods (Southwood, 1987; Sunderland *et al.,*1995; Brown & Matthews, 2016).

A pitfall trap catches animals, mostly invertebrate macrofauna that move across the soil surface. The use of Tullgren funnels for extracting soil fauna, which consists of separating arthropods from a soil sample using heat and desiccation that induce migration of trapped organisms towards a collecting device, is also followed by some. Pitfall trap methodologies and designs vary considerably among studies and investigators. In this study, however, the pitfall trapping technique was used to study the soil fauna. A literature review was conducted to know the most common methods used by past investigators who placed pitfall traps for the purpose of collecting and identifying soil fauna and this information was used for the pitfall trapping methods. A common garden experiment beside the college premises with lots of trees and a good amount of litter beneath them was a good opportunity to conduct this study.

Methodology

The research was carried out beside Sree Chaitanya College (Habra), North 24 Parganas, West Bengal, India for two consecutive years. The study site included an area full of different kinds of large and small trees and grasses. Some common trees and plants include *Azadirachta indica, Polyalthia longifolia, Ficus religiosa, Mangifera indica, Terminalia arjuna, Shorea robusta, Areca catechu, Madhuca longifolia, Neolamarckia cadamba, Psidium guajava, Thuja occidentalis, Agave tequilana, Adhatoda vasica, Rauwolfia serpentina, Ocimum sanctum, Hibiscus rosasinensis, etc.*

Soil macrofauna was collected quarterly by pit fall trapping for estimating the abundance and diversity of the fauna obtained. The pitfall trap consisted merely of a jar into which a small quantity of alcohol/water with detergent was placed. The experiment was laid out in a randomised design to control for possible habitat heterogeneity within the area. The traps were installed by burying the jar in the ground up to a depth of 20 cm. The upper rim of the jar was at the same level as the ground so that organisms moving on the ground may fall in it without noticing it. Ten traps placed about 5 m from each other were kept overnight. The number of organisms was counted after removing the jar from the soil. The number of faunas obtained in all the jars was averaged to get the number of each group of organisms each year. The organisms were identified up to the order level. The data obtained from all the pitfalls were compiled each year to calculate the abundance of the fauna obtained. Pitfall trapping is one of the most widely used methods for collecting soil arthropods (Southwood, 1987; Sunderland *et al.,* 1995; Brown & Matthews, 2016).

Results and Discussion

Altogether, 11 types of organisms belonging to 8 orders were identified (Table 1). As indicated in Fig1, the main fauna in all the pitfall samples was spider (order Araneae). The other dominant groups following spiders included orders Collembola, Hymenoptera and Orthoptera. The rest of the groups contributed to the community in small numbers. The abundance of the orders was not significantly different in the two years. Both years, the dominant fauna were the spiders (order Araneae) with a relative abundance of 30.47% followed by spring tails (Collembola -19.04%) while ants and wasps (order Hymenoptera) and crickets (order Orthoptera) showed almost equal relative abundances of 18%.

Many factors affect pitfall catches (Sunderland *et al.,* 1995), such as trapping technique, structure of the habitat and specific characteristics of the animals to be caught. In this study, the population of spiders was found to be the dominant ones. Spiders are actually common predators of forest floor food webs (Wise & Chen,1999).They are able to control the abundance of prey organisms micro detritivorous collembolans (Lawrence & Wise, 2000; Wise, 2004; Lensing*,* Todd & Wise, 2005). The population of spiders obtained in all the pitfalls was high compared to the populations of collembolans. This may be due to the prey-predator relationship of the forest floor or due to the soil characteristics as found by Verheof and Van Selm, 1983.

Plant species richness positively affected litter decomposition by increasing soil fauna (Sauvadet *et al*., 2017; Tresch *et al*., 2019). In this study, the orders recorded were found throughout the year. However, earthworms, which are most common residents of the forest floor, were not found, which may be due to the very dry nature of the soil.

Table 1: *Relative abundance of organisms obtained in pitfall catches in college campus area*

Orders	Organisms	Relative Abundance
Araneae	Spider	30.47%
Diptera	Fly	10.47%
Orthoptera	House Cricket	2.85%
Collembola	Spring tail	19.04%
Hymenoptera	Red ant	9.52%
Hymenoptera	Black ant	6.66%
Orthoptera	Mole cricket	15.23%
Hymenoptera	Wasp	1.9%
Coleoptera	Beetle	0.95%
Hemiptera	Bugs	0.95%
Isoptera	Termite	1.9%

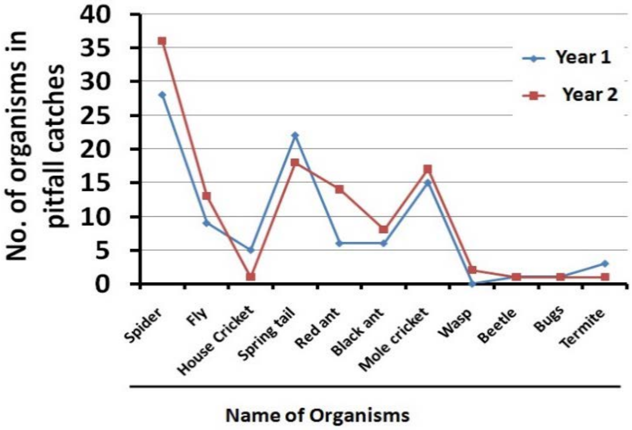

Figure 1: Abundance of organisms (average no.) in pitfall catches in two consecutive years in college campus area, Habra, West Bengal

Conclusion

Plant species richness positively affected litter decomposition but no difference in the composition of the soil fauna was observed due to the difference in the species of plants. In this study, the orders recorded were found throughout the year. However, earthworms which are the most common resident of the forest floor were not found may be due to the very dry nature of the soil.

Acknowledgement

The author is highly grateful to the principal of the college for providing every possible support for carrying out this research work.

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doi: 10.31674/book.2024scibe.006

Synthesis, Characterization and Biological activity of Schiff Base Metal (II) Binuclear Complexes with Alkali metal salt of *o*-Nitrophenol

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Abstract

A series of binuclear complexes with copper(II) and nickel(II) and alkali metals derived from Schiff bases were studied. Schiff base was prepared by the condensation of 1,2-phenylenediamine and 2-hydroxy-1-naphthaldehyde. The FT-IR and UV-Vis spectra have been used to explain the structures of the synthesized complexes. The bonding of Schiff base's complexes of copper(II) and nickel(II) with alkali metals are occurred by oxygen atoms. The outcome of spectral and magnetic results showed that the binuclear Schiff base complexes of transition metal(II) and alkali metal have coordination number four with square planar geometry. The ligands are found to be bonded to the transition metal atom through the nitrogen atoms of imine and oxygen atoms of the hydroxyl groups. The molar conductance values are low, indicating that the complexes are non-electrolytic. These complexes show significant results against the bacteria *E. coli* and *S. aureus* and also against the fungus viz. *C. albicans*.

Keywords: *Alkali Metal; Antimicrobial Studies; Binuclear Complexes; Infrared Spectra; Schiff Base; UV-Vis*

Introduction

Appreciable attention has been devoted in recent years to the field of preparation and characterization of heterobinuclear complexes due to their significant approach in biological inorganic chemistry as well as in material science (Rao & Zacharias, 1997; Zanello *et al*., 1987). The synthesis of transition metal complexes with Schiff bases is regarded as a great passion in inorganic chemistry and has been studied significantly (Patel, Parekh, & Patel, 2005). Several binuclear Cu(II) complexes with Schiff bases derived from 1,2-diamino-2-propanol and 2-hydroxy-1-naphthaldehyde have been synthesized and considerably interpreted (Cheng *et al*., 1996). The Schiff base complexes of many transitions metal possess the great antimicrobial activity (Panchal & Patel, 2006). A series of biologically active bimetallic complexes of Copper Schiff base are synthesized and significantly characterized (Zhong *et al*., 1994), with the antimicrobial effect of the transition metal complexes being higher as compared to the ligand. The synthesis of a large number of heterobinuclear complexes with Schiff base and their characterization are reported (Kumar, 2017; Kumar, 2023). This work reported herein has concentrated on developing a series of new binuclear complexes of transition metals and alkali metals.

Methodology

Chemicals of AR grade was used for synthesizing the Schiff bases and complexes. IR spectra and electronic spectra have been recorded through FTIR spectrophotometers, Shimadzu-8201PC in KBr phase and Perkin Elmer Lambda 15 UVB-VIS spectrophotometers, respectively. The magnetic results were recorded through the Gouy balance method. Molar conductance and melting point were measured using a Systronics digital conductivity meter and electrical melting point apparatus, respectively. The Elemental analysis results were taken out through Thermo Fisher Scientific Flash Smart instrument.

Synthesis

The Schiff base was synthesized by condensation of 1,2-phenylenediamine with alcoholic solution of 2-hydroxy-1-naphthaldehyde in 1:2 molar ratios. This mixture was continuously stirred at 70-75^{0}C for 25 minutes. The solid yellow Schiff base, N,N′-1,2-phenylene-bis(naphthaldimine), PHDND, was filtered and then recrystallized with alcohol.

Synthesis of Cu (II) and Ni (II) complexes: A solution of copper(II) acetate hydrate (2.0 g) in ethanol was slowly added to the hot solution of the Schiff base (PHDND, 4.16 g). This mixture was stirred up to 20 minutes at 70-75 ^{0}C. The solution on cooling, golden brown Cu(II) complex was separated out. Similarly, the Ni(II) complexes were prepared by adding nickel(II) acetate tetrahydrate (2.5g) in solution of the Schiff base (PHDND, 4.16g). The mixture on cooling, the deep orange Ni(II) complex was separated. These transition metal complexes were filtered, washed with ethanol, and then dried.

Synthesis of binuclear complexes containing Cu(II) metal and alkali metal: The N,N′-1,2-phenylene-bis(naphthaldiniminato)copper(II) [CuPHDND] was taken in absolute alcohol and the prepared alkali metal salts of *o*-nitrophenol were added in 1:1 molar proportion. This mixture was stirred and refluxed for 1 hour at 75-80^{0}C. The specific coloured complexes were deposited in hot conditions and then cooled, filtered, washed with alcohol and dried.

Synthesis of binuclear complexes containing Ni(II) metal and alkali metal: The N,N′-1,2-phenylene-bis(naphthaldiniminato)nickel(II) [NiPHDND] was taken in absolute alcohol and the prepared alkali metal salts of *o*-nitrophenol were added to it in 1:1 ratio. This mixture was stirred and refluxed for 1 hour at 75-80^{0}C. The specific-coloured complexes were separated in hot conditions, then cooled, filtered, washed with alcohol and then dried.

Results and Discussion

Both the copper(II) and nickel(II) transition metal complexes and their alkali metal adducts are stable and have characteristic coloured solids. The colour, melting point, conductivity, elemental analysis data and yields are presented in Table 1. These adducts are mostly soluble in organic solvents such as acetone and DMF, but in water they are insoluble. The molar conductivities of complexes at temperature 30($\pm$0.5)^{0}C in DMF at 10^{-3} M (Table 1)range from 0.6-1.5 $\Omega^{-1}cm^2mol^{-1}$. These values are low, which suggests their covalent (Geary, 1971) nature.

Table 1: *Physical characteristics of the complexes*

Complexes (CuPHDND. ML)	***Colour***	***m.p. (^{0}C)***	***Mol. Cond. Ω^{-1} cm^2 mol^{-1}***	***Elemental analysis (%) Found (Calculated)***					***Yield (%)***
				C	***H***	***N***	***Cu***	***M***	
CuPHDND	Golden brown	>300	1.3	69.89 (70.37)	3.62 (3.77)	5.73 (5.86)	13.15 (13.30)	-	70.6
CuPHDND.LiONP	Yellowish brown	248	1.5	65.48 (65.54)	3.49 (3.53)	6.65 (6.75)	10.16 (10.20)	1.05 (1.12)	77.11
CuPHDND.NaONP	Golden brown	296	0.9	63.83 (63.90)	3.40 (3.45)	6.51 (6.58)	9.87 (9.95)	3.58 (3.60)	71.26
CuPHDND.KONP	Golden brown	290	0.8	62.27 (62.34)	3.28 (3.36)	6.35 (6.42)	9.65 (9.70)	5.92 (5.96)	68.37
NiPHDND	Deep orange	>300	1,1	70.48 (71.08)	3.72 (3.81)	5.78 (5.92)	12.28 (12.42)	-	67.5
NiPHDND.LiONP	Reddish brown	>300	0.6	65.97 (66.12)	3.51 (3.56)	6.69 (6.80)	9.43 (9.50)	1.07 (1.13)	81.75
NiPHDND.NaONP	Reddish brown	>300	0.8	65.32 (64.38)	3.39 (3.47)	6.61 (6.63)	9.22 (9.26)	3.55 (3.63)	75.75
NiPHDND.KONP	Reddish brown	>300	0.6	62.74 (62,80)	3.35 (3.39)	6.42 (6.46)	8.96 (9.03)	5.91 (6.00)	72.73

IR Spectra: The Infrared spectral bands of the transition metal complexes and their binuclear complexes with alkali metals show bands in the range 1535-1610 cm^{-1}, this may be due to the phenolic C-O stretching (El-Sonbati, Al-Shihri & El-Bindary, 2004). The C-O bands for both Cu (II) and Ni(II) transition metal complexes as ligands are a little higher as compared to those of their binuclear complexes. The copper and nickel metal complex as ligands show absorption at 1535 cm^{-1} and 1597 cm^{-1} respectively, due to υ_{C-O} (phenolic). This band shifts towards the higher energy side of the complex formation by up to 55 cm^{-1} and 13 cm^{-1} in copper and nickel, respectively, in binuclear complexes. This is due to the coordination of metals by phenolic oxygen (El-Sonbati, Diab & El-Bindary, 2012) and suggests the existence of a phenoxo-bridge.

Table 2: *Spectral results of complexes*

Compound	IR spectra (cm^{-1}) υ(C-O)phenolic/ υ(M-O)/υ(M-N)	UV-Vis spectra (in nm)	Magnetic moment (in BM)
CuPHDND	1535, 556,470	225, 237, 324, 651	1.97
CuPHDND.LiONP	1570, 565, 490	228, 240, 330, 651	1.85
CuPHDND.NaONP	1539, 563, 470	224, 262, 328, 652	1.75
CuPHDND.KONP	1590, 561, 485	225, 238, 338, 652	1.92
NiPHDND	1597, 550, 460	205, 238, 340, 653	Dia
NiPHDND.LiONP	1610, 555, 485	206, 239, 328, 652	Dia
NiPHDND.NaONP	1598, 571, 490	207, 242, 324, 653	Dia
NiPHDND.KONP	1598, 561, 480	206, 240, 359, 652	Dia

These are expected because of a ring current arising from the delocalization of electrons in the chelating ring and also because of the phenolic C-O link. The far IR bands from medium to strong range at 550-571 cm^{-1} and 460-490 cm^{-1} correspond to υ_{M-O} and υ_{M-N} bonds, respectively (Nakamoto, 2009; Jasim, Kadhum & Badr, 2024; Golcu *et al*., 2005). These positive shifts in the absorption band in the binuclear complex compared to those of the transition metal complex assigned to the synthesis complex contribute to their coordination through oxygen atom of the Schiff base. These are suggested on the basis of electronegativity. The electronegativity of oxygen is higher as compared to the nitrogen atom, which is why M-O bond is considerably more ionic than that of M-N. The infrared spectral results suggest the coordination of oxygen in the phenolic group of the transition metal complex with nitrogen in the alkali metal salt of o-nitrophenol in binuclear complexes.

UV-Vis Spectra and Magnetic moment: Both copper (II) and nickel (II) metal chelate of Schiff base and their binuclear complexes show UV-Vis absorption between 224-262 and 205-242 nm, respectively (Table 2). These absorptions are due to the p-p* transition (aromatic ring) and C=N (chromophore) (Jabbar, Kadhum & Hassan, 2023). The band ranges at 324-653 nm are due to the d-d transition as well as charge transfer (Condrate & Nakamoto, 1965; Jaffer & Orclin, 1962; Thirumavalavan, Akilan & Kandaswamy, 2006). These results suggested coordination number four with square planar geometry (Jaffer & Orclin, 1962) in metal chelate and its adducts. The absorption of both metal complexes and their binuclear complexes is almost the same, which indicates that the stereochemistry of complexes does not change after heterobinuclear complex formation.

The magnetic moment of binuclear alkali complexes ranges from 1.75 to 1.92 BM (Table 2), and copper(II) Schiff base complex shows it at 1.97 BM. These results indicate the presence of one unpaired electron and also their square planar geometry with coordination number four. Nickel(II) metal complex and its alkali metal complex show very low values (about to zero), these suggest the diamagnetic nature and four coordination numbers with square planar geometry.

Antimicrobial activity: This activity of some of the binuclear complexes was carried out against bacteria, viz. *Escherichia coli* and *Staphylococcus aureus* and also with the fungus viz. *Candida albicans* in DMF at a concentration between 25-200 µg ml^{-1} by the serial dilution method. The results are shown in Table 3 and Figure1, the antimicrobial activity (Sharma *et al*., 2022) of the compounds gradually increases as its concentration increases and compounds show significantly better results at high concentrations.

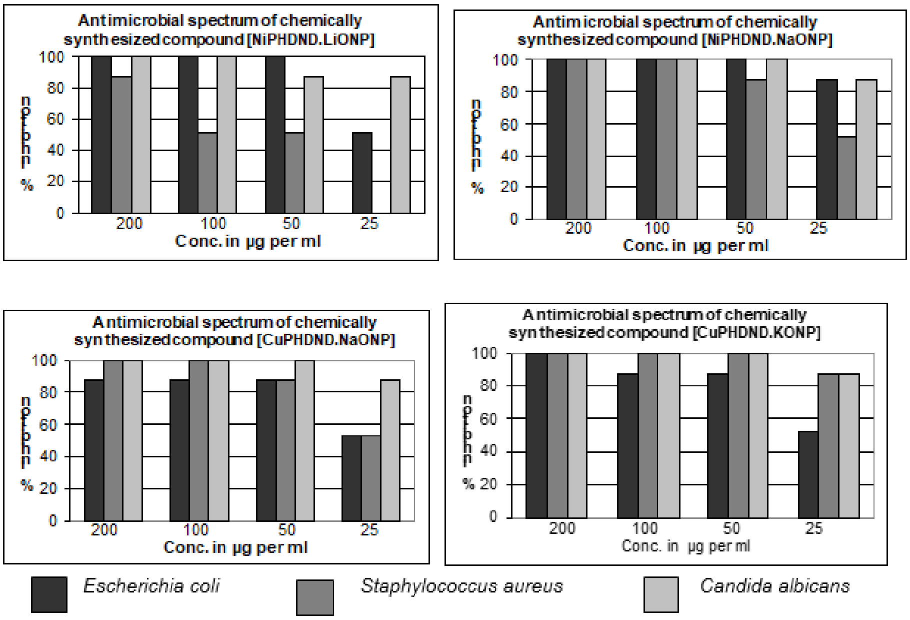

Figure 1: Antimicrobial data of binuclear complexes

Table 3: *Antimicrobial result of compounds*

Compound	Conc. (µgml^{-1})	Percentage inhibition		
		E.coli	*S.aureus*	*C.albicans*
NiPHDND.LiONP	200	100	85-90	100
	100	100	50-55	100
	50	100	50-55	85-90
	25	50-55	0	85-90
NiPHDND.NaONP	200	100	100	100
	100	100	100	100
	50	100	85-90	100
	25	85-90	50-55	85-90
CuPHDND.NaDNP	200	85-90	100	100
	100	85-90	100	100
	50	85-90	85-90	100
	25	50-55	50-55	85-90
CuPHDND.KONP	200	100	100	100
	100	85-90	100	100
	50	85-90	100	100
	25	50-55	85-90	85-90

These results have explained, based on the chelation theory, that the lipophilicity of the compound increases as the polarizability of the metal cloud decreases, which leads to the breakdown of the permeability of the cells (Ghosh *et al*., 2012). The chelation reduced the polarity of metal- ions due to its positive charge and share by p electron delocalization and donor groups (Panchal & Patel, 2006).

Structure and bonding: The proposed general formula of binuclear complexes of copper(II) and nickel(II) with alkali metal is considered $M_aPHDND.M_bL$ on the basis of quantitative results, where M_a = Cu(II)/Ni(II); M_b = Li/Na/K; PHDND = N,N′-1,2-phenylene-bis(naphthaldimine) and L = *o*-nitrophenol (deprotonated). The analytical results and spectral analysis suggested the square planar geometry (Figure. 2). The bonding between the metal(II) complexes and the alkali metals is caused by two oxygen atoms (phenolic) in the Schiff base.

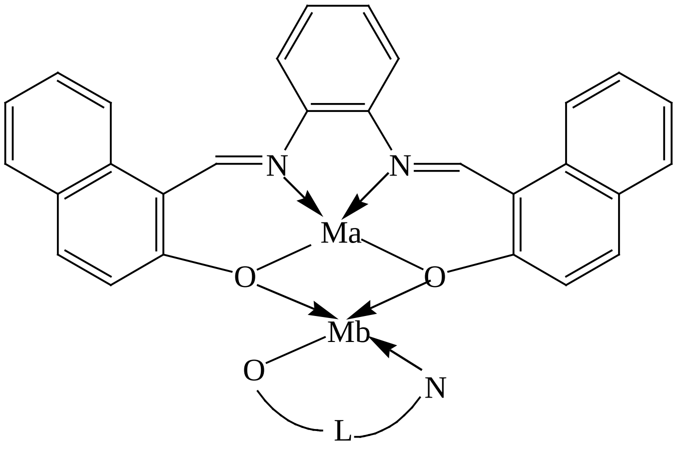

Figure 2: Structure of the complex

Conclusion

The synthesis and coordination chemistry of some novel binuclear complexes derived from the multi-dentate Schiff-base ligand PHDND are explored in this paper. The results are supported by analytical, IR spectral, UV-visible spectral and magnetic results. The structure and bonding of the complexes are established; the geometry of the complexes is square-planar. The compounds give significant antimicrobial results against *E. coli*, *S. aureus* and *C. albicans.*

Acknowledgement

The author is grateful to the CDRI, Lucknow and Department of Chemistry, BHU, India

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doi: 10.31674/book.2024scibe.007

Innovations in Waste Management: A Review

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Abstract:

Waste management has become a pressing global issue due to the swift urbanization, industrialization, and population expansion in recent years. This surge has prompted significant strides in waste management techniques and technologies, aimed at tackling the environmental, economic, and social repercussions associated with waste disposal. This review paper offers a comprehensive overview of these advancements, encompassing various facets of waste management, such as recycling, waste-to-energy conversion, landfill management, and novel strategies for handling hazardous waste. In the realm of recycling, innovative methods and technologies have emerged to enhance the efficiency and effectiveness of recycling processes, thereby reducing the strain on natural resources and minimizing landfill overflow. Additionally, waste-to-energy conversion technologies have gained traction as a sustainable means of generating energy while concurrently addressing waste disposal challenges. These approaches not only mitigate the environmental impacts of waste but also contribute to renewable energy production, fostering a circular economy model. Furthermore, effective landfill management strategies, including waste segregation and leachate treatment, are crucial for minimizing environmental contamination and maximizing resource recovery from landfill sites. Moreover, innovative solutions for hazardous waste management, such as advanced treatment processes and containment technologies, are essential for safeguarding human health and the environment from the adverse effects of hazardous materials. Despite notable advancements, waste management still faces numerous challenges, including inadequate infrastructure, insufficient funding, and limited public awareness. Addressing these challenges requires concerted efforts from governments, industries, and communities to promote sustainable practices and integrated waste management approaches. Putting sustainability first and adopting state-of-the-art technologies sets the stage for a waste management system that's resilient and environmentally conscious, ultimately protecting a healthier planet for future generations.

Keywords: *Challenges; Evolution; Infrastructure; Innovation; Sustainability; Waste Management*

Introduction:

In the intricate web of modern civilization, waste management stands as an indispensable thread, weaving its way through the fabric of sustainability, public health, and environmental stewardship (Robertson, 2021). From the ancient days of rudimentary disposal methods to the sophisticated systems of today, the journey of waste management is a testament to human ingenuity, adaptation, and the evolving relationship between society and its refuse. The importance of waste management transcends mere cleanliness; it is a cornerstone of sustainable development and a safeguard for the well-being of both current and future generations (Abdelfattah & El-Shamy, 2024). As global populations grow and urbanization accelerates, the volume and complexity of waste generated reach unprecedented levels. Within this context, the effective management of waste (Figure 1) assumes paramount significance, serving as a bulwark against pollution, disease outbreaks, and ecological degradation (Chilunjika & Gumede, 2021). The evolution of waste management practices is a chronicle of human innovation and responses to environmental challenges. In ancient civilizations, waste disposal primarily consisted of simple methods such as open dumping, where refuse was haphazardly discarded, often leading to unsanitary conditions and health hazards. However, as societies advanced, so too did their approaches to waste. The emergence of organized municipal waste collection in the 19th century marked a pivotal turning point, ushering in an era of systematic waste management. Innovations such as incineration, composting, and recycling gradually gained traction, offering more sustainable alternatives to traditional disposal methods (Ali *et al*., 2023).

Despite significant progress, the contemporary landscape of waste management is fraught with a myriad of challenges and issues. One of the foremost concerns is the sheer magnitude of waste generated worldwide, exacerbated by population growth, urbanization, and industrialization. The exponential rise in consumption patterns, coupled with the proliferation of single-use plastics and electronic waste, has placed immense strain on existing waste management infrastructure. In many regions, inadequate funding, limited resources, and outdated technologies further exacerbate the problem, resulting in insufficient capacity to handle the ever-mounting tide of waste. Moreover, the improper disposal and mismanagement of waste pose grave environmental and public health risks. Landfills, once considered a panacea for waste disposal, now loom as environmental liabilities, leaching harmful chemicals into soil and waterways and emitting greenhouse gases that contribute to climate change. Similarly, incineration, while offering a means of reducing waste volume, can release toxic pollutants into the atmosphere if not properly regulated. The indiscriminate dumping of electronic waste, laden with hazardous substances such as lead and mercury, threatens ecosystems and human health, particularly in developing countries with lax regulatory frameworks (Daum, Stoler & Grant, 2017). Furthermore, the globalized nature of waste has rendered it a transboundary issue, with waste often shipped across borders in search of cheaper disposal options. This practice, while ostensibly cost-effective, can lead to environmental injustice, as marginalized communities bear the brunt of pollution and contamination associated with waste disposal sites (White, 2013).

Figure 1: A schematic drawing of a waste management system

In light of these challenges, the imperative for sustainable waste management has never been more pressing. Addressing the multifaceted dimensions of waste requires a holistic approach that encompasses not only technological innovations but also social, economic, and policy interventions. Investment in infrastructure upgrades, recycling facilities, and waste-to-energy technologies is crucial to bolstering the resilience of waste management systems. Likewise, public education and awareness campaigns play a pivotal role in fostering responsible consumption habits and promoting waste reduction at the source. Moreover, fostering international cooperation and coordination is indispensable to tackling the global dimensions of waste management. By sharing best practices, expertise, and resources, nations can work collaboratively to develop innovative solutions and mitigate the adverse impacts of waste on a planetary scale (Sharma *et al*., 2020). The journey of waste management is a testament to human adaptability and resilience in the face of environmental challenges. From humble beginnings to the complexities of the modern era, their collective quest for sustainability and stewardship of the planet is reflected in the evolution of waste management. While navigating through the complexities of waste management, it's important to learn from the past, tackle present challenges, and steer towards a sustainable future for future generations.

Recycling and circular economy

Advances in recycling technologies have heralded a new era in waste management, offering innovative solutions to mitigate environmental impact and conserve finite resources (Zaman, 2022). Traditional recycling methods, such as sorting and reprocessing, have been revolutionized by cutting-edge technologies that enhance efficiency and efficacy. Automated sorting systems equipped with advanced sensors and robotics enable precise identification and segregation of recyclable materials, streamlining the recycling process and minimizing contamination. Similarly, breakthroughs in material recovery techniques, such as chemical recycling and pyrolysis, hold promise for transforming previously unrecyclable plastics into valuable feedstocks, thus closing the loop on resource utilization (Hinton *et al.*, 2022). The integration of circular economy principles has emerged as a driving force behind sustainable waste management practices. Unlike the linear "take-make-dispose" model, the circular economy seeks to maximize resource efficiency and minimize waste generation by promoting reuse, remanufacturing, and recycling (Lazarevic & Brandão, 2020). By designing products with recyclability in mind and establishing closed-loop supply chains, businesses can reduce their reliance on virgin materials and decrease environmental footprint. Moreover, the circular economy fosters economic resilience and innovation, creating new markets for recycled materials and stimulating job creation across various sectors (Le, Ferraris & Dhar, 2023).

However, despite significant strides, challenges persist in recycling infrastructure and material recovery. Inadequate collection systems and inconsistent recycling practices hinder the efficient recovery of recyclable materials, leading to contamination and reduced material quality (Arya & Kumar, 2020). Moreover, the lack of standardized recycling processes and limited market demand for recycled products pose barriers to scalability and viability. Additionally, the globalization of recycling markets has exposed vulnerabilities in supply chains, with disruptions in trade and fluctuations in commodity prices impacting recycling operations worldwide. Addressing these challenges requires concerted efforts from stakeholders across the value chain. Investment in recycling infrastructure upgrades and collection network expansion is critical to improving material recovery rates and reducing reliance on landfill disposal. Furthermore, incentivizing innovation and collaboration through public-private partnerships can spur the development of breakthrough technologies and business models that drive circularity. Legislative measures, such as extended producer responsibility (EPR) schemes and recycled content mandates, can also incentivize eco-design and promote market demand for recycled materials (Arora, Mutz & Mohanraj, 2023). Recycling and the circular economy represent powerful tools in the transition towards a more sustainable and resource-efficient future. Through continued investment in technological innovation, adoption of circular economy principles, and collaborative action, society can overcome the challenges posed by recycling infrastructure and material recovery. This paves the way for a circular economy that thrives on the principles of reuse, recycle, and regenerate.

Waste-to-energy technologies

Waste-to-energy (WtE) technologies offer a multifaceted approach to waste management by converting various forms of waste into valuable energy sources, thereby addressing both waste disposal and energy generation needs (Ferdoush *et al*., 2024). Among the diverse array of WtE technologies, anaerobic digestion, incineration with energy recovery, and gasification and pyrolysis processes stand out as prominent solutions, each with distinct advantages and considerations. Anaerobic digestion represents a sustainable method of treating organic waste by harnessing naturally occurring microbial processes to break down biodegradable materials in the absence of oxygen. This biological process yields biogas, primarily composed of methane and carbon dioxide, which can be captured and utilized as a renewable energy source for electricity generation, heating, or vehicle fuel (Damyanova & Beschkov, 2020). Moreover, anaerobic digestion generates nutrient-rich digestate, a valuable byproduct that can serve as fertilizer, thus completing the cycle of resource utilization and fostering circularity. Incineration with energy recovery is a well-established WtE technology that involves the combustion of waste materials at high temperatures in specially designed facilities known as waste-to-energy plants. During incineration, the heat generates steam that powers turbines to produce electricity. Additionally, the combustion process reduces the volume of waste and mitigates the need for landfill disposal, thereby alleviating environmental pressures associated with waste accumulation. However, concerns persist regarding air emissions and the release of pollutants such as dioxins, heavy metals, and particulate matter, necessitating stringent emissions controls and regulatory oversight to minimize environmental impact. Gasification and pyrolysis processes represent advanced thermochemical conversion technologies that offer efficient and environmentally sound alternatives to traditional incineration. Gasification involves the partial oxidation of carbonaceous materials at high temperatures to produce synthesis gas (syngas), a versatile fuel comprising carbon monoxide, hydrogen, and methane (Alves *et al*., 2023). Syngas can be combusted directly for energy generation or further processed into liquid fuels or chemicals. Pyrolysis, on the other hand, involves the thermal decomposition of organic materials in the absence of oxygen, yielding biochar, bio-oil, and syngas as end products. These bio-based fuels and chemicals can substitute for fossil fuels in various applications, offering a renewable and sustainable alternative.

While WtE technologies hold significant promise for waste management and energy production, they also pose environmental implications and regulatory considerations that must be carefully addressed (Wilson *et al*., 2015). Emissions from combustion processes, such as air pollutants and greenhouse gases, can impact air quality and contribute to climate change if not effectively controlled. Additionally, the handling and disposal of ash residues generated during incineration or gasification require proper management to prevent soil and water contamination. Furthermore, the siting of WtE facilities must consider local environmental and community concerns, ensuring minimal adverse impacts on human health and well-being. Regulatory frameworks play a crucial role in governing the deployment and operation of WtE technologies, establishing standards for emissions control, waste handling, and environmental monitoring (Jain, Sharma & Gupta, 2022). Striking a balance between promoting energy recovery and safeguarding environmental quality requires robust enforcement mechanisms and stakeholder engagement to foster transparency and accountability. Moreover, incentivizing the adoption of cleaner and more efficient WtE technologies through policy incentives and market mechanisms can accelerate the transition towards a more sustainable and circular economy. Waste-to-energy technologies offer viable solutions for addressing the dual challenges of waste management and energy security. By leveraging anaerobic digestion, incineration with energy recovery, and advanced thermochemical conversion processes, the potential of waste as a valuable resource can be harnessed while mitigating environmental impacts. However, achieving sustainable WtE deployment requires careful consideration of environmental implications, regulatory frameworks, and stakeholder engagement to ensure that the benefits of energy recovery are realized without compromising environmental integrity or public health.

Landfill management and remediation

Landfills, once viewed as convenient solutions for waste disposal, now pose significant environmental and health challenges. However, advancements in landfill engineering, leachate and gas management strategies, and landfill mining and reclamation techniques offer innovative approaches to mitigate these issues and transform landfill sites into sustainable assets (Madadian, Haelssig & Pegg, 2020). Landfill engineering and design have undergone considerable advancements to enhance containment, minimize environmental impact, and maximize resource recovery. Modern landfill design incorporates impermeable liners, leachate collection systems, and gas extraction infrastructure to prevent the migration of contaminants into surrounding soil and water (Touze-Foltz *et al*., 2021). Additionally, engineered caps and covers help mitigate odor emissions, control erosion, and promote vegetation growth, thereby restoring the aesthetic and ecological integrity of landfill sites. Furthermore, advances in geosynthetic materials and landfill liner technologies offer opportunities for cost-effective and durable containment solutions, ensuring the long-term stability and safety of landfill facilities. Leachate and gas management are critical components of effective landfill operations, requiring proactive strategies to mitigate environmental risks and ensure regulatory compliance. If not properly managed, leachate, a complex mixture of organic and inorganic compounds generated from decomposing waste, poses contamination threats to groundwater and surface water bodies. Engineered wetlands, bioreactors, and membrane filtration technologies are some of the more advanced leachate collection and treatment systems that can be used to get rid of pollutants and safely release or reuse treated effluent. Similarly, landfill gas, predominantly composed of methane and carbon dioxide, presents both environmental and safety hazards due to its flammable nature and potent greenhouse gas emissions. Utilizing landfill gas as a renewable energy resource through gas extraction and recovery systems not only reduces greenhouse gas emissions but also provides a sustainable source of electricity, heat, or vehicle fuel (Mac Kinnon, Brouwer & Samuelsen, 2018).

Landfill mining and reclamation techniques offer innovative solutions for remediation and resource recovery from legacy landfill sites. Landfill mining involves the systematic excavation and separation of waste materials, followed by sorting, recycling, and disposal of residual waste. This process not only reduces the volume of waste requiring long-term management but also recovers valuable resources, such as metals, plastics, and organic matter, for reuse or recycling (Nanda & Berruti, 2021). Furthermore, reclamation of post-closure landfill sites offers opportunities for land restoration and redevelopment, transforming former waste sites into productive and sustainable land uses. Reclaimed landfill sites can be repurposed for recreational areas, green spaces, solar farms, or even sustainable agriculture, providing economic, environmental, and social benefits to surrounding communities. However, despite these advancements, challenges remain in landfill management and remediation, including regulatory compliance, financial constraints, and public perception. Meeting stringent regulatory requirements for landfill design, operation, and closure necessitates substantial investment in infrastructure and ongoing monitoring to ensure environmental protection and public health. Additionally, securing funding for landfill remediation and reclamation projects can be challenging, particularly for municipalities or private entities facing budgetary constraints. Moreover, addressing public concerns and perceptions regarding landfill sites requires transparent communication, community engagement, and stakeholder collaboration to build trust and foster acceptance of remediation efforts (Perko *et al*., 2019). Landfill management and remediation represent critical aspects of sustainable waste management, offering opportunities to mitigate environmental impacts, recover valuable resources, and transform waste sites into productive assets. By leveraging advancements in landfill engineering, leachate and gas management strategies, and landfill mining and reclamation techniques, more sustainable outcomes for current and future generations can be achieved. However, addressing the challenges associated with landfill management requires concerted efforts from government, industry, and communities to prioritize environmental stewardship, innovation, and collaboration.

Innovative solutions for hazardous waste

Chemical treatment and detoxification methods offer effective means of mitigating the environmental and health risks associated with hazardous waste. These methods involve the use of chemical agents or processes to neutralize or transform hazardous substances into less harmful or inert forms (Kumar, Singh & Chandra, 2021). For instance, oxidation-reduction reactions can be employed to break down organic contaminants, while precipitation and ion exchange techniques can remove heavy metals from contaminated soil or water. Also, advanced oxidation processes like ozonation and photocatalysis use reactive species to break down persistent organic pollutants, making them less harmful or easier to treat later (Mouele *et al*., 2021). Bioremediation and phytoremediation represent nature-inspired approaches to hazardous waste management, harnessing the power of microorganisms and plants to degrade or immobilize contaminants. Bioremediation utilizes microbial metabolic processes to break down organic pollutants into harmless byproducts, often under conditions optimized for microbial growth and activity (Pal *et al*., 2020). In contrast, phytoremediation involves the uptake, accumulation, and transformation of contaminants by plants, which can then be harvested or disposed of, effectively removing pollutants from the environment. These green remediation techniques offer cost-effective and sustainable solutions for contaminated sites, leveraging natural processes to restore environmental quality (Kurade *et al*., 2021). Nanotechnology applications hold promise for revolutionizing hazardous waste management by offering precise and targeted approaches to pollutant remediation and detection. Nanomaterials, like nanoparticles and nanocomposites, have special qualities like a high surface area-to-volume ratio, reactivity, and catalytic activity. These qualities make them perfect for detecting, removing, and adsorbing pollutants (Roy *et al*., 2021). Nano remediation uses engineered nanoparticles to clean up polluted soil or groundwater by adsorbing them, changing their chemical makeup, or making microbes stronger. Additionally, nano sensors enable real-time monitoring of environmental pollutants, providing valuable data for decision-making and risk assessment (Chakraborty, Kaur & Chaudhary, 2021). However, the potential environmental and health impacts of nanomaterials require careful consideration, necessitating robust risk assessment and regulatory oversight to ensure their safe and responsible use in hazardous waste management.

Digitalization and smart waste management

Internet of Things (IoT) enabled waste monitoring systems utilize sensors and connected devices to gather real-time data on waste generation, collection, and disposal. These systems enable waste management authorities to remotely monitor fill levels, schedule pickups based on demand, and optimize route efficiency, reducing operational costs and environmental impact (Hussain *et al.,* 2024). Moreover, IoT sensors can detect anomalies or hazardous conditions, facilitating timely interventions and mitigating potential risks. Big data analytics play a pivotal role in optimizing waste management processes by analyzing vast quantities of data to identify patterns, trends, and opportunities for improvement. By leveraging predictive analytics and machine learning algorithms, waste managers can forecast waste generation patterns, optimize collection schedules, and allocate resources more effectively (Munir, Li & Naqvi, 2023). Furthermore, data-driven insights enable informed decision-making, empowering stakeholders to identify inefficiencies, reduce waste generation, and optimize recycling and recovery efforts. Blockchain technology offers a decentralized and immutable ledger for tracking and tracing waste throughout its lifecycle, enhancing transparency, accountability, and trust. By recording transactions, from waste generation to disposal, on a distributed ledger, blockchain enables stakeholders to verify the authenticity and origin of waste, ensuring compliance with regulations and standards. Additionally, blockchain-based smart contracts can automate payment processes and incentivize responsible waste management practices, fostering a circular economy and promoting sustainability.

Policy and regulatory frameworks

At the international level, agreements and conventions serve as foundational pillars for cooperation and collaboration among nations in addressing global waste challenges (Batista *et al*., 2021). Conventions such as the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal and the Stockholm Convention on Persistent Organic Pollutants establish norms and standards for the management and disposal of hazardous wastes, facilitating cross-border cooperation and harmonization of regulations (Mitsilegas *et al*., 2022). Similarly, initiatives such as the Sustainable Development Goals (SDGs) and the Paris Agreement underscore the importance of waste management in achieving broader environmental and social objectives, fostering a shared commitment to sustainable development and climate action. National waste management policies and initiatives provide a framework for governments to articulate priorities, set targets, and allocate resources for waste management at the domestic level. These policies encompass a range of strategies, including waste reduction, recycling and recovery, landfill diversion, and hazardous waste management, tailored to the specific needs and circumstances of each country (Kaza *et al*., 2018). Through regulatory mechanisms such as waste management plans, permits, and enforcement measures, governments seek to ensure compliance with environmental standards, protect public health, and minimize adverse impacts on ecosystems and natural resources. Government regulations play a pivotal role in promoting sustainable waste practices by establishing legal requirements, incentives, and penalties to encourage responsible waste management behaviors. Regulations may encompass a wide range of issues, including waste collection and transportation, recycling targets, landfill operation and closure standards, and producer responsibility schemes (Leclerc & Badami, 2020). By establishing clear rules and incentives, governments can create a conducive environment for innovation, investment, and public-private partnerships in waste management, driving the transition towards a circular economy and a more sustainable future.

Future directions and challenges

Research in waste management is increasingly focused on innovative solutions to improve efficiency, sustainability, and environmental outcomes. Emerging trends include the development of advanced recycling technologies, such as chemical recycling and bioplastics, as well as the exploration of bio-based materials and circular economy models. Additionally, there is growing interest in leveraging artificial intelligence (AI), robotics, and automation to enhance waste sorting, processing, and resource recovery processes, leading to greater accuracy, speed, and cost-effectiveness (Salem *et al*., 2023). Integration of emerging technologies like AI and robotics holds promise for revolutionizing waste management practices, offering opportunities for increased efficiency, precision, and scalability. AI-powered systems can optimize waste collection routes, predict waste generation patterns, and automate sorting processes, while robotics enable autonomous operation in hazardous or challenging environments (Andeobu, Wibowo & Grandhi, 2022). By leveraging the power of these technologies, waste management stakeholders can improve operational performance, reduce environmental impact, and increase resource recovery rates. Addressing socio-economic disparities in waste management remains a critical challenge, as marginalized communities often bear the brunt of environmental pollution and inadequate waste services. Efforts to promote equitable access to waste management infrastructure, education, and resources are essential for ensuring that all individuals and communities benefit from sustainable waste practices. Moreover, fostering inclusive decision-making processes and partnerships with local stakeholders can empower communities to participate in waste management solutions that address their specific needs and concerns.

Conclusion

In conclusion, this review paper has elucidated the remarkable advancements and persistent challenges within the realm of waste management. Notably, key advancements include the integration of innovative technologies such as IoT-enabled monitoring systems, big data analytics, and blockchain, which have revolutionized waste management processes by enhancing efficiency, transparency, and accountability. Additionally, the development of waste-to-energy technologies, such as anaerobic digestion and gasification, opens up new ways to recover resources and generate renewable energy. This leads to less waste going to landfills and reduces environmental impact. However, amidst these advancements, significant challenges remain. Socio-economic disparities in waste management access and environmental justice persist, underscoring the imperative for equitable solutions that address the needs of all communities. Moreover, regulatory frameworks must continue to evolve to keep pace with technological advancements and emerging waste streams, ensuring that environmental standards are upheld, and public health is protected. Central to addressing these challenges is the importance of collaboration and innovation in sustainable waste management. Cross-sectoral partnerships between government, industry, academia, and civil society are essential for fostering knowledge exchange, leveraging resources, and driving collective action toward shared sustainability goals. Likewise, fostering a culture of innovation and entrepreneurship is crucial for identifying and scaling up transformative solutions that promote resource efficiency, waste reduction, and circularity. In essence, sustainable waste management requires a multifaceted approach that encompasses technological innovation, policy reform, and social engagement. By embracing collaboration, innovation, and a shared commitment to sustainability, the challenges posed by waste can be overcome, paving the way for a more resilient, equitable, and environmentally sustainable future.

Acknowledgment

The authors are thankful to their departmental colleagues for their valuable suggestions and assistance in preparing this chapter.

Conflict of interest

There is no conflict of interest

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doi: 10.31674/book.2024scibe.008

Effects of Solvent Polarity in the Sonogashira Coupling: A Brief Overview

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Abstract

The Sonogashira cross-coupling reaction is a powerful and widely utilized synthetic method for the formation of carbon-carbon bonds. Over the years, extensive research has been conducted to explore the influence of different solvents on the reaction efficiency and selectivity. The solvent choice in Sonogashira cross-coupling reactions greatly affects the reaction rate and yield. A diverse range of solvents, including polar protic, polar aprotic, and nonpolar solvents, have been investigated. This chapter examines the impact of solvent polarity, dielectric constant, hydrogen-bonding ability, and solubility on the reaction outcome. Furthermore, solvent effects on the reactivity of the reactants as well as the stability of intermediates and catalysts are also discussed. The understanding and manipulation of solvent parameters in this reaction provide valuable insights for the development of improved protocols and the design of new catalytic systems. This chapter provides a comprehensive overview of the various facets of solvent effects in the Sonogashira cross-coupling, highlighting the significant role played by solvents in this transformation. This article aims to stimulate further research in the field, facilitating the advancement of the Sonogashira cross-coupling methodology towards more efficient and sustainable synthetic processes. Overall, the findings highlight the crucial influence of solvent polarity on the efficiency and selectivity of Sonogashira coupling, offering valuable insights for optimizing reaction conditions in synthetic organic chemistry.

Keywords: *Alkynylation; Carbon-Carbon Bond Formation; Catalysis; Solvent Effects; Sonogashira Cross-Coupling*

Introduction

Transition-metal-catalyzed carbon-carbon (C-C) bond-forming reactions have emerged as transformative processes in the realm of organic synthesis, playing a pivotal role in modern chemical methodologies. The utilization of transition metals as catalysts imparts unique reactivity, selectivity, and efficiency to these transformations, enabling the formation of C-C bonds under milder conditions compared to traditional methods (Docherty *et al*., 2023). Within this array, the palladium-catalyzed sp^2-sp coupling reaction, employing aryl or alkenyl halides or triflates with terminal alkynes, emerges as an important method for synthesizing arylalkynes and conjugated enynes. These compounds serve as key precursors for natural products (Tabassum *et al*., 2022), pharmaceuticals (Cruz*,* Mateus & Peterson, 2021), and molecular organic materials (Gao *et al*., 2022). Alkynes are pivotal in synthesizing carbocycles and heterocycles via metal catalysis, where they undergo diverse cyclization reactions. Alkynes are versatile intermediates in metal catalyzed cyclization reactions like cycloisomerization (Chan *et al*., 2020), benzannulation (Amin *et al*., 2024), etc. Additionally, under organocatalytic conditions, alkynes participate in cyclization processes facilitated by organic catalysts, enabling efficient formation of complex molecular structures (Zhang *et al*., 2024). The inception of this reaction can be traced back to independent reports in 1975 by Heck and Cassar. Heck's approach relied on the Mizoroki-Heck reaction, utilizing a phosphane-palladium complex as a catalyst, triethylamine or piperidine as a base, and a corresponding solvent (Dieck & Heck, 1975). Cassar's method involved a phosphane-palladium catalyst with sodium methoxide as a base and DMF as the solvent, with both methods typically requiring high temperatures, up to 100°C (Cassar, 1975).

In the same year, Sonogashira, Tohda and Hagihara (1975) introduced a pivotal observation, noting that the addition of a catalytic amount of copper(I) iodide significantly accelerated the reaction (figure 1). This innovation allowed for performing the alkynylation at room temperature, marking a significant advancement. The Sonogashira-Hagihara protocol, commonly known as the Sonogashira coupling, rapidly became the preferred choice for alkynylation reactions involving aryl or alkenyl halides. Notably, even primary and secondary alkyl bromides have been successfully alkynylated using this protocol, although the exploration of sp3-sp coupling in this context is relatively recent.

However, the inclusion of copper salts as co-catalysts in Sonogashira cross-coupling reactions present certain drawbacks. This addition introduces another environmentally unfriendly reagent that is challenging to recover. The in-situ generation of copper acetylides during the reaction conditions can lead to undesired side reactions, such as the Glaser coupling, particularly when the terminal acetylene is scarce or costly. Over the years, various alternatives to the copper(I) co-catalyst have been explored to address issues arising from competitive homocoupling to the diyne. These alternatives include the use of stoichiometric amounts of silver oxide or tetrabutylammonium salts as activators, as well as the exploration of palladium-only procedures. This versatile and robust reaction has greatly contributed to the advancement of modern synthetic chemistry and continues to be an active area of research and development.

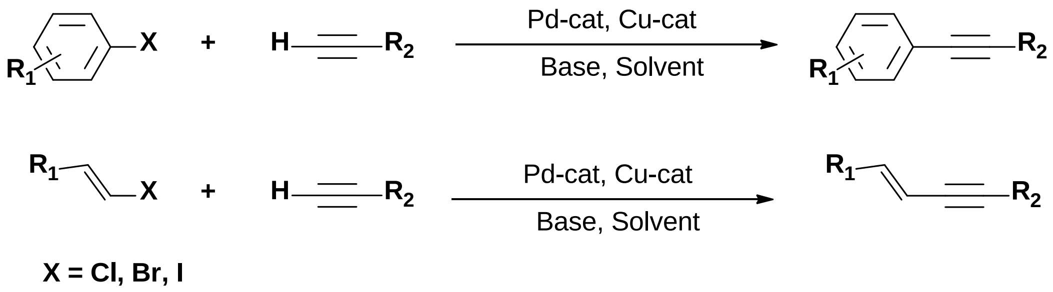


Figure 1: The Sonogashira Coupling

While the Sonogashira cross-coupling reaction has witnessed significant advancements in recent years, the choice of solvent plays a crucial role in influencing the reaction outcomes (Choy, Gan & Kwong, 2023). Solvents are not merely inert reaction media but actively participate in the reaction by influencing reaction rates, selectivity, and catalyst stability. By stabilising the ionic intermediates of the catalytic cycle, the solvents' polarity and hydrogen bonding ability help to accelerate the reaction, while steric bulk reduces this ability. These findings are consistent with the mechanistic investigations into the Cu-free version of the Sonogashira reaction (Ljungdahl *et al.*, 2006). The selection of an appropriate solvent can enhance the efficiency and control of the cross-coupling process. Table 1 shows the polarity of various commonly used protic and aprotic solvents along with their boiling points.

***Table 1:** Boiling points and dielectric constants of commonly used solvents*

Solvent	**Boiling Point (ºC)**	**Dielectric constant (ε)**	**Protic/Aprotic**
Water	100	80.4	Protic
Methanol	65	32.6	Protic
Ethanol	78	24.3	Protic
Acetonitrile	82	37.5	Protic
Ethylene glycol	197	37.0	Protic
Acetone	56	20.7	Protic
N, N-Dimethyl formamide	153	36.7	Aprotic
N, N-Dimethyl acetamide	165	37.8	Aprotic
Dimethyl sulfoxide	189	45.0	Aprotic
Tetrahydrofuran	66	7.6	Aprotic
Diethyl ether	35	4.3	Aprotic
Chloroform	61	4.8	Aprotic
Dichloromethane	40	8.9	Aprotic
Dichloroethane	84	10.4	Aprotic
Benzene	80	2.3	Aprotic
Toluene	111	2.4	Aprotic
o-Xylene	144	2.6	Aprotic
n-Hexane	69	1.9	Aprotic

The importance of solvent choice in the Sonogashira cross-coupling reaction arises from its influence on several key aspects. Firstly, solvents can affect the reaction rates by modulating the accessibility of reactants to the catalyst and the kinetic barriers involved in the reaction steps. Secondly, solvents play a vital role in determining the selectivity of the cross-coupling process, influencing regioselectivity and stereoselectivity. Solvent effects can also impact the stability and activity of the catalyst, which are crucial for achieving high yields and prolonged catalyst lifetimes. The purpose of this chapter is to explore the role of solvents in the Sonogashira cross-coupling reaction, with a specific focus on their impact on reaction rates, selectivity, and catalyst stability.

Methodology

Various solvents are applicable for cross-coupling reactions, with particular significance in palladium-catalyzed processes, akin to most solution-based chemical transformations. The chosen solvent profoundly influences reaction kinetics, selectivity, and equilibrium. It regulates product partitioning, facilitating by-product removal or clean product separation, while also impacting catalyst stability through coordination effects and modulating the activity of acids and bases via complementary functionalities. Proper solvent selection enhances catalyst lifespan, acid-base activity, and process benefits, serving as a heat sink for temperature control and allowing substances to be pumped as solutions. This article is designed in such a way that the readers can get the idea about the effect of the solvent in Sonogashira cross-coupling reaction. How the solvent polarity affects the overall outcome of the coupling process by influencing both the reactivity and selectivity of the reaction. In some cases, solvent molecules are not innocent, they also participated in the catalytic cycle by co-ordinating the metal centre and influencing the ligand etc.

Results and Discussion

Understanding solvent interactions is crucial for comprehending their impact on cross-coupling reactions. Among intermolecular forces, the most prevalent are weak, spontaneously induced dipoles (dispersion forces), inherent in all solvents due to organic molecule polarizability. Solvents with high polarizability, like aromatic and chlorinated solvents such as toluene, can stabilize induced and permanent dipoles in other molecules. Those with strong permanent dipoles are termed polar or dipolar, while cyclic solvents, with restricted conformations favoring higher dipole moments, exhibit greater polarity compared to equivalent acyclic counterparts (e.g., tetrahydrofuran over diethyl ether). Additionally, hydrogen bonding, a potent force with specific directionality, distinguishes solvents as hydrogen bond donors (e.g., alcohols) and/or acceptors (e.g., ethers), while those lacking hydrogen donors are termed aprotic.

The Sonogashira coupling reaction presents a challenge for solvent selection due to the diverse nature of its components. The solvent must effectively dissolve a range of solutes, including lipophilic aryl halides, copper acetylide organometallics, inorganic palladium complexes, and sometimes salts like bases and additives. A suitable choice for this purpose is a dipolar aprotic solvent, with N, N-Dimethylformamide (DMF) serving as a classic example. DMF, a polar and aprotic solvent, is cost-effective, capable of coordinating in metal complexes, and dissolves most organic compounds and many inorganic salts to varying extents. With a boiling point of 153 °C, DMF enhances reaction rates and can be easily recovered via distillation, making it a common solvent choice for the Sonogashira coupling. It is hypothesized that DMF's high electron-donating capacity facilitates alkyne deprotonation by coordinating with the Pd metal center and promoting product dissociation at the catalytic cycle's conclusion (Sherwood *et al*., 2019). However, DMF's reproductive toxicity necessitates its substitution. Yet, alternative polar solvents like DMSO and 1,4-dioxane present challenges due to their stability and toxicity concerns in the Sonogashira reaction (Gao *et al*., 2020).

Solvent polarity and nucleophilicity

Solvent polarity refers to the distribution of charge within a solvent molecule, with polar solvents having a separation of positive and negative charges. Nucleophilicity, on the other hand, refers to the ability of a solvent molecule to donate an electron pair. These properties are closely related and can affect the reaction kinetics and reactivity of the cross-coupling partners. Solvent polarity and nucleophilicity are critical factors to consider when screening solvents for Sonogashira cross-coupling reactions. Zhou and

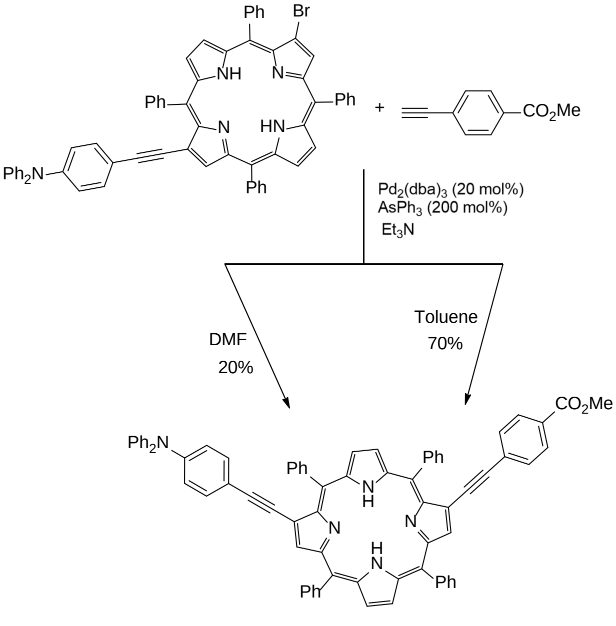


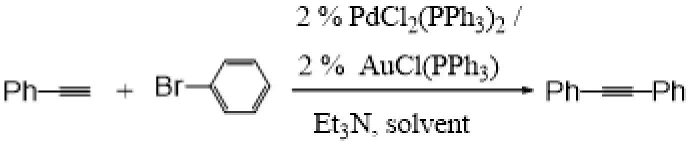
Figure 2: Sonogashira coupling of *β*-bromoporphyrin

co-workers (2014) reported a protocol for the copper-free Sonogashira coupling of *β*-bromoporphyrin using the $Pd_2(dba)_3/AsPh_3$ system as the catalyst. They found that a better yield was obtained when the reaction was performed in toluene solvent (70%) compared to DMF (20%) (Figure 2). The authors indicated that DMF may have slowed the reaction by displacing the $AsPh_3$ ligands from the active palladium complex. Therefore, a solvent screening approach should include solvents with a range of polarities to evaluate their effects on the reaction outcome.

Influence of polar solvents on reaction rates and yields

Polar solvents, such as acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), can enhance the reaction rates in Sonogashira coupling reactions. The polar nature of these solvents allows for effective solvation of the reactants and catalyst, increasing their accessibility and promoting favorable interactions. The solvation of the reactants can also facilitate the deprotonation step, promoting the activation of the acetylenic or aryl halide coupling partners. The enhanced solvation of the intermediates and transition states can stabilize the reactive species, resulting in improved yields. For example, palladium and gold dual catalytic sonogashira coupling of aryl halides were found to be most effective in polar solvents like DMF and DMA (96% yield) compared to non-polar solvent toluene (33%) (Table 2 & Figure 3) (Panda & Sarkar, 2010a). Here $Pd(PPh_3)_2Cl_2$ and $AuCl(PPh_3)$ were used as effective synergistic catalytic systems. The generality of this protocol was proved through the application of a wide range of aryl halides under this condition (Panda & Sarkar, 2013). Aryl halides containing various functional groups were coupled nicely with alkynes effectively and provided the desired coupled products in good to excellent yields. Similarly, the Pd-Au dual catalytic Sonogashira coupling of arene diazonium salts also

Table 2: *Solvent optimization of Pd-Au dual catalytic Sonogashira Coupling*



Entry	Solvent	Yield (%)
1	THF	81
2	H_2O	40
3	Et_3N	67
4	Toluene	33
5	MeCN	84
6	DMSO	89
7	**DMF**	**96**
8	**DMA**	**96**

Source: Panda & Sarkar, 2010a

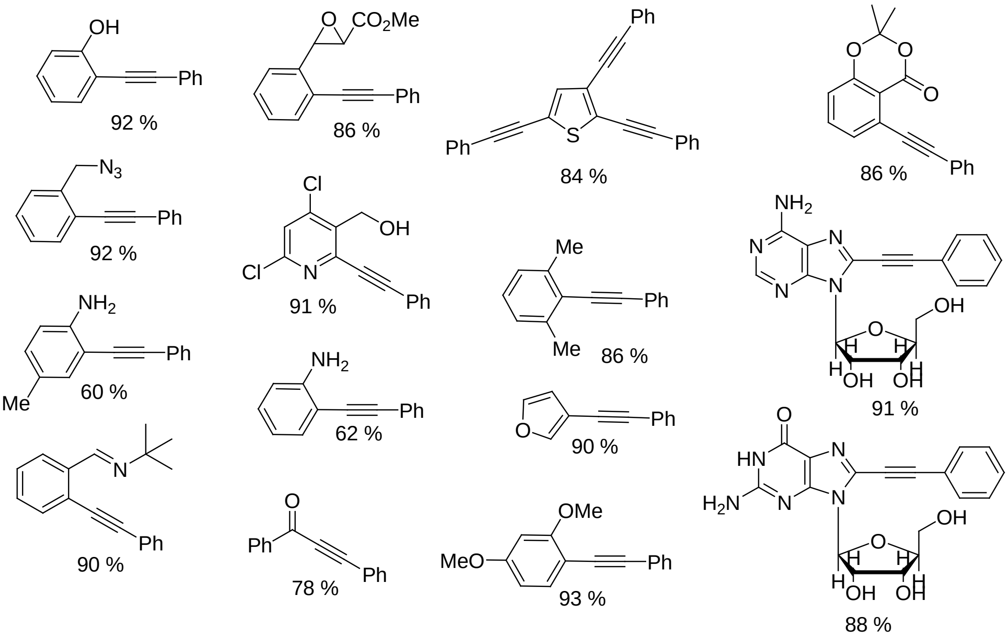
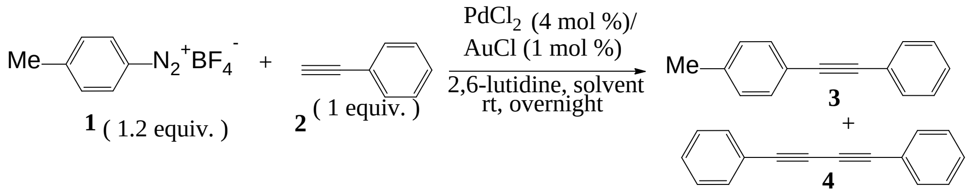


Figure 3: Pd-Au dual catalytic Sonogashira coupling

***Table 3:** Sonogashira Coupling of Arenediazonium Salts under Various Conditions*



Entry	Solvent	Yield(%) of 3	Yield(%) of 4
1	THF	62	8
2	1,4-dioxane	74	5
3	H_2O	62	14
4	MeCN-H_2O(1:1)	76	9
5	**MeCN**	**74**	**0**
6	Toluene	11	27

Source: Panda & Sarkar, 2010b

provides the best yield in acetonitrile solvent (Table 3 & Figure 4) (Panda & Sarkar, 2010b). Arenediazonium salts, derived from inexpensive anilines, serve as readily available and highly reactive aryl surrogates, demonstrating superior reactivity compared to aryl halides and triflates in diverse cross-coupling reactions (Panda, 2021).

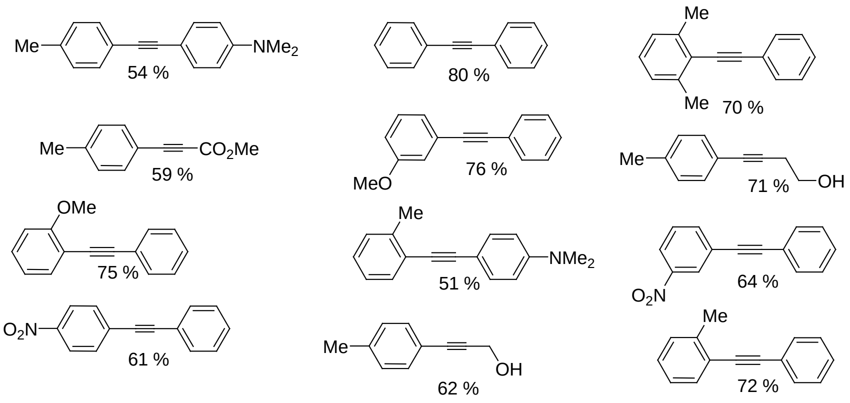
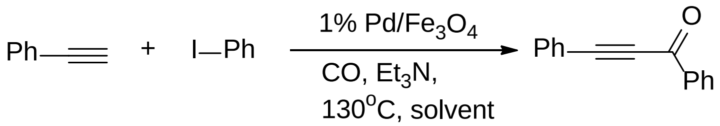


Figure 4: Pd-Au dual catalytic Sonogashira Coupling of Arenediazonium salts

Impact of Nonpolar Solvents on Reaction-on-Reaction Kinetics

Nonpolar solvents, such as benzene, toluene, and xylene, are often employed in Sonogashira coupling reactions. These solvents have low polarity and reduced nucleophilicity compared to polar solvents. While nonpolar solvents may decrease the solubility of polar reactants and catalysts, they can still play a crucial role in the reaction kinetics. In nonpolar solvents, the reactants and catalysts may have reduced solvation and experience decreased steric hindrance. This can lead to increased collision frequency between reactant molecules, promoting faster reaction kinetics. Additionally, nonpolar solvents can also influence the regioselectivity of the cross-coupling reaction by reducing competing side reactions, resulting in improved selectivity. In 2008, Liu and co-workers reported a carbonylative Sonogashira coupling of aryl iodides in the presence of a magnetically separable palladium catalyst under copper and phosphene-free conditions. Optimization studies revealed that, non-polar solvent toluene was found to be the best solvent compared to polar solvents like DME, THF, 1,4-dioxane and CH_3CN (Table 4). In their method, various functionalized aryl iodides were coupled successfully with alkynes to produce internal alkynes in high

***Table 4:** Solvent optimization of Pd/Fe_3O_4 catalytic Sonogashira Coupling*



Entry	Solvent	Yield (%)
1	THF	63
2	**Toluene**	**93**
3	MeCN	64
4	DME	49
5	1,4-dioxane	51

Source: Liu et al., 2008

yields. It is important to note that the choice of solvent in Sonogashira coupling is a delicate balance between the desired reactivity and selectivity. While polar solvents generally enhance reaction rates and yields, they may also lead to undesired side reactions or catalyst deactivation. Conversely, nonpolar solvents can promote faster reaction kinetics but may result in reduced solubility and limited reaction control.

Influence of solvent polarity on regioselectivity of cross-coupling reactions

Solvent polarity can have a profound impact on the regioselectivity of Sonogashira coupling reactions. The orientation of the reactants, particularly the terminal alkyne and the aryl or vinyl halide, is influenced by the solvation and electrostatic interactions within the reaction medium. Polar solvents, such as DMF or DMSO, can enhance regioselectivity by solvating and stabilizing charged or polar intermediates. The solvation effects can promote the formation of the desired regio-isomer in Heck and Hiyama reactions by reducing steric hindrance or providing specific interactions. A nice review by Fairlamb and co-workers (2006) lucidly described the regioselective cross-coupling reactions.

Li and co-workers reported the Sonogashira reaction of multifunctional 2-iodophenyl-acetylenes, aimed at generating cyclic products, exhibits favorable outcomes in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]) (Figure 5) (Li *et al*., 2005). However, when attempted in organic solvents (DMF, THF) under identical conditions, the reaction proves less effective. Copper(I) iodide, employed to facilitate the coupling, leads to undesirable homocoupling emerging as the major reaction pathway in organic solvents, even in the presence of an inert atmosphere. In contrast, the use of the ionic liquid allows for a significant reduction in the amount of CuI required (1 mol%), thereby enhancing the selectivity of the reaction.

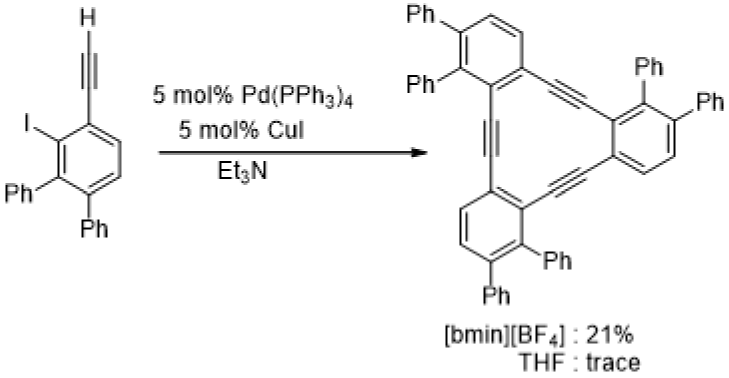


Figure 5: Sonogashira reaction of multifunctional 2-iodophenyl-acetylenes

In 2020, Al-zoubi and co-workers have revealed that solvent has a strong influence in regioseletivity of the Sonogashira coupling. According to their studies, when 1,2,3-triiodobenzene coupled with phenylacetylene in a polar aprotic solvent, DMF provides an inseparable mixture of alkynylated product mixture, thus showing poor regioselectivity (Figure 6). On the other hand, using anhydrous toluene as solvent, the Sonogashira coupling produced mono-alkynylated products selectively. During the optimization studies in the regioselective Sonogashira coupling reaction, Al-zoubi and co-workers also observed that in DMF solvent, full consumption of the starting material needs 12 hours, whereas in toluene solvent it needs 24 hours. This indicates that the rate of the reaction is higher in DMF compared to non-polar solvent toluene. High reactivity and low selectivity in DMF solvent and reverse effect in toluene were observed. Under these optimized reaction conditions, various highly functionalized tri-iodobenzenes were coupled efficiently with terminal alkynes and provided the desired products in moderate to good yields (Figure 7).

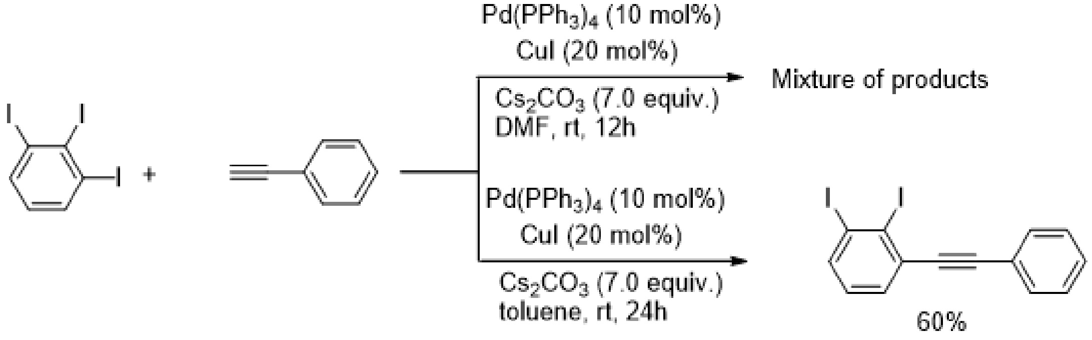


Figure 6: Solvent dependent selective Sonogashira coupling

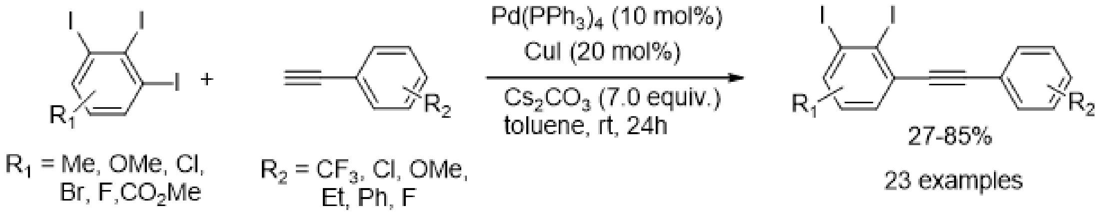


Figure 7: Selective Sonogashira coupling of functionalized tri-iodobenzenes

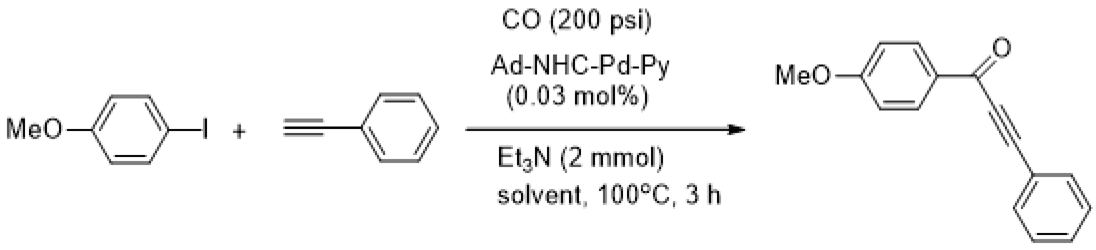
Solvent-induced effects on steric interactions and selectivity

Solvents can also influence the selectivity of Sonogashira coupling reactions by modulating steric interactions between the reactants and the catalyst. The choice of solvent can affect the accessibility of reactive sites, the relative orientation of reactants, and the efficiency of sterically demanding cross-coupling partners. Nonpolar solvents, such as toluene or hexane, can minimize steric hindrance and improve selectivity by reducing the interaction between bulky substituents.

Mansour and co-workers (2020) used isopropyl, benzyl, and adamantyl N-substituted (NHC) ligand-based palladium(II) complexes for the carbonylative Sonogashira coupling for the synthesis of ynones (Table 5). From their studies, they have found that adamentyl N-substituted N-heterocyclic carbene ligand-based palladium(II) complex was found to be most efficient in toluene solvent. Solvent screening reveals that polar solvents like THF, DMF, and MeCN are found to be less effective. The adamentyl-NHC-Pd complex is the softest species in this complex series, according to the frontier orbital quantum mechanical descriptors obtained through DFT analysis. This may be due to the unique steric and electronic properties of the adamantyl group relative to the isopropyl and benzyl groups. This observation is consistent with the complex's frequently observed maximum catalytic activity towards soft substrates.

It is important to note that the solvent-induced selectivity in Sonogashira coupling reactions can be complex and dependent on a variety of factors, including the nature of the reactants, catalyst, and reaction conditions. The understanding of solvent effects on selectivity is an active area of research, and further investigations are necessary to uncover the underlying mechanisms and develop strategies for controlling selectivity through solvent choice.

Table 5: *Carbonylative Sonogashira Coupling*



Entry	Solvent	Yield (%)
1	THF	61
2	DMF	73
3	MeCN	84
4	**Toluene**	97

Source: Mansour et al., 2020

Application of green and sustainable solvents

In the realm of Sonogashira coupling, the quest for green and sustainable solvent choices has gained significant traction. Researchers are increasingly focused on identifying solvents that not only promote efficient reaction outcomes but also minimize environmental impact. One promising avenue lies in the utilization of renewable and non-toxic solvents such as ethanol, water, or supercritical carbon dioxide. These solvents offer distinct advantages, including low toxicity, biodegradability, and reduced energy consumption during purification processes. Additionally, the implementation of solvent-free or solvent-minimized conditions has emerged as an attractive strategy, further enhancing the sustainability profile of Sonogashira coupling reactions. Through innovative solvent selection and process optimization, chemists aim to achieve greener synthetic pathways without compromising reaction efficiency or product yields.

Moreover, the exploration of alternative reaction media such as ionic liquids and deep eutectic solvents presents exciting opportunities for advancing the green credentials of Sonogashira coupling. These novel solvents offer unique properties such as tunable polarity, high stability, and recyclability, making them attractive candidates for sustainable reaction environments. By harnessing the potential of green solvents, researchers endeavor to mitigate the environmental footprint associated with traditional solvent-based approaches while fostering the development of more eco-friendly synthetic methodologies in Sonogashira coupling and beyond. In addition to the use of green solvents, various non-conventional techniques such as microwave irradiation sonochemistry (Safaei-Ghomi & Akbarzadeh, 2015), and photochemistry have achieved remarkable success in recent years.

Conclusion

In this chapter, the role of solvents in the Sonogashira cross-coupling reaction has been thoroughly explored. The discussion encompassed the influence of solvent polarity and nucleophilicity on reaction rates and yields, as well as the impact of solvents on selectivity and regioselectivity. Mechanistic insights into solvent effects were also examined, including solvent coordination with palladium catalysts, solvent-mediated activation of reactants, and solvent-dependent ligand effects. Additionally, the importance of solvent screening approaches for optimizing Sonogashira coupling reactions was highlighted.

The findings reveal that solvent choice has a significant impact on the outcome of the Sonogashira cross-coupling reaction. Different solvents can modulate reaction rates, selectivity, and catalyst stability, ultimately affecting the efficiency and success of the reaction. Polar solvents tend to enhance reaction rates and yields by facilitating the solvation and stabilization of intermediates, while nonpolar solvents can improve selectivity by minimizing steric hindrance. Solvent effects on regioselectivity were also observed, with polar solvents favoring specific regioisomers.

The implications of solvent choice in the Sonogashira cross-coupling extend beyond reaction outcomes. Sustainable solvent choices, such as green solvents, renewable and bio-based solvents, and solventless or solvent-minimized approaches, can significantly contribute to greener and more environmentally friendly processes. By reducing the use of hazardous solvents, utilizing renewable resources, and minimizing waste generation, researchers can align Sonogashira coupling reactions with the principles of green chemistry.

Looking ahead, there are several exciting opportunities for further research in this field. Future studies can focus on developing more sustainable solvent choices and solvent screening strategies, considering not only reaction performance but also environmental impact. Additionally, exploring solvent effects on different classes of substrates and reactions can provide a broader understanding of the solvent-dependent behavior in Sonogashira cross-coupling. Furthermore, investigating solvent effects in combination with other catalytic systems for cascade transformations can open new avenues for complex molecule synthesis.

Acknowledgement

Biswajit Panda would like to express gratitude to City College, Kolkata, India, for their generous support in accomplishing this work. He extends heartfelt thanks to all the faculty members of the Department of Chemistry, City College, Kolkata, for their help and support. The author is also thankful to Dr. Bhaskar Paul, Dr. Moumita Ganguli, Kirtika Dutta, Suban Kundu, Barnali Roy, Dr. Sujay Nandi, Dr. Totan Mondal and Atanu Ghosh for their continuous assistance.

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doi: 10.31674/book.2024scibe.009

Molecular Structure-Affinity Relationship of Flavonoids in Mango Pulp on Binding to Human Serum Albumin

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Abstract:

Mango pulp extract has gained growing attention as nutraceutical due to its various pharmacological functions. The polyphenolic phytochemical, flavonoids are considered as one of the main functional components of mango pulp. The structural variation present in flavone compounds such as hydroxylation in different positions and glycoconjugation in flavonoid structure, affect their binding properties with human serum proteins. Human serum proteins such as albumin, alpha fetoprotein, transferrin etc. can act as carrier proteins for flavonoid group of ligands, which can transport the ligands to their target sites. During transportation the binding affinity of the ligands with serum protein albumin can regulate their biological activities. In this study, the presence of four flavonoids in ethanolic extract of mango pulp is confirmed by UV-spectroscopic study. The molecular interaction studies between four flavonoids and human serum albumin are explored by in-silico method in molecular level. The connection between the molecular structures of flavonoids and their binding affinities for human serum albumin (HSA) is compared with the help of molecular docking method. The hydroxylation on 5 and 7 positions of A ring of flavone structure increases the affinities of ligands towards human serum albumin protein. Apart from the hydroxylation on 5 and 7 positions, the glycosylation on 3 position of C ring structure of flavone residue, also causes affinity induction for the same protein. It is revealed from the molecular docking study, that not only hydrogen bonds, but also, non-covalent interactions like, Pi-alkyl, Pi-Pi T shaped and Van der Waals interactions, play important roles in binding of flavonoids present in mango pulp to serum human albumin.

Keywords: *Binding Affinity; Flavonoids in Mango Pulp; Human Serum Albumin; Molecular Docking; Non-Covalent Interactions* Introduction

Throughout the plant kingdom, flavonoids are a vast class of naturally occurring low molecular mass polyphenol compounds that serve a variety of crucial roles, including chelating and antioxidant capacities. In vitro studies have demonstrated that flavonoids possess a broad spectrum of biological and pharmacological properties, such as anti-allergic, anti-inflammatory, antioxidant, antimicrobial, antibacterial, antiviral, and antifungal properties, as well as anti-diarrheal and anti-cancer properties (Fang *et al*., 2024). They are primarily found in vegetables (Eramma *et al*., 2025), fruits (Maheshwari, Rajawat & Parashar, 2024), as well as in wines, cocoa (Singh, Khedkar & Chandra, 2024), and teas consumed in the human diet.

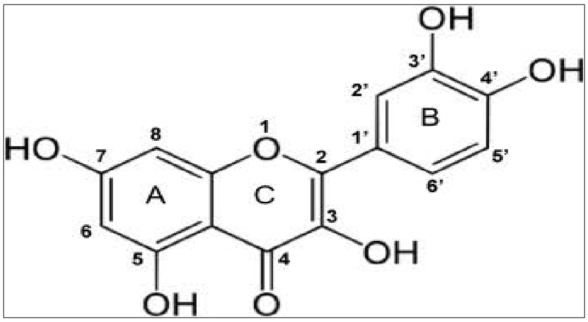


Figure 1: General Structure of Flavonoids *(Source: PubChem)*

Flavonoids are a broad class of polyphenolic compounds derived from plants that have a general structure (Figure 1). They are primarily found in fruits (Mehmood, Mehmood & Zulfiqar 2024), vegetables, and medicinal plants and are important in the detoxification process of free radicals. According to reports, quercetin and rutin are used to treat obesity and cardiovascular diseases. They also have antiviral, antibacterial, anti-inflammatory, antioxidant, and radical-scavenging properties. They are also immune-modulator agents and have therapeutic activity in conditions resulting from oxidative stress (Alsaif *et al*., 2020). Flavonoids are anticancer compounds, present in edible mango pulp, considered as nutraceuticals. Four flavonoids e.g. 5 hydroxyflavone (primuletin), 7 hydroxyflavone, 5, 7 dihydroxyflavone (chrysin) and kaempherol-3-glucuronide (Figure 2) are present in ethanolic extract of himsagar mango (Basu, 2024). All four phytochemicals after absorption through epithelial cells of GIT, transported to target cells after binding with albumin protein.

About 7% of the protein in human blood serum is found in the albumin fraction, which makes up two thirds of the total, and the globulin fraction, the remaining third. A big albumin peak and three smaller globulin peaks—the alpha, beta, and gamma globulins—are visible on serum electrophoresis. The single free sulfhydryl (—SH) group present in albumin (molecular weight 68,000) oxidizes to form a disulfide bond (S-S) with the sulfhydryl group (-SH) of another serum albumin molecule, forming a dimer. Serum albumin has an isoelectric point of pH 4.7.

About 60% of human plasma proteins are made up of serum albumin, a biomolecule that is crucial for the distribution and transportation of medications, metabolites, hormones, and other substances. It appears to function as a carrier for specific biological substances in living things (Ghosh & Bhadra, 2024). Serum albumin, a protein that stabilizes other proteins and is found in blood serum at a comparatively high concentration, serves as a protective colloid. For this reason, information about the ligands' binding mechanism on the available human serum albumin (HAS) binding sites is provided by the spectroscopic, docking, and molecular dynamic simulation methods. Sudlow sites I and II, which are situated in subdomains IIA and IIIA, are the two well-known binding sites that are accessible on HSA (Wang *et al.*, 2020).

The rationale for finding and creating naturally occurring compounds that are pharmacologically active and capable of binding the target plasma proteins has been greatly advanced by the latest developments in computational techniques. In order to demonstrate the biological activities of the natural compounds derived from mangos, computational methods have been employed for analysis (Basu, 2024). In our earlier study, we have identified, kaempherol-3-glucuronide, 5-hydroxy flavone (primuletin), 7-hydroxy flavone, chrysin, as potential therapeutic compounds present in himsagar mango pulp by using both UV visible spectroscopy and computational approaches (Basu, 2024).

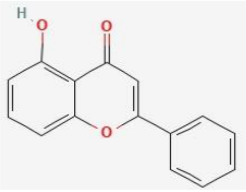
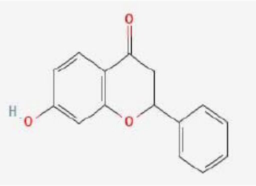
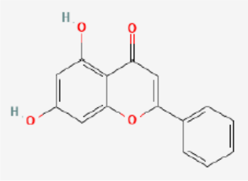
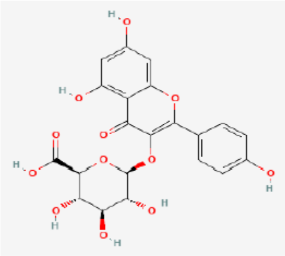
5-Hydroxy flavone (Primuletin)	7-Hydroxy flavone	5,7-Dihydroxy flavone (Chrysin)	Kaemferol-3-glucuronide
			

Figure 2: Chemical Structures of Four Flavonoids *(Source: PubChem)*

Flavonoids interact with various water-soluble proteins, especially albumins (López-Yerena *et al.*, 2020), when they are present in blood. Research on luteolin (Sarmah *et al.*, 2020), taxifolin, catechins (Shi *et al.*, 2011), galangin, naringenin (Yazdani *et al.*, 2022), kaempferol, diosmetin (Zhang, Wang & Pan, 2012), and other flavonoids described this interaction (Xue *et al.*, 2021). Dihydrochalcone and bovine serum albumin (BSA) were found to interact spontaneously, under the influence of hydrophobic forces, and with the release of energy (Curvale *et al*, 2012). While apigenin comes into contact with site I of subdomain II of BSA (Zhao *et al.*, 2012), morin was found to spontaneously interact with site II of subdomain IIIA of BSA (Hu *et al.*, 2012). Fisetin occupied a site similar to that of human serum albumin (HSA) (Singha Roy *et al.*, 2012). Hesperetin's binding constant to HSA was 1.941 × 10^{-4} M (Ding *et al.*, 2012), while EGCG's binding constant to site I of BSA's subdomain IIA was 6.6 × 10^{-7} M. EC's binding constant to site

II of subdomain IIIA was 10^{-6} M. It was proposed that the impact of galloyl groups could explain the observed variation in catechin binding (Pal *et al*., 2012).

Methodology

A. UV-Spectrophotometric screening for determination of Flavonoids present in mango pulp

The ethanolic sample of himsagar mango pulp was subjected to UV-spectrophotometric screening between 200 and 450 nm. The absorbance and peaks are recorded to order to identify the flavonoids in the mango sample. In order to accurately identify the flavonoids, found in mango pulp extracts, the ethanolic extract is treated with a UV shift reagent, such as NaOAc, and the absorption spectra are examined. During UV spectrometric analysis, various absorption maxima (peaks and shoulders) are observed.

B. Molecular docking study of plasma proteins with flavonoids present in mango extract

A crucial tool in computer-assisted drug design and structural molecular biology is molecular docking. Predicting the predominant binding mode(s) of a ligand with a protein that has a known three-dimensional structure is the aim of ligand-protein docking. Effective docking techniques use a scoring function that appropriately ranks candidate dockings and efficiently searches high-dimensional spaces. Protein-ligand interaction research benefits greatly from the use of docking, which can be used to virtually screen huge libraries of compounds, rank the outcomes, and suggest structural hypotheses about how the ligands bind to the target. Molecular docking techniques have demonstrated how these natural products interact with human serum albumin (Patil & Rohane, 2021; Bugnon *et al*., 2024).

C. 2D plot generation of Protein-ligand interaction for human serum albumin and flavonoids

By using Discovery studio visualizer software (Jejurikar & Rohane, 2021), four 2D interaction plots of human serum albumin and four flavonoids interactions, are studied to elucidate their types of bindings interactions and amino acid residues of human serum albumin which are involved in flavonoids binding.

Results and Discussion

A. UV spectrophotometric absorption curve for mango extract

With the ethanolic sample of himsagar mango pulp, UV-spectrophotometric screening has been completed within the range of 200-450 nm. The peaks and absorbance are noted and the presence of the four flavonoids has been identified in mango sample.

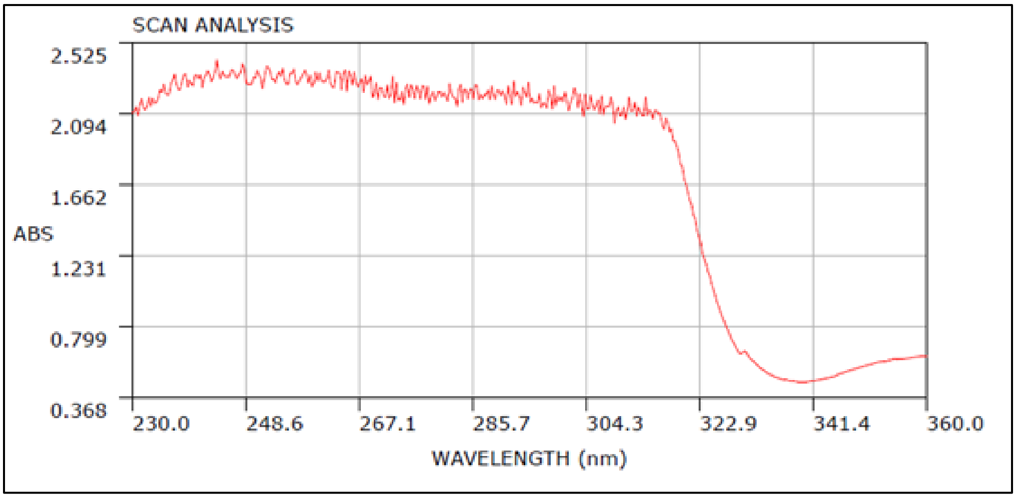


Figure 3: UV Spectrophotometric Absorption Curve for Mango Extract *(Source: PubChem)*

B. Observation of absorption maxima after addition of the UV shift reagent sodium acetate

In presence of UV shift reagent such as sodium acetate, a bathochromic shift is observed in in the ethanolic extract, of himsagar mango sample (as shown in Table 1) and the existence of 5-Hydroxyflavone, 7-Hydroxyflavone and 5,7-Dihydroxyflavone in himsagar sample is confirmed.

Table 1: *Absorption Band in Presence of Sodium Acetate*

Sample	Band Obtained with UV Shift Reagent: Sodium Acetate	Inference
5 (Himsagar sample)	295 (BAND II)	The bathochromic shift from 263 nm to 295 nm confirm the presence of 5-Hydroxyflavone, 7-Hydroxyflavone and 5,7-Dihydroxyflavone

C. Molecular docking study of plasma proteins with flavonoids present in mango extract

The molecular docking study of human serum albumin (PDB ID 6M4R) with four flavonoids such as 5-Hydroxyflavone, 7-Hydroxyflavone, 5,7-Dihydroxyflavone and kaempherol-3-glucuronide for binding affinity estimation has been conducted. The binding energies, ΔG

(Kcal/mol) and different parameters for binding energy calculations are shown in Table 2.

***Table 2:** The Binding Energies, ΔG (kcal/mol) and Different Parameters for Docking Structures*

Docking Structure	**ΔG (Kcal/ mol)**	**ΔG-electro (Kcal/ mol)**	**ΔG-vdw (Kcal/ mol)**	**ΔG-ligand solvent polar (Kcal/ mol)**	**ΔG-ligand solvent non-polar (Kcal/ mol)**	**ΔG-protein solvent polar (Kcal/ mol)**	**ΔG-protein solvent non-polar (Kcal/ mol)**	**ΔG-component solvent polar (Kcal/ mol)**	**ΔG-component solvent non-polar (Kcal/mol)**
1. Albumin _Primuletin (Cluster 0, Element 0)	-6.90	0.0	-30.61	-5.76	5.33	-4343.73	419.991	-4339.64	418.769
2. Albumin _7-OH flavone (Cluster 13, Element 1)	-6.98	0.0	-40.82	-7.92	5.35	-4343.73	419.991	-4326.3	418.107
3. Albumin _Chrysin (Cluster 0, Element 4)	-7.05	0.0	-32.98	-8.32	5.84	-4343.73	419.991	-4340.62	419.058
4. Albumin _Kaempherol-3-glucuronide (Cluster 1, Element 3)	-8.87	0.0	-64.64	-23.72	10.55	-4343.73	419.991	-4329.68	419.203

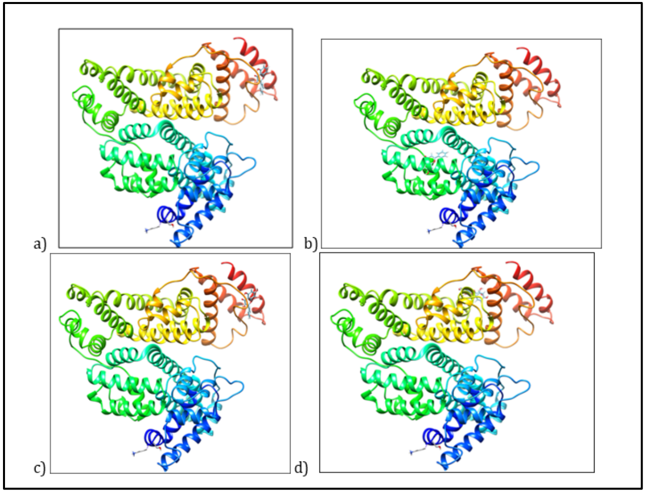


Figure 4: Molecular Docking Structures of Human Serum Albumin and Four Flavonoids: A) Molecular Docking Structure of Albumin (Alpha Chain) with Primuletin; B) Molecular Docking Structure of Albumin (Alpha Chain) with 7-Hydroxy Flavones; C) Molecular Docking Structure of Albumin (Alpha Chain) with Chrysin; D) Molecular Docking Structure of Albumin (Alpha Chain) with Kaemferol-3-Glucuronide

Molecular docking study (Bugnon *et al*., 2024) shows that the hydroxylation on 5 and 7 position increases the binding affinities of flavones towards human serum albumin. Glycosylation on position 3 of kaempherol-3-glucuronide also increases the binding affinity for human serum albumin. Different binding sites of human serum albumin with four flavonoids are shown in Figure 4.

D. 2D plot generation of Protein-ligand interaction for human serum albumin and flavonoids

From 2D plot generation study (Jejurikar & Rohane, 2021) of protein-ligand interaction for human serum albumin (HAS) and four flavonoids present in himsagar mango, shows that hydrogen bonds, Pi-alkyl, Pi-Pi T shaped and Van der Waals interactions play significant roles in binding flavonoids to HAS (Figure 5).

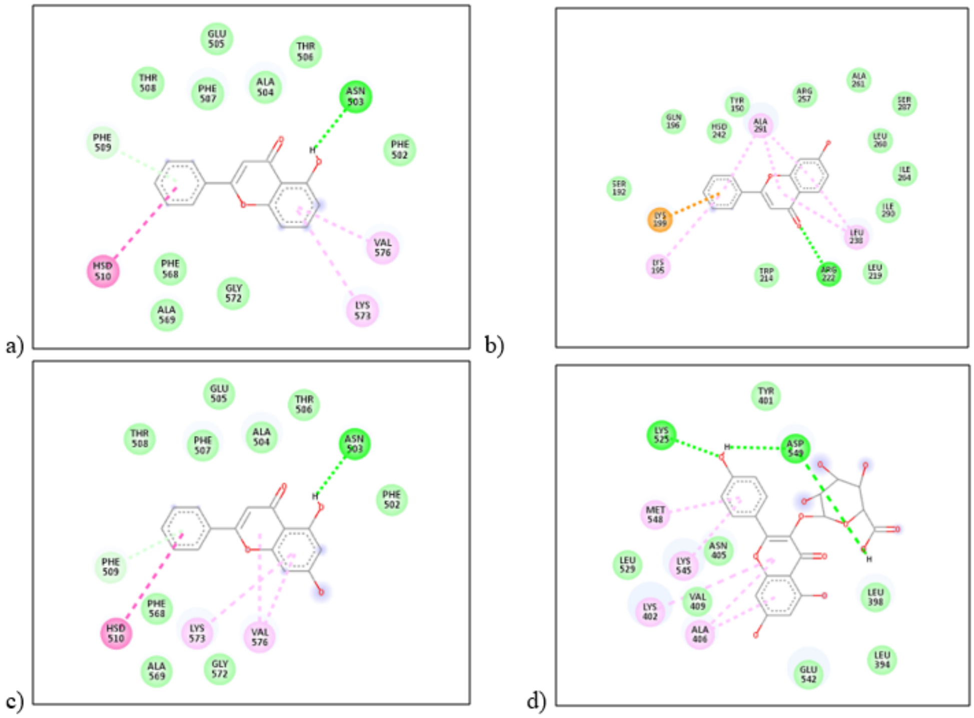


Figure 5: Generation of 2D Plot of Protein-Ligand Interaction for Human Serum Albumin and Flavonoids: a) Molecular Docking Structure of Albumin (Alpha Chain) with Primuletin; b) Molecular Docking Structure of Albumin (Alpha Chain) with 7-Hydroxy Flavones; c) Molecular Docking Structure of Albumin (Alpha Chain) with Chrysin; d)Molecular Docking Structure of Albumin (Alpha Chain) with Kaemferol-3-Glucuronide

The hydroxylation on 5 and 7 positions of A ring of flavone structure increases the affinities of ligands towards human serum albumin protein. Apart from the hydroxylation on 5 and 7 positions, the glycosylation on 3 position of C ring structure of flavone residue, also causes affinity induction for the same protein. The molecular docking study reveals that, in addition to hydrogen bonds, Pi-alkyl, Pi-Pi T-shaped, and Van der Waals interactions (Figure 5) also play significant roles in the binding of flavonoids found in mango pulp to human serum albumin.

Discussion

Drugs, fatty acids, vitamins and minerals, bilirubin, metabolites, and amino acids are among the endogenous and exogenous substances that human serum albumin (HAS) transports in blood (Varshney *et al*., 2010; Siddiqui *et al*., 2021; Leboffe *et al*., 2020). HSA's remarkable capacity to reversibly bind a variety of medications in plasma (Tayyab & Feroz, 2021) allows it to regulate their pharmacokinetics, osmotic pressures, and distribution patterns to distinct target tissues during plasma circulation (Zhivkova, 2015; Fanali *et al*., 2012). On the other hand, weak binding has been linked to poor drug absorption, delayed drug delivery rates, and delayed drug reach of action sites, while strong binding has been linked to an increase in release time and a subsequent decrease in the therapeutic values of drugs. The preferred model protein for researching the physiochemical and as well as biophysical behaviors of drug transports to target tissues is HSA, due to its moderate binding capacity (Kratz, 2008; Rahimizadeh, Yang & Lim, 2020).

A single polypeptide chain comprising 585 amino acid residues in three structurally related domains (I, II, and III) forms the basis of human serum albumin, which is divided into two subunits and joined by 17 disulfide bonds (Kragh-Hansen, 2016; Park *et al*., 2021). The polypeptide chain creates a structure that resembles a heart and has a thickness of 30 Å and approximate dimensions of 80×80×80 Å3. In the three structurally homologous domains (I, II, and III), approximately 67% of HSA is composed of α-helices, with no β-sheets (He & Carter, 1992; Belinskaia *et al*., 2020). There are ten helices in each domain; helices 1-6 make up sub-domains A, and helices 7–10 make up sub-domains B. The sub-domains IIA and IIIA contain two hydrophobic pockets where aromatic and heterocyclic ligands bind. The sub-domain interfaces, IIIA, IIIB, and IB are home to seven binding sites for fatty acids. Sudlow 1 and Sudlow 2 are the names of the two main binding sites found in subdomains II and III. For HSA, a number of additional binding sites have been found (Fig. 6) (Salem *et al*., 2019; Wang *et al*., 2022).

Using in-silico molecular docking, it was discovered that HAS has a moderate binding capacity when compared to compounds like primuletin (-6.90 Kcal/mol) and kaempherol-3-glucuronide (-8.87 Kcal/mole). Chrysin selectively exhibits exothermic binding on six binding sites, with binding energies ranging in −7.05 Kcal/mol. With a binding energy of −6.98 kcal/mol, 7 hydroxy flavone exothermally bound to a new large pocket on subdomain IIA (Sudlow 1).

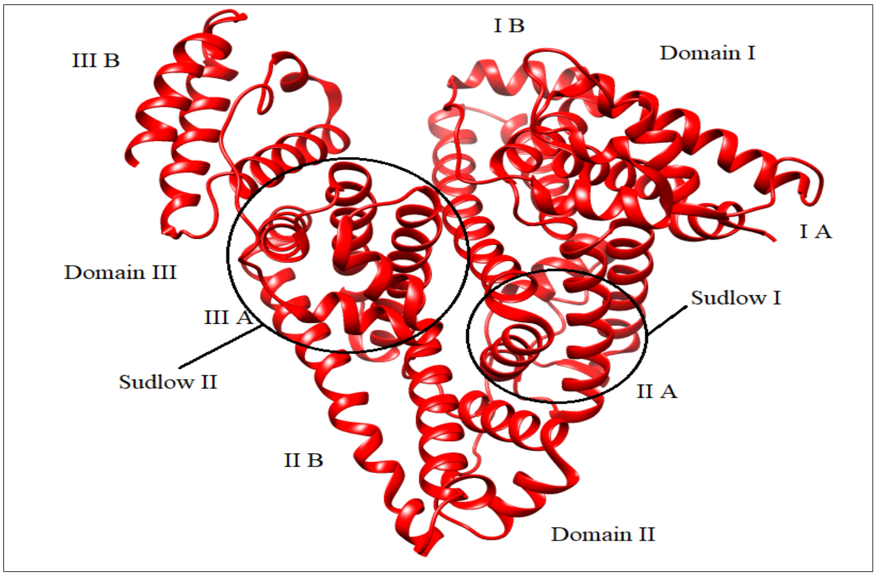


Figure 6: Domains, Subdomains and Binding Sites of Human Serum Albumin

Conclusion

These findings supported the formation of stable HSA complexes involving kaempherol-3-glucuronide and 7 hydroxy flavones. They also advanced our knowledge of the binding properties of these compounds, including their affinities towards HSA, binding sites, mode of bindings, and non-covalent interactions involved in binding, as well as the structural alterations of HSA that occur during interactions. Strong binding between kaempherol-3-glucuronide and 7 hydroxy flavone has been linked to longer release times and a subsequent decline in the therapeutic benefits of medications, whereas weak binding of primuletin, has been linked to slower drug absorption, delayed delivery rates, and delayed action site reach. It has been demonstrated through molecular docking studies that HSA is capable of solubilizing and transporting chrysin compounds through blood with a moderate binding affinity to target tissues. This information is important for ascertaining the pharmacological characteristics of the four phytochemical compounds and their future development as anticancer therapeutic agents.

Acknowledgment

The authors would like to express their deepest gratitude to the Principal, Professors and other staffs of Biochemistry Department, for their motivation and support throughout this research.

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doi: 10.31674/book.2024scibe.010

Exploring “Jhora Fishery”: A Study from Darjeeling, West Bengal, India

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Abstract

Introduction: The Jhora fishery, a traditional and sustainable fish farming practice prevalent in the Darjeeling region, utilizes the natural streams (Jhoras) flowing from the Himalayan foothills. This work aims to provide a holistic understanding of the evolution and status of Jhora fisheries, elucidating the need for sustainable management strategies to ensure their preservation and resilience. **Methods:** The review compiles data from various sources, including academic journals, government reports, and local case studies. Field observations and interviews with local fishermen were conducted to gain firsthand insights. **Results:** Findings indicate that the Jhora fishery supports a diverse range of fish species, contributing to the region's biodiversity. The practice enhances food security and provides a significant source of income for local communities. Ecologically, Jhora fishery helps maintain water quality and ecosystem balance. However, Jhora fishery is facing a number of challenges due to water pollution, climate change, and modernization. **Conclusion:** Despite facing modern challenges, with proper management and conservation efforts, Jhora fishery can continue to thrive, preserving both the ecological and socio-economic fabric of the region. In a nutshell, Jhora fishery in Darjeeling exemplifies a harmonious relationship between humans and nature, fostering sustainable development. There are challenges that need to be mitigated through policies aimed at enhancing traditional knowledge, improving resource management and reducing other threats to ensure the longevity of this indigenous practice.

Keywords: *Darjeeling; Fish Species; Government Initiative; Jhora Fishery*

Introduction

The region often referred to as the "Queen of the Hills" for its breathtaking beauty and renowned tea culture, Darjeeling is situated in the northern part of West Bengal, India. Nestled at an elevation of 6,700 feet, Darjeeling spans from 27°13'N to 26°27'N latitude and 88°53'E to 87°59'E longitude.

Darjeeling's landscape is adorned with numerous streams, locally known as "Jhora," a term derived from the Nepali language meaning "spring water" and "Jharna" in

Bengali. Jhoras may be of two types: perennial Jhora, which flows throughout the year, and seasonal Jhora, which is dependent on rainfall patterns.

The cold temperate climate and year-round water availability in perennial Jhoras have fostered the cultivation of cold-tolerant exotic carps, colloquially referred to as "Jhora Fishery." This is the first of its kind in India. It is a traditional way of fish culture (Sarma, 2015) and this practice has become a significant source of livelihood for the local communities inhabiting the Darjeeling hills.

Despite its importance, detailed information regarding Jhora fishery in Darjeeling has been scarce. Therefore, a comprehensive study was conducted to provide detailed insights into the Jhora fisheries in the Darjeeling-Kalimpong region of West Bengal. This research involved a thorough analysis of both primary and secondary data. Primary data were gathered through field visits and surveys conducted in the Darjeeling and Kalimpong (Pedong region) areas during the period of 2021-2022.

By delving deeper into the intricacies of Jhora fisheries, this study aims to shed light on this vital aspect of genesis, management and constrains of Jhora fishery. The support delivered by the government is also documented here.

Historical Perspective

The history of hill stream fisheries in Darjeeling can be traced back to indigenous fishing practices deeply embedded in local cultures and traditions. Early settlers relied on these streams for sustenance, and fishing techniques evolved over generations, reflecting a profound understanding of aquatic ecosystems. Colonial influences introduced modern fishing practices, altering traditional management systems and setting the stage for subsequent changes in Jhora fisheries dynamics. The idea of fish culture in Jhora ponds in the Darjeeling Kalimpong region of West Bengal came into a structured form about 40–50 years ago (Lepcha, Prithwiraj Jha & Sudip Barat, 2003). The initiative was taken by the Department of Fisheries, Govt. of West Bengal and Darjeeling Gorkha Hill Council in around 1981–1986 in the Kalimpong subdivision of Darjeeling district. The Fisheries Department set up nine small ponds, each about 13 sq m, that were fed by perennial springs called Jhora at different altitudes to study fish growth. The economically important fish that could thrive in the cold climatic conditions were selected. Following nine months of proper management, edible fish of good size were obtained from this Jhoras. Encouraged by the success, the fisheries department launched such a fishery on a much larger scale, with 50% subsidy assistance from the government for the beneficiaries. Since then, many Jhora fishery units have been constructed in this area by individuals as well as various fish farmer development agencies.

Site selection for Jhora fishery

Key factors to consider in selecting an ideal site for a Jhora fishpond include topography, water availability, and soil quality. Optimal locations typically feature flat or gently sloping terrain, minimizing the risk of flooding and landslides. In regions like Darjeeling, where perennial hill springs are abundant, setting the pond near one ensures a constant water supply. A running water system is essential for trout culture. It is necessary to arrange alternative water sources during periods of drought. Clay-loamy soil is ideal for such ponds as it minimizes seepage and leakage while maintaining soil fertility. Additionally, for ease of management, it's advantageous to construct the pond near a household or within a vegetable garden, commonly referred to as kitchen ponds. This proximity enhances accessibility and facilitates day-to-day maintenance tasks.

Pond Construction

Jhora ponds come in various shapes and sizes, including oval, round, rectangular or square, with an average area ranging from 15 to 20 square meters. However, to accommodate more extensive fish farming operations, larger ponds are currently under construction. The depth of these ponds usually ranges from 0.8 to 1.0 metres, although variations may occur depending on the cultured species (Jha, Barat & Lepcha, 2003; Jha, Barat & Lepcha, 2004).

The pond depth is very crucial, as extremely deep ponds can result in very low water temperatures, while very shallow ponds make fish more susceptible to predation. Additionally, the bottom of the pond should slope gently towards the outlet, typically at around 0.2%, to ensure proper water circulation and drainage. Both overflow and complete drying are avoided. Usually, bamboo grating or a wire net guard the inlet and outlet to prevent fish from escaping. An ideal Jhora pond needs a slow, continuous flow of water.

Types of Jhora ponds

In Darjeeling Kalimpong region different types of Jhora ponds, each offering distinct characteristics and construction methods are found.

(i) General/ Normal Pond: These ponds feature muddy embankments surrounding them entirely.

(ii) Mud Bottom Pond: These ponds have a muddy bottom, while the embankments on all four sides are made of concrete.

(iii) Cemented Bottom Pond: In these ponds, the bottom is covered with a cement mortar mixture, providing a more solid foundation.

(iv) Total Cemented Pond: This type involves constructing both the bottom and walls (embankments) using materials such as rods, stones, gravel, or bricks.

Fish species selection, stocking management and feeding

A prudent selection of compatible, fast-growing species is crucial for maximizing fish production. In the Darjeeling Hill area, more than 120 fish species have been documented, some of which thrive in torrential streams and demonstrate remarkable adaptation to clinging to rocks in swift currents. These indigenous and exotic species are chosen for commercial culture in the Jhora based on criteria such as growth performance, maturation, fecundity, and breeding. The commonly selected species include Golden Himalayan Mahasol (Tor putitora), Katli (Neolissochilushexagonolepis), Asala (Schizothoraxrichardsonii), Kalabans (Labeodero), goldfish (Carassius auratus), Common Carp (Cyprinus carpio), Grass Carp (Ctenopharyngodonidella), and Silver Carp (Hypophthalmichthys molitrix).

However, the cultivation of fish in the Jhora has not been extensively researched, and stocking combinations and densities are often chosen on an ad-hoc basis. Most farmers tend to prefer monoculture when stocking indigenous fish species.

The stocking density is usually about 15000–20000 fingerlings of 6–8 cm per hector. The cultural period runs from March to October. Low temperatures adversely affect the growth of the fish; hence, stocking times are adjusted in areas with very low temperatures. Common carp and grass carp exhibit much higher growth rates compared to Indian major carps.

In the Jhora fishery, there is a predominant focus on supplementary feeding rather than pond manuring, as commonly practiced in traditional aquaculture setups. This supplementary feeding regime involves the utilization of inexpensive and readily available waste products, such as slaughterhouse waste and grain waste. Additionally, alternative natural feeds like squash leaves, pumpkin leaves, and halhal leaves are used to nourish fish, particularly grass carp.

Recently, the Directorate of Coldwater Fisheries Research (DCFR) has initiated efforts to develop balanced, formulated feeds tailored specifically for cold-water fish species, with a particular emphasis on species like mahseer. This initiative aims to optimize the nutritional content of fish feeds to enhance fish growth and health while minimizing environmental impacts. By formulating feeds that meet the dietary requirements of cold-water fish, the DCFR aims to improve the efficiency and sustainability of Jhora fishery practices in the region.

This shift towards formulated feeds represents a promising step towards enhancing the productivity and profitability of Jhora fishery operations, while also promoting environmental sustainability. By utilizing balanced feeds, fish farmers can optimize feed utilization efficiency, reduce nutrient waste, and improve overall fish health and growth rates. Additionally, the adoption of formulated feeds may help to mitigate the reliance on unconventional feed sources, thereby addressing concerns related to food safety and environmental contamination. Overall, the development and adoption of balanced, formulated feeds signify a positive advancement towards enhancing the sustainability and productivity of Jhora fishery practices in the region.

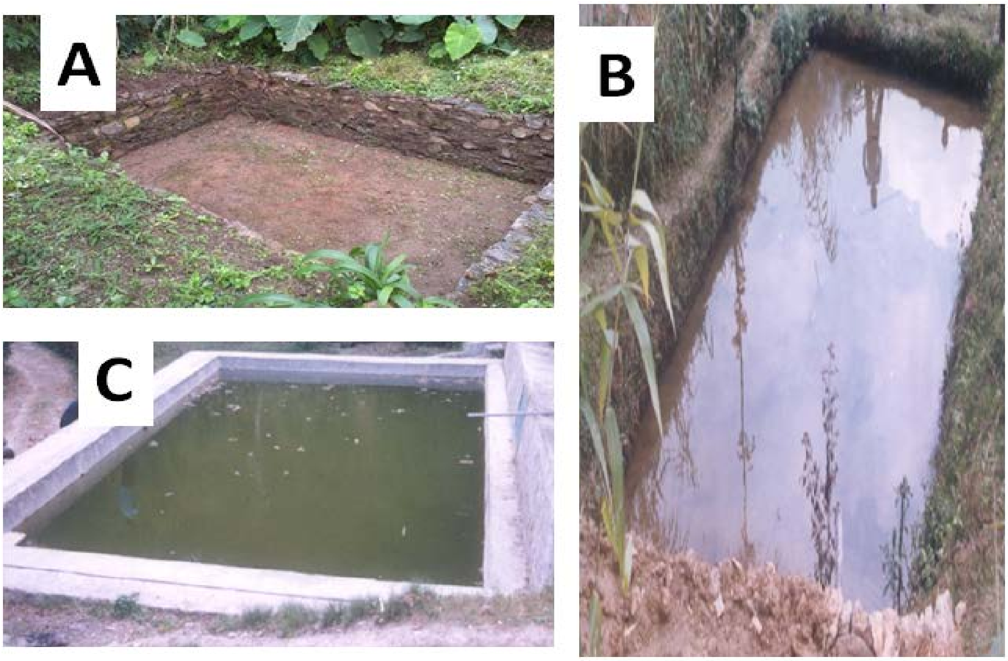
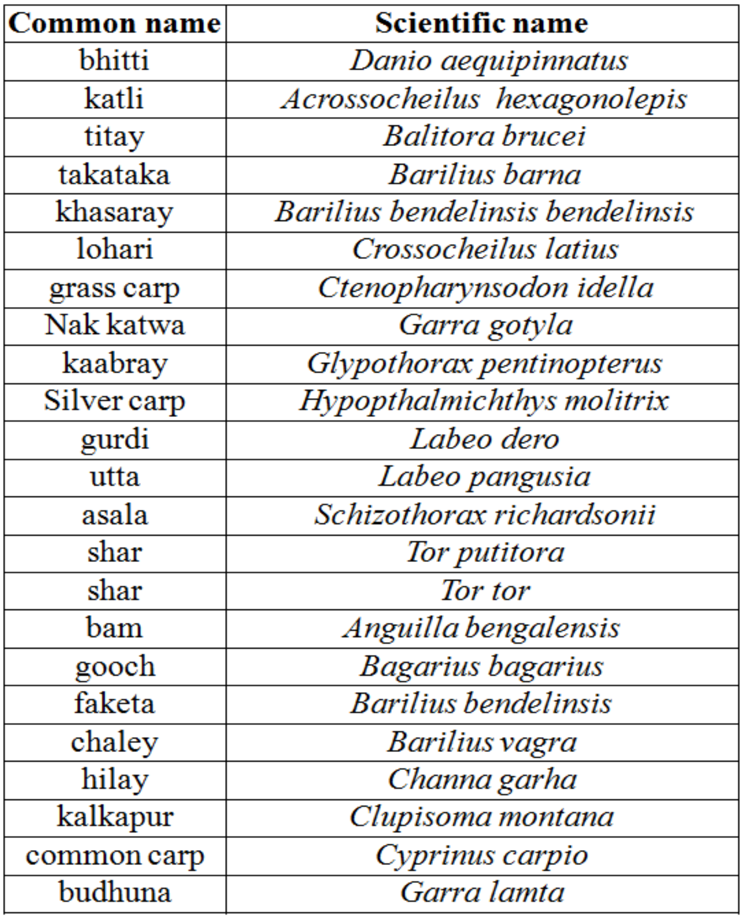


Figure 1: Jhora ponds. A: Normal Jhora pond without water. B. Normal Jhora pond with water, C: concrete Jhora pond

Socioeconomic Importance:

The Jhora fishery serves as a cornerstone of the socioeconomic landscape in Darjeeling's rural areas, deeply intertwined with the lives and livelihoods of local communities. Fishing in Jhoras represents a vital source of both protein and income for many households, particularly in remote and economically marginalized areas of Darjeeling. With limited access to alternative livelihood opportunities, residents often rely on the fishery as a primary means of sustenance and financial support. Fishermen rely on Jhora streams for food security, income generation, and cultural practices, reinforcing the integral connection between fisheries and community well-being. Moreover, the trade of indigenous fish species contributes to local economies and tourism, highlighting the economic value of Jhora fisheries.

Table 1: *Commonly cultured fishes in Jhora fishery*



Common name	Scientific name
bhitti	*Danio aequipinnatus*
katli	*Acrossocheilus hexagonolepis*
titay	*Balitora brucei*
takataka	*Barilius barna*
khasaray	*Barilius bendelinsis bendelinsis*
lohari	*Crossocheilus latius*
grass carp	*Ctenopharynsodon idella*
Nak katwa	*Garra gotyla*
kaabray	*Glypothorax pentinopterus*
Silver carp	*Hypopthalmichthys molitrix*
gurdi	*Labeo dero*
utta	*Labeo pangusia*
asala	*Schizothorax richardsonii*
shar	*Tor putitora*
shar	*Tor tor*
bam	*Anguilla bengalensis*
gooch	*Bagarius bagarius*
faketa	*Barilius bendelinsis*
chaley	*Barilius vagra*
hilay	*Channa garha*
kalkapur	*Clupisoma montana*
common carp	*Cyprinus carpio*
budhuna	*Garra lamta*

Constrains of Jhora fishery in Darjeeling kalimpong region:

Since 1981, Jhora fish farming has played a vital role in fostering economic opportunities for the economically disadvantaged community in Darjeeling's hilly terrain (Thapa *et al*., 2021). However, various challenges, as outlined below, have hindered its efficacy.

Technical and Infrastructural Challenges

The primary obstacles encountered by Jhora farmers in the Darjeeling region include a lack of access to quality feed and seeds. Insufficient hatcheries in the area compel farmers to procure fish seeds from neighbouring districts like Jalpaiguri. A similar finding was previously reported, stating that limited or non-availability of good seed is the top infrastructural constraint in Meghalaya (Das, 2018; Niangti *et al.,* 2020).

Additionally, farmers lack modern knowledge and techniques in fish farming, leading to issues such as water seepage, maintenance difficulties, and high mortality rates. Transportation challenges, inadequate marketing facilities, and an erratic power supply further exacerbate infrastructural constraints. Despite these hurdles, the Fisheries Department of the West Bengal Government has initiated efforts to provide technical guidance and ensure the availability of feed and seeds to farmers (Thapa *et al.,* 2023)

Environmental Constraints

Predation by birds, snakes, and other animals poses a significant threat to small fish in Jhora ponds. (Thapa *et al.,* 2023) Although measures like leaf netting have been employed to mitigate this issue, natural disasters such as frequent landslides during the monsoon and pollution from waste dumping near Jhora exacerbate environmental constraints.

Economic Challenges

Jhora farmers face significant economic hurdles, including a lack of self-financing, high initial investments, and limited financial support. The high costs of feed (Mishra *et al.,* 2022) and seeds add to the financial burden for poor farmers in different parts of West Bengal, including Darjeeling. Subsidies, primarily accessible to Scheduled Tribe category farmers under the Tribal Sub-Plan, have left other farmers deprived of financial assistance (Thapa *et al.,* 2023). However, the government now extends aid in the form of fingerlings and fish feed to alleviate economic constraints. Along with this, as previously also reported (Rahaman, Bera & Ananth, 2013; Das *et al.,* 2018) had reported theft/poaching as the most important constraint of fish production in West Bengal and Assam., theft/poaching is a big constrain in fish farming in West Bengal and Assam.

Government initiatives and support

Since the inception of Jhora fisheries, which significantly aid protein consumption among the economically disadvantaged communities in the hills, the Government of West Bengal has spearheaded efforts to promote Jhora fisheries practices across the Darjeeling Himalayan region. The Jhora fishery, unique to the cold-water hilly terrain, stands as a pioneering endeavour in India's fisheries landscape. The Jhora fishery had developed significantly from 1996 to 2013 (Ghosh, Mohapatra & Roy, 2017)

Under the West Bengal Accelerated Development of Minor Irrigation (ADMI) project of 2018, the state government identified and supported over 500 financially vulnerable locals by constructing tanks and supplying them with 150 fingerlings of tilapia, common carp, grass carp, and rohu. However, due to the inability of certain species, like tilapia and rohu, to adapt to the extreme cold, this initiative faced setbacks.

In response, a novel approach termed the 'Kalimpong model' emerged to mitigate fish mortality in jhora farming. This model involved the construction of poly tank-houses made of iron bars and blue polythene sheets, housing PVC tanks within. While cemented tanks developed cracks over time, the polyhouse tanks proved resilient.

The Department of Fisheries, Aquaculture, Aquatic Resources, and Fishing Harbour, Government of West Bengal, now extends support in terms of providing fingerlings and fish feed. Furthermore, the Government of India has integrated the Jhora fisheries of the hill districts of West Bengal into the Blue Revolution scheme (2016) under the Central Sector Scheme on integrated development and management of fisheries, which is now part of the larger framework for fisheries development under PMMSY.

As per the West Bengal Inland Fisheries Policy of 2023, issued by the Government of West Bengal, initiatives have been outlined to enhance cold water pisciculture in the hilly regions of Darjeeling and Kalimpong districts.

One of the key strategies involves the utilization of existing natural ponds known as "Jhoras," which have inlets and outlets, for cold water pisciculture. The government has pledged to provide 40 percent of financial assistance to support this endeavour.

Furthermore, the promotion of re-circulatory Aquaculture Systems (RAS) is prioritized, with progressive farmers being encouraged to adopt this advanced aquaculture technique. The government is committed to helping up to 40 percent to facilitate the implementation of RAS among interested farmers.

Additionally, the policy emphasizes the establishment of hapa, which are small rearing or grow-out ponds, for the purpose of raising fingerlings for table fish. Financial aid of up to 40 percent will be provided to support the construction of such hapas and the associated activities.

These initiatives underscore the government's commitment to promoting sustainable aquaculture practices and supporting the development of the fisheries sector in the hilly regions of Darjeeling and Kalimpong.

Conclusion

In this work, information regarding the history of the Jhora fishery, its management and feeding, constraints and government initiatives has been discussed in detail. In conclusion, Jhora fisheries in Darjeeling represent invaluable natural resources that require careful stewardship and sustainable management to safeguard their ecological integrity and socio-economic contributions. By acknowledging the historical legacy and socio-economic significance of Jhora fisheries, stakeholders can work together to address existing challenges and chart a path towards a more sustainable and resilient future.

Acknowledgment

The author would like to acknowledge the Jhora fish farmers for providing the information and the Principal, Sree Chaitanya College, Habra, India

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doi: 10.31674/book.2024scibe.011

Metal Organic Frameworks (MOFs): An Overview of Synthesis Methods

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Abstract

Metal organic frameworks (MOFs) are crystalline porous organic and inorganic hybrid materials composed with metal centers and organic linkers, creating one-, two-, or three-dimensional networks with high porosity and surface areas that make the compounds very useful in adsorption/separation, catalysis, sensing luminescence, and biomedical applications. This chapter presents a comprehensive, up-to-date overview of the synthesis methods, including conventional solvothermal/hydrothermal synthesis, microwave-assisted, electrochemical, sonochemical, and mechanochemical synthesis of currently available MOFs with specific examples. Recently, newly attempted ionothermal, dry-gel conversion, and microfluidic synthesis methods are also utilized for synthesizing more environmentally benign MOFs. In most of the methods, solvents play an important role, whereas mechanochemical synthesis involves solvent less process or uses a minimum amount of solvent. Most of the MOFs have been synthesized by using aromatic ligands as linkers in conjuction with metal nodes of transition metal ions, alkaline earth metal ions, rare earth metal ions and nitrate, sulphate, acetate, chloride and oxides of metal.

Keywords: *Electrochemical; Mechanochemical; Metal Organic Frameworks (MOFs); Microwave; Solvothermal/Hydrothermal; Sonochemical*

Introduction

In the last few decades, metal organic frameworks (MOFs) have attracted great attention from scientists for their wide range of applications in energy storage, gas adsorption, hydrocarbon adsorption and separation, sensors, catalysis, magnetic and electronic devices, drug delivery, cancer therapy, photoluminescence, etc. due to their high surface area, high pore volumes, and high metal content (Furukawa *et al.,* 2013; Safaei *et al.,* 2019; Chattopadhyay, Mandal & Maiti, 2024). MOFs are crystalline materials made up of organic and inorganic hybrid materials that are formed by joining metals with organic linkers. The organic linkers are called organic secondary building units (SBU), whereas the metal centers act as joints in the MOF structure. The structure has high porosity due to the extended size of inorganic metals and the length of the linker used (Lee, Kim & Ahn, 2013; Wang, 2017). Different types of metals and ligands are used to synthesize MOFs as secondary building blocks for their flexibility in physical and chemical properties. The atomic-level structural uniformity in network topology and geometry, as well as the excellent chemical stability of MOFs, make them have great potential for their various applications. Different first-row transition metals, such as Co^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+} are used as joints in the formation of MOFs compounds. The synthesis of MOFs also incorporates alkaline earth metal ions and rare earth metal ions (Dey *et al*., 2014). Since MOFs compounds are dependent on the choice of metal ions and ligands, different ligands are used to create large volume and high porosity in the cavity of the MOFs. Sometimes, nitrate, sulphate, acetate, chloride and oxides of metal are also used as precursors for the synthesis of MOFs (Soni, Bajpai & Arora, 2019). The reactivity of the pores is enhanced by incorporating organic units and metal organic complexes through reactions with linkers in post-synthetic modification of MOFs. This chapter comprehensively reviewed different synthesis methods for MOFs with suitable examples (Table 1).

Table1: Some selective MOFs with their synthesis methods

Synthesis method	MOF	Metal salt	Ligand	Solvent	Conditions	Ref
Slow evaporation	$[Cu(pya)_2(H_2O)_2]_n$	$Cu(ClO_4)_2\cdot 6H_2O$	Hpya	$MeOH/H_2O$	7 days	Du, Li & Zhao, 2006
	$[Hg(pya)Cl]_n$	$HgCl_2$	Hpya	$MeOH/H_2O$	21 days	Du, Li & Zhao, 2006
	MOF-Co/PDA	$CoCl_2\cdot 6H_2O$	PDA	H_2O/ Pyridine	14 days	Murinzi, Hosten & Watkins, 2017
Slow Diffusion	$Zn_3(BDC)_3\cdot 6CH_3OH$	$Zn(NO_3)_2\cdot 6H_2O$	H_2BDC	DMF/Methanol/ n-propanol	12 days	Li *et al.,* 1998
	$[Ag(dpma)(H_2O)](NO_3)$	$AgNO_3$	dpma	$MeOH/H_2O$	14 days	Wu, Chao & Zhong, 2013
Solvothermal	MOF-5	$Zn(NO_3)_2\cdot 6H_2O$	H_2BDC	DMF/Chlorobenzene	120ºC, 2 days	Eddaoudi *et al.,* 2002
	$[Mg_4(bdc)_4(DEF)_4]_n$	$Mg(NO_3)_2\cdot 6H_2O$	H_2BDC	DEF	120ºC, 18 hrs	Biswas *et al.,* 2016
	UiO-66	$ZrCl_4$	H_2BDC	DMF	120ºC, 2 days	Abid *et al.,* 2012
	IRMOF-3	$Zn(NO_3)_2\cdot 4H_2O$	$H_2BDC-NH_2$	DEF	85ºC, 4 days	Millward & Yaghi, 2005
	Bi-TMA	$Bi(NO_3)_3\cdot 5H_2O$	H_3TMA	DMF/ Methanol	120ºC,1 day	Nguyen *et al*., 2021
Hydrothermal	HKUST-1	$Cu(NO_3)_2\cdot 3H_2O$	H_3BTC	$EtOH/H_2O$	180ºC, 12 hrs	Chui *et al.,* 1999
	Hf-MOF-808	$HfClO_2$	H_3BTC	H_2O/ CH_3COOH	100ºC, 37 hrs	Bohigues *et al.,* 2021
Microwave-assisted	UiO-66	$ZrCl_4$	H_2BDC	Acetone	80ºC, 6 hrs	Yahia *et al.,* 2024

	MOF-808	$ZrCl_4$	H_3BTC	Acetone/ H_2O	95ºC, 5 hrs	Yahia *et al.,* 2024
	Cr-MIL-100	Metallic Cr with HF	H_3BTC	H_2O	220ºC, 4 hrs	Jhung, Lee & Chang, 2005
	HKUST-1	$Cu(NO_3)_2\cdot 3H_2O$	H_3BTC	EtOH	140ºC, 1 hr	Seo *et al.,* 2009
	ZiF-8	$Zn(NO_3)_2\cdot 6H_2O$	HMeIm	DMF	140ºC, 3 hrs	Park, Park & Jhung, 2009
	Fe-MIL-53	$FeCl_3\cdot 6H_2O$	H_2BDC	DMF	150ºC, 10 mins	Horcajada *et al.,* 2006
	Co-MOF-74	$Co(NO_3)_2\cdot 6H_2O$	H_4DHBDC	DMF/ EtOH/H_2O	130ºC, 1 hr	Cho *et al.,* 2012
Electrochemical	HKUST-1	Bulk Cu plate	H_3BTC	MeOH	12-19 V, 1.3A, 150 mins	Mueller *et al.,* 2006
	Al-MIL-53	$Al(NO_3)_3\cdot 9H_2O$	H_2BDC	H_2O/DMF	90ºC, 10 mA	Martinez Joaristi *et al.,* 2012
	Al-MIL-53-NH_2	$Al(NO_3)_3\cdot 9H_2O$	H_2BDC-NH_2	H_2O/DMF	90ºC, 10 mA	Martinez Joaristi *et al.,* 2012
	Mn–DABDC	Mn strips	DABDC	DMF/H_2O	20-22ºC, 70 mA, 2 hrs	Asghar *et al.,* 2021
	Fe-MIL-101	$FeCl_2$	H_2BDC/ $TBAPF_6$	DMF	0.75 V, 14h	Wu *et al.*, 2021
Sonochemical	MOF-5	$Zn(NO_3)_2\cdot 6H_2O$	H_2BDC	NMP	60W, 30 mins	Son *et al.,* 2008
	Mg-MOF-74	$Mg(NO_3)_2\cdot 6H_2O$	H_4DHBDC	DMF/ EtOH/H_2O	500W, 1 hr	Yang *et al.,* 2012
	MIL-53(Fe)	$FeCl_3\cdot 6H_2O$	H_2BDC	DMF	70ºC, 2 hrs	Lee, Ahn & Kwak, 2022
Mechanochemical	HKUST-1	$Cu(OAC)_2\cdot 6H_2O$	H_3BTC	-	15 mins	Pichon & James, 2008
	ZIF-8	ZnO	HMeIm	DMF	5-60 mins	Beldon *et al.,* 2010
	ZIF-4	ZnO	HIm	DMF	5-60 mins	Beldon *et al.,* 2010
	MOF-74	ZnO	H_4DHBDC	DMF	2-90 mins	Beamish-Cook *et al.,* 2021

Hpya = 4-pyridylacetic acid, PDA = 2,6-pyridinedicarboxylic acid, H_2BDC = 1,4-benzenedicarboxylic acid, dpma = Di(3-pyridylmethyl)amine, H_2BDC-NH_2 = 2-amino-1,4-benzenedicarboxylic acid, H_3TMA = trimesic acid, H_3BTC=1,3,5-benzenetricarboxylic acid, HMeIm = 2-methyl imidazole, H_4DHBDC = 2,5-dihydroxy-1,4-benzenedicarboxylic acid, DABDC = 2,5-diaminoterephthalic acid, HIm = imidazole.

Methodology

Slow evaporation method

The slow evaporation method is a conventional method where the crystallization of MOFs starts at room temperature by evaporating solvents, making the solution more concentrated. The process needs no external energy, but the process is too slow to get the crystals. The process can be faster by using different solvents or mixtures of solvents that dissolve the starting reagents, and the low-boiling solvents evaporate more quickly. The major advantage is that the reaction takes place at room temperature (Du, Li & Zhao, 2006).

Slow diffusion method

The slow diffusion method is applied when it is difficult to get a single crystal of MOFs by mixing metal ions and ligand solutions at room temperature. The gentle, steady diffusion of two solutions of metal ions and ligands in appropriate portions of solvents forms single crystals over time as two layers of different densities of solvents diffuse to generate larger and better-quality single crystal at the interface of two solutions (Li *et al.,* 1998; Wu, Chao & Zhong, 2013). This method is useful for microcrystalline powder compounds that are not soluble.

Solvothermal/ hydrothermal synthesis

In solvothermal synthesis, the metal salt and organic linker are mixed in a solvent and heated in glass vials (low-temperature reactions), whereas for high-temperature reactions, Teflon lined auto-clave is used (Wang & Ying, 1999). When water is used as a solvent, the process is called hydrothermal synthesis. The boiling point of the solvents should be high for a solvothermal reaction, in which temperature, pressure, solvent composition, and reagent concentration are the important parameters to get the MOFs (Lee, Kim & Ahn, 2013). The most commonly used solvents are dimethyl formamide (DMF), diethyl formamide (DEF), dimethyl sulphoxide (DMSO), dimethylacetamide (DMA). Different mixtures of solvents are used to avoid the difficulties of dissolving the starting reagents.

Microwave-assisted synthesis

Microwave-assisted synthesis is a rapid process in which the energy is provided in the form of a microwave. It is generally useful in organic synthesis, but in recent times, nanoporous compounds have also been synthesised by using microwaves. In this process, the heating time is generally one hour for getting the nanosized crystals after heating the solution with microwave (Lee, Kim & Ahn, 2013). The alternative name of the process is microwave-assisted solvothermal synthesis for the preparation of MOFs. Fast crystallisation along with phase selectivity, particle size distribution, and morphological controls, are the major advantages of the process.

Electrochemical synthesis

Electrochemical synthesis involves anodic dissolution as a metal source instead of metal salts. Anodic dissolution is the electrosynthesis method in which a high anodic voltage or current is applied to the electrode immersed in supporting electrolytes and organic linkers and metal gets oxidised to metal ions and released into a solution containing organic linkers (Dey *et al.,* 2014; Ren & Wei, 2022). Mueller and co-workers (2006) introduced the process. The metal ions and the organic linker react on the surface of the electrode as a thin layer of MOF. Different factors, such as the nature of solvents, electrolyte concentration, applied voltage, electro deposition time etc. govern the crystallization process. Polar protic solvents play an important role in electrochemical synthesis, as the solvent ensures hydrogen generation and avoids the reduction of metal ions on the cathode. The nucleation of MOF crystals increases with increasing the rate of applied voltage and regulating the crystal size.

Sonochemical synthesis

Sonochemical synthesis is a rapid, efficient, and promising method in which high temperature and pressure are generated and high-quality MOFs are produced in a short period compared to other conventional methods, as ultrasonic waves can facilitate the nucleation and growth of MOFs in high energy conditions produced by the wave through cavitation (formation of bubbles, growth and collapse due to altering pressure) (Dey *et al.,* 2014). Sonochemical synthesis can produce narrow size distributions of MOFs and it is useful in different applications.

Mechanochemical synthesis

Mechanochemical synthesis is a process in which mechanical force is produced by milling or grinding solid starting materials and thus the chemical reactions proceed with minimal amounts of solvents or without solvents at all. The process is the most environment friendly methodology, as a minimum amount of toxic solvent is used or without using solvents, the reactions are most sustainable for the earth. The solid-solid reaction has potential advantages to get high amounts of MOFs (Stock & Biswas, 2012). However, in purification steps, solvents are used despite solvent-free or solvent less mechanochemical synthesis. This mechanochemical route is considerable interest for the construction of bonds through environment friendly process in modern synthetic chemistry.

Beside these methods as discussed above, Ionic Liquids (ILs) have attained great attention because of their unique properties such as excellent solvating properties as well as high thermal stability and easy recyclability and used as solvent for chemical synthesis (Himeur *et al.,* 2010; Pérez Fernández *et al.,* 2019; Azbell *et al.,* 2023). The majority of the researchers have used ILs derived from 1-alkyl-3-methylimidazolium. Other synthetic method Microfluidic MOF Synthesis (Bendre *et al.,* 2023) is also a continuous, faster and viable processes for MOF synthesis. Dry-gel conversion (DGC) synthesis method has also been used in the preparation of MOFs (Kim, Lee & Ahn, 2013).

Discussion

Different synthetic methods have been used in MOFs synthesis, most of them are liquid phase synthesis, where metal salts and ligand solutions or solvents are added to the mixture. Solvent plays an important role in determining the geometry and shape, i.e., the crystallization process for favouring thermodynamics and activation energy for the reaction process. The reactivity, solubility, stability constant etc. greatly influenced by the solvent used by the solvent used for a particular reaction (Dey *et al.,* 2014). Therefore, different solvents in the same ratio of reactants can proceed to form different MOFs. Researchers also attempted to synthesise MOFs in the solid phase, which is quicker and easier, but the success of obtaining a single crystal is comparatively low. Slow evaporation and slow diffusion methods are well suited for the researchers, but it takes a long time to get single crystals of MOFs, depending on the solvents used. Today, the solvothermal/hydrothermal method is quite common and convenient for synthesising an enormous number of MOF compounds (Table-1). Some of them are MOF-5 (Eddaoudi *et al.,* 2002), UiO-66 (Abid *et al.,* 2012), IRMOF-3 (Millward & Yaghi, 2005), HKUST-1 (Chui *et al.,* 1999). Microwave-assisted synthesis, electrochemical synthesis, and sonochemical synthesis are also used as alternatives to MOF synthesis (Dey *et al.,* 2014; Lee, Kim & Ahn, 2013). Cr-MIL-100 (Jhung, Lee & Chang, 2005) is the first MOF that has been synthesized via microwave method. HKUST-1 (Seo *et al.,* 2009), ZiF-8 (Park, Park & Jhung, 2009), Fe-MIL-53 (Horcajada *et al.,* 2006), Co-MOF-74 (Cho *et al.,* 2012), UiO-66 (Yahia *et al.,* 2024) and MOF-808 (Yahia *et al.,* 2024) are also well-known microwave-assisted MOFs. The process is very useful as both compounds have better CO_2 adsorption abilities. Several metal ions, such as Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+} containing MOFs have been reported using the microwave method. The first and most often electrochemically synthesized MOF is HKUST-1 or $Cu_3(BTC)_2$ (Mueller *et al.,* 2006). Al-MIL-53 (Martinez Joaristi *et al.,* 2012), Al-MIL-53-NH_2 (Martinez Joaristi *et al.,* 2012), Fe-MIL-101 (Wu *et al.,* 2021), and Mn-DABDC (Asghar *et al.,* 2021) are also synthesized by electrochemical method. Aluminium containing MOFs have been synthesized by using $Al(NO_3)_3.9H_2O$ as metal salt and 1,4-benzene dicarboxylic acid or 2-amino-1,4-benzene dicarboxylic acid or 1,3,5-benzenetricarboxylic acid as ligand. Using sonochemical irradiation, MOF-5 (Son *et al*., 2008) compounds (5-25 mm crystals) obtained in 1-methyl-2-pyrrolidinone (NMP) in 30 min, compounds are similar to the MOF-5 crystals that are obtained in solvothermal or microwave methods. Mg-MOF-74 (Yang *et al.,* 2012), MIL-53(Fe) (Lee, Ahn & Kwak, 2022) are also synthesized by sonochemical method. Using mechanochemical synthesis method, HKUST-1 was successfully obtained without using a solvent (Pichon & James, 2008). ZIF-8 was successfully synthesized by using ZnO and 2-methylimidazole in the presence of NH_4NO_3 in DEF solvent whereas ZIF-4 was successfully produced by using ZnO and imidazole in presence of $NH_4NCH_3SO_3$

using DMF as a solvent (Beldon *et al.,* 2010). MOF-74 was synthesized by using ZnO and 2,5-dihydroxy-1,4-benzenedicarboxylic acid in DMF solvent by mechanochemical process (Beamish-Cook *et al.,* 2021).

Conclusion

The porous coordination polymer or metal organic framework has been widely used in gas adsorption and desorption, separation, sensing, magnetism, catalysis etc. Different synthetic methods, such as slow evaporation synthesis, solvothermal/ hydrothermal synthesis, microwave-assisted synthesis, electrochemical synthesis, sonochemical synthesis and mechanochemical synthesis, have been applied to get porous crystalline MOFs. In most of the methods, solvents play an important role in the synthesis of MOFs as well as in deciding morphology of the MOFs. In solvothermal synthesis, the most common solvents are DMF, DEF, DMA, DMSO, ethanol/methnol, acetonitrile, and acetone, whereas in hydrothermal synthesis, water is used as solvent. MOFs having different morphology are obtained in same reaction condition with varying solvents as degree of deprotonation of organic linker is different in different solvents. Besides, reactions are greatly influenced by the temperature and pH of the reaction medium. The microwave-assisted synthesis of MOFs is comparable to that of conventional methods, but the progress of the reaction is very fast compared to hydrothermal methods. In the electrochemical synthesis method, there is no need to use metal salts, as metal ions are continuously supplied through anodic dissolution. Sonochemical synthesis involves homogeneous solution with formation and collapse of bubbles, termed acoustic cavitation, which produces high local temperature and pressure and results in a in a fine MOF crystal with a reduction in crystallization time. Mechanochemical synthesis, which is an environment-friendly method, produces a quantitative number of small MOFs in short reaction times and in this method, metal oxide is generally used as the starting material. In most cases, the solvent is minimized, or reaction is done without using a solvent. Using Ionic Liquids as a solvent, Microfluidic MOF Synthesis and Dry-gel conversion synthesis are now a days getting attention for more environmentally benign MOF synthesis. The reported methods are confined to very small-scale production with crystal structure analysis and the MOFs that were reported are mostly unstable except Zr-containing MOFs. Therefore, researchers should focus on producing large-scale stable crystals that will be highly demanded in industry.

Acknowledgement

The author expresses sincere thanks to Department of Biotechnology, Government of India, for the funding from DBT-STAR College grant under which this review project was conducted. They are also grateful to the Principal and the DBT-STAR Coordinator at Surendranath College, West Bengal, India for their support.

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doi: 10.31674/book.2024scibe.012

C-H Bond Activation in Five-Membered Oxa- and Aza-Heterocycles: Recent Applications of Rh-Catalysis

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Abstract

This review paper offers an insight into the topic by demonstrating the revolutionary effects and wide range of applications of rhodium chemistry in the carbon-hydrogen bond activation of and aza-heterocycles with 5 ring members. The author hopes to see the scientific community use these works on pyridine and oxazole derivatives to inspire further research and collaboration through an examination of recent developments and future opportunities in various subfields. This will promote a deeper comprehension of the limitless potential of chemistry to shape the world and overcome future challenges.

Keywords: *Aza-Heterocycle; C-H Activation; Oxa-Heterocycle; Rhodium Catalysis*

Introduction

In the scientific community, Chemistry has always played a central role in shaping the understanding of modern scientific advancements globally. It has always pushed the boundaries between the scientific realms to merge into one another and paved the pathway to understanding numerous complex protocols (Blakemore *et al*., 2018). From unveiling the molecular-level understanding of complex biological cycles to developing complex materials of unparalleled properties, chemistry has always emerged as the core subject to set a heavy footprint in that field (Campos *et al*., 2019). Among the various applications, scientific research and technological advancements, the role of transition metals in carbon-hydrogen bond activation has caught the attention of researchers with high level of interest recently (Lam, Wu & Yu, 2021). In this article, the author has highlighted plethora of applications of carbon-hydrogen activation by Rh accelerator in heterocyclic substances and the potential opportunities they offer for the future. The author also dug into the current breakthroughs and significant discoveries in the field of organometalics. Heterocyclic derivatives, especially five-membered oxa- and aza-heterocycles, are widely used in many different fields of science and industry. Whether it's inventing novel drugs to treat illnesses, producing environmentally friendly materials to lessen their influence on the environment, or coming up with energy storage options for a sustainable future. The author's goal is to highlight the last decade's outstanding developments in the array of organometallic chemistry derivatives, from physical and analytical chemistry to organic and inorganic chemistry. The author anticipates that the present article will provide a thorough understanding of the subject and its possible ramifications by showcasing the most important discoveries and advancements in the area of five-membered oxa- and aza-heterocycles. The potential that these compounds' activation will bring to chemistry in the future is really intriguing. It can be expected that, with the emergence of new materials with remarkable properties, the discovery of more effective catalysts for chemical reactions, and the development of sustainable energy sources, the energy landscape will completely transform as the understanding of transition metal chemical processes continues to advance. Furthermore, there is a good chance that the combination of organometallic chemistry with other scientific disciplines like biology and materials science will result in previously unheard-of breakthroughs in biotechnology, nanotechnology, and medication development.

Recent developments:

I. A direct Bis-cyanation reaction with double C-H activation by Rh-catalysis:

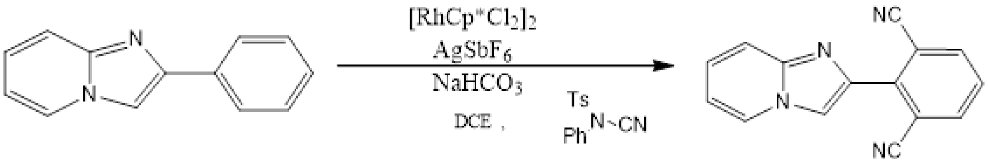


Figure 1: Bis-cyanation reaction with double C-H activation (*Zhu et al., 2017*)

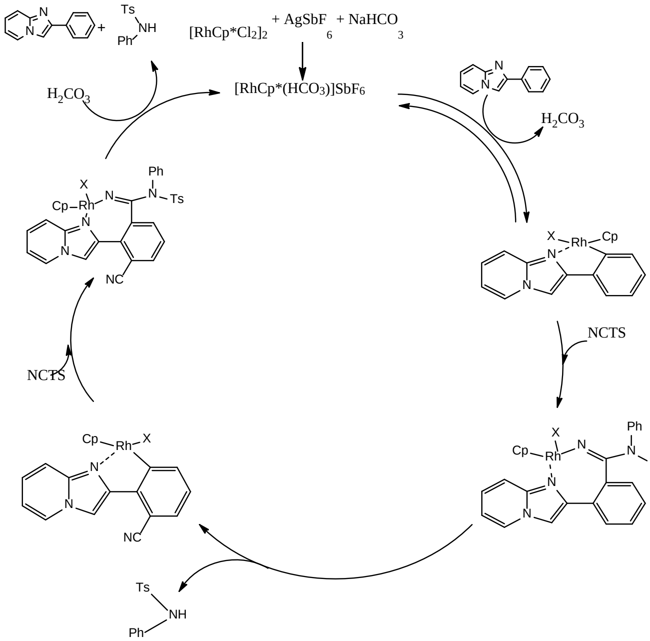


Figure 2: Mechanism of the reaction (Zhu *et al*., 2017)

First, in the presence of $AgSbF_6$ and $NaHCO_3$ the $[RhCp^*Cl_2]_2$ was converted to an active cationic Rh(III) species A. The five-membered rhodacycle B was then formed by chelating N1 at the imidazo[1,2-α]pyridine ring with in situ generated Rh(III) active complex A through a reversible C−H rhodation of 2-phenylimidazo[1,2-α]pyridine. Next, intermediate C was created when the cyano group was coordinated and moved into the C-Rh bond. It then underwent proto-demetalation, roll-over activation, and β-amine elimination to produce mono-cyanated intermediate D. The intended bis-cyanated product was then released and the catalytic cycle got completed (Figure 1, Figure 2). by the regeneration of the active Rh(III) species A when a new NCTS molecule joined with intermediate D to form intermediate E (Zhu *et al.*, 2017).

In order to achieve lucrative yields of bis-cyanated products, substituents with both electron-donating and electron-withdrawing motifs at the para-, meta-, and ortho-positions were permitted (Figure 3). For the C-H cyanation of meta- and ortho-substituted substrates, only electron-donating groups at the benzene ring are beneficial, whereas substrates with electron-withdrawing groups delivered low yields.

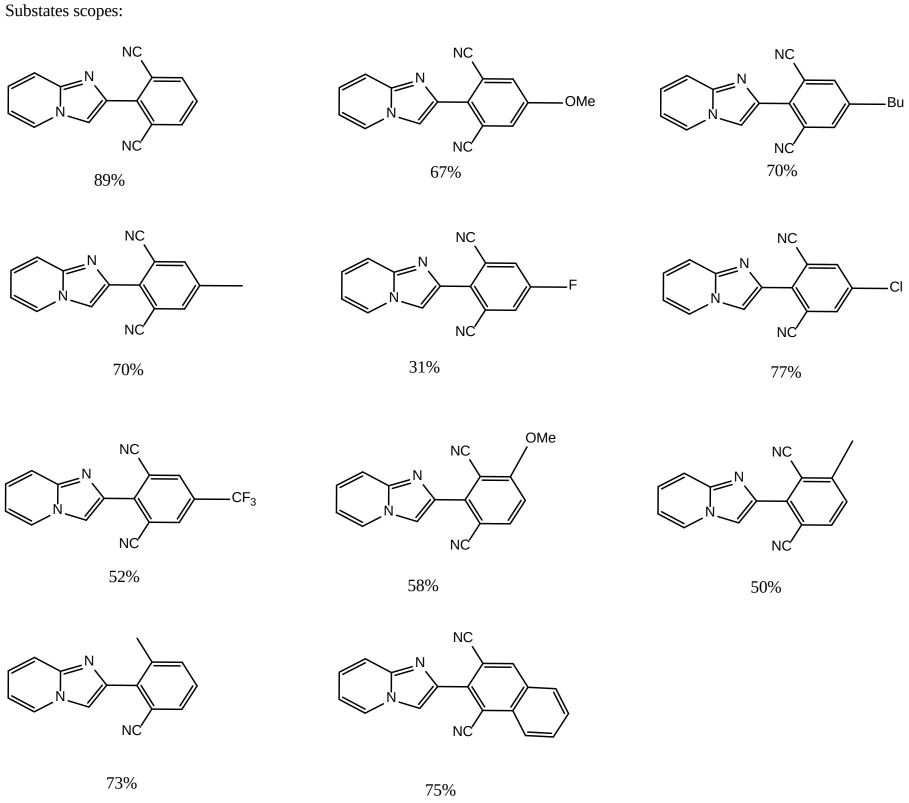


Figure 3: Substarte Scope (Zhu *et al.*, 2017)

II. A direct NHC-Driven Cascade C/H bond activation by Rh-catalysis:

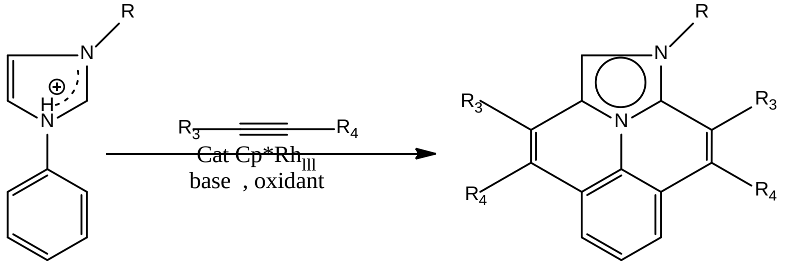


Figure 4: A direct NHC-Driven Cascade C/H bond activation (*Ghorai & Choudhury, 2015*)

The first step is the ortho C-H bond activation of the imidazolium substrate (Figure 4), which forms a five-membered rhodacycle. This activation is controlled by the NHC ligand. The seven-membered rhodacycle intermediate is produced by alkyne insertion into the Rh−aryl bond. In the presence of Ag^I, further reductive elimination from alkyl Rh-caryl yields the monoannulated product on one side, which is then repeated to get the other annulated (Figure 5) side product (Ghorai & Choudhury, 2015).

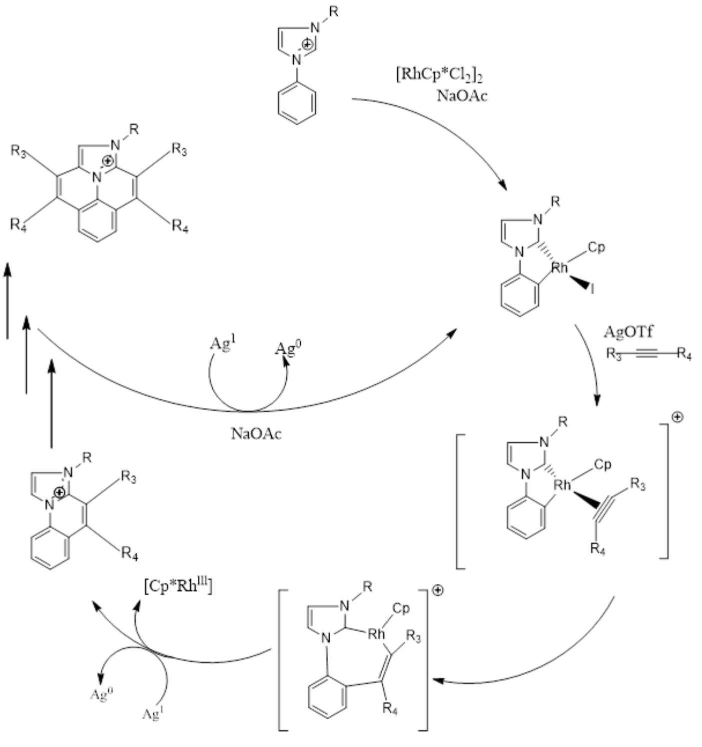


Figure 5: Mechanism of the reaction (*Ghorai & Choudhury, 2015*)

The matching products yielded good results (Figure 6) in this case when the groups on an N-phenyl wingtip that donate and withhold electrons were present. The yield is good when utilizing an alkyne that has a strongly electron withdrawing group, according to the results.

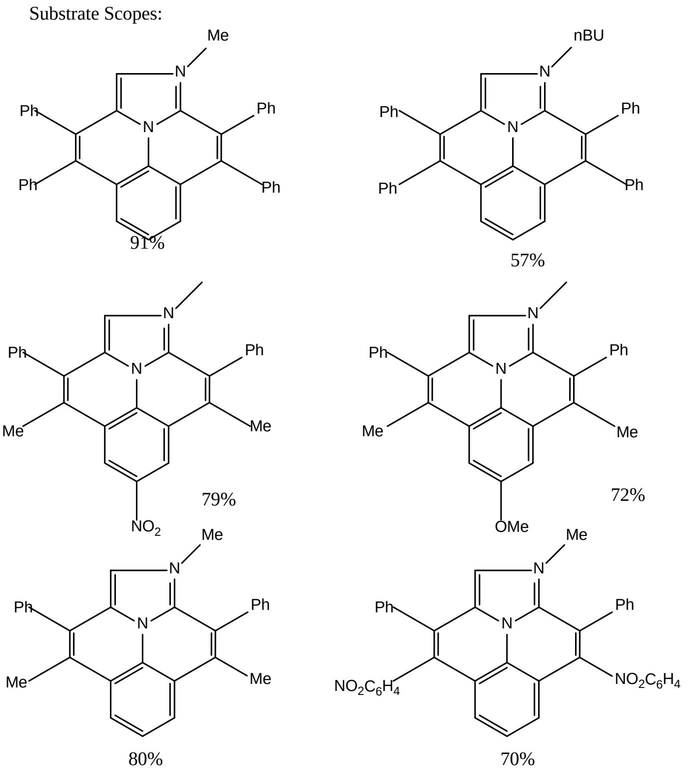


Figure 6: Substarte Scope (*Ghorai & Choudhury, 2015*)

III. An arylation protocol of heterocycles via C/H Bond Activation: Broadened perspective via mechanistic understanding:

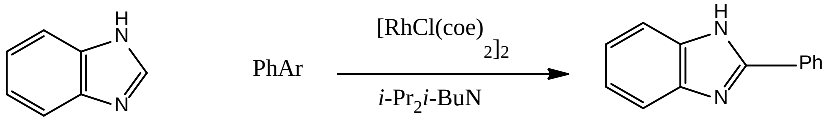


Figure 7: An arylation protocol of heterocycles (*Berman et al., 2008*)

The dimer complex is produced by combining $[RhCl(coe)_2]_2$ with the initial material (see above). The heterocycle complex would be produced by dissociating this complex and coordinating the heterocycle (Figure 7). The mechanism of carbon-hydrogen activation/tautomerization is thought to be responsible for the production of the carbene complex. The (aryl)(carbene)rhodium complex can be produced by oxidatively adding aryl halides to this low-valent, electron-rich Rh complex. Then, an HBr molecule gets removed from this complex, either intramolecularly or with the help of the additional amine base (Figure 8). Finally, the Rh catalyst was regenerated along with the required product by a reductive elimination step (Berman *et al*., 2008).

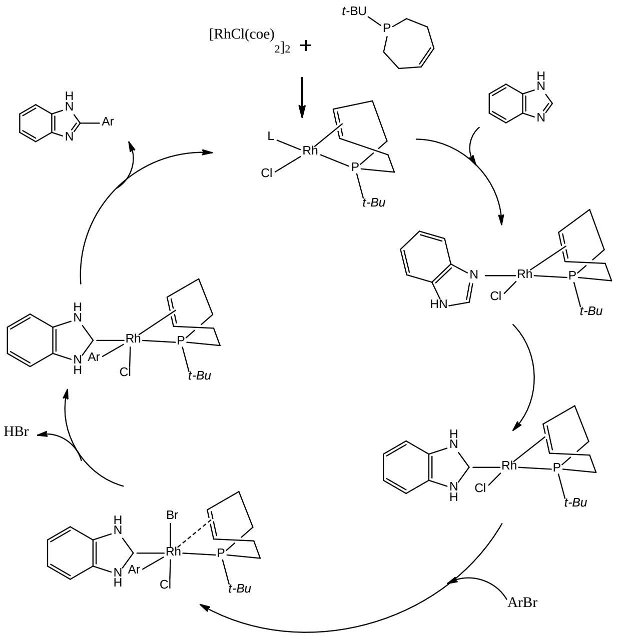
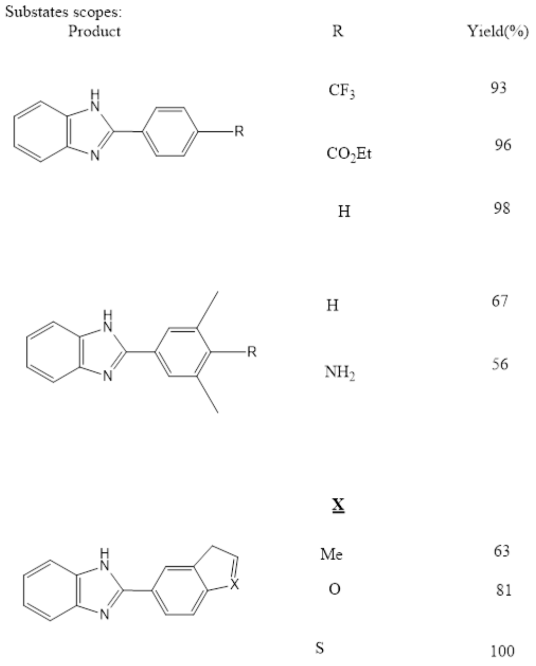


Figure 8: Mechanism of the reaction (*Berman et al., 2008*)



Substates scopes:

Product	R	Yield(%)
	CF_3	93
	CO_2Et	96
	H	98
	H	67
	NH_2	56
	X	
	Me	63
	O	81
	S	100

Figure 9: Substarte Scope (*Berman et al., 2008*)

When para and meta substitutions were used, products with high yields were produced (Figure 9). But, ortho-substitution was not fruitful. Additionally, electron-rich compounds paired with good yields. Please note that, in the structures mentioned in Table 9, the "R" groups are referred to as the substituents at the phenyl rings used for the arylation protocol. These findings are highly significant, given that electrophilic metalation occurs at a high yield percentage for these electron-rich heterocycles.

IV. A Hydroformylation reaction of heterocyclic Olefins: A highly selective asymmetric process:

Phosphine-phosphonites are a new class of chiral hybrid diphosphorus ligands that have a novel use in the asymmetric hydroformylation of heterocyclic olefins catalyzed by Rh (Figure 10). The notoriously challenging substrate 2,5-dihydrofuran is enantio selectively converted by the same catalyst under mild reaction conditions, with up to 91% ee contemporaneous with complete regioselectivity to 3-carbaldehydes (Figure11) (Chikkali *et al*., 2012).

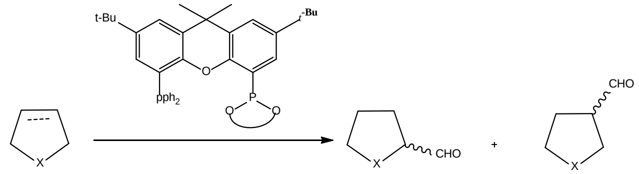


Figure 10: Hydroformylation reaction of heterocyclic Olefins (*Chikkali et al., 2012*)

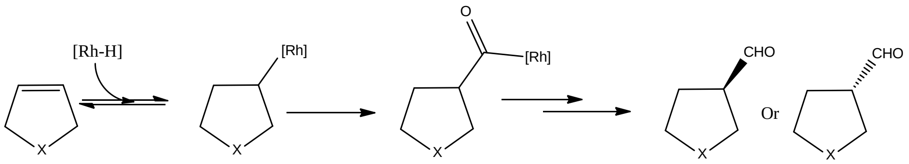


Figure 11: Mechanism of the reaction (*Chikkali et al., 2012*)

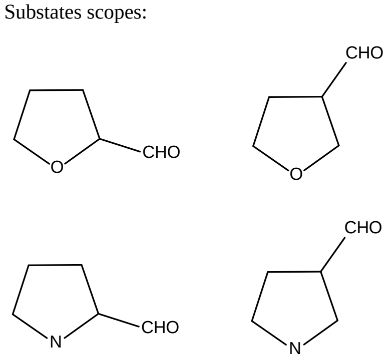


Figure 12: Substarte Scope (*Chikkali et al., 2012*)

Using a sterically more hindered ligand, the 3-carbaldehyde product showed excellent regioselectivity and a promising ee of 89% at room temperature (Figure 12). In product 4, there is a notable reversal of enantio selection from substrate 1 (resulting in (R)-4) to substrate 2 (resulting in (S)-4).

V. Double C-H activation for direct selective C/H oxidative annulations of alkynes and substituted imidazoles with rhodium(III) Catalysis:

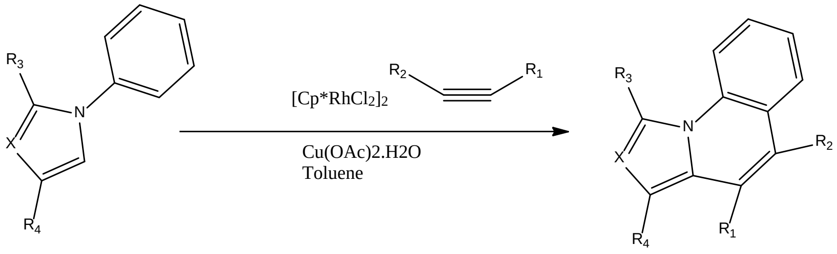


Figure 13: Selective C/H oxidative annulations of alkynes and substituted imidazoles (*Huang et al., 2013*)

Rhodium(III) catalyst was used (Figure 13) to achieve double CH activations of ortho-substituted vinyl/arylimidazoles without the need for a heteroatom-based directing group. Aza-fused heterocycles were effectively and highly yielded by another oxidative annulation with alkynes (Huang *et al*., 2013).

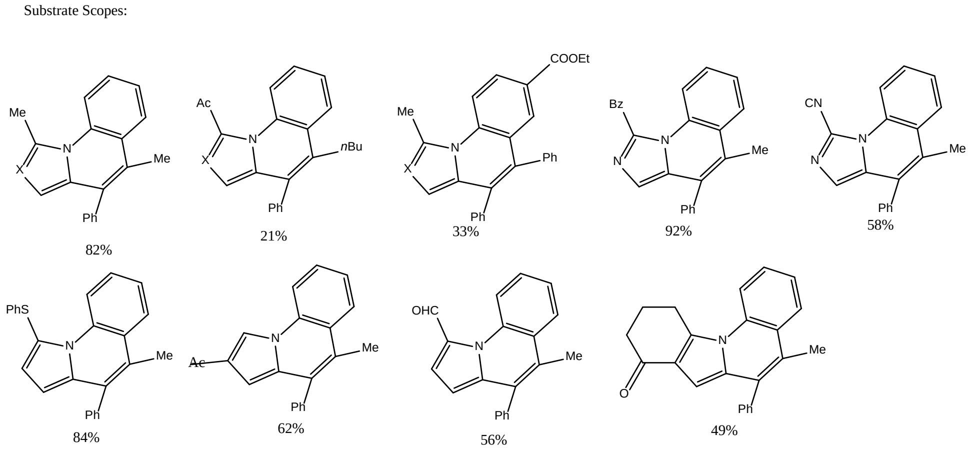


Figure 14: Substarte Scope (*Huang et al., 2013*)

The imidazoles with groups that are either withdrawing or donating electrons at para-position exhibited excellent product yield (Figure 14). Nevertheless, because to steric restriction, an ortho-substituted aryl substrates gave the desired tricycles at much lower yield.

VI. An alternative pathway to Epibatidine for the asymmetric hydroarylation of azabicyles:

A novel rhodium-based chiral NHC-complex, Rh(IBiox[(-)-menthyl](CO)$_2$Cl, has been synthesized and characterized (Figure 15). Furthermore, as a catalyst, this complex's extremely high enantioselectivity was proven and used in the production of epibatidine during an asymmetric hydroarylation reaction of azabicycles (Figure 16) (Bexrud & Lautens, 2010).

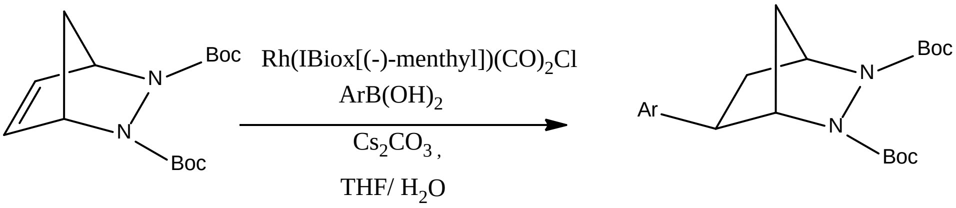


Figure 15: Asymmetric hydroarylation of azabicyles (*Bexrud & Lautens, 2010*)

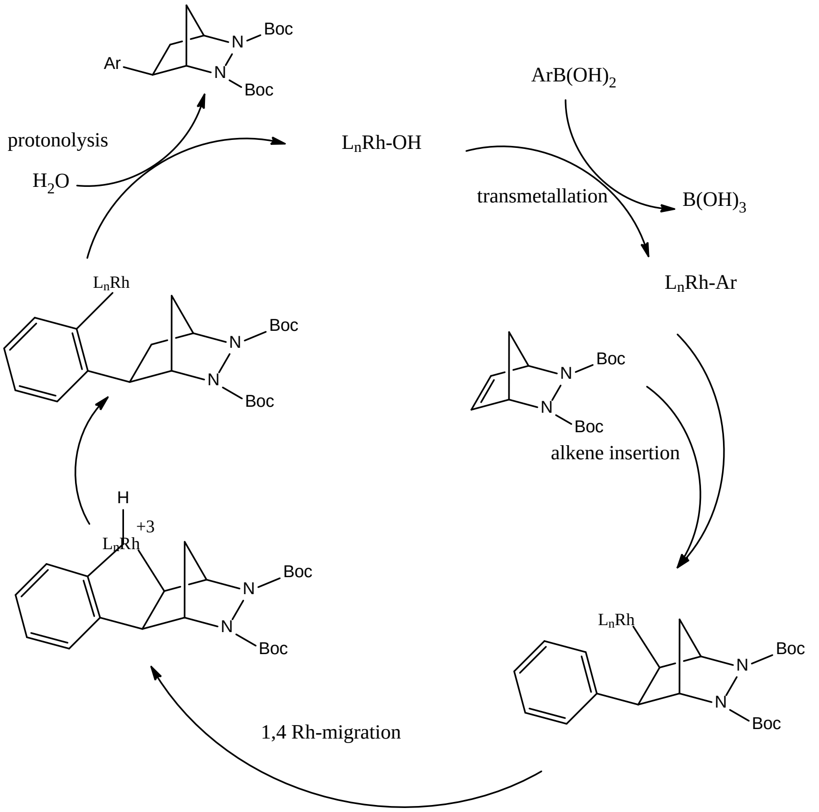


Figure 16: Mechanism of the reaction (*Bexrud & Lautens, 2010*)

Unfavorable steric interactions between the substituents are probably the cause of the low yields found, while electron donating groups can also produce large yields (Figure 17).

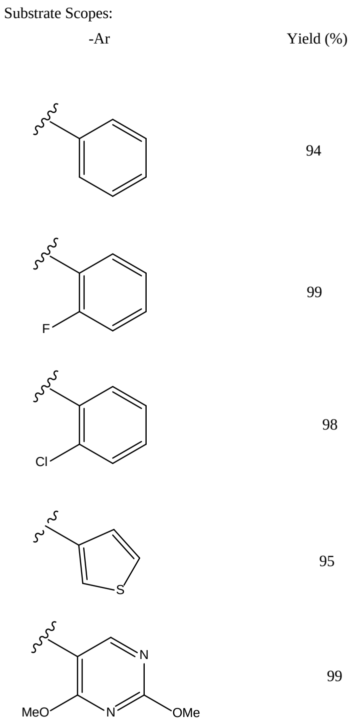


Figure 17: Substarte Scope (*Bexrud & Lautens, 2010*)

VII. Divergent synthesis of indoles and pyrroles by Rh(III)-catalyzed C/H activation:

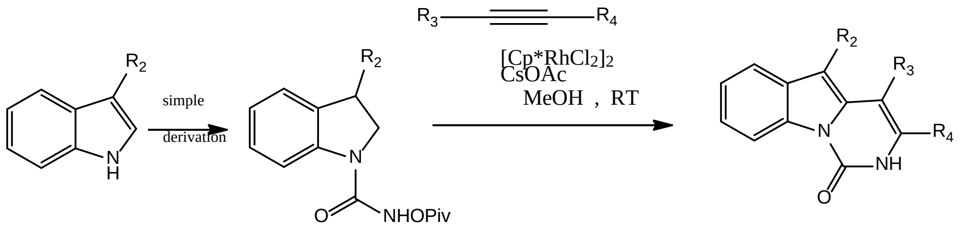


Figure 18: Divergent synthesis of indoles and pyrroles (*Zhang, Zheng & Cui, 2014*)

In this protocol (Figure 187), in presence of CsOAc, a carboxylate was produced from $[Cp^*RhCl_2]_2$, which promoted the C-H activation of indole/pyrrole-N-carboxamides through an initial metalation, followed by a deprotonation pathway (Figure 19), resulting in the formation of rhodacycle (Zhang, Zheng & Cui, 2014).

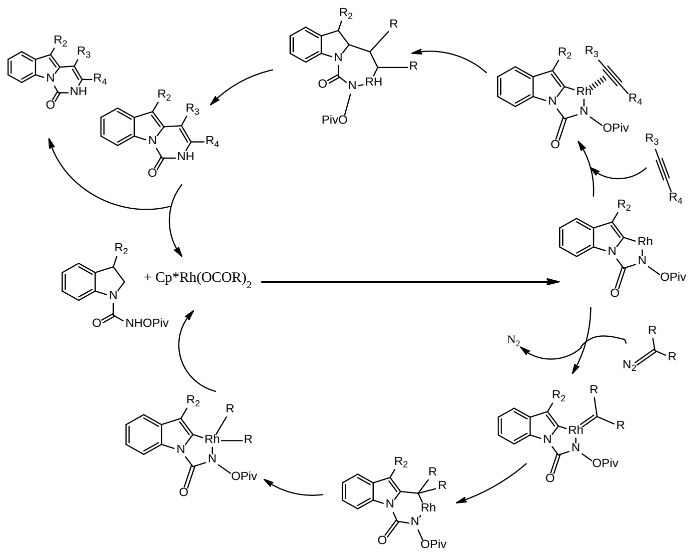


Figure 19: Mechanism of the reaction (*Zhang, Zheng & Cui, 2014*)

The scope of this protocol was expanded by examining the usage of the alkenes under the typical reaction conditions, since these are another excellent coupling partner in this C-H activation/cyclization protocol. The product yield is decreased by the electron-withdrawing group (Figure 20).

Substates scopes:

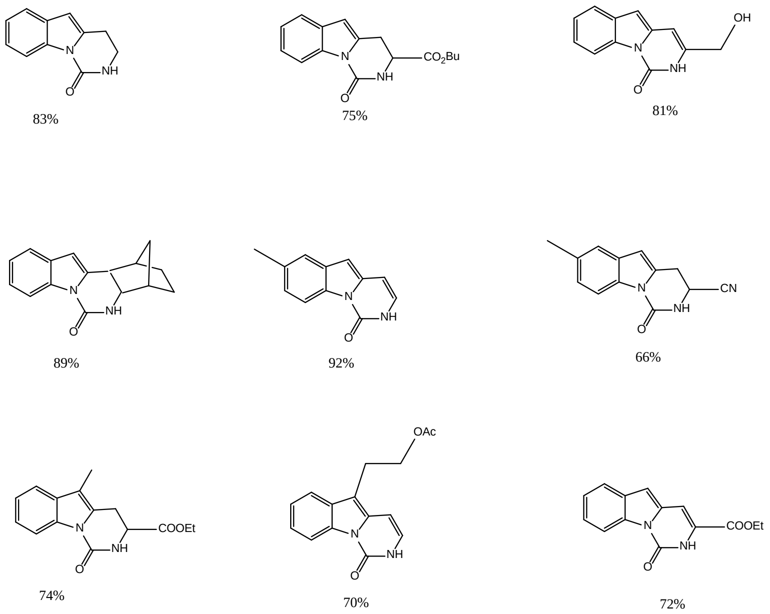


Figure 20: Substarte Scope (*Zhang, Zheng & Cui, 2014*)

VIII. C-H activation at the indole C4-position with allyl alcohols: An example of Rh-carbonyl directed reaction

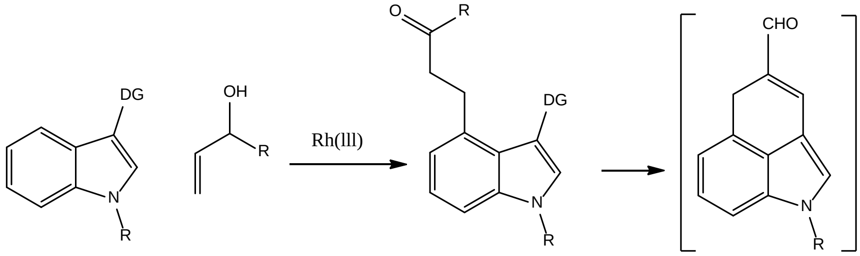


Figure 21: Rh-carbonyl directed reaction (*Sherikar, Devarajappa & Prabhu, 2020*)

In this reaction (Figure 21), the authors report that, a weak coordination of the carbonyl group with the Rh(III) center, directs the coupling of allyl alcohols at the C-4 site of indole derivatives under the optimized activation condition (Figure 22). As a result, indole derivatives only experience alkylation at C–4 site. Under aldol reaction conditions, the resultant product creates a tricyclic derivative as a synthetic precursor to construct certain alkaloid molecules, including hapalindole or ergot alkaloids and similar heterocycles (Sherikar, Devarajappa & Prabhu, 2020).

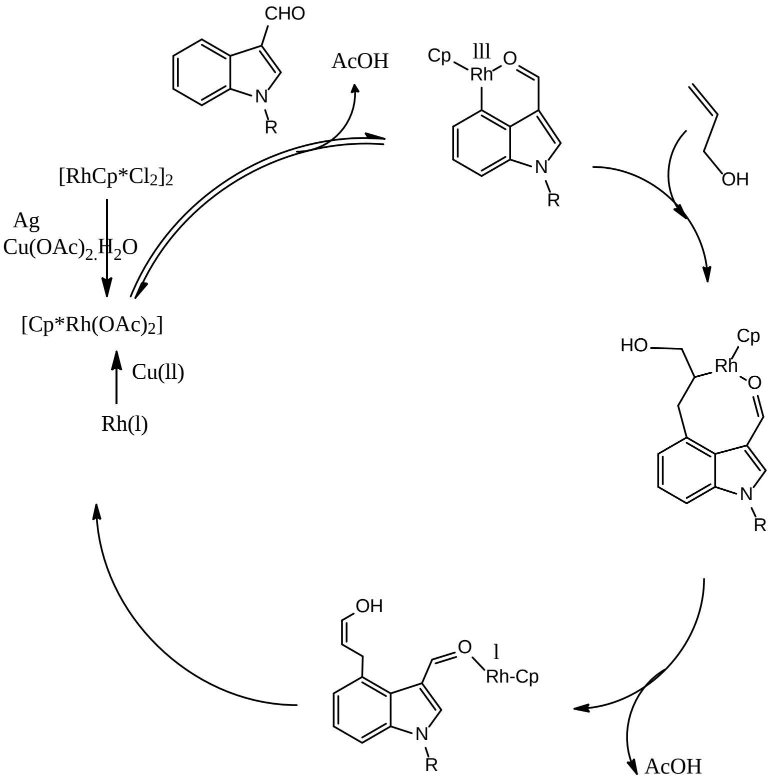


Figure 22: Mechanism of the reaction (*Sherikar, Devarajappa & Prabhu, 2020*)

The intended products were not produced by the substituted indole derivatives that withdrew electrons or by various carbonyl directing such at the indole's C3-position (Figure 23). N-protected derivatives and indole-3-carbaldehyde derivatives with a free NH group failed to create the intended product.

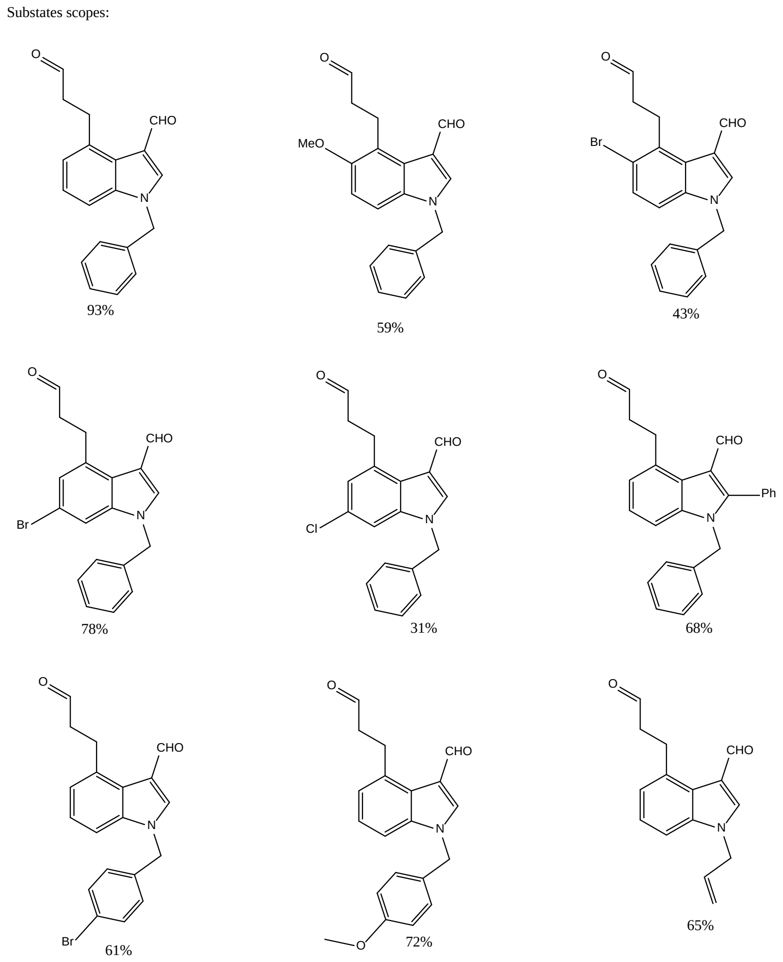


Figure 23: Substarte Scope (*Sherikar, Devarajappa & Prabhu, 2020*)

IX. Rh(III)-catalyst's dual function in the regioselective halogenation of heterocycles:

It is reported (Figure 24) that electron-rich heterocycles can be selectively brominated and iodinated with Rh(III). According to kinetic studies, rhodium has two functions in the bromination process: first, it catalyzes the directed halogenation, and second, it stops these substrates from naturally halogenating. It is possible to use furans, thiophenes, benzothiophenes, pyrazoles, quinolones, and chromones (Schröder, Lied & Glorius, 2015).

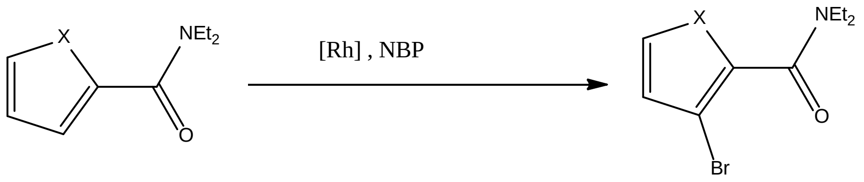


Figure 24: Regioselective halogenation of heterocycles (*Schröder, Lied & Glorius, 2015*)

In order to guarantee high levels of regioselectivity, the rhodium catalyst plays two functions in facilitating the halogenation of substrates, where both the 3- and 5-positions are free (Figure 25). Here, the 5-position becomes less reactive, as rhodium inhibits the intrinsic reaction by delaying the generation of Br$_2$. Consequently, the directing effect on the halogenation reaction at C3-site was also catalysed, having NBP as the bromine source.

Substates scopes:

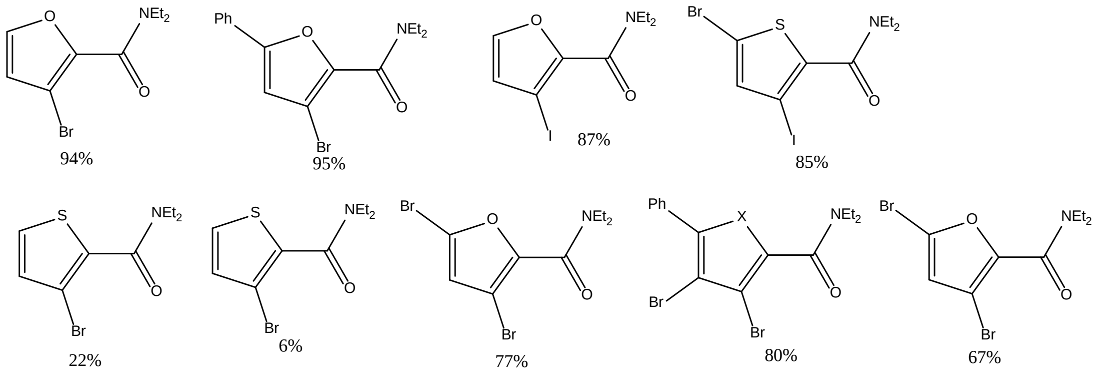


Figure 25: Substarte Scope (*Schröder, Lied & Glorius, 2015*)

Conclusion:

The wide range of applications and revolutionary effects of Rhodium chemistry in the carbon-hydrogen bond activation of oxa- and aza-heterocycles, having 5 ring members, are demonstrated in this review article, which provides an insight into the field. Through an examination of current advancements and forthcoming prospects in diverse subfields, the scientific community now aims to apply these works on pyridine and oxazole derivatives to stimulate additional investigation and cooperation, cultivating a more profound understanding of the infinite capacity of chemistry to mould the world and confront the obstacles that lie ahead.

Acknowledgment:

The author would like to acknowledge the Teacher-in-charge of Maharaja Manindra Chandra College for providing office space and internet facilities. The author also acknowledges the constant support extended by his colleagues in the Department of Chemistry at Maharaja Manindra Chandra College.

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Published by:

Lincoln University College, Malaysia

e ISBN 978-967-2819-32-5

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ISBN 978-967-2819-31-8

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