ISBN: 978-93-95847-85-8

FRONTIERS IN CHEMICAL, BIOLOGICAL AND PHARMACEUTICAL SCIENCES VOLUME III

EDITORS:
MR. MUKUL M. BARAWNT
DR. BASSA SATYANNARAYANA

BHUMI PUBLISHING
FIRST EDITION: 2024

www.bhumipublishing.com

FRONTIERS IN CHEMICAL, BIOLOGICAL AND PHARMACEUTICAL SCIENCES
VOLUME III

(ISBN: 978-93-95847-85-8)

Edited by

Mr. MUKUL MACHHINDRA BARWANT
Assistant Professor,
Department of Botany,
Sanjivani Arts Commerce and Science College,
Kopargaon, Maharashtra, India.
Email: mukulbarwant97@gmail.com

Dr. BASSA SATYANNARAYANA
Assistant Professor,
Department of Chemistry,
Govt. M. G. M P. G. College, Itarsi, MP-461111
Email: satyanarayana. bassa@gmail.com

BHUMI PUBLISHING
Nigave Khalasa, Tal – Karveer,
Dist – Kolhapur, Maharashtra, INDIA 416 207
E-mail: bhumipublishing@gmail.com

Title: **Frontiers in Chemical, Biological and Pharmaceutical Sciences Volume III**

ISBN: 978-93-95847-85-8

Editors: **Dr. Bassa Satyannarayana, Mr. Mukul Machhindra Barwant**

First Published, 2023

Bhumi Publishing

Published by:

BHUMI PUBLISHING
Nigave Khalasa, Tal – Karveer,
Dist – Kolhapur, Maharashtra, INDIA 416 207
E-mail: bhumipublishing@gmail.com

PREFACE

Embarking on the journey into the pages of Frontiers in Chemical, Biological, and Pharmaceutical Sciences Volume III is like setting sail into uncharted waters of scientific exploration. This volume stands as a testament to the ceaseless quest for knowledge, innovation, and breakthroughs in the ever-evolving realms of chemistry, biology, and pharmaceutical sciences.

Within these pages, you will find a symphony of ideas, discoveries, and advancements orchestrated by brilliant minds from diverse corners of the scientific landscape. Each chapter is a gateway to a frontier where the boundaries of understanding are pushed further, unveiling new vistas and unraveling the intricacies of nature at molecular and cellular levels.

The preface serves as a compass, guiding you through the thematic richness of this volume. From the intricacies of chemical synthesis to the mysteries of biological systems and the cutting-edge developments in pharmaceutical sciences, these chapters weave a tapestry that reflects the interdisciplinary nature of modern scientific inquiry.

As we delve into this intellectual odyssey, may you be inspired by the passion, dedication, and collaborative spirit that permeate the scientific community. Frontiers in Chemical, Biological, and Pharmaceutical Sciences Volume III beckons you to explore, question, and marvel at the frontiers of knowledge, where every turning page is an invitation to expand your understanding of the intricate dance of molecules and the profound impact it has on our world. Welcome to a world where curiosity knows no bounds and the pursuit of knowledge is a journey with no final destination.

Editors:

Dr. Bassa Satyannarayana

Mr. Mukul Machhindra Barawnt

TABLE OF CONTENT

Chapter 1

ROLE OF SUPER ADSORBING HYDROGELS FOR WASTE WATER TREATMENT

RAJASHREE A. MARKANDEWAR

Department of Chemistry, Rashtrapita Mahatma Gandhi Arts, Commerce and Science College, Saoli, Dist. Chandrapur. MS
Corresponding author E-mail: rajashree.markandewar@gmail.com

ABSTRACT

One of the most pressing challenges of the twenty-first century is to find less expensive and environmentally friendly ways to treat wastewater that contains heavy metals and dyes without harming the environment and causing freshwater sources to dry up. The removal of heavy metal ions and monolayers that have accumulated on the surface of an adsorbent is commonly accomplished by adsorption. Therefore, the recent results of using hydrogel adsorbents to remove heavy metal ions are the main focus of this discussion. The review focuses on the key elements of adsorption and provides an understanding of the removal of heavy metal ions by hydrogels according to the chemical entity employed.

KEYWORDS: Hydrogels, Heavy Metal Ions, Waste Water Treatment, Adsorption

INTRODUCTION

Because of the careless disposal of both organic and inorganic pollutants, water source pollution has become a global issue. Managing wastewater purification prior to its flow into water reservoirs is still a challenging task. One of the most pressing challenges of the twenty-first century is locating low-cost, environmentally acceptable ways to remove heavy metal and dye contamination from wastewater without contributing to the depletion of accessible freshwater sources [1]. Adsorption is still the most straightforward and affordable method of treating wastewater; in fact, naturally occurring adsorbent materials have attracted a lot of interest [2]. One promising instance of such adsorbents is hydrogels (HGs), which represent a 3-dimensional polymeric network of hydrophilic groups that is highly capable of adsorbing a large number of metal ions and dyes from wastewater.

With the expansion of human activity and industry, such as the plating and electroplating sector, batteries, pesticides, mining, rayon, tanning, fluidized bed bioreactors, textile, metal smelting, petrochemical, paper, and electrolysis applications, the amount of heavy metals in wastewater has been rising. Even though there are traces of heavy metal ions, their effects are still quite dangerous. The risks that heavy metal ions pose to the human body are shown in the following table [3].

The metals listed above as well as others that are frequently found in wastewater, such as silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), cobalt (Co), etc., must be eliminated [4].

Concerns about the increasing effects of effluent pollution on the atmosphere are shared by researchers worldwide. Wastewater is difficult to clean up before it enters water reservoirs. Therefore, wastewater treatment is still required before it can be released into natural water streams. The treatment of wastewater is a comparatively new technique.

Table 1: Heavy metals and their health hazards

Heavy Metals	Desirable amount in Traces	Potential Negative IMPACT on Health after desirable amount
Zn	3000	Stomach Cramps, dermal irritations, vomiting, nausea and anemia
Cu	2000	Severe Toxological complications such as vomiting, cramps, convulsions, even death
Ni	50	Acute lung, kidney and gastrointestinal pain, pulmonary fibrosis and skin dermatitis.
Hg	0. 1	Pulmonary kidney and Chest pain, dyspnea impairments.
Co	0. 1	Paralysis, asthama, pneumonia, diarrhea, lung irritations, weight loss, vomiting, nausea, damage thyroid hormone and liver
Cd	3	Renel Dysfunction and even death
Pb	10	Failure of kidney, liver, reproductive system, basic cellular process, brain function and even central nervous system of human body.
Cr	50	Destruction of human metabolism, skin irritation, food chain disruption and lung carcinoma

All elements in μ gm/l

ROLE OF HYDROGELS

Hydrogels can be positioned as multipurpose platforms for the targeted detection of pollutants and the deep purification of micropolluted water. Hydrogels are endowed with high sensibility and adsorption ability, which are somewhat superior to those of carbon nanomaterials. Their enrichment ability is brought about by their relatively large surface area, porous structures, rich functional group, specific functional DNA, and specific surface charge [6]. In contrast to certain commonly used materials for treating wastewater, such as carbon-based materials, clay minerals, metallic materials, and carbon-based materials, [7–9]. DNA hydrogels are better suited for treating micropolluted water, which is defined as water that has trace amounts of different types of pollutants in it.

SUPER ABSORBANT HYDROGELS

Wastewater treatment is still a major problem worldwide, despite numerous technological advancements and successes. If untreated, the toxins in wastewater present a serious risk to human health. The most widely used adsorbent for eliminating toxic ions from wastewater is cellulose biomass-based hydrogel because of its macro-porous structure and distinct surface functionalization. A number of novel materials derived from cellulose have recently been introduced, proving to be competitive in the removal of harmful ions. This promising material is better described by a number of outstanding properties, such as its high mechanical strength, large surface area, and chemical inertness [11]. India has also seen a notable increase in interest in the research.

A low-cost superabsorbent polymer hydrogel (SPH) made of acrylic acid and acrylamide in various compositions was prepared by a single step free radical polymerization technique using ammonium persulphate and N, N-methylene bis-acrylamide as an initiator and cross-linker, respectively. Luqman Shah *et al.,* . [12] report an efficient removal of selected heavy metal ions using this method. For superabsorbent polymer hydrogels, the morphological, thermal, and mechanical properties were evaluated. After a thorough analysis of the effects of pH and monomer content on the swelling behavior

of SPH, a composition with the highest possible content of acrylic acid (AA) was found to have a maximum swelling capacity of 1841%. Using Freundlisch adsorption model and pseudo-second order kinetics, all samples removed Cd^{2+}, Ni^{2+}, Cu^{2+}, and Co^{2+} from aqueous medium at pH range of 2–10. Furthermore, in a competitive removal process, the materials demonstrated high selectivity towards Co^{2+} and Cu^{2+} and a greater removal capacity at pH 7. These materials have a high removal ability of more than 75% for each metal ion, which makes them an effective, accessible, and environmentally friendly product.

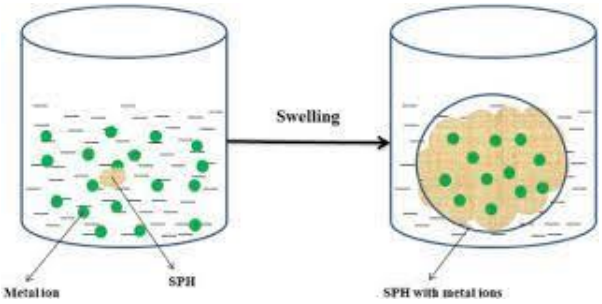


Fig. 1: Illustration of swelling of Chitosin based Hydrogels [40]

The CSIR-CIMAP Research Centre in Boduppal, Hyderabad, carried out field research in 2016–17 on red sandy soil in a semi-arid region of south India to investigate the effects of varying hydrogel dosages on the growth, yield, and economics of senna, one of the most economically significant and export-oriented crops in India. The findings indicate that when compared to the other treatment, applying 3000 g of hydrogel per hectare significantly increased the yield of leaves and pods (2324. 7 kg ha−1 and 675. 7 kg ha−1, respectively) [13].

The widespread use of cotton textiles has resulted in a significant issue with the disposal of waste cotton fabrics (WCFs). It is generally acknowledged that there will be significant business opportunities if WCFs can be repurposed. For the purpose of removing heavy metals, Jainhu Ma and colleagues [14] created a double network hydrogel based on WCFs and polyacrylamide (Cellulose/PAM DNHs). The porous and sheet-like laminar structures of the DNHs allow for fast kinetics, with sorption equilibrium being reached in 5 minutes. Additionally, the DNHs show good reusability and excellent adsorption properties. Both simulated and real-world wastewater can be efficiently processed by the tandem two columns packed with Cellulose/PAM-3, and after three adsorption-desorption cycles, the adsorption discrepancy is minimal. For Cd (II), Cu (II), and Pb (II), the treatment volumes of the simulated wastewater are 172. 5 BV (7935 mL), 195 BV (8970 mL), and 292. 5 BV (13455 mL), in that order. In addition, 42 BV (1932 mL) of Cd (II), 63 BV (2898 mL) of Cu (II), and 87 BV (4002 mL) of Zn (II), Pb (II), and Fe are the treatment volumes of actual industrial wastewater, respectively. The construction of a resource-sustainable and environmentally friendly society greatly benefits from this work's new avenue for the combination of WCFs reuse and heavy metal removal.

Saravanakumar *et al.,* 2020 [15] came to the conclusion that Superabsorbent hydrogels have superior performance, eco-friendly benefits, and a wide range of applications in the preparation of polymer packing films [16]. Khalid *et al., (*2020) as a catalyst carrier [19], Dwivedi *et al., (*2020) as antibacterial materials [18], and Kassem *et al., (*2020) as superabsorbent hydrogel [20] all carried out the synthesis of natural hydrogels as the drug-delivery vehicle.

Ningmei Wu and Zeingkei Lee created a novel poly (Hydroxyethyl methacrylate/Maleamic acid) (p (HEA/MALA)) hydrogel [21]. Using 60Co-γ induced copolymerization, Pb^{2+}, Cd^{2+}, Ni^{2+}, and Cu^{2+} are extracted from aqueous solutions. Three different analyses were used to characterize the prepared copolymer: FTIR, TGA, and XPS. The effects of pH, time, initial metal ion concentration, and solution

competition properties on the adsorption of Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} ions were studied in batch equilibrium experiments. The presence of HEA and Maleamic acid copolymer in the p (HEA/MALA) hydrogel was confirmed by FTIR spectra and TGA analysis. Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} ion adsorption kinetics on p (HEA/MALA) were characterized by a pseudo-second-order kinetic model, and the order of the adsorption rates was Cd^{2+} > Pb^{2+} > Ni^{2+} > Cu^{+2}The competitive adsorption results showed that Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} was the priority order in multi-component adsorption. According to these results, hydrogel shows promise as an adsorbent for removing and recovering heavy metal ions from contaminated water. Scientists at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), located in Bengaluru, have created a novel method that holds promise for creating hydrogels that could be applied to a range of tasks, such as the treatment of industrial wastewater.

The process entails using molecular binders to facilitate the self-assembly of small cubes of metal-organic compounds into hydrogels. The size, shape, and geometry of the molecular binder determine the composition of the resulting hydrogel. For example, the hydrogel produced by using a cationic ammonia-based molecular binder had a nano-tubular shape and a negatively charged surface. It can be applied to any material as a gel-chromatography separator to separate cationic from anionic species (Science Wire, India) [23].

The goal of research is to create an efficient adsorbent hydrogel that can remove several heavy metal ions from waste water completely and simultaneously. The practical application of manufactured waste water adsorbents for the removal of multiple heavy metal ions is possible, particularly when using an affordable, easily accessible adsorbent.

Fig. 2: Polycyclic Aromatic hydrocarbons [24]

Dominik Pilnaj and co workers [24] stated the Magnetic sorbents represent very promising materials for environmental applications due to their simple synthesis, separability in a magnetic field, low toxicity, wide range of possible modifications, and usability in heterogeneous systems. We report on the synthesis, characterization, and application of magnetically separable Fe_3O_4/SiO_2 sorbent surface-modified with octadecyl chains (C18). Since PAHs are formed as by-products of pyrolysis, a rapidly evolving technology for transformation of waste into green chemicals, there is a need for efficient sorbents suitable for PAHs removal from the environment. The use of Fe_3O_4/SiO_2-C18 for adsorption of 16 different PAHs has not yet been reported. The adsorption was examined by gas chromatography with mass spectrometry and studied using molecular modeling comparison of adsorption efficiency η for Fe_3O_4, Fe_3O_4/SiO_2, and Fe_3O_4/SiO_2-C18 revealed a positive effect of C18. The highest η values were found for medium-heavy PAHs (178. 2–228. 2 g/mol). Exhibiting high efficiency and average capacity of ~1μg/g, the Fe_3O_4/SiO_2-C18 is suitable for pre-concentration purposes of PAHs in analytical sample extractions from water [25,26].

CONCLUSION

In our review, we looked at conducting hydrogel composites, a cutting-edge and adaptable class of materials that are becoming more and more popular for the adsorption of heavy metals in wastewater. A

few synthesis techniques and strategies for achieving the Adsorption method—which removes heavy metal ions and monolayers of ions formed by accumulation on an adsorbent surface—are summarized in this review. Numerous methods are extremely straightforward, efficient in removing metal ions, adaptable in adsorbent design, and impervious to harmful pollutants. Researchers can use this review to help them create new, straightforward adsorbing hydrogels for the treatment of wastewater, which will contribute to a better, more environmentally friendly future.

REFERENCES

[1]. Taseidifar, M., Makavipour, F., Pashley, R. M. & Rahman, A. F. M. M. (2017). Removal of heavy metal ions from water using ion flotation. Environ. Technol. Innov. 8, 182–190.

[2]. Gupta, V. K., Ali, I., Saleh, T. A., Siddiqui, M. N. & Agarwal, S. (2013). Chromium removal from water by activated carbon developed from waste rubber tires. Environ. Sci. Pollut. Res. 20, 1261–1268

[3]. Mahdavinia, G; Pourjavadi, A; Hosseinzadeh, H; Zohuriaan, M. (2004). Modified chitosan 4. Superabsorbent hydrogels from poly (acrylic acid-co-acrylamide) grafted chitosan with salt-and pH-responsiveness properties. Eur. Polym. J. 2004, 40, 1399–1407.

[4]. Renu; Madhu Agarwal; K. Singh. (2017). Heavy metal removal from wate water using various adsorbents: a review. Journal of Water Reuse and Desalination 7 (4): 387–419.

[5]. O. Suárez-Iglesias, S. Collado, P. Oulego, M. Díaz, (2017). Chem. Graphene-Family Nanomaterials in Wastewater Treatment Plants. Eng. J. 2017, 313, 121;

[6]. C. Santhosh, V. Velmurugan, G. Jacob, S. K. Jeong, A. N. Grace, A. Bhatnagar, (2016). Role of nanomaterials in water treatment applications: A review. Chem. Eng. J. 2016, 306, 1116;

[7]. Wang, F., Zhu, Y. F., Xu, H., and Wang, A. Q. (2019). Preparation of Carboxymethyl Cellulose-Based Macroporous Adsorbent by Eco-Friendly Pickering-MIPEs Template for Fast Removal of Pb^{2+} and Cd^{2+}. *Front. Chem.* 7, 603. doi:10. 3389/fchem. 2019. 00603

[8]. Vakili, M., Deng, S., Cagnetta, G., Wang, W., Meng, P., Liu, D., *et al.,* . (2019). Regeneration of Chitosan-Based Adsorbents Used in Heavy Metal Adsorption: A Review. *Separat. Purif. Technol.* 224, 373–387. doi:10. 1016/j. seppur. 2019. 05. 040

[9]. Li L, Ai J, Zhang W, Peng S, Dong T, Deng Y, Cui Y, Wang D. (2020). Relationship between the physicochemical properties of sludge-based carbons and the adsorption capacity of dissolved organic matter in advanced wastewater treatment: Effects of chemical conditioning. Chemosphere. 2020 Mar 1;243:125333.

[10]. Ezeokonkwo, M. A., Ofor, O. F., and Ani, J. U. (2018). Preparation and Evaluation of Adsorbents from Coal and IrvingiaGabonensis Seed Shell for the Removal of Cd (II) and Pb (II) Ions from Aqueous Solutions. *Front. Chem.* 5, 132. doi:10. 3389/fchem. 2017. 00132

[11]. Alyafei A, AlKizwini RS, Hashim KS, Yeboah D, Gkantou M, Al Khaddar R, Al-Faluji D, Zubaidi SL. (2020). Treatment of effluents of construction industry using a combined filtration-electrocoagulation method. InIOP Conference Series: Materials Science and Engineering 2020 Jul 1 (Vol. 888, No. 1, p. 012032). IOP Publishing.

[12]. Fabrication of Hydrogels via Host–Guest Polymers as Highly Efficient Organic Dye Adsorbents for Wastewater Treatment Nan HouRan WangFan WangJiahui BaiJingxin Zhou*Lexin ZhangJie HuShufeng Liuand Tifeng Jiao*ACS Omega (2020), 5, 10, 5470–5479

[13]. Yadav, M., Mishra, D. K., Sand, A., and Behari, K. (2011). Modification of Alginate through the Grafting of 2-acrylamidoglycolic Acid and Study of Physicochemical Properties in Terms of Swelling Capacity, Metal Ion Sorption, Flocculation and Biodegradability. *Carbohydr. Polym.* 84, 83–89. doi:10. 1016/j. carbpol. 2010. 10. 065

[14]. Khan, Samiullah & Ranjha, Nazar. (2014). Effect of degree of cross-linking on swelling and on drug release of low viscous chitosan/poly (vinyl alcohol) hydrogels. Polymer Bulletin. 71. 2133-2158. 10. 1007/s00289-014-1178-2.

[15]. Luqman Ali Shah, Majid Khan, Rida Javed, Murtaza Sayed, Muhammad Saleem Khan, Abbas Khan, Mohib Ullah, (2018). Superabsorbent polymer hydrogels with good thermal and mechanical properties for removal of selected heavy metal ions, Journal of Cleaner Production, Volume 201, 2018, Pages 78-87.

[16]. Jianhong Ma, Yutang Liu, Omar Ali, Yuanfeng Wei, Shuqu Zhang, Yuanmeng Zhang, Tao Cai, Chengbin Liu, Shenglian Luo, (2018). Fast adsorption of heavy metal ions by waste cotton fabrics based double network hydrogel and influencing factors insight, Journal of Hazardous Materials, Volume 344, 2018, Pages 1034-1042,

[17]. Saravanakumar, K., Sathiyaseelan, A., Mariadoss, A. V. A., Xiaowen, H., and Wang, M. -H. (2020). Physical and Bioactivities of Biopolymeric Films Incorporated with Cellulose, Sodium Alginate and Copper Oxide Nanoparticles for Food Packaging Application. *Int. J. Biol. Macromolecules* 153, 207–214. doi:10. 1016/j. ijbiomac. 2020. 02. 250

[18]. Mishra, A., Pandey, V. K., Shankar, B. S., and Melo, J. S. (2021). Spray Drying as an Efficient Route for Synthesis of Silica Nanoparticles-Sodium Alginate Biohybrid Drug Carrier of Doxorubicin. *Colloids Surf. B: Biointerfaces* 197, 111445. doi:10. 1016/j. colsurfb. 2020. 111445

[19]. Dwivedi, L. M., Baranwal, K., Gupta, S., Mishra, M., Sundaram, S., and Singh, V. (2020). Antibacterial Nanostructures Derived from Oxidized Sodium Alginate-ZnO. *Int. J. Biol. Macromolecules* 149, 1323–1330. doi:10. 1016/j. ijbiomac. 2020. 02. 011

[20]. Khalid, I., Ahmad, M., Minhas, M. U., and Barkat, K. (2018). Preparation and Characterization of Alginate-PVA-Based Semi-IPN: Controlled Release pH-Responsive Composites. *Polym. Bull.* 75, 1075–1099. doi:10. 1007/s00289-017-2079-y

[21]. Kassem, I., Kassab, Z., Khouloud, M., Sehaqui, H., Bouhfid, R., Jacquemin, J., *et al.,* . (2020). Phosphoric Acid-Mediated green Preparation of Regenerated Cellulose Spheres and Their Use for All-Cellulose Cross-Linked Superabsorbent Hydrogels. *Int. J. Biol. Macromolecules* 162, 136–149. doi:10. 1016/j. ijbiomac. 2020. 06. 136

[22]. Ningmei Wu, Zhengkui Li, (2013). Synthesis and characterization of poly (HEA/MALA) hydrogel and its application in removal of heavy metal ions from water, Chemical Engineering Journal, Volumes 215–216, 2013, Pages 894-902,

[23]. Katoch A, Goyal N, Gautam S. (2019). Applications and advances in coordination cages: Metal-Organic Frameworks. Vacuum. 2019 Sep 1;167:287-300.

[24]. Dominik Pilnaj, Pavel Kuráň, Martin Šťastný, VěraPilařová, Pavel Janoš, Martin Kormunda, JonášTokarský, (2021). C18-functionalized Fe3O4/SiO2 magnetic nano-sorbent for PAHs removal from water, Environmental Technology & Innovation, Volume 24, 2021, 101905,

[25]. Abdellaoui K, Pavlovic I, Bouhent M, Benhamou A, Barriga C (2017) A comparative study of the amaranth azo dye adsorption/desorption from aqueous solutions by layered double hydroxides. Appl Clay Sci 143:142–150.

[26]. Nan Hou, Ran Wang, Fan Wang, Jiahui Bai, Jingxin Zhou,* Lexin Zhang, Jie Hu, Shufeng Liu, and Tifeng Jiao (2020) Fabrication of Hydrogels via Host−Guest Polymers as Highly Efficient Organic Dye Adsorbents for Wastewater Treatment Mar 5;5 (10):5470-5479

Chapter
2

MICRO- AND NANOSCALE ORAL DRUGS DELIVERY SYSTEM

PRAKASH KUMAR SAHOO

Post Graduate Department of Chemistry, Dhenkanal Autonomous College, Dhenkanal, Odisha.
Corresponding author E-mail: prakashchemistry1989@gmail.com

ABSTRACT

Micro- and nanoscale oral drug delivery platforms have revolutionized the field of pharmaceutical sciences by enabling targeted and controlled release of therapeutics for the treatment of various diseases. These platforms utilize advanced materials and engineering techniques to enhance drug stability, improve bioavailability, and achieve site-specific delivery within the gastrointestinal (GI) tract. In recent years, there has been significant progress in the development of micro- and nanoscale delivery systems, such as microspheres, nanoparticles, and nanocarriers, that can protect drugs from degradation in the harsh GI environment and facilitate their absorption into systemic circulation. These platforms offer numerous advantages, including the ability to overcome physiological barriers, prolong drug release, and enhance therapeutic efficacy while minimizing side effects.

Microspheres, typically ranging in size from 1 to 1000 micrometers, are solid or hollow spherical particles that can be loaded with drugs and coated with protective materials to control drug release. Nanoparticles, on the other hand, are smaller in size, typically below 1000 nanometers, and offer high drug loading capacity, improved stability, and increased cellular uptake. Nanocarriers, including liposomes, micelles, and dendrimers, are designed to encapsulate drugs within their structures, providing protection and targeted delivery to specific tissues or cells. The design and fabrication of these delivery platforms involve various techniques such as emulsion/solvent evaporation, spray drying, electrostatic assembly, and self-assembly. Surface modification and functionalization can be employed to enhance stability, prolong circulation time, and achieve targeted drug release at the desired site of action.

Micro- and nanoscale oral drug delivery platforms have demonstrated significant potential in addressing challenges associated with conventional oral drug administration, such as poor solubility, low permeability, and rapid metabolism. These platforms have been successfully employed for the delivery of diverse therapeutic agents, including small molecules, peptides, proteins, and nucleic acids, opening new avenues for personalized medicine and targeted therapies. Despite the progress made, several challenges remain, including scale-up manufacturing, regulatory considerations, and ensuring the safety and biocompatibility of these advanced delivery systems. Ongoing research aims to optimize the design, fabrication, and performance of micro- and nanoscale oral drug delivery platforms to enhance their clinical translation and improve patient outcomes. In conclusion, micro- and nanoscale oral drug delivery platforms hold great promise for revolutionizing drug delivery and personalized medicine. With further advancements and interdisciplinary collaborations, these platforms have the potential to overcome current limitations and significantly impact the future of pharmaceutical sciences and healthcare.

KEYWORDS: Nanofabrication, Oral Drug Delivery, Targeted Delivery, Nanoparticles, Therapeutic Agents.

INTRODUCTION

In recent years, there has been a significant surge of interest in developing innovative drug delivery systems that can enhance the therapeutic efficacy and safety of oral medications. Oral administration is the most commonly utilized route for drug delivery due to its convenience, non-invasiveness, and patient compliance. However, the bioavailability and effectiveness of orally administered drugs can be limited by various factors, such as poor solubility, enzymatic degradation, and inadequate absorption. To overcome these challenges, researchers have turned their attention to micro- and nano scale drug delivery platforms. These platforms offer remarkable opportunities to optimize drug delivery, improve drug stability, and enhance the targeting of specific sites within the gastrointestinal tract. By harnessing the unique properties of materials at the micro- and nano scale, novel oral drug delivery systems have been developed, enabling controlled release kinetics, targeted delivery, and enhanced therapeutic outcomes.

Oral administration has emerged as one of the most commonly employed approaches for drug delivery within the human body, owing to its high level of patient compliance, cost-effectiveness, non-invasiveness, and user-friendliness. A wide array of therapeutic compounds, encompassing both synthetic small molecules and biologics, has been administered orally. Nevertheless, effective drug delivery via the oral route presents considerable challenges. These challenges predominantly arise from the numerous biological barriers that a drug carrier must navigate throughout the gastrointestinal (GI) tract. Some of these barriers include the harsh acidic pH environments in the stomach, degrading enzymes that diminish the efficacy of drugs, inadequate penetration of drugs across GI tissue barriers and into the systemic circulation, and the subsequent elimination of drugs through the GI tract before drug release can occur. To surmount these obstacles, the dosage of delivered drugs is often higher than the therapeutic requirement due to reduced bioavailability caused by factors such as enzymatic degradation and limited permeation through the intestinal wall. Nonetheless, it remains crucial to ensure that the concentration of the drug does not exceed a toxic level within the body, as observed in certain cases involving DNA and protein-based drugs at concentrations surpassing the critical threshold. Conversely, even if a drug reaches the target site at a non-toxic concentration level after successfully traversing the physiological barriers of the GI tract, its delivered dosage may prove ineffective.

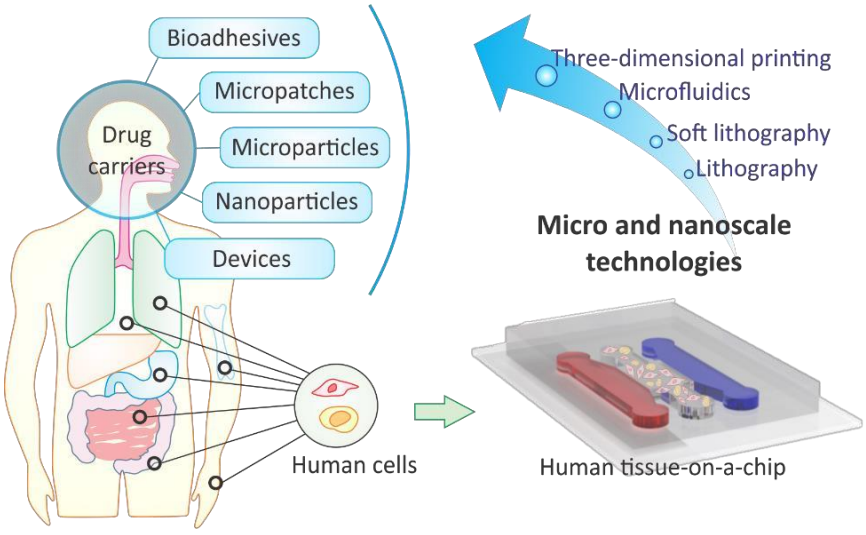


Fig. 1: Micro- and nanoscale technologies enable the fabrication of oral drug carriers as well as human tissue-on-a-chip models for precision medicine applications (Ahadian *et al.*, 2020)

Micro and nanotechnologies have experienced widespread implementation in oral drug delivery systems with the objective of enhancing delivery efficiency. These technologies have found applications in diverse areas, including drug discovery through the development of high-throughput screening assays, the miniaturization of therapeutic and diagnostic tools, tissue engineering, and oral drug delivery. The fabrication of micro and nanocarriers with precise control over their architecture and size has resolved several significant issues associated with oral drug delivery. These efforts are an extension of controlled drug delivery systems dating back to the 1950s. In recent years, dynamic oral delivery systems have been created utilizing micro and nanofabrication technologies, enabling sensing, recording, and stimulation of biological systems to optimize drug delivery.

ORAL DRUG DELIVERY SYSTEM

Oral drug delivery refers to the administration of medications via the oral route, typically in the form of tablets, capsules, or liquids that are ingested and pass through the gastrointestinal (GI) tract. It is one of the most common and convenient routes of drug administration due to its ease of use, patient compliance, and non-invasive nature.

Advantages of oral drug delivery system

(a) Convenience

Oral medications are easy to administer and do not require specialized medical personnel or equipment. Patients can self-administer their medications at home, improving convenience and independence.

(b) Patient Compliance

Oral drugs are generally well-accepted by patients and have high patient compliance rates compared to other routes of administration. This is important for chronic conditions where long-term adherence to medication regimens is necessary.

(c) Wide Acceptance

Oral drug delivery is a widely accepted and familiar method of drug administration among patients, healthcare providers, and regulatory authorities. Extensive regulatory guidelines and approval processes exist for oral pharmaceutical products.

(d) Cost-Effectiveness

Oral medications are typically less expensive to manufacture and distribute compared to other delivery methods, such as injections or intravenous infusions. This makes oral drug delivery more cost-effective for patients and healthcare systems.

(e) Safety

In general, oral drug delivery is considered a safe route of administration. The risk of infections or complications associated with invasive procedures, as seen with injections, is minimized.

(f) Flexibility

Oral medications can be formulated in various dosage forms, including tablets, capsules, powders, and liquids, providing flexibility in dosing and formulation design. Controlled-release formulations can be developed to achieve sustained drug release over an extended period.

LIMITATIONS AND CHALLENGES OF ORAL DRUG DELIVERY SYSTEM

Despite its advantages, oral drug delivery also faces certain limitations and challenges, including:

(a) Variable Absorption

The GI tract presents barriers to drug absorption, such as enzymatic degradation, low solubility, limited permeability, and efflux transporters, which can result in inconsistent drug absorption and variable bioavailability among individuals.

(b) First-Pass Metabolism

Drugs absorbed from the GI tract are initially transported to the liver through the portal vein, where they may undergo significant metabolism before reaching systemic circulation. This can lead to reduced bioavailability and the need for higher drug doses.

(c) Patient Variability

Variations in gastric emptying time, pH levels, and GI motility among individuals can affect drug absorption and therapeutic outcomes. Factors such as food intake, disease conditions, and concomitant medications can also impact oral drug delivery.

(d) Drug Stability

Some drugs are susceptible to degradation in the acidic environment of the stomach or under enzymatic activity in the gut, which can affect their effectiveness. Formulation strategies are often required to enhance drug stability and protect the active compound.

Researchers and pharmaceutical scientists employ various strategies to overcome these challenges and enhance oral drug delivery, including the development of prodrugs, nanoparticles, microparticles, liposomes, and formulation approaches to improve drug solubility, permeability, stability, and targeted delivery within the GI tract. Continued advancements in formulation design, drug delivery technologies, and personalized medicine hold the potential to further optimize oral drug delivery and improve therapeutic outcomes.

BARRIER TO ORAL DRUG DELIVERY

One of the major barriers to oral drug delivery is the physiological barriers present within the gastrointestinal (GI) tract. These barriers can significantly limit the absorption and bioavailability of orally administered drugs, impacting their therapeutic efficacy. Some of the key barriers include:

(a) Poor aqueous solubility

Many drugs exhibit low solubility in water, which hinders their dissolution and subsequent absorption in the GI tract. Poorly soluble drugs may form aggregates or precipitates, reducing their effective concentration and limiting their absorption across the intestinal epithelium.

(b) Limited permeability

The intestinal epithelium acts as a selective barrier, controlling the absorption of drugs into systemic circulation. Drugs must pass through the epithelial cells (transcellular route) or between the cells (paracellular route) to be absorbed. However, many drugs, particularly those with large molecular sizes or hydrophilic properties, face limited permeability across the intestinal epithelium, resulting in poor absorption.

(c) First-pass metabolism

After absorption, drugs from the GI tract are transported to the liver via the portal vein, where they may undergo extensive metabolism before reaching systemic circulation. This "first-pass metabolism" can lead to a significant reduction in drug concentration, limiting the bioavailability and therapeutic effect of the drug.

(d) Enzymatic degradation

The GI tract contains various enzymes, such as proteases, lipases, and esterases, which can degrade drugs and reduce their stability. Enzymatic degradation can occur in the stomach, intestine, or during passage through the gut lumen, thereby reducing the concentration of active drug available for absorption.

(e) Efflux transporters

Efflux transporters, such as P-glycoprotein (P-gp), are membrane proteins expressed in the intestinal epithelial cells. They actively pump drugs back into the gut lumen, limiting their absorption and increasing their elimination. Drug substrates of these transporters may experience decreased absorption and reduced bioavailability.

(f) pH-dependent drug solubility

The pH along the GI tract varies significantly, ranging from highly acidic in the stomach to more alkaline in the small intestine. Some drugs may exhibit pH-dependent solubility, leading to precipitation or reduced dissolution in specific regions of the GI tract, affecting their absorption.

Overcoming these barriers is crucial for enhancing oral drug delivery. Researchers employ various strategies, such as formulation approaches (e. g., using solubilizing agents, nanoparticles, or prodrugs), enzyme inhibitors, permeation enhancers, and targeted delivery systems, to improve drug solubility, permeability, stability, and bypass first-pass metabolism. Innovative technologies and formulations are continuously being developed to overcome these challenges and improve the effectiveness of oral drug delivery. There are various barriers to oral drug delivery system. These are discussed below.

(a) PHYSIOLOGICAL BARRIER TO ORAL DRUG DELIVERY

Several constraints associated with oral drug delivery systems are dictated by the anatomy, physiology, and biochemistry of the gastrointestinal (GI) tract. While the skin serves as the primary interface between the human body and the external environment, the absorption mechanism of orally administered drugs in the intestinal epithelium encounters more chemical and physical limitations due to its significantly larger surface area of approximately 300-400 m2 (2) compared to the skin's surface area of approximately 2 m2. Upon ingestion, the drug enters the GI tract and gradually releases within the intestine, diffusing through the mucus layer as illustrated in Figure 2. The mucus layer in the small intestine is non-continuous, while the stomach and large intestine (colon) consist of two layers (3). The drug traverses the mucus layer and further diffuses through pathways involving tight junctions (TJs) and epithelial cells. This process continues until the drug successfully traverses the capillary layer covering the epithelium.

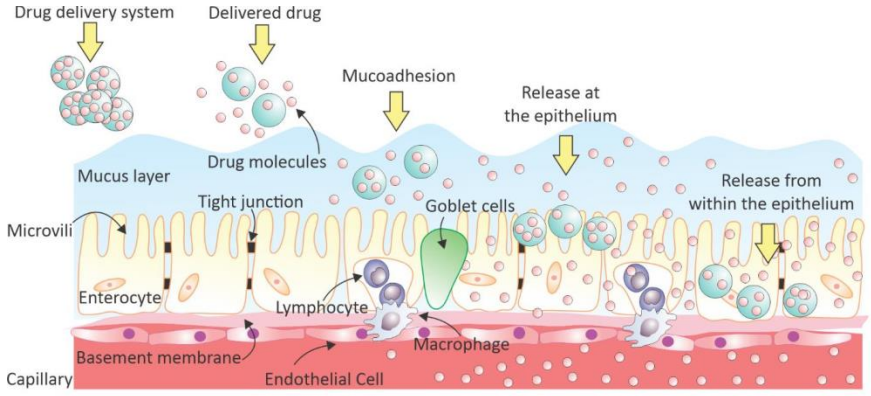


Fig. 2: Schematic illustration of drug release and absorption mechanisms for orally delivered drugs in the large surface area of the human intestinal epithelium (Ahadian *et al.*, 2020)

The GI tract encompasses the oral cavity, oesophagus, stomach, small intestine, and colon, each possessing distinct characteristics that must be considered during the design of delivery systems and the study of drug release mechanisms. Generally, drug absorption in the GI tract faces various physiological barriers across different regions. The GI tract naturally exhibits low permeability to foreign molecules, including orally delivered drugs, due to complex physiological barriers (4). Factors such as the

bottlebrush-like structure of mucin within the lipid-rich matrix of mucus, gastric glands embedded in the stomach with its acidic environment, residence time, microbiome, and permeability across the intestinal epithelium should all be considered when designing carriers to facilitate the oral delivery of small molecules, proteins, and peptides. The key obstacles encountered in oral drug delivery encompass biochemical, mucus diffusional, and cellular permeability barriers within the GI tract. The specific site of drug absorption is determined by the drug type as well as local environmental conditions such as pH, enzymes, mucus barriers, drug residence time, and the surface area of the GI tract.

Table 1: Characteristics of different segments of the human GI tract (4)

Part of body	pH	Length (cm)	Mean Diameter	Mucus thickness (μm)	Mucus Turnover rate (hrs)
Stomach	0. 8-5	20	NA	245± 200	24-48
Duodenum	~7	17-56	4	15. 5	
Jejunum	>= 7	280-1000	2-2. 5	15. 5	
Ileum	>= 7	280-1000	3	15. 5	
Colon	7-8	80-313	4-4. 8	135±25	

(b) Biochemical Barrier To Oral Drug Delivery

The combined effect of enzymatic degradation and pH deterioration serves as the primary biochemical impediments to the bioavailability of therapeutics administered orally. The existence of drug-degrading enzymes and the presence of an acidic pH lead to an approximate loss of 94-98% of ingested biological drugs due to deamidation, oxidation, or hydrolysis. The gastric fluid in the stomach comprises hydrochloric acid, the protein-digesting enzyme pepsin, and the mucus secreted by gastric glands, which collectively create an acidic environment with a pH range of 1. 2-3. Apart from the harsh acidity of the stomach, the presence of digestive enzymes, such as pepsin, also poses challenges for oral drug delivery. Moreover, lipases present in the stomach can contribute to the hydrolysis of drugs with hydrophobic regions. Furthermore, the small intestine plays a role in drug digestion, as it contains high concentrations of digestive enzymes, including trypsin, chymotrypsin, carboxypeptidases, and elastases. Lastly, the colon offers an extended residence time of up to 20 hours, low concentrations of digestive enzymes, relatively neutral pH values ranging from 6 to 6. 7, and low fluid volumes compared to drug ratios.

(c) Mucosal Diffusion Barrier to Oral Drug Delivery

In conjunction with the aforementioned physiological hindrances involving pH and enzymes, the presence of mucus with a viscoelastic and hydrogel-like structure poses a formidable barrier to the penetration of therapeutics from the intestinal lumen to the underlying epithelium (Figure 3b). The direct interaction between therapeutics and epithelial cells is limited by two layers of mucus: the outer loosely adherent layer and the inner firmly adherent layer. Goblet cells secrete mucus, with a turnover rate of approximately 24-48 hours, to prevent the attachment of potentially harmful compounds and bacteria. The majority of mucus consists of mucin glycoproteins, which form a viscous gel that entraps foreign particles. Additionally, mucus contains proteins, carbohydrates, nucleic acids, lipids, salts, antibodies, and other active proteins. Consequently, it acts as a protective barrier while providing a nutrient-rich environment for bacterial colonization and the presence of antimicrobial molecules.

(d) Cellular Permeability Barrier to Oral Drug Delivery

The intestinal epithelium represents the outermost layer of cells that are exposed to the contents of the intestinal lumen. It is comprised of tight junctions (TJs) and three distinct types of cells: enterocytes,

goblet cells, and Microfold cells (M-cells). Enterocytes, which are the most abundant cells within the epithelium layer, play a vital role in facilitating the transportation of nutrients and water from the gut lumen into the bloodstream. Goblet cells, responsible for secreting mucus, constitute approximately 10-20% of the epithelial cells, while M-cells, which cover Peyer's patches, account for less than 1% of the total. M-cellsserve as crucial agents for antigen sampling and are particularly significant targets for drug delivery due to their relatively lower protection by mucus. TJs act as paracellular barriers, regulating the transportation of drugs between adjacent intestinal epithelial cells.

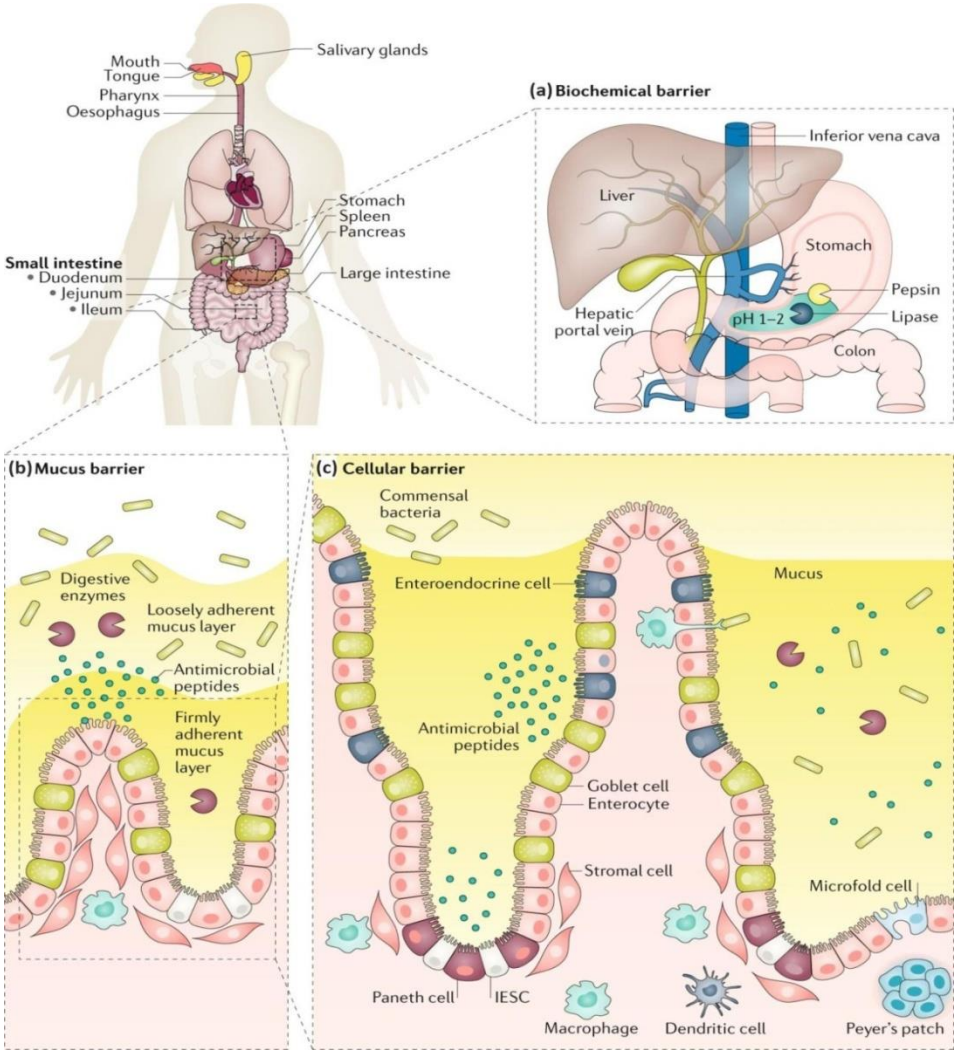


Fig. 3: A schematic of physiological barriers in oral drug delivery including (a) biochemical barriers, (b) mucus barriers, and (c) cellularbarrierstooraldrug delivery (Brown *et al.*, 2019)

The methods employed for drug absorption into the bloodstream rely on interactions between therapeutic agents and epithelial cells, occurring either through direct transport across the cells themselves (transcellular pathways) or via the passage between the cells by utilizing the TJs (paracellular pathways). Furthermore, drug absorption can also take place through lymphatic absorption, facilitated by M-cells present in Peyer's patches. Another mechanism involves receptor-mediated and transcytosis-mediated endocytosis, commonly facilitated by pathways such as the vitamin B_{12} uptake pathway or hydrogen-coupled peptide transporters. Additionally, receptors for transferring receptors and IgG neonatal receptors play a role in this process. In the subsequent sections, we will delve into how micro

and nanoscale technologies enable the circumvention of biochemical and mucosal diffusion barriers, thus facilitating successful cellular uptake.

MICROSCALE ORAL DRUG DELIVERY PLATFORMS

In recent years, the field of drug delivery has witnessed significant advancements, particularly in the development of microscale oral drug delivery platforms. These innovative platforms offer a promising approach to enhancing the efficacy and safety of therapeutic treatments. By utilizing microscale technologies, drug delivery systems can overcome various challenges associated with conventional oral drug administration. This chapter aims to explore the concept of microscale oral drug delivery platforms, their advantages, and the potential applications they hold in the field of medicine. Microscale oral drug delivery platforms refer to systems that utilize micro and nanotechnologies to formulate and deliver drugs through the oral route. These platforms encompass a range of techniques, including microencapsulation, microemulsions, microparticles, and nanotechnology-based drug delivery systems. By harnessing the advantages of microscale technologies, these platforms offer improved drug solubility, enhanced bioavailability, controlled release, and targeted drug delivery.

Advantages of Microscale Oral Drug Delivery Platforms

1. **ENHANCED DRUG SOLUBILITY**

Microscale platforms enable the formulation of drugs with poor solubility, enhancing their bioavailability and therapeutic efficacy. Techniques such as nanoemulsions and nanoparticle-based drug delivery systems improve the solubility and dissolution rate of poorly water-soluble drugs.

2. **CONTROLLED RELEASE**

Microscale oral drug delivery platforms allow for precise control over drug release kinetics. By manipulating the formulation parameters, such as particle size and composition, sustained, pulsatile, or delayed release profiles can be achieved, ensuring optimal drug delivery and therapeutic outcomes.

3. **TARGETED DRUG DELIVERY**

Microscale technologies facilitate targeted drug delivery to specific sites within the body. By incorporating ligands, antibodies, or specific receptors on the surface of microcarriers or nanoparticles, drugs can be selectively delivered to the desired tissues or cells, minimizing off-target effects, and reducing systemic toxicity.

4. **PROTECTION AND STABILITY**

Microscale platforms provide protection to drugs that are susceptible to degradation or have low stability. Microencapsulation techniques, such as microspheres or liposomes, can shield the drug molecules from environmental factors, enhancing their stability and shelf life.

Applications of Microscale Oral Drug Delivery Platforms

1. **CANCER THERAPY**

Microscale oral drug delivery platforms have shown great potential in improving cancer treatment outcomes. By encapsulating anticancer drugs within targeted nanoparticles, these platforms can enhance drug accumulation at the tumor site, minimize systemic toxicity, and improve patient compliance.

2. **INFECTIOUS DISEASES**

Microscale platforms offer opportunities for targeted drug delivery to combat infectious diseases. By incorporating antimicrobial agents within microcarriers or nanocarriers, these platforms can deliver drugs directly to the infection site, increasing efficacy and reducing the risk of drug resistance.

3. CHRONIC CONDITIONS

Microscale oral drug delivery platforms hold promise in the management of chronic conditions such as diabetes and cardiovascular diseases. These platforms can provide controlled and sustained drug release, allowing for improved patient adherence and better disease management.

Future Perspectives and Challenges

While microscale oral drug delivery platforms show great promise, several challenges and opportunities for further development remain. Here are some future perspectives:

1. BIOCOMPATIBILITY AND SAFETY

Ensuring the biocompatibility and safety of microscale platforms is crucial. Extensive preclinical and clinical studies are necessary to assess their potential side effects, toxicity, and long-term safety profiles.

2. MANUFACTURING SCALABILITY

The scalability of microscale platforms is essential to meet the growing demand for efficient drug delivery systems. Optimization of manufacturing processes and cost-effective production methods are areas that require further attention.

3. REGULATORY CONSIDERATIONS

Microscale platforms may pose unique regulatory challenges due to their novel nature. Collaboration between researchers, regulatory bodies, and pharmaceutical companies is necessary to establish guidelines and standards for their development, evaluation, and commercialization.

4. INTEGRATION WITH DIGITAL HEALTH TECHNOLOGIES

The integration of microscale platforms with digital health technologies, such as smart sensors and wireless communication, can enable real-time monitoring of drug release, patient adherence, and therapeutic outcomes. This integration has the potential to revolutionize personalized medicine and improve patient care.

The micro-scale oral drug delivery platforms have emerged as a promising approach to enhancing drug delivery efficiency, efficacy, and patient compliance. By utilizing micro and nanotechnologies, these platforms offer advantages such as enhanced drug solubility, controlled release, targeted delivery, and stability. They hold tremendous potential for various applications, including cancer therapy, infectious diseases, and chronic conditions. However, further research, collaboration, and regulatory considerations are necessary to overcome challenges and unlock the full potential of these platforms. With continued advancements, microscale oral drug delivery platforms can transform the landscape of drug delivery and contribute to improved healthcare outcomes.

NANOSCALE ORAL DRUG DELIVERY PLATFORMS

In recent years, the field of nanotechnology has witnessed remarkable advancements, revolutionizing various industries, including medicine. One particular area where nanotechnology has shown immense potential is in the development of drug delivery systems. Nanoparticles, defined as particles with sizes ranging from 1 to 100 nanometers, have emerged as promising tools in targeted drug delivery. This chapter aims to explore the applications, benefits, and challenges associated with utilizing nanoparticles as drug delivery systems.

Applications of Nanoparticles in Drug Delivery

The applications of nanoparticles in drug delivery are diverse and extensive. These tiny particles can be engineered to encapsulate a wide range of therapeutic agents, including small molecules, proteins, and nucleic acids. Their versatility enables them to address various diseases, such as cancer, cardiovascular disorders, infectious diseases, and neurological conditions. By precisely tailoring the characteristics of

nanoparticles, researchers can enhance drug solubility, stability, and bioavailability, thus optimizing their therapeutic effects.

Benefits of Nanoparticle-based Drug Delivery Systems

Nanoparticle-based drug delivery systems offer numerous advantages over conventional drug administration methods. Firstly, their small size allows for enhanced permeation and retention in target tissues, enabling more efficient drug delivery to specific sites of action. This targeted approach reduces systemic side effects and increases drug efficacy, leading to improved patient outcomes. Additionally, nanoparticles can protect drugs from premature degradation and clearance, ensuring a sustained release of therapeutic agents and prolonging their circulation time in the body. Furthermore, nanoparticles can be surface modified to achieve targeted drug delivery. By attaching ligands or antibodies to the nanoparticle surface, drugs can be selectively delivered to cells or tissues expressing corresponding receptors or antigens. This active targeting strategy improves drug localization, reduces off-target effects, and minimizes systemic toxicity. Such precision in drug delivery is particularly crucial in the treatment of complex diseases, where site-specific action is desired.

Challenges and Considerations

While nanoparticles hold immense promise as drug delivery systems, several challenges and considerations need to be addressed. One significant concern is the potential toxicity of nanoparticles themselves. Due to their unique physicochemical properties, nanoparticles may interact with biological systems in unpredictable ways, potentially leading to adverse effects. Thorough characterization and evaluation of nanoparticle toxicity are necessary to ensure their safety for clinical use.

Moreover, the scalability and cost-effectiveness of nanoparticle production pose challenges for large-scale manufacturing and commercialization. As the demand for nanoparticle-based therapies grows, it becomes essential to develop scalable and reproducible manufacturing processes that meet regulatory standards. Advances in nanomaterial synthesis, purification, and quality control are actively pursued to overcome these challenges. Regulatory considerations also play a vital role in the development and approval of nanoparticle-based drug delivery systems. Regulatory agencies are actively working to establish guidelines and standards for the evaluation of safety, efficacy, and quality of nanoparticle formulations. These regulations aim to ensure the responsible translation of nanomedicine from the laboratory to the clinic, promoting patient safety and fostering innovation in the field.

Nanoparticles have opened up new possibilities in the field of drug delivery, offering targeted and controlled release of therapeutic agents. Their unique properties, including size-dependent behavior, tunable surface characteristics, and multifunctionality, make them invaluable tools in modern medicine. However, the full potential of nanoparticle-based drug delivery systems can only be realized through continued research and development. Addressing the challenges related to toxicity, scalability, and regulatory considerations is crucial for the successful translation of nanoparticle-based drug delivery systems into clinical practice. With ongoing research, scientists are actively exploring novel strategies to enhance the performance and functionality of nanoparticles as drug carriers. Surface engineering techniques, such as the incorporation of targeting ligands, stimuli-responsive coatings, and stealth materials, are being employed to improve nanoparticle stability, circulation time, and targeting efficiency. Additionally, efforts are being made to optimize drug loading and release kinetics, ensuring the controlled and sustained delivery of therapeutics.

The development of advanced characterization techniques is another crucial aspect of nanoparticle-based drug delivery. Scientists are employing cutting-edge imaging and spectroscopic methods to study the behavior and fate of nanoparticles within the body. This knowledge aids in understanding the

biodistribution, cellular uptake mechanisms, and intracellular trafficking of nanoparticles, providing insights into their efficacy and potential toxicity. In the quest for safer and more efficient drug delivery systems, researchers are exploring the use of biocompatible and biodegradable materials for nanoparticle synthesis. Biomimetic nanoparticles that mimic the natural structures and functions of cells and tissues are gaining attention due to their enhanced biocompatibility and reduced immunogenicity. These bioinspired systems hold great promise for targeted and personalized medicine, allowing for precise drug delivery and therapeutic interventions.

The field of nanomedicine is also witnessing exciting advancements in the area of theragnostic, which combines therapeutic and diagnostic functionalities. Nanoparticles can be designed to carry both therapeutic agents and imaging probes, enabling simultaneous drug delivery and real-time monitoring of treatment response. This integrated approach offers a powerful tool for personalized medicine, allowing physicians to tailor treatment strategies based on individual patient characteristics and disease progression. In conclusion, nanoparticles have emerged as valuable platforms for drug delivery, holding immense potential to revolutionize the field of medicine. Their unique properties and capabilities offer advantages such as targeted delivery, enhanced drug stability, and controlled release. However, it is essential to address challenges related to toxicity, scalability, and regulatory considerations to ensure the safe and effective translation of nanoparticle-based drug delivery systems. With continued research and innovation, nanoparticles are poised to play a transformative role in improving patient outcomes and advancing healthcare.

CONCLUSION AND FUTURE PERSPECTIVES

Micro- and nanoscale oral drug delivery platforms have the potential to revolutionize the field of medicine by improving drug delivery and enhancing therapeutic outcomes. These platforms offer advantages such as targeted delivery, controlled release kinetics, and increased bioavailability. However, further research is needed to fully understand the underlying mechanisms, optimize the design parameters, and evaluate the long-term safety and efficacy of these systems.

The future perspective of micro- and nanoscale oral drug delivery platforms is promising, with several exciting developments on the horizon. Here are some key areas that hold great potential for advancement:

1. PERSONALIZED MEDICINE

Micro- and nanoscale drug delivery platforms can contribute to the realization of personalized medicine. By tailoring the design of these platforms to specific patient needs, including individual drug dosages, release kinetics, and targeted delivery, healthcare providers can optimize treatment outcomes. This approach has the potential to revolutionize patient care by maximizing therapeutic efficacy while minimizing adverse effects.

2. COMBINATION THERAPIES

micro- and nanoscale platforms offer opportunities for *c*ombination therapies, where multiple drugs or therapeutic agents are delivered simultaneously to address complex diseases. By encapsulating different drugs within a single delivery system, synergistic effects can be achieved, enhancing therapeutic outcomes. Furthermore, the precise control over drug release kinetics provided by these platforms allows for the customization of combination therapy regimdiaens tailored to individual patient requirements.

3. INTEGRATION OF DIAGNOSTIC CAPABILITIES:

The integration of diagnostic capabilities within micro- and nanoscale drug delivery platforms opens up new avenues for theranostics. Theranostic systems combine therapeutic and diagnostic functionalities, enabling simultaneous treatment and monitoring of disease progression. By incorporating sensors or

imaging agents into the drug delivery platforms, healthcare professionals can gain real-time insights into drug distribution, efficacy, and patient response. This integration facilitates personalized treatment adjustments and enhances patient management.

4. BIORESPONSIVE AND TARGETED DELIVERY

Future developments in micro- and nanoscale platforms will focus on achieving even greater precision and control over drug delivery. Bioresponsive systems that can sense specific physiological cues, such as pH, enzymes, or biomarkers, will enable on-demand drug release at the target site. Additionally, advancements in targeting strategies will enhance the specificity of drug delivery, minimizing off-target effects and improving therapeutic efficiency.

5. REGULATORY CONSIDERATIONS AND COMMERCIALIZATION

As micro- and nanoscale oral drug delivery platforms progress towards clinical translation, addressing regulatory considerations and ensuring commercial viability will be crucial. Robust preclinical studies, comprehensive safety assessments, and effective manufacturing processes will be essential to obtain regulatory approvals. Moreover, collaborations between academia, industry, and regulatory agencies will play a pivotal role in facilitating the successful transition of these platforms from the lab to the market.

In conclusion, micro- and nanoscale oral drug delivery platforms hold great promise in the field of medicine. Their ability to enhance drug bioavailability, enable targeted delivery, and provide controlled release kinetics make them valuable tools for improving therapeutic outcomes. However, it is crucial to conduct further research to address challenges related to scalability, biocompatibility, and regulatory approval. With continued advancements in this field, micro- and nanoscale oral drug delivery platforms have the potential to revolutionize the way we administer medications, leading to more effective treatments and improved patient care.

REFERENCES

[1]. S. Ahadian, J. A. Finbloom, M. Mofidfar, *et al.,* . (2020). Micro andnanoscale technologies in oral drug delivery, Advanced Drug Delivery Reviews. https://doi. org/10. 1016/j. addr. 2020. 07. 012

[2]. Prausnitz MR, Elias PM, Franz TJ, Schmuth M, Tsai J-C, Menon GK, Holleran WM, Feingold KR. Skin barrier and transdermal drug delivery.

[3]. Li H, Limenitakis JP, Fuhrer T, Geuking MB, Lawson MA, Wyss M, BrugirouxS, KellerI, Macpherson JA, Rupp S. (2015). The outer mucus layer hosts a distinct intestinal microbial niche. Nature communications. 2015;6 (1):1-13.

[4]. Homayun B, Lin X, Choi HJ. (2019). Challenges and Recent Progress in Oral Drug DeliverySystems for Biopharmaceuticals. Pharmaceutics. 2019;11 (3):129. Epub 2019/03/22. doi:10. 3390/pharmaceutics11030129. PubMed PMID: 30893852; PMCID: PMC6471246.

[5]. Brown TD, Whitehead KA, Mitragotri S. (2019). Materials for oral delivery of proteins andpeptides. Nature Reviews Materials. 2019:1-22.

[6]. Cade B. Fox, Jean Kim, Long V. Le, Cameron L. Nemeth, Hariharasudhan D. Chirra, Tejal A. Desai. (2015). Micro/nanofabricated Platforms for OralDrug Delivery, Journal of Controlled Release 2015, doi: 10. 1016/j. jconrel. 2015. 07. 033.

[7]. Sant S, Tao SL, Fisher OZ, Xu Q, Peppas NA, Khademhosseini A. (2012). Microfabrication technologies for oral drug delivery. Adv Drug Deliv Rev. 2012;64 (6):496-507. Epub2011/12/15. doi: 10. 1016/j. addr. 2011. 11. 013. PubMed PMID: 22166590; PMCID: PMC3534972.

[8]. Sastry SV, Nyshadham JR, Fix JA. (2000). Recent technological advances in oral drug delivery–a review. Pharmaceutical science & technology today. 2000;3 (4):138-45.

[9]. Maham A, Tang Z, Wu H, Wang J, Lin Y. (2009). Protein-based nanomedicine platforms for drug delivery. Small. 2009;5 (15):1706-21. Epub 2009/07/03. doi: 10. 1002/smll. 200801602. PubMedPMID: 19572330.

[10]. Koziolek M, Grimm M, Schneider F, Jedamzik P, Sager M, Kuhn JP, Siegmund WWeitschies W. (2016). Navigating the human gastrointestinal tract for oral drug delivery: Unchartedwaters and new frontiers. Adv Drug Deliv Rev. 2016;101:75-88. Epub 2016/04/03.

[11]. Petit J, Meurice N, Kaiser C, Maggiora G. (2012). Softening the rule of five—where to draw theline? Bioorganic & medicinal chemistry. 2012;20 (18):5343-51

[12]. Peyrot M, Rubin RR, Kruger DF, Travis LB. (2010). Correlates of insulin injection omission. Diabetes care. 2010;33 (2):240-5.

[13]. Gedawy A, Martinez J, Al-Salami H, Dass CR. (2018). Oral insulin delivery: existing barriersand current counterstrategies. Journal of pharmacy and pharmacology. 2018;70 (2):197-213.

[14]. Ahadian S, Civitarese R, Bannerman D, Mohammadi MH, Lu R, Wang E, DavenportHuyer L, Lai B, Zhang B, Zhao Y. (2018). Organ-on-a-chip platforms: a convergence of advanced materials, cells and microscale technologies. Advanced healthcare materials. 2018;7 (2):1700506.

[15]. Ahadian S, Ramón-Azcón J, Estili M, Obregón R, Shiku H, Matsue T. (2014). Facile and rapidgeneration of 3D chemical gradients within hydrogels for high-throughput drug screeningapplications. Biosensors and Bioelectronics. 2014;59:166-73.

[16]. Bae H, Chu H, Edalat F, Cha JM, Sant S, Kashyap A, Ahari AF, Kwon CH, Nichol JW, Manoucheri S, Zamanian B, Wang Y, Khademhosseini A. (2014). Development of functionalbiomaterials with micro- and nanoscale technologies for tissue engineering and drug delivery applications. J Tissue Eng Regen Med. 2014;8 (1):1-14, Epub 2012/06/20.

[17]. Caldorera-Moore M, Peppas NA. (2009). Micro- and nanotechnologies for intelligent andresponsive biomaterial-based medical systems. Adv Drug Deliv Rev. 2009;61 (15):1391-401. Epub 2009/09/18.

[18]. Pan J, Chan SY, Lee WG, Kang L. (2011). Microfabricated particulate drug-delivery systems. Biotechnol J. 2011;6 (12):1477-87. Epub 2011/11/15. doi: 10. 1002/biot. 201100237. PubMedPMID: 22076813.

[19]. Khademhosseini A, Langer R. (2006). Drug delivery and tissue engineering. Chem Eng Prog. 2006;102 (2):38-42

[20]. Park K. (2014). Controlled drug delivery systems: past forward and future back. J ControlRelease. 2014;190:3-8. Epub 2014/05/06. doi: 10. 1016/j. jconrel. 2014. 03. 054. PubMed

[21]. Dahan A, Hoffman A. (2008). Rationalizing the selection of oral lipid based drug delivery systems by an in vitro dynamic lipolysis model for improved oral bioavailability of poorly water soluble drugs J control Release. 2008;129 (1):1-10. Epub 2008/05/24.

[22]. Son G-H, Lee B-J, Cho C-W. (2017). Mechanisms of drug release from advanced drugformulations such as polymeric-based drug-delivery systems and lipid nanoparticles. Journal ofPharmaceutical Investigation. 2017;47 (4):287-96.

[23]. Prausnitz MR, Elias PM, Franz TJ, Schmuth M, Tsai J-C, Menon GK, Holleran WM,Feingold KR. (2012). Skin barrier and transdermal drug delivery. J Dermatology. 2012;3:2065-73.

[24]. Groeber F, Holeiter M, Hampel M, Hinderer S, Schenke-Layland K. (2011). Skin tissueengineering—in vivo and in vitro applications. Advanced drug delivery reviews. 2011

[25]. Prausnitz MR, Elias PM, Franz TJ, Schmuth M, Tsai J-C, Menon GK, Holleran WM,Feingold KR. Skin barrier and transdermal drug delivery.

[26]. Li H, Limenitakis JP, Fuhrer T, Geuking MB, Lawson MA, Wyss M, Brugiroux S, KellerI, Macpherson JA, Rupp S. (2015). The outer mucus layer hosts a distinct intestinal microbial niche. Nature communications. 2015;6 (1):1-13.

[27]. Homayun B, Lin X, Choi HJ. (2019). Challenges and Recent Progress in Oral Drug DeliverySystems for Biopharmaceuticals. Pharmaceutics. 2019;11 (3):129. Epub 2019/03/22.

[28]. Ensign LM, Cone R, Hanes J. (2012). Oral drug delivery with polymeric nanoparticles: thegastrointestinal mucus barriers. Adv Drug Deliv Rev. 2012;64 (6):557-70. Epub 2012/01/04.

[29]. Renukuntla J, Vadlapudi AD, Patel A, Boddu SH, Mitra AK. (2013). Approaches for enhancingoral bioavailability of peptides and proteins. Int J Pharm. 2013;447 (1-2):75-93.

[30]. Moreno Raja M, Lim PQ, Wong YS, Xiong GM, Zhang Y, Venkatraman S, Huang Y. (2019). Polymeric Nanomaterials. Nanocarriers for Drug Delivery2019. p. 557-653.

[31]. Brown TD, Whitehead KA, Mitragotri S. (2019). Materials for oral delivery of proteins andpeptides. Nature Reviews Materials. 2019:1-22

[32]. Durán-Lobato M, Niu Z, Alonso MJ. (2019). Oral delivery of biologics for precision medicine. Advanced Materials. 2019:1901935.

[33]. Li XJ, Zhou Y. (2013). Microfluidic devices for biomedical applications: Elsevier; 2013.

[34]. Kawaguchi H. (2000). Functional polymer microspheres. Progress in polymer science. 2000;25 (8):1171-210.

[35]. Makadia HK, Siegel SJ. (2011). Poly lactic-co-glycolic acid (PLGA) as biodegradable controlleddrug delivery carrier. Polymers. 2011;3 (3):1377-97.

[36]. Varde NK, Pack DW. (2004). Microspheres for controlled release drug delivery. Expert Opin BiolTher. 2004;4 (1):35-51. Epub 2003/12/19. doi: 10. 1517/14712598. 4. 1. 35. PubMed

[37]. McClements DJ. (2012). Advances in fabrication of emulsions with enhanced functionality usingstructural design principles. Current Opinion in Colloid & Interface Science. 2012;17 (5):235-45.

[38]. Ignatious F, Sun L, Lee C-P, Baldoni J. (2010). Electrospun Nanofibers in Oral Drug Delivery. Pharmaceutical Research. 2010;27 (4):576-88.

[39]. Thakkar S, Misra M. (2017). Electrospun polymeric nanofibers: New horizons in drug delivery. European Journal of pharmaceutical sciences. 2017;107:148-67.

[40]. Sanjay ST, Zhou W, Dou M, Tavakoli H, Ma L, Xu F, Li X. (2018). Recent advances ofcontrolled drug delivery using microfluidic platforms. Adv Drug Deliv Rev. 2018;128:3-28. Epub 2017/09/19.

[41]. Dittrich PS, Manz A. (2006). Lab-on-a-chip: microfluidics in drug discovery. Nat Rev DrugDiscov. 2006;5 (3):210-8. Epub 2006/03/07. doi: 10. 1038/nrd1985. PubMed

Chapter
3

PESTICIDES AND THEIR EFFECTS ON CROPS

SHWETA[1], M. L. JOSHI[2], RUCHI TRIPATHI[1] AND RASHMI TEWARI[1]

[1]Department of Plant Pathology, College of Agriculture,
G. B. Pant University of Agriculture and Technology, Pantnagar-263 145, Uttarakhand, India
[2]Department of Botany, G. P. G. C. Champawat, S. S. J. University, Almora Uttarakhand, India

ABSTRACT

The harm caused by pesticides to human health and the environmentinvolves some sensitive issues such as drinking water contamination, the health of users and the harmful effects on wildlife, plants and other biodiversity. Pesticide transmission into the environment causes harm to non-target organisms. By controlling pests, diseases, and weeds, farmers can protect their crops from significant losses. The development of synthetic agrochemicals and their widespread use have contributed to the enormous increase in agricultural yield. However, concerns over the harmful impact of pesticides on human health and the environment have led to the reconsideration in pesticide registration procedures. The science of modern pest management is becoming more and more diverse, with thousands of different management techniques so, by investigating the effectiveness of specific insect, disease or insect problems in various cropping systems, a suitable management strategy could be applied by keeping in view all the benefits and risks associated with the used approach.

KEYWORDS: Pesticides, Biodiversity, Agricultural Yield, Disease Management**,** Insecticides

INTRODUCTION

The harm caused by pesticides to human health and the environment is a major subject of concern which involves some sensitive issues such as drinking water contamination, the health of users and the harmful effects on wildlife, plants and other biodiversity. The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others. The introduction of synthetic insecticides – organophosphate (OP) insecticides in the 1960s, carbamates in 1970s and pyrethroids in 1980s and the introduction of herbicides and fungicides in the 1970s–1980s contributed greatly to pest control and agricultural output (Akhtar,2009). In agricultural production, pesticides are indispensable for reducing the crop losses and to increase global food supply for world's increasing population. Chemical pesticides have significantly increased agricultural productivity in last few decades. Pesticides are employed to boost agricultural productivity, but they are applied carelessly and are also known to harm the biota. Pesticide transmission into the environment causes harm to non-target organisms. Several pesticides have the potential to harm to both the environment and human health. Pesticides are thought to only affect the intended organisms in about 0. 1% of cases, with the remainder polluting the environment and harming the environment (Carriger *et al.,* 2006). Pesticides have been used by farmers to control weeds and insects, and their remarkable increases in agricultural products have been reported. About one-third of agricultural products are produced depending on the application of pesticides. Without the use of pesticides, there would be a 78% loss of fruit production, a 54% loss of vegetable production, and a 32% loss of cereal production.

Therefore, pesticides play a critical role in reducing diseases and increasing crop yields worldwide (Tudi *et al.,* 2021).

The development of synthetic pest control chemicals and their widespread use have contributed to the enormous increase in agricultural yield. However, concerns over the harmful impact of pesticides on human health and the environment have led to the reconsideration in pesticide registration procedures. The worldwide pesticide production increased at a rate of about 11% per year, from 0. 2 million tons in the 1950s to more than 5 million tons by 2000 (Carvalho, 2017). Three billion kilograms of pesticides are used worldwide every year (Hayes *et al.,* 2017), while only 1% of total pesticides are effectively used to control insect pests on target plants. The large amounts of remaining pesticides penetrate or reach non-target plants and environmental media. As a consequence, pesticide contamination has polluted the environment and caused negative impacts on human health (Hernandez *et al.,* 2013). However, there is a decline in the usage of the quantity of synthetic pesticides due to the availability of new safer options in the form of bio pesticides. This chapter provides information about the historical perspective of pesticide usage, general types of pesticide in use, and the role of pesticides in agriculture.

HISTORY OF PESTICIDES

Prior to the 1870s, a variety of natural compounds were used to manage pests. Insecticides were used for the first time by the Sumerians around 4500 years ago. Insects and mites were managed with sulphur-based chemicals. Initially volatile compounds were applied frequently by "smoking". The idea was to burn straw, chaff, hedge clippings, manure, or other animal products to create smoke that would spread throughout the orchard, crop, or vineyard (Unsworth, J., 2010). Weeds were controlled mainly by hand weeding. Pyrethrum obtained from the dried flowers of the chrysanthemumhas also been used as an insecticide for over 2000 years.

Because of the urgency to improve food production and control insect-borne diseases, the development of pesticides increased during World War II (1939-1945). Additionaly, from the 1940s onwards, the increased use of synthetic crop protection chemicals permitted a further increase in food production (Bernardes *et al.,* 2015). A copper acetoarsenite inorganic compound known as "Paris Green" was first made available as a pigment in 1814. Paris Green was successfully used as a rodenticide and pesticide by 1867. Paris Green paints were indeed still being made in the 1960s. Elements such as sulphur, heavy metals and salt were the earliest documented chemical pesticide compounds. People started using inorganic synthetic pesticides between 1870 and 1945. Copper and sulphur compounds were used to protect fruit and potatoes from fungal attack around the end of 1800sby Swedish. Since then, several inorganic chemicals have been used, including the Bordeaux mixture (Sheail J., 1993).

Many organochloride compounds, such as DDT (dichlorodiphenyltrichloroethane) and BHC (Benzene hexachloride), were first synthesized in the 1800s, but their properties as insecticides fully discovered and exploited in 1939 and 1944 respectively. Since the start of the boom in pesticide production in the 1940s to present day thousands of synthetic insecticides, herbicides, and general pesticides have been developed that include organochlorides (DDT, BHC), organophosphates (Malathion,Parathion, Azinophos Methyl),Carbamates (Aldicarb, Carbofuran, Oxamyl, Methomyl),phenoxyacetic acids (2,4-D, MCPA, 2,4,5-T), Captan, neonicotinoids (Imidacloprid, Acetamiprid, Clothianidin, Nitenpyram), and Glysophates. Publication of Rachel Carson's Silent Spring in 1962, challenged the notion that chemicals brought benefits but risks and widespread toxicity, the approach shifted towards safer means for pest control. However, biopesticides based on plants and microorganisms have been used for pest control for centuries but an increasing number of studies involving biopesticides emerged during the rapid

institutional expansion of agricultural researchin the early 20th century. The bacterium Bacillus thuringiensis (Bt) was the first biopesticide and is being used most widely till now (O'neal*et al.,* 2018).

PRODUCTION AND USAGE OF PESTICIDES IN INDIA

During World War II (1939–1955), pesticide development accelerated due to the pressing need to raise food production and to reduce diseases and insects. A further increase in food production was also made possible by the greater use of synthetic crop protection chemicals starting in the 1940s (Bernardes *et al.,* 2015). In addition, global pesticide production rose from 0. 2 million tonnes in the 1950s to more than 5 million tonnes by 2000 at a pace of around 11% annually.

Being an agrarian economy, India places a strong emphasis on agricultural growth. India is one of the top producers and consumers of pesticides in Asia as well as in the world. The Green Revolution played a significant role in the several hundred-foldincreases in pesticide consumption in India from 154 MT in 1953–1954 to 80,000 MT in 1994–1995. Due to ban and restriction on the use of organochlorine pesticides and the introduction of the Integrated Pest Management programme the consumption steadily decreased in 2000s. According to the report of Directorate of Plant Protection Quarantine and Storage India consumed an average of 58,429. 7 MT of chemical pesticides over the past ten years, from 2012–13 to 2021–22. In 2021-22 the pesticides consumption was recorded around 63284 MT. 40% of the chemical pesticides used in the nation are consumed in Maharashtra and Uttar Pradesh (GOI, 2023).

BENEFICIAL EFFECTS OF PESTICIDE USE IN CROP PLANTS

Pesticides have played a crucial role in boosting agricultural productivity. By controlling pests, diseases, and weeds, farmers can protect their crops from significant losses. Pesticides help minimize yield losses caused by insects, fungi, viruses, and other pests, ensuring a stable food supply for a growing global population.

PESTICIDES FOR DISEASE MANAGEMENT

Disease management must be a crucial part of crop production if we are to prevent the development of famine, severe food shortages, or intolerable crop losses by farmers. An estimated 20% loss is caused by plant diseases globally. In order to tackle the large range of fungal diseases that endanger agricultural crops, plant disease control has become heavily reliant on fungicides since no new, efficient plant disease control technologies are present at a time.

The first significant landmark in the development of chemical disease control was the discovery of Bordeaux mixture in 1885 (Ragsdale and Sisler,1991). It belongs to the first generation of fungicidesthat also includeother inorganic agents, includes Bordeaux combination. With the invention of dithiocarbamates, the second generation of fungicides, which are organic compounds, began in 1934. This class also includeorganotins, quinones, captan and related compounds, chlorothalonil etc. Similar to inorganic fungicides, all of these substances are surface protectants and are only effective when used before infection. They do not penetrate plant tissue.

Infection thathas already spread and established is controlled by third-generatioragn fungicides, which are also organic but penetrate the plant tissue and are known as systemic fungicides. The majority of these include 2-aminopyrimidines, benzimidazoles, fosetyl-AI, azoles and related compounds, and morpholines. The fourth generation of fungicides comprises of substances that arenonfungitoxic in vitro but manage plant diseases by interfering with the processes necessary for fungal penetration into the plant or by boosting host-plant resistance. Examples include probenazole, which causes plants to activate their defence mechanisms, and tricyclazole, which results in the dysfunction of fungal appressoria (Waard *et al.,* 1993).

Many specific fungicides having protective as well as curative properties with systemic action that gives users flexible application windows came in limelight recently (Knight *et al.,* 1997; Morton and Staub 2008).

HERBICIDES FOR WEED MANAGEMENT

Weeds result decline in crop quality and yield losses. Prior to the invention of selective herbicides, farmers were compelled to follow a set of weed control strategies by carefully combining crop rotation, suitable tillage, and fallow systems because of the tediousness of hand weeding. Discovery of herbicides as"the chemical hoe" made things easier. It allowed them to think about weed control more independently from the crop production system than they have in the past thanks to the introduction of selective herbicides in the late 1940s and the continuous flow of new herbicides in the following decades (Kudsk & Streibig,2003).

A new era in weed research emerged on the brink of the Second World War when accidental discovery of two auxin herbicides, MCPA and 2, 4 D were made accessible for the selective control of broad-leaved weeds in cereal crops. The challenge was accepted by a number of agrochemical firms, and from then until the 1970s, the market for herbicides grew by 6. 3% actual per growth year (Cobb & Kirkwood, 2000). Thousands of urea compounds were used for their selectivity for controlling weeds (Geissbuhler*et al.,* 1975). Other families of herbicides including bipyridylium (diquat and paraquat) to control broad leaved weeds and aryloxyphenoxyproprionates (fops) and the cyclohexanediones (dims) in the mid-70s for the control of annual and perennial grasses in a range of crops were discovered (Cobb & Kirkwood, 2000). Subsequently, several other herbicides and chemical groups like glyphosate, sulfonylureas, imidazolinones, triazolpyrimidines, pyrimidinylthiobenzoates also discovered (Beyer *et al.,* 1988; Los, 1991; Franz *et al.,* 1997).

PESTICIDES FOR MANAGING INSECT INFESTATION

Due to environmental and technological changes, insect pest problems in agriculture have significantly changed throughout the first decade of the twenty-first century. Crop losses in India have decreased from 23. 3% in the years following the "green revolution" to 17. 5% at the moment. In terms of money, insect pests currently cost Indian agriculture an estimated Rs 8,63,884 million every year (Dhaliwal *et al.,* 2010). It is estimated that due to changing climate the ranges of numerous species will also expand. Chemicals called insecticides are used to kill insects or stop them from acting in an unwanted or destructive way. They are classified based on their structure and mode of action. Some insecticides, such as cholinesterase inhibitors, affect an insect's nervous system, while others operate as growth regulators or endotoxins. 4. 7% of the world's pesticide and 10% of its insecticide sales come from cotton growing to manage ballworm.

Different insecticides are available for specific pest in different formulations. For example, Dust (Quinolphos 4), Wettable powder or WP (Carbaryl 75 WP), Granules (Phorate 10G), Emulsifible concentrates (EC), aerosol or foliar spray. Most of the insecticides are available in this formulation, e. g., Cypermethrin 5EC, Malathion 50EC, etc.

HARMFUL EFFECTS OF PESTICIDES

While pesticides offer numerous benefits, their use has raised concerns about potential risks and adverse effects. Due to their chemical compositionthe pesticides can also be poisonous to other organisms, including fish, birds, beneficial insects, non-target plants, and to non-target plants themselves. Their chemical residue can also affect human health through environment and contaminated food. Additionally, pesticide contamination spreads away from the target plants and pollutes the environment.

Pesticides can spread by the air, wind currents, water, runoff, or leaching, as well as plants, animals, and people.

Their mobility in water can cause contamination of water resources. There are many reports throughout the world. For example, United States Geological Survey (USGS) have found several pesticides in more than 90% of water and fish samples collected from US streams. The residues not only persist and transfer to the water bodies but also in terrestrial area contaminating the soil. Some pesticides such as organochlorine DDT, endosulfanare strongly bound to soil particles due to their persistency.

Pesticide behaviour in the environment, such as volatilization from the treated area to the air, soil, and non-target plants, as well as residual pesticides transmitted from soil and water to crops, vegetables, and fruits, all contribute to food contamination which has toxic effect on human health. This occurs when pesticide residuals in crops and vegetablesexceedsthe WHO maximum food contamination standards or above the maximum residue limits (MRLs) set by WHO. When pesticides are applied to the target plants, non-target organisms are also affected adversely. This includes harm to wildlife, birds, aquatic environments, honeybees, and beneficial insects as well as the natural enemies of insect pests. There are 293 pesticides that are registered in India, and according to Goi (2021), 104 pesticides are still manufactured or used despite being banned in two or more other countries. According to Mooventhan*et al.*, . (2020), 50% of pesticides used for pest control in India are diverted to cotton pest control.

FOOD SAFETY CONCERNS, PRECAUTIONS, AND SAFETY MEASURES

Harmful effects of excessive and unauthorized use of pesticides are well known. In India Central Insecticides Board & Registration Committee (CIB & RC) under Ministry of Agriculture and Farmers Welfare is responsible for registration of pesticides, under the provisions of Insecticides Act, 1968. Pesticide residue in food commodities and their entry into food chain has become one of the major concerns globally. An independent scientific body "Scientific Panel on Pesticide Residues" constituted by Food Safety & Standards Authority of India (FSSAI), recommends the maximum residue limits (MRL) of pesticides for different crops by utilizing the Good Agriculture Practice (GAP) and based on the safety and risk assessment of the data provided by the manufacturers through CIB & RC.

Exposure to pesticide concentrations or vapour drift can affect applicators, bystanders, and the environment. To reduce the danger, those who handle pesticides must be aware of and adhere to safe procedures. Farmers and other farm workers who handle pesticides are frequently exposed to high concentrations of pesticides; the dermis and inhalation are the most prevalent routes of exposure. Pesticides can be ingested by them at any time while handling. These steps involve loading/mixing, spraying, cleaning associated equipments, and entering or reentering farms where pesticides have been used. Therefore, the hazards related to pesticide exposure can be decreased by wearing PPE, selecting the right type of PPE, and using safe practises when handling pesticides (Yarpuz-Bozdogan, 2018; Macfarlane *et al.,* 2013). The World Health Organisation (WHO) and the Food and Agriculture Organisation (FAO) of the United Nations (FAO) released the International Code of Conduct on Pesticide Management in 2015, which outlines rules for licencing public health pest management professionals.

MOVING TOWARDS SAFER APPROACH

Nowadays, biopesticides derived from natural resources such as plants, animals, microbes, and certain minerals are becoming more and more well-liked due to its advantages in terms of environmental safety, target-specificity, efficacy, biodegradability, and application in integrated pest management (IPM) programmes. Biopesticides have a well-known potential for use that is safe for the environment. Attention has been growing in light of rising demand for organic food (Kumar and Singh, 2015).

Currently, it is estimated that the biopesticide market will be worth between USD 3 and USD 4 billion in the USD 56 billion global pesticide market. It is predicted that the development of biopesticides will surpass that of chemical pesticides, with compound annual growth rates of 14. 1%. In India, the consumption of biopesticides makes up about 9% of total pesticide consumptionand, by 2050, is estimated to represent up to 50% of the entire pesticide market. The entire usage of biopesticides in India increased by 40% between 2014–2015 and 2018–2019 and reached 8847 and 8645 metric tons in 2019–2020 and 2020–2021, respectively based on PPQS statistics (GOI, 2022). The Central Insecticides Board and Registration Committee (CIBRC) currently have 970 biopesticide products registered. According to the Insecticide Act of 1968, only 12 different types of biopesticides have been identified in India (Kandpal, 2014). Neem-based insecticides, Beauveria bassiana,Bacillus thuringiensis, NPV, Pseudomonas,and Trichoderma are the principal biopesticides produced and used in India. According to statistics, Maharashtra has used the most biopesticides, whereas Goa has used the least in 2021-22.

CONCLUSION

Chemical control is still a major part of managing pests and diseases. Because choosing the right pesticides can be challenging when there are no viable alternatives, pesticide resistance may become more common in the future. Pesticides are undeniably valuable tools for protecting crops and ensuring food security. However, their use must be carefully managed to mitigate potential risks to human health and the environment. By embracing integrated pest management, promoting research and innovation, providing education and training, and implementing effective regulations, we can strike a balance that allows for sustainable agriculture. The science of modern pest management and control is becoming more and more diverse, with thousands of different management techniques so, byinvestigating the effectiveness of specific insect, disease or insect problems in various cropping systems a suitable management strategy could be applied by keeping in view all the benefits and risks associated with the used approach.

REFERENCES

[1]. Abhilash, P. C., & Singh, N. (2009). Pesticide use and application: an Indian scenario. Journal of hazardous materials, 165 (1-3), 1-12.

[2]. Aktar, M. W., Sengupta, D., & Chowdhury, A. (2009). Impact of pesticides use in agriculture: their benefits and hazards. Interdisciplinary toxicology, 2 (1), 1.

[3]. Bernardes, M. F. F., Pazin, M., Pereira, L. C., Dorta, D. J. (2015). Impact of Pesticides on Environmental and Human Health. In Toxicology Studies—Cells, Drugs and Environment. IntechOpen, London, UK.

[4]. Beyer, J., Duffy, M. J., Hay, J., & Schlueter, D. (1988). Herbicides Chemistry, Degradation and Mode of Action, (Vol. 3, pp. 117–189). PC Kearney & DD Kaufman, Marcel Dekker, New York, USA.

[5]. Carriger, J. F., Rand, G. M., Gardinali, P. R., Perry, W. B., Tompkins, M. S., & Fernandez, A. M. (2006). Pesticides of Potential Ecological Concern in Sediment from South Florida Canals: AnEcologicalRiskPrioritizationforAquaticArthropods. Soil and Sediment Contamination: An International Journal, 15 (1), 21–45.

[6]. Carvalho, F. P. (2017). Pesticides, environment, and food safety. Food Energy Security, 6, 48–60.

[7]. Chakraborty, N., Mitra, R., Pal, S., Ganguly, R., Acharya, K., Minkina, T., & Keswani, C. (2023). Biopesticide Consumption in India: Insights into the Current Trends. Agriculture, 13 (3), 557.

[8]. Cobb, A. H.,& Kirkwood, R. C. (2000). Challenges for herbicide development. In: Herbicides and Their Mechanisms of Action. Sheffield Academic Press, Sheffield, UK.

[9]. Dhaliwal, G. S., Jindal, V., &Mohindru, B. (2015). Crop Losses due to insect pests: Global and Indian Scenario. Indian Journal of Entomology, 77 (2), 165–165.

[10]. Franz, J. E., Mao. M. K. & Sikorski, J. A. (1997). Glyphosate: a Unique Global Herbicide. ACS Monograph 189, American Chemical Society, Washington DC, USA.

[11]. Geissbuhler, H., Martin, H., & Voss, G. (1975). The substituted ureas. In: Herbicides. Chemistry, Degradation, and Mode of Action, (Vol. 1, pp. 209-291). PC Kearney & DD Kaufman, Marcel Dekker, New York, USA.

[12]. GOI. (2022). Statistical Database | Directorate of Plant Protection, Quarantine & Storage | GOI. Retrieved from http://ppqs. gov. in/statistical-database

[13]. GOI. (2023). Statistical Database | Directorate of Plant Protection, Quarantine & Storage | GOI. Retrieved from http://ppqs. gov. in/statistical-database

[14]. Hayes, T. B., Hansen, M., Kapuscinski, A. R., Locke, K. A. Barnosky, A. (2017). From silent spring to silent night: Agrochemicals and the anthropocene. Elem Sci Anth., 5, 1–24.

[15]. Hernández, A. F., Gil, F., Lacasaña, M., Rodríguez-Barranco, M., Tsatsakis, A. M., Requena, M., Alarcón, R. (2013). Pesticide exposure and genetic variation in xenobiotic-metabolizing enzymes interact to induce biochemical liver damage. Food Chemical Toxicology, 61, 144–151.

[16]. Kandpal, V. (2014). Biopesticides. Res. India Publ, 4, 190–196.

[17]. Knight, S. C., Anthony, V. M., Brady, A. M., Greenland, A. J., Heaney, S. P., Murray, D. C., Powell, K. A., Schulz, M. A., Spinks, C. A., Worthington, P. A., Youle, D. (1997). Rationale and perspectives on the development of fungicides. Annu. Rev. Phytopathol. 35:349–372.

[18]. Kudsk, P., & Streibig, J. C. (2003). Herbicides–a two-edged sword. Weed Research, 43 (2), 90-102.

[19]. Kumar, S., & Singh, A. (2015). Biopesticides: Present Status and the Future Prospects. J. Fertil. Pestic, 6.

[20]. Los M., (1991). Discovery of the imidazolinone herbicides. In: The ImidazolinoneHerbicides. CRC Press, Boca Raton, Florida, USA.

[21]. Macfarlane, E., Carey, R., Keegel, T., El-Zaemay, S., Fritschi, L., (2013). Dermal exposure associated with occupational end use of pesticides and the role of protective measures. Saf. Health Work. 4 (3), 136–141.

[22]. Mooventhan, P., Murali, R. B., Kumar, J., & Kaushal, P. (2020). NIBSM Publ. yar

[23]. Morton, V, Staub, T. (2008). Short history of fungicides.

[24]. O'neal, M., Bio, M., & Dara, S. (2018). Brief history of botanical and microbial pesticides and their current market.

[25]. Ragsdale, N. N.,& Sisler, H. D. (1991). The nature, modes of action, and toxicity of fungicides. Handbook of Pest Management in Agriculture, 2:461-96. CRC Press. Boca Raton, FL.

[26]. Sapbamrer, R., &Thammachai, A. (2020). Factors affecting use of personal protective equipment and pesticide safety practices: A systematic review. Environmental research, 185.

[27]. Savary, S., Willocquet, L., Pethybridge, S. J., Esker, P., McRoberts, N., & Nelson, A. (2019). The global burden of pathogens and pests on major food crops. Nature Ecology & Evolution, 3 (3), 430–439.

[28]. Sheail, J. (1991). The regulation of pesticides use: An historical perspective. Innovation and Environmental Risks. Belhaven Press,London, UK.

[29]. Tudi, M., Daniel Ruan, H., Wang, L., Lyu J, Sadler, R., Connell, D., Chu, C., Phung, D. T. (2021). Agriculture Development, Pesticide Application and Its Impact on the Environment. International

Journal of Environmental Research and Public Health, 18 (3):1112. https://doi. org/10. 3390/ijerph18031112

[30]. Unsworth, J. (2010). History of pesticide use. IUPAC (International Union of Pure and Applied Chemistry).

[31]. Waard, M. A., Georgopoulos, S. G., Hollomon, D. W., Ishii, H., Leroux, P., Ragsdale, N. N., & Schwinn, F. J., (1993). Chemical control of plant diseases: problems and prospects. Annual review of phytopathology, 31 (1), 403-421.

[32]. Waard, M. A., Georgopoulos, S. G., Hollomon, D. W., Ishii, H., Leroux, P., Ragsdale, N. N., & Schwinn, F. J. (1993). Chemical control of plant diseases: problems and prospects. Annual review of phytopathology, 31 (1), 403-421.

[33]. Yarpuz-Bozdogan, N., (2018). The importance of personal protective equipment in pesticide applications in agriculture. Curr. Opin. Environ. Sci. Health. 4, 1–4.

Chapter 4

ETHNO-BOTANICAL STUDY OF MEDICINAL PLANTS FROM WARANGAL DISTRICT, TELANGANA STATE, INDIA

D. NAGARAJU

Department of Botany, Govt. City College (A), Nayapul, Hyderabad, Telangana State, India.
Corresponding author E-mail: drdnr123@gmail.com

ABSTRACT

Ethno-botanical study deals with the documentation of the indigenous, time immemorial, traditional knowledge of plants used by the ethnic people. In the present Ethno botanical study (2017-2018) collected the data by conversation, structured questionnaire from various, traditional, tribal, koya, guthikoya, chenchu, kondareddlu, Lambadi and other indigenous group of people in Pasra, Thadvai, Eturnagaram, Mangapeta, Pakhal, Gudur, Bhupalapally and Mahabubabad mandal tribal areas in Warangal district of Telangana. The majority of data was collected from herbal practitioners, traditional healers, tribes and journals. The present study provided information about medicinal plants which are predominantly using in remedies by local peoples. The tribal people, herbal practitioners, traditional healers and rural peoples are helped to identify and collect medicinal plants data which are using in medicine. Present study having a scope for screening of presently recorded plants for active compounds having specific effects on various diseases.

KEYWORDS: Ethanobotany, Herbal, Indigenous, Medicine, Tribes, Traditional.

INTRODUCTION

The utilization of medicinal plants is known since times immemorial. The utility of medicinal plants played important role in Ayurveda, Unani, Siddha and also in modern medicine. The World Health Organization (WHO) estimated that 80% of the population of developing countries rely on traditional medicines, mostly plant based drugs, for their primary healthcare needs and security especially in Asia and African Countries., Even in modern pharmacopoeia still contains at least 25% drugs derived from plants and many others which are synthetic analogues built on prototype compounds isolated from plants. India and other countries have rich floristic yielding herbal drugs. The world market includes herbal drugs, pharmaceuticals, fragrances, flavors, dyes and other ingredients and their marketing exceeds several billion dollars per year.

The collection of ethnobotanical knowledge is the main source for the discovery of drugs. Field study in a tribal area gives first hand information. the first step in ethnobotanical field work is to identify the local inhabitants or primitive societies and their regional jurisdiction. Ethanobotanist apart from collection of plant, also need to discuses and records the uses of plants with the help of informants (Jain, S. K. 1964). The primitive communities, who hold the traditional knowledge and practice the traditional way of treatment to cure ailments are the custodians of it, such knowledge of tribal's has only oral traditions without any written documents. This knowledge was even passed through generation to generation and play an important role in conservation and sustainable use of biodiversity. Unfortunately, Due to the changing life style of tribals and fast urbanization, globalization, modernization, availability of hospitals in remote areas the ethnobotanical knowledge on useful plants acquired and accumulated through

generations is gradually getting lost. Hence there is an urgent need of recording all ethnobotanical information before they are lost and continuous efforts should be made to collect the information which will provide avenue for future generation.

STUDY AREA

The Warangal district is a part of northern Telangana. It lies between17^{0}19/ and 18^{0}36/ N latitude and 78^{0}. 49/ and 80^{0}. 43/E longitude. It surrounded with Khammam, Karimnagar, Nalgonda districts and Chhattisgarh and Maharashtra states. The forest cover occupies on area of 3, 71,314 hectorswhich bear 28. 89% of the total geographical area of the district (gov. in map 2017). Warangal district is rich in area under forest cover, plant diversity and the ethnic people also have more in reserve as traditional botanical knowledge (Pullaiah, T. 2015).

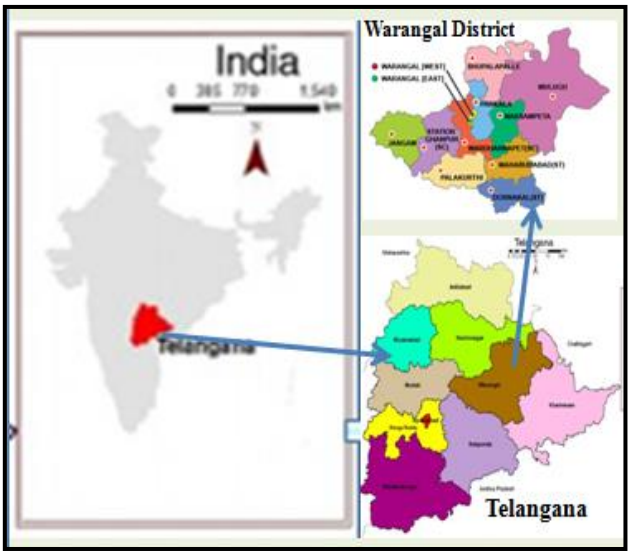


Fig. 1: Study Area Map

MATERIAL AND METHODS

In the part of Ethanobotanical study Field trips were conducted and ethnomedicinal data were collected during the 2017-2018 through conversation, structured questionnaire from various, traditional healers, herbalists, tribal, koya, guthikoya, chenchu, kondareddlu, Lambadi, other indigenous group of people and elder people in the field trips of Pasra, Thadvai, Eturnagaram, Mangapeta, Pakhal, Gudur, Bhupalapally and Mahabubabad mandal tribal areas in Warangal district of Telangana (Narender and Mustafa 2016, Reddy *et al.,* 2007 & 2016, Sreeramulu *et al.,* . 2016)). During the conversation local names, useful plant parts, method of preparation and dosage were recorded (Hemadri *et al.,* 1986). In the present account, 80 species belonging to 32 families are reported. They are used as ethnomedicines for various severe diseases. The tribal people, herbal practitioners, traditional healers and elder peoples are helped to identify and collect medicinal plants data which are using as ethanomedicine in the study area.

Fig. 2: Field Visit to Ethno-botanical Study

RESULTS

Ethno botanical survey was conducted during 2017-2018, with the regular field visits by once in two weeks as a field visit in Warangal district of Telangana. The Ethanobotanical information was collected from herbal practitioners, traditional healers, and local tribes. The present study provided information about eighty medicinal plants with ethno-botanical study to explore about ethno-medicinal plants using for curing various diseases with medicinal properties. (Table-1).

Table-1: List of Medicinal Plants which are using by Local tribes of Warangal District, Telangana State.

S. No	Scientific Name	Vernacular name/ Local Name	Family	Plant /Partused	Usages by Tribes in various remedies
1.	*Abrus precatorius L.*	Gurija	Fabaceae	Leaf	Insectbite
2.	*Abutilon indicum (L.) Sweet*	Thutturu benda	Malvaceae	Whole plant	Infertility
3.	*Acacia leucophloea (Roxb.) Willd.*	Tellatumma	Fabaceae	Stem bark	Wounds
4.	*Acacia chandra (Raxb. Ex. Roxb) Willd)*	Sandra	Mimosaceae	Stem bark	Ulcer
5.	*Acalypha indicaL.*	Muripinda, pippaku	Euphorbiaceae	Leaf	Scorpionbite, gas trouble
6.	*Achyranthes aspera L.*	Uttareni	Amaranthaceae	Root	Scorpionsting, tooth-ache
7.	*Adenanthera pavonine L.*	Bandi guriginja	Fabaceae	Leaf	Dysentery, hemorrhage
8.	*Aegle marmelos (L.) Corrêa*	Maredu	Rutaceae	Fruit	Diarrhoea, skindisease, constipation
9.	*Alangium salviifolium (L. f.) Wangerin*	Udugu	Alangiaceae	Stem bark	Bonefracture
10.	*Albizia lebbeck (L.) Benth.*	Dirisena	Fabaceae	Stembark	Insect bite, knee pain, Skin disease
11.	*Andrographis paniculata (Burm. f.) Nees*	Nelavemu	Acanthaceae	Leaf	Edema, viral fever, typhoid
12.	*AnnonasquamosaL.*	Seethaphalam	Annonaceae	Seed	Insectbite, licein hair, tooth-ache
13.	*Anogeissus latifolia (Roxb. ex DC.) Wall. exGuillem. &Perr.*	Tiruman	Combretaceae	Stembark	Insectbite
14.	*Argemone Mexicana L.*	Pichikusuma	Papaveraceae	Leaf	Itching, sexually Transmitted diseases

15.	*Aristolochia indica L.*	Nalleswari	Aristolochiaceae	Root	Snakebite, aphrodisiac
16.	*Arva lanataL (L) Juss.*	Pindikura	Amaranthaceae	Whole Plant	Break Kidney stones
17.	*Asclepias curassavica L.*	Jilledu mandara	Apocynaceae	Whole plant	Piles, gonorrhoea, tumors
18.	*Asparagus recemousus Willd*	Shatamuli	Asparagaceae	Tuber	Increase Breast Milk, Diarrhoea, Aphrodisiac
19.	*Azadirachta indica L.*	Vepa	Meliacae	Youngleaf	Constipation, skindisease
20.	*Bauhinia recemosa Lamk*	Aare	Caesalpiniaceae	Leaf	Sticky Motion, Maleria
21.	*Barleria prionitis L.*	Mulla gorinta	Acanthaceae	Root	Fever, immuno restorative
22.	*Boerhavia diffusa L.*	Atikamamidi	Nyctaginaceae	Whole plant	Anaemia, night blindness
23.	*Boswellia serrata Roxb.*	Andugu	Burseraceae	Bark	Rheumatism, Knee Pain
24.	*Buchanania axillaris (Desr.) Ramamoorthy*	Pedda morli	Anacardiaceae	Flower	Wounds
25.	*Butea monosperma (Lam.) Taub.*	Moduga	Fabaceae	Stem bark	Menstrual pain, high bleeding
26.	*Calotropis gigantea (L.) Dryand.*	Jilledu	Apocynaceae	Stem bark	Knee pain
27.	*Capparis zeylanica L.*	Adonda	Capparaceae	Fruit	Ear ache, scorpion bite
28.	*Cardiospermum helicacabum L.*	Buddateega	Sapindaceae	Root	Arthritis
29.	*Cassia fistula*	Rala	Caesalpiniaceae	Bark, Root	Whooping cough, Diarrhea
30.	*Celosia argentia*	Gunugu	Amaranthaceae	Leaf, Seed	Pisonous insect bite, Diarrhea
31.	*Centella asiatica (L.) Urb.*	Saraswati aku	Apiaceae	Whole plant	Memory
32.	*Cissus quandrangularis L.*	Nalleru	Vitaceae	Stem Bark	Bone fracture
33.	*Cissampelos pareira L.*	Boddi kura	Menispermaceae	Root	Digestion
34.	*Cleistanthus collinus (Roxb.) Benth. ex Hook. f.*	Kodisha	Euphorbiaceae	Stem bark	Wounds
35.	*Cleome viscosa L.*	Kukka vaminta	Cleomaceae	Whole plant	Arthritis, Infantine convulsions

36.	*Cocculus hirsutus (L.) W. Theob.*	Dusari teega	Menispermaceae	Root	Gonorrhoea, fertility
37.	*Curcuma longa L.*	Pasupu	Zingiberaceae	Rhizome	Antiseptic
38.	*Cynodon dactylon (L.) Pers.*	Garika	Poaceae	Leaf	Kidney stone
39.	*Datura metel L.*	Ummetta	Solanaceae	Leaf	Scorpion bite
40.	*Delonix elata (L.) Gamble*	Chilukapari chettu	Fabaceae	Leaf	Bone fracture
41.	*Dichrostachys cinerea (L.) Wight & Arn.*	Velturu chettu	Fabaceae	Root	Rheumatism, urinary diseases
42.	*Dillenia pentagyna Roxb.*	Revadi	Dilleniaceae	Leaf	Constipation, stomach-ache
43.	*Dioscorea alata L.*	Bellam gadda	Dioscoreaceae	Tuber	Aphrodisiac
44.	*Dioscorea bulbifera L.*	Chenna gadda	Dioscoreaceae	Tuber	Dysentery
45.	*Dioscorea pentaphylla L.*	Govinda gadda	Dioscoreaceae	Tuber	Rheumatism
46.	*Dregea volubilis (L. f.) Benth. ex Hook. f.*	Bandi gurija	Apocynaceae	Leaf	Rheumatism
47.	*Euphorbia tirucalli L.*	Kaadajemudu	Euphorbiaceae	Whole plant	cold, cough
48.	*Gloriosa superba L.*	Potti dumpa	Colchicaceae	Tuber	Abortion
49.	*Gymnema sylvestre (Retz.) R. Br. ex Sm.*	Podapatri	Apocynaceae	Leaf	Diabetes
50.	*Hemidesmus indicus (L.) R. Br. ex Schult.*	Suganda pala	Apocynaceae	Leaf	Galactogogue
51.	*Holoptelea integrifolia Planch.*	Pedda nemali	Ulmaceae	Stem bark	Leprosy, dyspepsia
52.	*Hybanthus enneaspermus (L.) F. Muell.*	Nela kobbari	Violaceae	Whole plant	Urinary problem
53.	*Justicia adhatoda L.*	Addasaram	Acanthaceae	Leaf	Asthma, cough
54.	*Kigelia africana (Lam.) Benth.*	Enugu lavuda	Bignoniaceae	Stem bark	Leprosy, syphilis, rheumatism
55.	*Lawsonia inermis L.*	Gorinta	Lythraceae	Leaf	Reduce body heat
56.	*Leptadenia reticulata (Retz.) Wight & Arn.*	Mukku teega	Apocynaceae	Whole plant	Aphrodisiac
57.	*Litsea glutinosa (Lour.) C. B. Rob.*	Narra mamidi	Lauraceae	Stem bark	Bone fracture

58.	*Madhuca longifolia var. latifolia (Roxb.) A. Chev.*	Ippa	Sapotaceae	Flower	Galactogogue
59.	*Mimosa pudica L.*	Attipatti	Fabaceae	Whole plant	Fistula, hydrocele
60.	*Mucuna pruriens (L.) DC.*	Dulagondi	Fabaceae	Whole plant	Aphrodisiac, spermatorrhoea
61.	*Nyctanthes arbor-tristis L.*	Parijatham	Nyctanthaceae	Stem bark	Back-ache, scurvy, baldness
62.	*Ocimum basilicum L.*	Saidaku	Lamiaceae	Seed	Summer stroke (cooling agent)
63.	*Operculina turpethum (L.) Silva Manso*	Tella tagada	Convolvulaceae	Whole plant	Obesity, tuberculosis
64.	*Pergularia daemia (Forssk.) Chiov.*	Dustapu teega	Apocynaceae	Leaf	Wounds
65.	*Pueraria tuberosa (Willd.) DC.*	Nela gummadi	Fabaceae	Root	Rheumatism
66.	*Rauvolfia serpentina (L.) Benth. ex Kurz*	Sarpagandhi	Apocynaceae	Root	Snake bite
67.	*Senna auriculata (L.) Roxb.*	Tangedu	Fabaceae	Root	Blood purifier, urinary diseases
68.	*Senna occidentalis (L.) Link*	Adavi chennangi	Fabaceae	Leaf	Rheumatism
69.	*Smilax perfoliata Lour.*	Nageti dumpa	Smilacaceae	Tuber	Abortion
70.	*Solanum surattense Burm. f.*	Vakudu	Solanaceae	Whole plant	Dandruff, infections
71.	*Soymida febrifuga (Roxb.) A. Juss.*	Somidi	Meliacae	Stem bark	Stomach-ache
72.	*Spathodea campanulata P. Beauv.*	Patida	Bignoniaceae	Stem bark	Urine passage inflammation, kidney problem
73.	*Terminalia arjuna (Roxb. Ex DC.) Wight & Arn.*	Tella maddi	Combretaceae	Stem bark	Wounds
74.	*Tridax procumbens (L.) L.*	Nallalam	Asteraceae	Leaf	Wounds, skin rashes
75.	*Tylophora indica (Burm. f.) Merr.*	Mekameyani aku	Menispermaceae	Leaf	Asthma
76.	*Vanda tessellate (Roxb.) Hook. ex G. Don*	Kodikalla chettu	Orchidaceae	Whole plant	Ephemeral fever
77.	*Vitex negundo L.*	Vavili	Lamiaceae	Leaf	Skin disease, body pains

78.	*Withania somnifera (L.) Dunal*	Domma dolu gadda	Solanaceae	Tuber	Paralysis
79.	*Xanthium strumarium L.*	Marulamathangi	Asteraceae	Plant extract, seed powder	Headache, Snakebite
80.	*Ziziphus oenopolia (L.) Mill.*	Pariki	Rhamnaceae	Leaf/ Fruits	Dysentery, stomach ache

CONCLUSION

India and other countries have rich floristic yielding herbal drugs. The world market includes herbal drugs, pharmaceuticals, fragrances, flavors, dyes and other ingredients and their marketing exceeds several billion dollars per year. The present paper deals with the tribes, elder people, their status of health and medicinal plants used for human health care by the ethnic tribes, traditional healers, elder people inhabiting Warangal District, Telangana State, India.

The above traditional knowledge enlightening the scope for screening of presently recorded plants for active parts having specific effects on various diseases. Unfortunately, due to the changing life style of tribals and fast urbanization, globalization, modernization, availability of hospitals in remote areas the ethnobotanical knowledge on useful plants acquired and accumulated through generations is gradually getting lost. Hence there is an urgent need of recording all ethnobotanical information before they are lost and continuous efforts should be made to collect the information which will provide avenue for future generation.

ACKNOWLEDGEMENT

The author is thankful to the ethnic, traditional tribal resource persons who shared their Ethano-Botanical knowledge in the study area, B. Sc students involved in this study project and also thankful to Commissioner of Collegiate Education for encouragement.

REFERENCES

[1]. Anonymous. Telangana State Information. (2017). Website: http:// www. telangana. gov. in /aboutdistricts.

[2]. Hemadri, K,K & C. R. R. Sharma & S. S. Rao (1986). Medicinal plant Wealth of Andhra Pradesh. Anc. Sci. Life (6):167-186.

[3]. Jain,S. K. (1964). The role of botanist in folklore research. Folklore (5):145-150.

[4]. Narendar, M and Mustafa, Md (2016). An Ethnobotanical study of medicinal plants used by koyatribesin and around malluruhill region,Warangal District,Telangana,India. 7 (2): 103-114.

[5]. Pullaiah T. (2015). Flora of Telangana State: The 29th State of India. Regency Publications, NewDelhi. pp. 1-826.

[6]. Reddy KN and Reddy CS. (2016). Flora of Telangana State, India. Bishen Singh Mahendra Pal Singh, DehraDun.,pp. 1-824.

[7]. Reddy,C. S.,Gopala krishna, P. and Raju V. S. (2007). Phototherapy at rural communities: A case study from the Gonds of Waragal district, Andhra Pradesh India. Res. J. Bot. 3 (2):97-102.

[8]. Sreeramulu, N., Sateesh S., Ragan, A and Raju, VS (2013). Ethno-botanico-medicine for common human ailments in Nalgonda and Warangal districts of Telangana, Andhra Pradesh, India.

Chapter 5

CURRENT SCENARIO OF MYCOSYNTHESISED BIOMOLECULES FROM MUSHROOMS

RIYAJ R. INAMDAR*, ANURADHA A. KAMBLE, PRATIKSHA S. JADHAV, AYODHYA D. KSHIRSAGAR AND NARAYAN M. GHANGAONKAR

Department of Botany, PG and Research Center Chandmal Tarachand Bora College, Shirur
*Corresponding author E-mail: riyajinamdar45@gmail.com

ABSTRACT

The diversity of living organism on the earth promotes variation in organism to organisms. Due to value added importance all organisms play important role in human life. Among them Mushrooms are one of leading and important group which associated with human life in various forms. From the producer to decomposer mushrooms have greater diversity. In this chapter, revealed the role of mushrooms in food, agriculture, biomedical, industrial and environment. This chapter studied the various biomolecules synthesised from mushrooms and help to handover data about medical application in the sense of antimicrobial, antiviral, antiinflamentary, anticancerous and antioxidant activity. Mushrooms are good source of primary and secondary metabolites. The nutritional values of mushrooms have increased consumption statistics.

KEYWORDS: Mushrooms, Biomolecules, Application, Medicinal Importance.

INTRODUCTION

The mushrooms are living, non-chlorophyllous, eukaryotic, heterotrophic organisms belong to kingdom Fungi. Mushrooms are large, asexual, macroscopic fruiting bodies which belongs to the sub-division of fungi Ascomycotina or Basidiomycotina. Mushrooms are good de-composers that mainly grow on dead and decaying organic matters, commonly known as "Saprophytes". In worlds population they are found in diversity. Among all around 1600 species of mushrooms, where 100 species have been recognized to be consumed for edible purposes. About 33 species of edible mushrooms are under cultivation throughout the world. There are many species of edible mushrooms are either harvested wild or cultivated in farm. (Kozarski *et al.,* 2015; Kumar *et al.,* 2021). Mushrooms have great history in worldwide. From origin of mushrooms to current year's mushrooms plays diverse role in environment. Mushrooms are one of important component of food web having great approaches towards sustainable food chain. Application of mushrooms revealed the unfolded principles and uses in various disciplines. Mushrooms have tremendous nutritional values in which proteins, fibres, vitamins and minerals. The core interest of mushrooms is in food, fodder, medicines, etc. the multiple application of mushrooms changes the world's attitude towards mushrooms and started mushrooms businesses.

Mushrooms have treasures of biomolecules and secondary metabolites which shows higher efficacy against disorders and diseases. Known metabolites are practices as anti-microbial (Huguet *et al.,* 2022), anti-diabetic (Kaewnarin *et al.,* 2020), anti-cancerous (Sadi *et al.,* 2016), anti-oxidant agents (Ferreira *et al.,* 2007) for controlling and maintaining human life style. Some mushrooms have ability to cure skin disorders (Taofiq *et al.,* 2020), inflammentation (Han *et al.,* 2023), eruption (Zhou *et al.,* 2020), infections and allergies (Ellertsen *et al.,* 2009). The statistical data for consumption of medicinal mushrooms in

functional food or dietary supplement is expected to markedly increase in the future. Medicinal mushroom global scenario projected to increase by USD 13. 88 billion from 2018 to 2022. The edible mushrooms of global market is forecasted to reach up to USD 62. 19 billion in 2023 (De Cianni *et al.,* 2023). Mushrooms are one of the best natural bioremediator in environment which remove toxic heavy elements from soil. The Mushroom fruiting bodies produces on agricultural wastes as well as industrial waste which are considered as a product from waste. In this article revealed the biochemistry of selected mushrooms. Due to the presence of those secondary metabolites in mushrooms, have to potential applications in biomedicines. These compounds have a wide range of therapeutic effects. Edible mushrooms typically lack transunsaturated fatty acids, but they do contain ergosterol. Ergosterol is used to prevent cardiovascular disease and is also a precursor for the production of vitamin D (Javed *et al.,* 2019). Edible mushrooms are a valuable protein source, with a protein content of 200 to 250 grams per kilogram of dry weight. The most prevalent amino acids present in mushrooms are leucine, aspartic acid, valine, glutamine, and glutamic acid (Thu *et al.,* 2020). While some wild mushrooms are safe to eat, it's crucial to correctly identify them before consumption (Thu *et al.,* 2020). Wild mushrooms offer significant nutritional benefits (Sifat*et al.,* 2020).

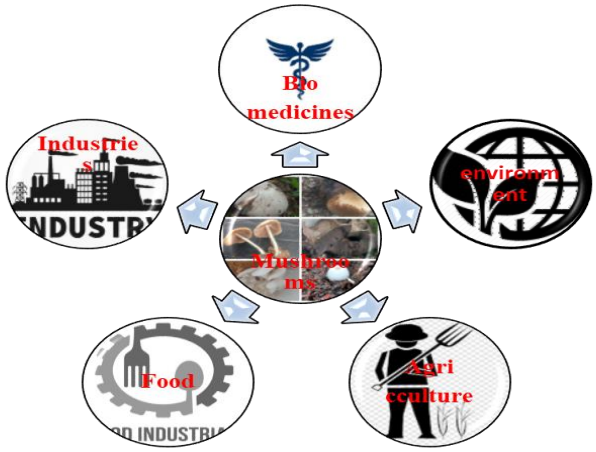


Fig. 1: Applications of mushrooms

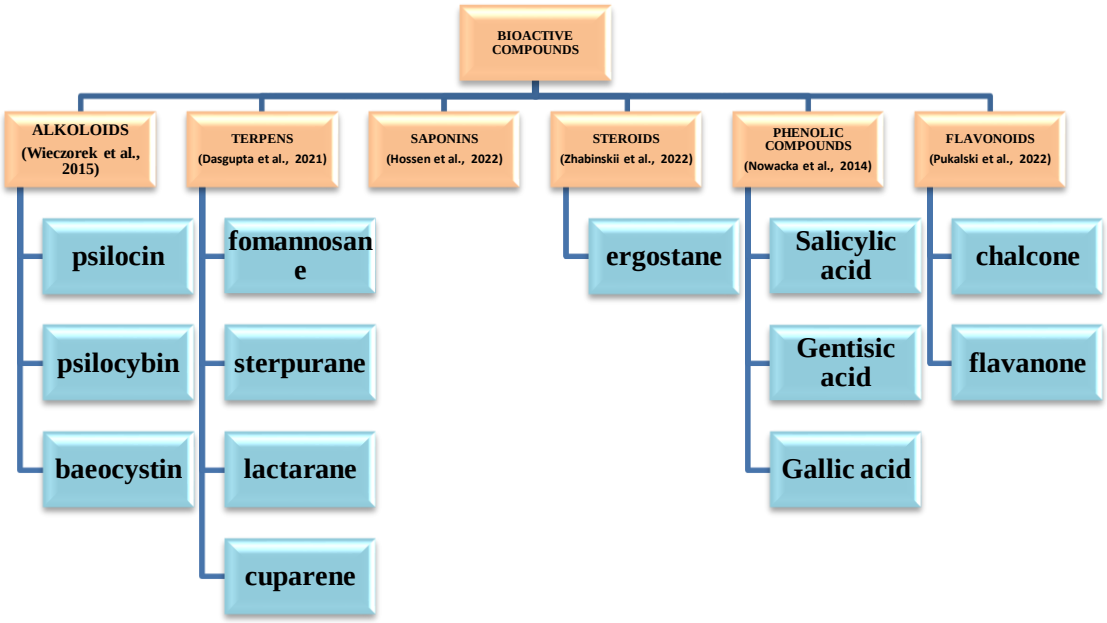


Fig. 2: List of all known compound's synthesis from macrofungi

They are a valuable source of protein, vitamins, minerals, and have a high water content. Wild mushrooms can provide approximately 0. 2 percent of daily protein intake and contribute to about 3% of the agricultural output in the Czech economy, which serves as a representation of Central Europe (Procházka *et al.,* 2023). Mushrooms contain higher protein content than vegetables, making them an essential source of nutrition for many Central Europeans who prefer non-animal-based protein sources. Wild mushrooms, in particular, are rich in essential amino acids and other vital nutrients, making them a valuable addition to a well-rounded diet. During times of war, wild mushrooms also serve as an important substitute for meat. Wild edible mushrooms are also a valuable source of primary and secondary bioactive compounds, such as proteins, carbohydrates, lipids, polyunsaturated fatty acids, alkaloids, terpenes, triterpene, sesquiterpenes, flavonoid, flavanone, saponins, alkaloids, polysaccharides, anthraquinone, tannins, steroids, glycoproteins, polyketides, phenolic compounds, melanin, β-glucan, dietary fibers, lectins, and many other compounds (Lalotra *et al.,* 2016). With the evolutionary phases, secondary metabolites serves as "playground" in the sense of chemically engineered sectors for the interaction in a changing environment. The Kissanga *et al.,* 2022 detected the oxalic acid, quinic acid, malic acid, citric acid and fumaric acids. Among the samples, Russula sp3 had the highest total organic acid content at 11. 80 g/100 g dry weight in distilled water extract. Quinic acid was the predominant compound in samples Russula aff. cellulata Buyck, Russula sp1 , Russula sp2 , Russula sp3, Russula sp3, and Amanitaloosei Beeli, with concentrations of 5. 33, 5. 65, 5. 01, 4. 72, 4. 57, and 1. 66 g/100 g dw, respectively. A. loosei had the lowest concentration of total organic acids among the analyzed mushrooms at 3. 86 g/100 g dw. The fruiting bodies of the three edible mushrooms Boletus edulis, Boletus mirabilis, and Lactarius deliciosus contained proteins ranging from 25% to 55%, carbohydrates ranging from 34% to 69%, ash content ranging from 3% to 6. 5%, and lipids ranging from 0. 8% to 5. 3%. The elemental concentrations varied depending on the species and their habitat (Rasalanavho *et al.,* 2020). A. auricula, uncooked A. auricula exhibited notably greater total antioxidant activity (TAA), the ability to chelate ferric ions, DPPH (diphenyl-i-picrylhydrazyl) radical-scavenging capacity, and reducing power. This enhanced antioxidant performance is attributed to the presence of additional bioactive compounds such as flavonoids, vitamin C, and l-DOPA (dihydroxyphenylalanine) in uncooked A. auricular (Karun *et al.,* 2016). Nine bioactive components found in tender Amanita sp., including total phenolics, tannins, flavonoids, vitamin C, phytic acid, lycopene, β-carotene, trypsin inhibition, and haemagglutinin, were more abundant in uncooked samples compared to cooked ones. Additionally, five antioxidant activities, such as total antioxidant activity, ferrous ion-chelating capacity, reducing power, and DPPH and ABTS radical-scavenging activities, were also higher in uncooked samples (Greeshma *et al.,* 2018). The study Thomas *et al.,* 2023 reported the compounds that are distinct to psilocybin mushrooms include 2-methylbutanal, valeraldehyde, benzaldehyde, 3-octen-2-one, 2-methyl-dodecane, and 2-butyl-2-octenal. In contrast, compounds unique to non-psilocybin mushrooms are 2-methyl-pyrazine, 2,3-butanediol, butyric acid, butyrolactone, benzyl alcohol, 2-pyrrolidinone, and estragole. Interestingly, among these mushrooms, the compound 1-octen-3-ol, which is commonly shared, exhibits a stronger response in psilocybin mushroom species. Morels are highly sought-after wild mushrooms globally because they are both delicious and relatively rare, making them a popular choice among foragers and culinary enthusiasts (Zhao *et al.,* 2022). The study of Yang *et al.,* 2019 estimated liquid fermentation of Morchella sp. YDJ-ZY-1 reported the four pyranoids and 2- (1-oxo-2-hydroxyethyl) furan, linoleic acid, Morelin (2-hydroxy-cinnamic acid methyl ester, and 1-O-β-D-ribofuranose-Morelin were obtained from EtOAc extraction and elucidated by spectral data where Antiradical activity was evaluated by free radical

scavenging effect on DPPH (1,1-Diphenyl-2-picrylhydrazyl radical 2,2-Diphenyl-1- (2,4,6-trinitrophenyl)hydrazyl).

CONCLUSION

The current scenario of fungal metabolites synthesised from wild mushrooms have opportunity to overcome the problems related to natural compounds. On the basis of this chapter enlist the mycosynthesised biomolecules and their role in various field also concluded the application in medical field. The secondary metabolites isolated from mushrooms have beneficially used as anticancerous, antioxidant, antipileptic, antiviral and antimicrobial role in our day-to-day life. The conducted data revealed mushrooms are one of important component in food web. Mushrooms have high nutrition such as protiens, vitamins, minerals and other. The data about secondary metabolites is also folded in this chapter and enlisted some selected examples. Alkaloids, terpens, saponin, steroid, phenolic compound and flavonoids are reported in this chapter.

REFERENCES

[1]. Dasgupta, A., & Acharya, K. (2021). Bioactive terpenoids from mushrooms. In New and Future Developments in Microbial Biotechnology and Bioengineering (pp. 145-154). Elsevier.

[2]. De Cianni, R., Varese, G. C., & Mancuso, T. (2023). A Further Step toward Sustainable Development: The Case of the Edible Mushroom Supply Chain. Foods, 12 (18), 3433.

[3]. Ellertsen, L. K., & Hetland, G. (2009). An extract of the medicinal mushroom Agaricus blazei Murill can protect against allergy. Clinical and Molecular Allergy, 7 (1), 1-10.

[4]. Ferreira, I. C., Baptista, P., Vilas-Boas, M., & Barros, L. (2007). Free-radical scavenging capacity and reducing power of wild edible mushrooms from northeast Portugal: Individual cap and stipe activity. Food chemistry, 100 (4), 1511-1516.

[5]. Greeshma, A. A., Sridhar, K. R., Pavithra, M., & Tomita-Yokotani, K. (2018). Bioactive potential of nonconventional edible wild mushroom Amanita. Fungi and their Role in Sustainable Development: Current Perspectives, 719-738.

[6]. Han, B., Luo, J., & Xu, B. (2023). Insights into the Chemical Compositions and Health Promoting Effects of Wild Edible Mushroom Chroogomphus rutilus. Nutrients, 15 (18), 4030.

[7]. Hossen, S. M., Hossain, M. S., Yusuf, A. T. M., Chaudhary, P., Emon, N. U., & Janmeda, P. (2022). Profiling of phytochemical and antioxidant activity of wild mushrooms: Evidence from the in vitro study and phytoconstituent's binding affinity to the human erythrocyte catalase and human glutathione reductase. Food Science & Nutrition, 10 (1), 88-102.

[8]. Huguet, C., Bourjot, M., Bellanger, J. M., Prévost, G., & Urbain, A. (2022). Screening for antibacterial activity of French mushrooms against pathogenic and multidrug resistant bacteria. Applied Sciences, 12 (10), 5229.

[9]. Jaeger R. J. R., Lamshöft M., Gottfried S., Spiteller M., Spiteller P. (2013). HR-MALDI-MS imaging assisted screening of β-carboline alkaloids discovered from *Mycena metata*. J. Nat. Prod. 2013;76:127–134.

[10]. Javed, S., Li, W. M., Zeb, M., Yaqoob, A., Tackaberry, L. E., Massicotte, H. B., Egger K., N., Cheung C., K., Payne G., W., Lee, C. H. (2019). Anti-inflammatory activity of the wild mushroom, echinodontium tinctorium, in RAW264. 7 macrophage cells and mouse microcirculation. Molecules, 24 (19), 3509.

[11]. Kaewnarin, K., Suwannarach, N., Kumla, J., Choonpicharn, S., Tanreuan, K., & Lumyong, S. (2020). Characterization of polysaccharides from wild edible mushrooms from Thailand and their

antioxidant, antidiabetic, and antihypertensive activities. International Journal of Medicinal Mushrooms, 22 (3).

[12]. Karun, N. C., Sridhar, K. R., Niveditha, V. R., & Ghate, S. D. (2016). Bioactive potential of two wild edible mushrooms of the Western Ghats of India. In Fruits, Vegetables, and Herbs 343-362.

[13]. Kissanga, R., Liberal, Â., Diniz, I., Rodrigues, A. S., Baptista-Ferreira, J. L., Batista, D., . . . & Catarino, L. (2022). Biochemical and molecular profiling of wild edible mushrooms from Huila, Angola. Foods, 11 (20), 3240.

[14]. Kozarski, M., Klaus, A., Jakovljevic, D., Todorovic, N., Vunduk, J., Petrović, P., Niksic, M., Vrvic M., & Van Griensven, L. (2015). Antioxidants of edible mushrooms. Molecules, 20 (10), 19489-19525.

[15]. Kumar, K., Mehra, R., Guiné, R. P., Lima, M. J., Kumar, N., Kaushik, R., Ahmed N., Yadav A., & Kumar, H. (2021). Edible Mushrooms: A comprehensive review on bioactive compounds with health benefits and processing aspects. Foods, 10 (12), 2996.

[16]. Lalotra, P., Bala, P., Kumar, S., & Sharma, Y. P. (2016). Biochemical Characterization of Some Wild Edible Mushrooms from Jammu and Kashmir. Proceedings of the National Academy of Sciences, India Section B: Biological Sciences, 88 (2), 539–545.

[17]. Nowacka, N., Nowak, R., Drozd, M., Olech, M., Los, R., & Malm, A. (2014). Analysis of phenolic constituents, antiradical and antimicrobial activity of edible mushrooms growing wild in Poland. LWT-Food Science and Technology, 59 (2), 689-694.

[18]. Procházka, P., Soukupová, J., Mullen, K. J., Tomšík Jr, K., & Čábelková, I. (2023). Wild Mushrooms as a Source of Protein: A Case Study from Central Europe, Especially the Czech Republic. Foods, 12 (5), 934.

[19]. Pukalski, J., & Latowski, D. (2022). Secrets of flavonoid synthesis in mushroom cells. Cells, 11 (19), 3052.

[20]. Rasalanavho, M; Moodley, R; Jonnalagadda, S. (2020). Elemental Bioaccumulation and Nutritional Value of Five Species of Wild Growing Mushrooms from South Africa. Food Chem. 2020, 319, 126596.

[21]. Sadi, G., Kaya, A., Yalcin, H. A., Emsen, B., Kocabas, A., Kartal, D. I., & Altay, A. (2016). Wild edible mushrooms from Turkey as possible anticancer agents on HepG2 cells together with their antioxidant and antimicrobial properties. International journal of medicinal mushrooms, 18 (1).

[22]. Sifat, N., Lovely, F., Zihad, S. N. K., Hossain, M. G., Shilpi, J. A., Grice, I. D.,& Uddin, S. J. (2020). Investigation of the nutritional value and antioxidant activities of common Bangladeshi edible mushrooms. Clinical Phytoscience, 6, 1-10.

[23]. Taofiq, O., Barreiro, M. F., & Ferreira, I. C. (2020). The role of bioactive compounds and other metabolites from mushrooms against skin disorders-A systematic review assessing their cosmeceutical and nutricosmetic outcomes. Current Medicinal Chemistry, 27 (41), 6926-6965.

[24]. Thomas, S. L., Myers, C., & Schug, K. A. (2023).comparison of fragrance and flavor components in non-psilocybin and psilocybin mushrooms using vacuum-assisted headspace high-capacity solid-phase microextraction and gas chromatography–mass spectrometry. Advances in Sample Preparation, 8, 100090.

[25]. Thu, Z. M., Myo, K. K., Aung, H. T., Clericuzio, M., Armijos, C., & Vidari, G. (2020). Bioactive phytochemical constituents of wild edible mushrooms from Southeast Asia. Molecules, 25 (8), 1972.

[26]. Thu, Z. M., Myo, K. K., Aung, H. T., Clericuzio, M., Armijos, C., Vidari, G. (2020). Bioactive phytochemical constituents of wild edible mushrooms from Southeast Asia. Molecules, 25 (8), 1972.

[27]. Wieczorek, P. P., Witkowska, D., Jasicka-Misiak, I., Poliwoda, A., Oterman, M., & Zielińska, K. (2015). Bioactive alkaloids of hallucinogenic mushrooms. Studies in natural products chemistry, 46, 133-168.

[28]. Yang, C., Zhou, X., Meng, Q., Wang, M., Zhang, Y., & Fu, S. (2019). Secondary metabolites and antiradical activity of liquid fermentation of Morchella sp. isolated from Southwest China. Molecules, 24 (9), 1706.

[29]. Zhabinskii, V. N., Drasar, P., & Khripach, V. A. (2022). Structure and biological activity of ergostane-type steroids from fungi. Molecules, 27 (7), 2103.

[30]. Zhao, X., Hengchao, E., Dong, H., Zhang, Y., Qiu, J., Qian, Y., & Zhou, C. (2022).combination of untargeted metabolomics approach and molecular networking analysis to identify unique natural components in wild Morchella sp. by UPLC-Q-TOF-MS. Food Chemistry, 366, 130642.

[31]. Zhou, J., Chen, M., Wu, S., Liao, X., Wang, J., Wu, Q., & Ding, Y. (2020). A review on mushroom-derived bioactive peptides: Preparation and biological activities. Food Research International, 134, 109230.

Chapter 6

BIO-BASED BUSINESS MODELS: A REVIEW AND NEW DIRECTIONS FOR FUTURE RESEARCH

SHRUTI MAHESHWARI

Smt. SDM PG Girls College, Bhilwara

ABSTRACT

The "biomass to biofuel" biorefinery marked the beginning of the biobased business model, which upgraded otherwise wasted or degraded biological resources. It required significant investments due to its scale and provided a steady supply of low-cost, high-volume feedstock. A well-known commercial strategy for early biorefineries was a joint venture, which was frequently formed by two established companies to combine their expertise, experience, and skill sets with the possibility of a future merger or purchase. The commercial viability of the biofuel biorefinery was questioned due to its low-cost end product, and sustainability concerns were raised because it just uses the energy content and ignores the biomass structures. A range of new bioeconomy business models are made possible by this dual goal, which makes them appropriate for more complex biobased industries. These industries include higher-value products in the biobased portfolio, which are more complex, handle multiple process steps and streams, and produce a variety of biobased products. There are five instances of these business models described:

The commercial viability of the biofuel biorefinery was questioned due to its low-cost end product, and sustainability concerns were raised because it just uses the energy content and ignores the biomass structures. There are five instances of these business models described:

(1) The biobased industry, improving sidestreams of internal production.

(2) A biorefinery focused on biomass.

(3) Cooperatively owned biobased sidestream processing and agricultural residue valorization.

(4) The desired biobased business model is industry clusters.

(5) Local biobased product production owned by a public/private collaboration. Additionally, a forecast study of potential new business models that might work for the anticipated large range of new biobased industry types is offered.

KEYWORDS: Business Models, Sustainability, Biorefinery, Valorization.

INTRODUCTION

A biobased business is a forward-looking enterprise that leverages the power of nature to create sustainable and environmentally friendly products. By harnessing the potential of renewable resources like plants, microorganisms, and biomass, biobased businesses are at the forefront of a green revolution. These businesses prioritize innovation, sustainability, and the reduction of our dependence on fossil fuels. In this introduction, we'll explore the key aspects of biobased businesses, their importance in a world focused on environmental conservation, and the myriad opportunities they offer for a more sustainable future. Biobased business models represent a groundbreaking approach to entrepreneurship that is not only economically viable but also inherently eco-friendly. In an era where environmental sustainability is paramount, these business models have emerged as a beacon of hope. At their core, they

revolve around the utilization of renewable biological resources, such as plants, microorganisms, and waste materials, to develop products and services that are not only competitive in the market but also contribute to a greener, more sustainable future.

These business models have gained prominence due to the pressing need to combat climate change, reduce our reliance on fossil fuels, and curb the environmental degradation caused by traditional industries. By embracing biobased principles, these businesses are aligning themselves with the global shift towards sustainability, circular economies, and responsible resource management.

This introduction will delve into the intricate workings of biobased business models, exploring their diverse applications across various industries, the sustainable practices they champion, the economic advantages they offer, and the pivotal role they play in ushering in a new era of environmental consciousness and responsible entrepreneurship. Join us as we unravel the fascinating world of biobased business models, where innovation meets sustainability, and profit intersects with planet-friendly practices.

These business models are built upon the utilization of renewable biological resources, showcasing a deep commitment to sustainability, innovation, and eco-conscious entrepreneurship.

At the heart of biobased businesses is the recognition that the Earth's biological materials—ranging from agricultural crops and forestry products to microorganisms and organic waste—hold the potential to be harnessed as valuable assets. By tapping into this vast reservoir of natural resources, biobased businesses are redefining the rules of production, delivering a wide array of eco-friendly products and services.

Intriguingly, the appeal of biobased business transcends mere environmentalism. These enterprises, through a combination of scientific advancements and forward-thinking approaches, are pioneering solutions that simultaneously address the challenges of climate change, resource scarcity, and economic growth. Biobased business models are not just a niche within the commercial landscape; they are a critical part of the global transition toward sustainability and the reduction of our dependence on finite fossil fuels.

This introduction will take you on a comprehensive journey into the world of biobased business. We will explore the key principles that underpin these models, their applications across a wide spectrum of industries, the inherent advantages they offer, the technological breakthroughs that empower them, and the profound impact they have on our environment and economy. Get ready to dive deep into the fascinating realm of biobased business, where sustainable practices meet economic opportunity, and the future of commerce is intricately intertwined with the well-being of our planet.

Life cycle analysis, sustainability criteria and 360-degree, holistic thinking are essential and important components of biomass use and technology assessment [1]. Along with bio-actives and non-toxic biobased pesticide substitutes for toxic pesticides used in aquaculture and agriculture, this also includes innovative biobased products and solutions that replace fossil-based products. The use of natural solutions will coexist with the replacement of fossil fuel-based products. One potential use of natural solutions is the elimination or reduction of the need for chemical additions in agriculture. Carefully controlled and monitored production and consumption practices are necessary to achieve truly sustainable production and responsible consumption, meeting the environmental, economic, and social sustainability criteria. [2].

Globally, fossil resources are allocated unevenly. It is foreseeable that the concept of several bioeconomies with distinct geographic boundaries will emerge. More raw materials will probably be upgraded and

valorised in the nation where they are generated if effective biomass upgrading technologies, skills, and expertise are widely available.

In the agricultural sector, bio-based business models promote practices like precision farming and the use of genetically modified crops to increase yield and reduce the need for synthetic inputs. This not only benefits farmers but also has a positive impact on the environment by minimizing the use of pesticides and fertilizers.

In the chemical industry, bio-based models produce chemicals and materials from renewable sources, offering alternatives to petroleum-based products. This reduces greenhouse gas emissions and dependency on fossil fuels.

Moreover, bio-based energy solutions include biofuels and biomass energy, which provide a greener substitute for traditional fossil fuels, thereby mitigating climate change. The emergence of bio-based business models is also reshaping the food and beverage industry, where plant-based and lab-grown alternatives are becoming increasingly popular, addressing concerns related to animal agriculture and its environmental consequences.

In essence, bio-based business models are not only environmentally conscious but also economically viable. They align with the growing global emphasis on sustainability and offer innovative solutions to pressing issues like climate change, resource depletion, and food security. As the world seeks more sustainable, eco-friendly alternatives, bio-based business models are at the forefront of this transition, offering a promising and dynamic landscape for entrepreneurs and innovators.

DEVELOPING BUSINESS MODELS FOR THE FUTURE BIO-BASED INDUSTRIES

Developing business models for the future bio-based industries is a multifaceted endeavour that demands a forward-thinking approach. These industries, which are centred on sustainable and renewable resources, offer a promising avenue for economic growth and environmental stewardship. First and foremost, businesses in this sector need to prioritize research and development to harness the full potential of bio-based materials. This involves investing in cutting-edge biotechnology and green chemistry to create innovative and cost-effective products. Furthermore, collaboration and partnerships are paramount, as bio-based industries often require a complex supply chain. Leveraging circular economy principles is essential, with an emphasis on recycling and reusing materials to minimize waste. Flexibility in business models is also key, as regulations and consumer preferences in the bio-based sector are constantly evolving. Lastly, companies must embrace transparency and sustainability as core values to build trust with eco-conscious consumers and investors. In summary, the future of bio-based industries lies in technology, collaboration, sustainability, and adaptability, making these elements essential components of any successful business model in this field. Yeast biomass is already commercialized; it is effectively produced through fermentation and used as a wholesome and nutrient-dense food and feed ingredient (for both large- and small-scale food processing). [5].

These industries, which encompass biofuels, bioplastics, bio-pharmaceuticals, and more, are rapidly gaining prominence due to their environmentally friendly nature. To succeed in this landscape, businesses must embrace several key principles. Firstly, they need to invest in research and development to harness the full potential of bio-based materials and processes, driving innovation in product design and production. Collaboration with research institutions and government bodies can be crucial in this regard.

For example, bio-based companies can explore licensing their intellectual property, offering consulting services, or venturing into new markets or applications for their products. Flexibility is key in responding to changing market dynamics and consumer preferences.

Additionally, bio-based businesses must prioritize sustainability throughout their value chain, from sourcing renewable feedstock to implementing eco-friendly production processes. Transparency in the supply chain and adherence to rigorous environmental standards are critical for consumer trust and regulatory compliance. Moreover, embracing circular economy principles by reusing and recycling bio-based materials can enhance both economic and environmental sustainability. The next step involves cultivating yeast in enclosed environments using nutrients from sidestreams and genetically modifying yeast strains to generate proteins from milk and meat. Notably, the resulting food product does not contain the genetically modified yeast organisms. Well-known biotech firms that are currently leading the world's markets for industrial enzymes and have access to massive infrastructures for fermentation tanks may soon be producing food as well. These companies have vast experience in large-scale fermentation [6].

Table 1: https://oaj. fupress. net/index. php/bae/article/view/10820

<table>
<tr>
<td rowspan="2">Key Partnerships
· raw material providers
· sales partners
· partners in waste management
· R&D partners cooperating in successful plant operation
· financial advisory service, investors</td>
<td>Key Activities
· feedstock transport and storage
· technology steps: LX chemical pre-treatment process, precipitation of cellulose and lignin, separation / filtration of each component
· enzymatic hydrolysis
· recovery of solvent and precipitant
· technical problem solving
· product transport
· technology optimization and design for scale up</td>
<td rowspan="2">Value Proposition
· production of wide range of bio-based chemicals, non-toxic, sulphur-free, high-quality natural lignin, biofuels and biogas
· high feedstock flexibility: any lignocellulosic raw material can be processed (using only non-food biomass), meaning that the plant is not fixed to a single feedstock
· using the output materials from LX-Process technology, bio-processing plants can produce sugars by enzymatic hydrolysis which can be then converted through microbial fermentation processes into a multitude of valuable end products (e.g. biogas, ethanol, lactic acid, etc.)
· LX-Process leaves little inhibitors (such as furfural or formic acid) the presence of which is a principle hurdle faced in downstream bioprocessing, as they cannot not be removed economically
· simple, modular technology system
· decentralized bio-based production is possible
· circular bioeconomy approach supported by legislation on EU and national level
· GHG reduction</td>
<td>Customer Relationships
· B2B sales strategy
· operating a large-scale pilot plant
· personal follow-up contacts with stakeholders showing interest after presentations at conferences or website visits</td>
<td rowspan="2">Customer Segments
· chemical industrial enterprises interested in 2nd generation bio-chemicals
· key players in development of bio-based, "drop-in" replacement of petrochemicals
· customers seeking natural lignin of unique quality
· cosmetic industry
· 3D printing market
· sectors of construction industry interested in green construction materials
· producers of biopolymers (resins, plastics) and adhesives
· bioethanol and biogas consumers</td>
</tr>
<tr>
<td>Key Resources
· regionally available biomass feedstock (biogas digestate, agricultural and forestry residues)
· estate for the buildings and feedstock storage
· buildings and machinery for processes listed under Key Activities
· vehicles for transport and handling of feedstock and products
· specific-skilled workforce and their technical experiences</td>
<td>Channels
· marketing: company website
· presentations and workshops to inform stakeholders
· demonstration activities performed in the large-scale pilot plant</td>
</tr>
<tr>
<td colspan="3">Cost Structure
· CAPEX costs highly depend on scale and integration scenario
· main OPEX items: feedstock, energy (heat / electricity)
· feedstock price: as cheap as possible, but up to 100 EUR/tonne
· simplicity of the process keeps operational costs low: low temperature, around 70°C, enabling use of residual waste heat; normal atmospheric pressure/tolerance/corrosiveness</td>
<td colspan="3">Revenue Streams
· sales of the materials produced by LX-Process technology
· bulk products as lignin, cellulose, sugars generate revenue with relatively good margins but can also benefit from a wide market of niche products, such as vanillin, which generate high margins but in much lower volume markets
· 6-7 years long payback time is estimated for a plant with a capacity of 25 kt dry matter processed biomass per year
· deployment of the technology is already economical from ca. 10 000 tonnes of throughput (dry matter biomass) per year</td>
</tr>
</table>

Meadow grass silage biorefinery producing grass fibre reinforced plastic composite granulates and biobased insulation material, combined with biogas plant producing electrical energy from grass juice and food residues

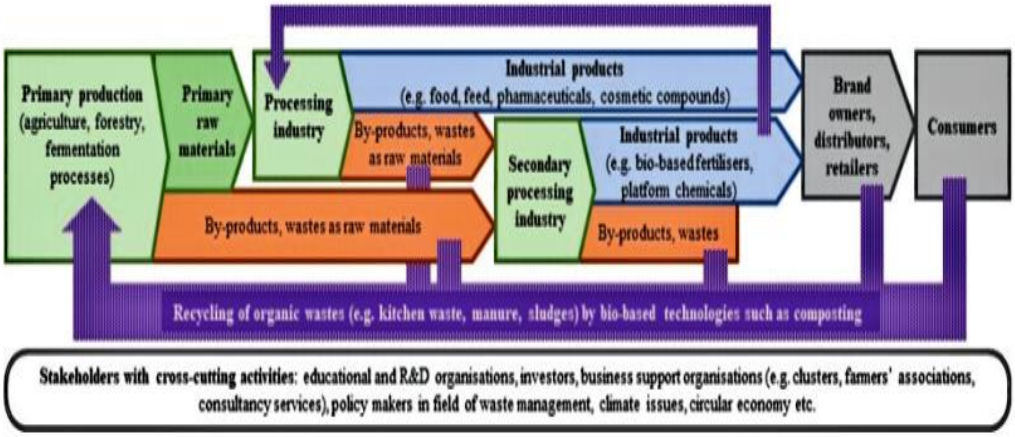


Fig. 1: https://oaj. fupress. net/index. php/bae/article/view/10820

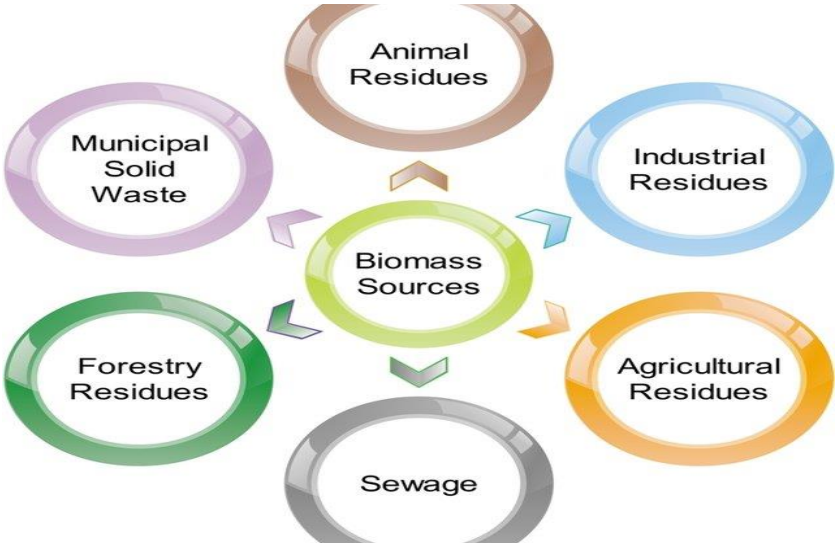


Fig. 2: https://www. frontiersin. org/articles/10. 3389/frsus. 2022. 789435/full

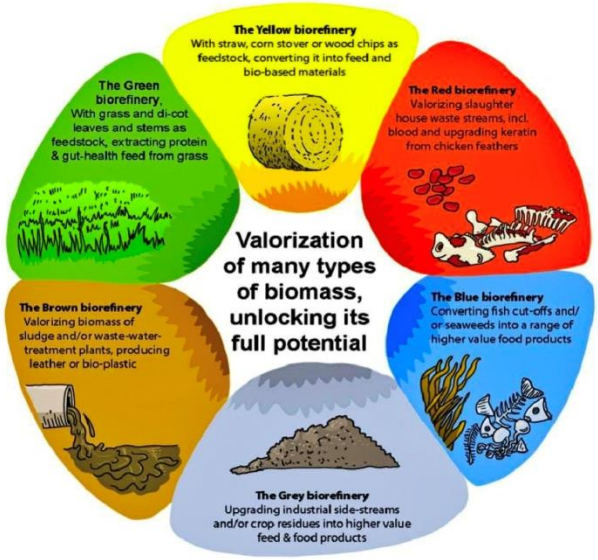


Fig. 3: https://www. frontiersin. org/articles/10. 3389/frsus. 2022. 789435/full

NEW TYPES OF BUSINESS MODEL FOR MORE COMPLEX, HIGHER-VALUE FOCUSED BIOBASED INDUSTRY

Due to its low-priced final product, the biofuel biorefinery faced challenges from both the commercial and sustainability fronts. This is because it simply uses the energy content, failing to fully utilize and valorize the biomass structures. A new phase of "Waste2Value" commercial operations and public research initiatives were launched concurrently. Here, the goal was to maximize the biomass's potential by using all or at least a larger portion of it in a cascading manner and by attempting to produce higher-value products from the biomass. This dual goal creates a range of new, more complicated bioeconomy business models that can handle many process steps and streams and generate multiple kinds of biobased products. This frequently featured goods for a variety of industrial business sectors, to satisfy a range of client needs, and subject to a variety of authority approval processes (of products, process, and production plants) (Sierra *et al.,* 2021). A variety of new business models are made possible by this novel form of biobased production, which is complicated in terms of both product and process, customer needs, and markets. Significantly and crucially, manufacturing a variety of goods can provide stability against changes in the market and the cost of particular goods. Additionally, increasing the value of biomass conversion through the use of multiple components, rather than just the energy content, and creating products that are significantly more valuable than fuels (such as new functional materials and chemicals, cosmetics, feed additives, and food ingredients) with a potentially larger profit margin opens up the possibility of improved sustainability, as evidenced by strengthened LCA analysis, as well as improved commercial viability. This is because bioresources are used more responsibly and efficiently. For the entire biobased industry sector, this was a game-changer. The requirement for building biobased business by economy at scale was no longer a general condition (Lange *et al.,* 2021b).

BARRIERS TO CIRCULAR BUSINESS MODEL IMPLEMENTATION IN A BIO-ECONOMY

Implementing a circular business model in a bioeconomy is a complex endeavour with several notable barriers. First and foremost, there are substantial technological hurdles. The bioeconomy relies on sustainable production and processing of biological resources, which often requires advanced biotechnological methods. Companies may struggle to develop and adopt these technologies, limiting their ability to create closed-loop systems.

Secondly, there is a substantial need for technological innovation. Circular business models often require advanced technologies for efficient resource recovery, recycling, and upcycling. In the context of the bioeconomy, this includes developing biodegradable materials, improving biomass conversion processes, and creating eco-friendly alternatives to traditional products. These innovations are not only costly but also demand substantial research and development efforts.

Additionally, regulatory and policy barriers pose significant hurdles. The bioeconomy operates within a complex web of regulations, including intellectual property rights, biosecurity, and environmental standards. These regulations can be inconsistent or even contradictory, making it challenging for businesses to navigate the legal landscape and integrate circular practices effectively. There is the issue of technology and infrastructure. Many circular bioeconomy models require advanced technologies for efficient waste conversion and resource recovery. However, not all regions have the necessary infrastructure in place, and small businesses may struggle to access or afford these technologies, hindering their ability to embrace circularity.

Another significant challenge is the risk associated with market demand and consumer behavior. The adoption of circular bioeconomy models often relies on consumers' willingness to accept alternative

products and packaging. Changing consumer habits and perceptions can be slow and unpredictable, making it difficult for businesses to justify the initial investments required for circular practices.

Additionally, securing a sustainable and consistent supply of bio-based feedstocks can be challenging. Weather-related factors, crop yield fluctuations, and competition for biomass resources can all impact the availability and cost of raw materials needed for bioeconomy processes.

Furthermore, consumer behavior and awareness play a crucial role. In many cases, consumers may not prioritize or understand the environmental benefits of circular products, which can impact demand. Educating and motivating consumers to embrace sustainable choices is an ongoing challenge.

Lastly, financial considerations cannot be overlooked. Transitioning to circular models may require substantial upfront investments, and the return on investment is often not immediate. Many businesses may be hesitant to make these investments, especially if they are unsure about the long-term economic viability of circular practices in the bioeconomy.

In conclusion, implementing a circular business model in a bioeconomy is a complex endeavor that involves overcoming challenges related to value chain fragmentation, technology, regulations, consumer behavior, and financial considerations. Addressing these barriers requires a holistic and coordinated approach involving governments, industries, and consumers to unlock the full potential of circularity in the bioeconomy.

RESEARCH METHODOLOGY

The starting point for the selection was a collection of nineteen bio-based solutions which were described in detail in a study in the framework of the POWER4BIO project. 17 In the first step, this collection was screened to select good practice solutions having high technological maturity and proven business potential. Additionally, sufficient quality and quantity of the data of the solutions should be available. In this step, knowing a reliable contact person at the company owning the bio-based solution who had permission for sharing necessary and relevant information for all nine building blocks of the Biobased was an important aspect.

1. Final product (a final product or finished product is a product that is ready for sale, distinguishable from a business's work in progress, which is not yet complete or ready for sale, e. g. tableware, biofuel, mushroom grown on agricultural wastes, etc.);
2. Material (he elements, constituents, or substances of which something is composed or can be madee. g. bio-based fibres, bio-based foam for packaging applications, hemp-based insulation material for buildings, plantbased material for clothes, etc.);
3. General building block or biopolymer (chemical monomer or polymer to produce materials, e. g. biobased 1,4-butanediol, an industrial chemical used as a building block for the production of plastics, elastic fibres and polyurethanes);
4. Technology licensing. The authors selected six recently developed biobased good practice cases and described them following the Biobased modelling system [8].

DATA COLLECTION

Intensive desk and literature research were carried out to extract the valuable information from publicly available sources such as webpages of the companies, (bio)economy news portals, press releases issued by the companies, by conference presentations, by economical/statistical databases, or by scientific articles, etc. Online or telephone interviews were conducted with the owners or experts of selected solutions. One person was interviewed per company. The company experts were informed of the aim and subject of the interviews in advance, during the appointment arrangement process. A set of relevant

questions was compiled before the meetings, structured by the elements of BMC, to help covering all relevant details during the interviews. For the case when a company preferred to fill in a questionnaire rather than giving an oral interview, this set of questions was sent to its representative expert. The collected data were processed and organized using BMC structure. 8 Companies have checked and endorsed the business model descriptions [8].

CONCLUSION

In conclusion, the bio-based business model represents a paradigm shift in the global economy, driven by the imperative to address environmental concerns and create a sustainable future. This model leverages renewable biological resources, such as agricultural crops and microorganisms, to produce a wide range of products, from biofuels and bioplastics to pharmaceuticals and food. The key advantages of this model are its reduced environmental footprint, decreased reliance on finite fossil fuels, and its potential to mitigate climate change. Furthermore, bio-based businesses often promote rural development, as they encourage the cultivation of biomass crops, fostering job creation and economic growth in agriculture-dependent regions. However, challenges exist, including the need for substantial investment in research and development, the establishment of robust supply chains, and addressing concerns about land use competition and potential monoculture. Nevertheless, as technology and consumer demand continue to advance, the bio-based business model holds great promise for a more sustainable and eco-friendly future, shaping not only industries. Its success hinges on continued innovation, collaboration, and a shared commitment to balancing economic growth with environmental stewardship.

Biobased business models represent a promising and sustainable approach to economic development. These models capitalize on renewable resources derived from living organisms, such as plants and microorganisms, to create a wide range of products and services. One key conclusion is that biobased business models contribute to environmental conservation by reducing reliance on non-renewable resources and minimizing greenhouse gas emissions. Additionally, they often align with consumers' increasing demand for eco-friendly and socially responsible products.

Moreover, biobased businesses have the potential to drive innovation and economic growth. The development of new biobased materials, biofuels, and biopharmaceuticals opens up novel market opportunities. This diversification fosters economic resilience by decreasing dependence on finite fossil resources. Furthermore, biobased business models often promote rural development, as they can be linked to agriculture and forestry, revitalizing these sectors and creating employment in rural areas.

However, challenges exist, including the need for investment in research and development to improve the efficiency and cost-effectiveness of biobased processes. Additionally, navigating regulatory frameworks and ensuring sustainable sourcing of biobased feedstocks can be complex. Despite these challenges, the shift towards biobased business models is a promising avenue for a more sustainable and environmentally responsible future, offering both economic and environmental benefits.

The review of the business model's components revealed glaring obstacles to the commercialization of what the bioeconomy has to offer. The main obstacle to value creation is the requirement for enhanced partner engagement in order to balance investments, capabilities, and resources. Furthermore, the primary obstacles to value capture include the high operating and investment costs as well as the reliance on subsidies due to the instability of revenue streams. Additionally, this research aids in the conception of the key areas of alignment needed to create a bioeconomy business model that works. More attention needs to be paid to the viewpoint of a business ecosystem, where the value created must be examined from all angles without concentrating on the individual value maximization of each actor [9].

REFERENCES

[1]. Fritsche, U., and Iriarte, L. (2014). Sustainability criteria and indicators for the bio-based economy in Europe: state of discussion and way forward. Energies 7, 6825–6836. doi: 10. 3390/en7116825

[2]. University of Wisconsin (2017). The Tripple Bottom Line. Available online at: https: //sustain. wisconsin. edu/sustainability/triple-bottom-line/ (accessed December 17, 2020).

[3]. Chesbrough, H; Rosenbloom, R. S. The role of the business model in capturing value from innovation: Evidence from Xerox Corporation's technology spin-off companies. Ind. Corp. Chang. 2002, 11, 529–555. [CrossRef].

[4]. Ronzon, T., Piotrowski, S., M'Barek, R., Carus, M. 2017. A systematic approach to understanding and quantifying the EU's bioeconomy. Bio-based and Applied Economics, 6 (1):1-17. DOI: 10. 13128/BAE20567

[5]. Gasser, B., Saloheimo, M., Rinas, U., Dragosits, M., Rodríguez-Carmona, E., Baumann, K., *et al.,* . (2008). Protein folding and conformational stress in microbial cells producing recombinant proteins: a host comparative overview. Microb. Cell Fact 7, 11. doi: 10. 1186/1475-2859-7-11

[6]. Lange, L., Bak, U. G., Mikkelsen, M. D., Meyer, A. S., Karlsson, E. N., Polymenakou, P., *et al.,* . (2021a). The Blue Bioeconomy - A Significant Contribution to Sustainable Development, Locally as Well as Globally. Copenhagen.

[7]. Bocken, N. M.; Schuit, C. S.; Kraaijenhagen, C. Experimenting with a circular business model: Lessons from eight cases. Environ. Innov. Soc. Transit. 2018, 28, 79–95. [CrossRef]. https://oaj. fupress. net/index. php/bae/article/view/10820

[8]. Osterwalder, A.; Pigneur, Y. Business Model Generation: A Handbook for Visionaries, Game Changers, and Challengers; Wiley: Hoboken, NJ, USA, 2010. Diagrams and charts from- https://www. frontiersin. org/articles/10. 3389/frsus. 2022. 789435/full

[9]. https://oaj. fupress. net/index. php/bae/article/view/10820

Chapter 7

REGULATORS AND WATER PROVIDERS ON DIRECTING CYANOBACTERIA IN DRINKABLE WATER SUPPLIES

AKANKSHA PAL*, ISHIKA SRIVASTAVA, SWEETY SAHU AND KIRTI RAJE SINGH*

Department of Botany, CMP Degree College,
University of Allahabad, Prayagraj-211002, Uttar Pradesh, India
Corresponding author E-mail: jayantipal208@gmail.com, dr.kirtiraje@gmail.com

ABSTRACT

This brief article offers a comprehensive overview of the control of cyanobacteria in drinking water sources to assist regulators and water providers in deciding when and how to intervene. It lists several ways to stop cyanobacterial blooms from growing as well as solutions for controlling them once they do. The control of other risks can also benefit from many of the methods, even though some of them are special to cyanobacteria. In order to address existing and potential dangers from cyanobacteria in drinking water, this evidence brief gives an overview of the scope of the problem and highlights important areas of relevance for public health (PH) experts and others involved in water management.

KEYWORDS: Drinking Water Treatment, Cyanotoxins, Cyanobacteria, Public Health.

INTRODUCTION

Cyanobacteria can thrive in a range of settings and are widespread around the world. The frequency of toxic cyanobacterial harmful algal blooms (CHABs), which endanger drinking and recreational water supplies worldwide, has been rising.

Water utilities around the world face challenges because of cyanobacteria and their persistence in drinking water sources. Cyanobacteria can lead to issues such as the emission of poisonous and/or offensive-tasting substances, an increase in the need for chemical treatment, or the clogging of filters (Chen *et al.,* 2009; Ma *et al.,* 2012; Shen *et al.,* 2011).

A concentration of particles and organic matter is produced in the settling floc, or sludge, as a result of the chemical coagulation, flocculation, clarifying, and filtration processes used in conventional water treatment. The sludge is taken to treatment facilities where it will be stored and given additional care. A cyanobacteria bloom that is healthy during the particle separation process, the secondary metabolites, such as toxins and taste and odour chemicals, are concentrated in the sludge since they can be up to 98% internalised within the cell (Chorus and Bartram, 2002). A significant difficulty for water supply is eliminating and controlling algae, which can produce toxins and alter the taste and odour of drinking water supplies.

Utility managers must comprehend the destiny and movement of cyanotoxins in their system in order to balance the removal economics against the risk of cyanotoxins in potable water.

HOW DO CYANOBACTERIA WORK?

Low to moderate levels of cyanobacteria, often known as blue-green algae, are found in surface waters naturally; extremely high levels are typically brought on by human activity enriching the water with phosphorus and nitrogen. Cyanotoxins are poisons that are produced by some cyanobacteria.

Cyanobacteria can exist as solitary cells, in colonies, filaments, or in groups. Fresh, marine, and brackish waters all contain them. Anabaena, Aphanizomenon, Cylindrospermopsis, Lyngbya, Microcystis, Oscillatoria, Phormidium, and Planktothrix are among the genera that are frequently found in surface waters. (Wood *et al.,* 2009)

Cyanobacterial genera such Anabaena, Phormidium, and Planktothrix create substances with disagreeable smells and scents (sometimes known as "off-flavours"). The two most prevalent substances are 2-methylisoborneol and geosmin. They give drinking water a musty, earthy flavour that, while not pleasant, is completely safe. The effects of cyanotoxins on human health can vary. Acute symptoms can include liver damage and neurotoxicity, in addition to gastroenteritis, fever, and irritation of the skin, eyes, throat, and respiratory tract. Tumour promotion is one of the chronic long-term consequences (World Health Organisation, 2015). Cyanobacteria are not contagious since they do not grow in the human body (Chorus & Bartram, 2002).

In the form of a thick mat or scum at the water's surface, cyanobacterial blooms (also known as cyanoblooms) can be bluish-green, green, red, or brownish in colour and have the look of pea soup or paint. (1) Cyanobacteria, sometimes referred to as blue-green algae, proliferate excessively in water, forming cyanobacterial harmful algal blooms (CHABs). Although certain cyanobacteria do not create toxins, it has been hypothesised that the aquatic environment will be more conducive to the bloom of toxic cyanobacteria such Microcystis sp. when water temperatures rise (Paerl 2008; Davis *et al.,* 2009; Ye *et al.,* 2011). A range of cyanotoxins, as well as taste and odour chemicals, can be produced by these blooms, endangering water supplies all around the world.

HEALTH CONSEQUENCES OF CYANOTOXINS

The presence of a bloom, as well as its general size, shape, and colour, are the first outward signs of a risk from exposure to polluted drinking water, food, or recreational contact. However, they do not indicate if a bloom is toxic. (Carmichael, 2008; Svirčev *et al.,* 2017; Miller & Russell, 2017) The main dangers posed by cyanobacteria are caused by the cyanotoxins produced intracellularly and released either throughout the organism's lifespan or when the cells die and burst.

Cyanotoxins are known to be produced by about 5% of the more than 2000 species of cyanobacteria that have been identified, and some cyanobacteria are capable of producing multiple cyanotoxins. 16 Acute exposures to cyanotoxins can cause nausea, vomiting, diarrhoea, skin irritation, rash, fever, and headaches, among other symptoms. Cyanotoxins can target a variety of organs, including the liver (hepatotoxins), nervous system (neurotoxins), and skin. Some of the cyanotoxins are as follow:

MICROCYSTINS

The cyanobacteria genera Microcystis, Anabaena, Planktothrix, Nostoc, and Anabaenopsis are the source of the hepatotoxin microcystin. The microcystins have over 80 reported variants and are highly soluble in water; however, the US Environmental Protection Agency (US EPA) is particularly concerned about four of them (LR, RR, LA, and YR) and they are on the US EPA Contaminant Candidate List III, which was created through a series of international panel discussions (Westrick *et al.,* 2010). The World Health Organisation (WHO) has established a provisional microcystin LR drinking water guideline of 1 ug/L.

CYLINDROSPERMOPSIN

Cylindrospermopsis, Anabaena, Umezakia, and Aphanizomenon are some of the cyanobacteria genera from which cylindrospermopsin is derived. Toxicology data are being assessed by the WHO (Christoffersen & Kaas, 2000), Falconer (Yoo, 1995) and the USA (EPA, 2006) to see if a drinking water guideline for cylindrospermopsin is necessary.

A provisional guideline value of 1 ug/L for cylindrospermopsin is suggested by Falconer (Yoo,1995). Cylindrospermopsin's uracil side chain prevents the translation of proteins, binds to DNA, breaks DNA strands, and promotes hepatotoxicity, cytotoxicity, and genotoxicity.

ANATOXIN-A

A frequent and dangerous neurotoxic is anatoxin-A. 1 ug/L is the recommended guideline concentration, according to Fawell *et al.,* . Anabaena, Planktothrix, and Aphanizomenon are the three genera that produce anatoxin-a. By binding to the acetylcholine receptors, this cholinergic agonist imitates the effects of acetylcholine.

SAXITOXINS

These neurotoxins, which are frequently linked to "red tides," are brought on by marine dinoflagellet blooms and behave as poisonous shellfish. Aphanizomenon, Anabaena, Lyngbya, and Cylindrospermopsis are four genera of freshwater cyanobacteria that have been reported to contain saxitoxins. The majority of animal fatalities associated with saxitoxins occur in freshwater.

ASPECTS THAT AFFECT THE OCCURENCE OF CYANOBLOOMS

Nutrients The most crucial nutrients are phosphorus (P) and nitrogen (N), with increased input from point sources like sewage effluent and diffuse sources like agricultural runoff increasing the likelihood of detecting a bloom (Fawel *et al.,* 1999).

Temperature – Long-term warm temperatures (over 20°C, for example) encourage the growth of cyanobacteria. Blooms flourish best during drought situations that have long stretches of warm weather and intervals of quiet, dry water (Qi YL *et al.,* 2015).

Characteristics Of Lakes - Eutrophic (nutrient rich) lakes are more likely to see blooms than oligotrophic (nutrient poor) lakes, as are lakes with low flushing rates and stratification, where the water column is divided into strata according to temperature (Miller *et al.,* 2017)

PHYTOCLIMATIC FACTORS THAT SUPPORT THE GROWTH OF CYANOBACTERIA

- High nutrient contents, especially phosphorus (more than 25 to 50 g of total phosphorus per litre1),
- Higher than 25 °C water temperature
- Longer than one month's worth of hydraulic retention, and
- Stratification of a steady water body (for some cyanobacteria) (World Health Organization, 2015)

THE DIFFICULTIES AND KNOWLEDGE SPACES FOR PUBLIC HEALTH

A number of issues have been raised by this review, such as certain knowledge and practise gaps for public health in controlling cyanobacterial threats to drinking water.

- There aren't enough common indicators for monitoring and predictive modelling, such as specifics about when blooms occur, cell volume, toxin concentration, and other environmental data (including temperature, precipitation, wind speeds, nutrient concentrations, etc (Merel *et al.,* 2013., Chorus and Bartram, 1999). It is challenging to compare research because there are no standards for sampling, analysis, or monitoring frequency. (Quiblin *et al.,* 2013; Ibelings *et al.,* 2015; Otten and Paerl, 2015; de *et al.,* 2017).
- The ability to react quickly to cyanobloom incidents is constrained by the lack of quick and accurate field tests. Real-time monitoring technologies or quick field tests could let the appropriate authorities conduct more thorough surveillance. (Otten and Paerl, 2015; Pham and Utsumi, 2018). This might enhance the timely identification and measurement of risk and assist PH experts in better communicating danger to the general public.

- Users receiving water from big treatment facilities may not be as protected from exposure as SDWS and PWS who draw water from contaminated water bodies with very minimal treatment (such as disinfection only).
- Multiple stakeholders, with varied levels of resources and opposing interests, must be involved in the management of cyanobloom risks. A more coordinated and uniform approach might be developed throughout provinces or regions with the assistance of local champions and organisational leadership.
- Water bodies affected by cyanoblooms currently lack easily accessible monitoring data. Some provinces (such as the PHSD and the Government of Manitoba) are expanding access to information by offering web-based interactive maps; however, long-term data could improve predictive models for future bloom events and help relevant authorities in effectively focusing monitoring and surveillance efforts.
- For a variety of cyanotoxins, including effects on other human systems (such as reproduction and kidneys), health risks from exposure to mixtures of cyanotoxins and other chemical stressors in water supplies, and information on the most vulnerable populations via various exposure routes (considering rates of ingestion, age, and underlying conditions), there are research gaps in the mechanisms and level of toxicity to human systems via various exposure routes. (Merel *et al.,* 2013; Ibelings *et al.,* 2015).

APPROACHES TO PURIFICATION

Activated carbon

Coal, coconut, and wood are typical precursors used in the large-scale synthesis of activated carbon. As a result of the various precursors and activation procedures, the activated carbons' adsorptive properties can be altered, and they can even be made slightly selective for particular pollutants.

In the drinking water industry, activated carbon is used in two different ways: powdered activated carbon is typically used as a short-term solution for transient contaminants and granular activated carbon (GAC) is used in fixed beds to remove organic matter, flavour and odorants, and synthetic organic compounds from industrial source waters. Activated carbon with a large mesopore capacity can absorb both microcystin and cylindrospermopsin (Newcombe and Nicholson, 2004; Ho *et al.,* 2008).

According to research by (Newcombe and Nicholson, 2004; Ho *et al.,* 2005), activated carbons having a high percentage of micropores—pores smaller than 1 nm—will have the greatest ability to adsorb saxitoxins. Otherwise, it is generally accepted that saxitoxins can be removed by carbons that are good at removing taste and odour substances, such as 2-methylisoborneol and geosmin (Newcombe and Nicholson, 2004).

MEMBRANE FILTRATION

Based on the physical/chemical properties of the membrane, reverse osmosis, nanofiltration, and ultrafiltration technologies separate pollutants by size and charge. According to studies on nanofiltration and reverse osmosis filtration, microcystin is completely removed in 82% of cases (Fawell *et al.,* 1993; Muntisov and Trimboli, 1996).

BIOLOGICALLY ACTIVE FILTRATION

Microcystins (Yoo, 1995; Bourne *et al.,* 2006; Lahti *et al.,* 2001; Westrick *et al.,* 2010) and cylindrospermopsin (Ho *et al.,* 2005) have been observed to be removed/ inactivated by biologically active river bank filtration and both slow and quick filtering. The creation and training of a microbial community competent to metabolise microcystins are necessary for acclimation prior to breakdown (Jones *et al.,* 1994; Cousins *et al.,* 1996; Christoffersen *et al.,* 2002; Rapala *et al.,* 1994). Predation, pH, and

temperature are further environmental factors (Newcombe and Nicholson, 2004). To investigate the elimination of microcystins by biologically active slow sand filtration, (Westrick *et al.,* 2010) carried out two full-scale trials.

OXIDANTS

This portion of the review addresses the more current literature that establishes the reaction rates and processes of the frequently employed oxidants and cyanotoxins in light of Lawton and Robertson's (Senogles *et al.,* 2000) analysis of probable reaction schemes for the oxidation of microcystin LR.

Chlorine, ozone, hydroxyl radicals, chloramines, potassium permanganate, and chlorine dioxide are the main oxidants in drinking water. These oxidants are frequently employed as disinfectants before chemical addition, before filtering, or after filtering. Total organic carbon, temperature, pH, and possibly even treatment chemicals might alter the oxidant demand, potentially reducing the efficiency of cyanotoxins to be inactivated. For instance, increasing the pH of the treatment water to 9 will result in lesser levels of halogenated compounds being formed, as will applying ozone before and after coagulation to reduce the quantity of halogenated compounds formed during chlorination.

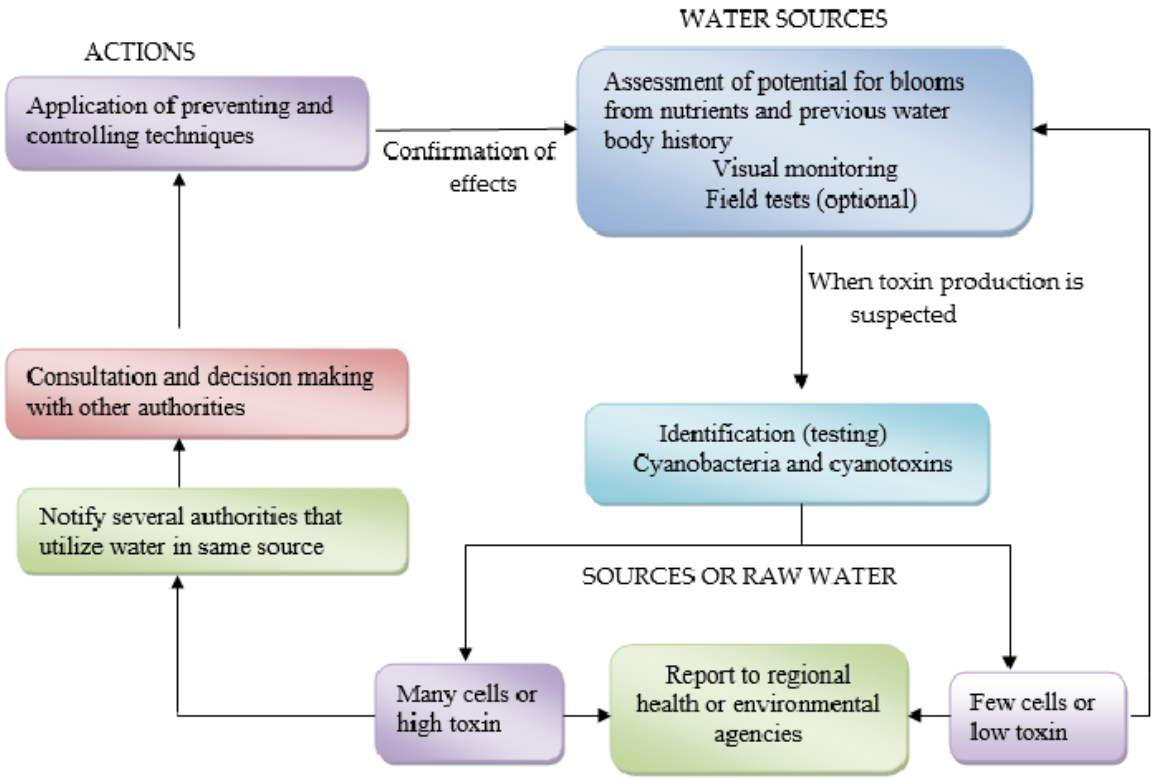


Fig. 1: An illustration of the water cyanobacteria management flow chart
(Source: Adapted from Health Canada, 2002)

ADVANCED OXIDATION PROCESSES

Advanced oxidation techniques produce and employ the hydroxyl radical. The hydroxyl radical is a kind of oxidant that is not very selective. Both photochemical and nonphotochemical methods can produce the hydroxyl radical. The inactivation of microcystin LR by UV/H2O2 (Lawton and Robertson, 1999), Fenton and photo-Fenton methods and TiO2/UV (Senogles *et al.,* 2000; Liu *et al.,* 2003; Westrick *et al.,* 2010) was demonstrated in earlier research. Mesoporous nitrogen-doped TiO2 photocatalysts were created by (Westrick *et al.,* 2010) with the goal of inactivating microcystin LR under UV and visible light. (Liang *et al.,* 2008) looked at the use of electrochemical oxidation with a Ti/RuO2 anode to render microcystin LR

inactive. The main drawback of this method is that it works best at pH 3, which is unsuitable for treating drinking water. These new technologies must include cylindrospermopsin, anatoxin-a, and saxitoxins in their research.

UV DISINFECTION

A low to medium pressure lamp with UV dosages between 10 and 40 mJ/cm2 is typically used in the UV treatment procedure to disinfect surfaces. Studies by (Tsuji *et al.*, 1994; Chorus and Welker, 2021; Senogles *et al.,* 2000) indicate that the anatoxin-a, cylindrospermopsin, and microcystin can be destroyed by photolysis.

CONCLUSION

When focusing on bloom prevention through catchment and water source management as part of a water safety plan strategy to controlling risks to a water supply system, cyanobacteria management is most effective. Establishing a cross-sectoral team to examine the local circumstances, evaluate the health hazards, and create management strategies are all part of adopting the water safety plan strategy. Water safety plans offer a helpful forum for discussion amongst catchment stakeholders who may be governed by several laws (such as those governing agriculture, wastewater, water management, and health).

The efficiency of the barriers put in place, from the catchment to the treatment plant outlet, will be evaluated using monitoring techniques and toxin testing together. To determine whether there may be a health risk during an occurrence, periodic testing for specific cyanotoxins is helpful (for example, during a bloom and as it diminishes). Small drinking water systems with restricted treatment capabilities and private water systems using damaged surface water bodies as a source of water may be more exposed than other drinking water users. There are examples of good practise in risk assessment, reporting of blooms, and public outreach, but approaches to managing threats to drinking water differ across the nation.

REFERENCES

[1]. Bourne, D. G., Blakeley, R. L., Riddles, P., & Jones, G. J. (2006). Biodegradation of the cyanobacterial toxin microcystin LR in natural water and biologically active slow sand filters. Water Research, 40 (6), 1294-1302.

[2]. Carmichael, W. (2008). Cyanobacterial harmful algal blooms: State of the science and research needs. Adv. Exp. Med. Biol, 619, 831-853.

[3]. Chorus, I., Bartram, J., (2002). Toxic Cyanobacteria inWater: A Guide to their Public Health Consequences, Monitoring and Management. Spon Press, London (ISBN 0-419-23930-8).

[4]. Chorus I, Bartram J. (1999). Toxic cyanobacteria in water: a guide to their public health consequences, monitoring and management. London; New York: E & FN Spon; 1999. Available from: https://apps. who. int/iris/handle/10665/42827

[5]. Chen, J. -J., Yeh, H. -H., & Tseng, I. -C. (2009). Effect of ozone and permanganate on algae coagulation removal – Pilot and bench scale tests. Chemosphere, 74 (6), 840-846. https://doi. org/10. 1016/j. chemosphere. 2008. 10. 009

[6]. Chorus, I., & Welker, M. (2021). Toxic cyanobacteria in water: a guide to their public health consequences, monitoring and management (p. 858). Taylor & Francis.

[7]. Christoffersen, K., Lyck, S., & Winding, A. (2002). Microbial activity and bacterial community structure during degradation of microcystins. Aquatic Microbial Ecology, 27 (2), 125-136.

[8]. Cousins, I. T., Bealing, D. J., James, H. A., & Sutton, A. (1996). Biodegradation of microcystin-LR by indigenous mixed bacterial populations. Water research, 30 (2), 481-485.

[9]. Davis, T. W., Berry, D. L., Boyer, G. L., & Gobler, C. J. (2009). The effects of temperature and nutrients on the growth and dynamics of toxic and non-toxic strains of Microcystis during cyanobacteria blooms. Harmful Algae, 8 (5), 715-725. https://doi. org/10. 1016/j. hal. 2009. 02. 004

[10]. de Boutray ML, Maghsoudi E, Ndong M, Dorner S. (2017). Revue de littérature sur les cyanotoxines dans les milieux aquatiques d'eau douce: leurs effets sur la santé des usagers et les critères ou seuils d'alerte de toxicité chronique et aigüe. Québec: Fonds de Recherche du Québec - Nature et Technologies; 2017. Available from: https://publications. polymtl. ca/2762/

[11]. EPA, U. (2006). Toxicological reviews of cyanobacterial toxins: cylindrospermopsin (external review draft). United States Environmental Protection Agency, Washington.

[12]. Fawell, J. K., Mitchell, R. E., Everett, D. J., & Hill, R. E. (1999). The toxicity of cyanobacterial toxins in the mouse: I Microcystin-LR. Human & Experimental Toxicology, 18 (3), 162-167. https://doi. org/10. 1177/096032719901800305

[13]. Fawell JK, Hart J, James HA, Parr W (1993) Water Supply11:109–122

[14]. Health Canada (2002). Cyanobacterial toxins – Microcystin-LR (Guidelines for Canadian Drinking Water Quality: supporting documentation). Ottawa (ON): Health Canada, Federal-Provincial-Territorial Committee on Drinking Water (http://hc-sc. gc. ca/ewh-semt/alt_formats/hecssesc/pdf/pubs/watereau/cyanobacterial_toxins/cyanobacterial_toxins-eng. pdf, accessed 27 May 2014).

[15]. Ho, L., Slyman, N., Kaeding, U., & Newcombe, G. (2008). Optimizing PAC and chlorination practices for cylindrospermopsin removal. Journal-American Water Works Association, 100 (11), 88-96.

[16]. Ho, L., Shaw, G., O'Donohue, M., Saint, C., & Newcombe, G. (2005). Biological filtration processes for the removal of algal metabolites. Water, 32 (5), 64-68.

[17]. Ibelings BW, Backer LC, Kardinaal WE, Chorus I. (2015). Current approaches to cyanotoxin risk assessment and risk management around the globe. Harmful Algae. 2015 Dec;49:63-74. Available from: https://doi. org/10. 1016/j. hal. 2014. 10. 002

[18]. Jones, G. J., & Orr, P. T. (1994). Release and degradation of microcystin following algicide treatment of a Microcystis aeruginosa bloom in a recreational lake, as determined by HPLC and protein phosphatase inhibition assay. Water research, 28 (4), 871-876.

[19]. Lahti, K., Rapala, J., Kivimäki, A. L., Kukkonen, J., Niemelä, M., & Sivonen, K. (2001). Occurrence of microcystins in raw water sources and treated drinking water of Finnish waterworks. Water science and technology, 43 (12), 225-228.

[20]. Lawton, L., & Robertson, P. J. (1999). Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters. Chemical Society Reviews, 28 (4), 217-224.

[21]. Liang, W., Qu, J., Wang, K., Wang, J., Liu, H., & Lei, P. (2008). Electrochemical degradation of cyanobacterial toxin microcystin-LR using Ti/RuO2 electrodes in a continuous tubular reactor. Environmental engineering science, 25 (5), 635-642.

[22]. Liu, I., Lawton, L. A., & Robertson, P. K. (2003). Mechanistic studies of the photocatalytic oxidation of microcystin-LR: an investigation of byproducts of the decomposition process. Environmental science & technology, 37 (14), 3214-3219.

[23]. Ma, M., Liu, R., Liu, H., & Qu, J. (2012). Chlorination of Microcystis aeruginosa suspension: Cell lysis, toxin release and degradation. Journal of Hazardous Materials, 217, 279-285. https://doi. org/10. 1016/j. jhazmat. 2012. 03. 030

[24]. Merel S, Walker D, Chicana R, Snyder S, Baurès E, Thomas O. (2013). State of knowledge and concerns on cyanobacterial blooms and cyanotoxins. Environ Int. 2013;59:303-27. Available from: https://doi. org/10. 1016/j. envint. 2013. 06. 013

[25]. Miller, A., & Russell, C. (2017). Food crops irrigated with cyanobacteria-contaminated water: An emerging public health issue in Canada. Environmental Health Review, 60 (3), 58-63.

[26]. Christoffersen, K., & Kaas, H. (2000). Toxic cyanobacteria in water. A guide to their public health consequences, monitoring, and management.

[27]. Miller, T., Beversdorf, L., Weirich, C., & Bartlett, S. (2017). Cyanobacterial Toxins of the Laurentian Great Lakes, Their Toxicological Effects, and Numerical Limits in Drinking Water. Marine Drugs, 15 (6), 160. https://doi. org/10. 3390/md15060160

[28]. Muntisov, M., & Trimboli, P. (1996). Removal of algal toxins using membrane technology. WATER-MELBOURNE THEN ARTARMON-, 23, 34-34.

[29]. Newcombe, G., & Nicholson, B. (2004). Water treatment options for dissolved cyanotoxins. Journal of Water Supply: Research and Technology-Aqua, 53 (4), 227-239. https://doi. org/10. 2166/aqua. 2004. 0019

[30]. Otten TG, Paerl HW. (2015). Health effects of toxic cyanobacteria in U. S. drinking and recreational waters: Our current understanding and proposed direction. Curr Environ Health Rep. 2015 Mar;2 (1):75-84. Available from: https://doi. org/10. 1007/s40572-014-0041-9.

[31]. Paerl, H. (2008). Nutrient and other environmental controls of harmful cyanobacterial blooms along the freshwater–marine continuum. Advances in Experimental Medicine and Biology, 217-237. https://doi. org/10. 1007/978-0-387-75865-7_10

[32]. Pham TL, Utsumi M. (2018). An overview of the accumulation of microcystins in aquatic ecosystems. J Environ Manage. 2018 May 1;213:520-9. Available from: https://doi. org/10. 1016/j. jenvman. 2018. 01. 077.

[33]. Qi YL, Rosso L, Sedan D, Giannuzzi L, Andrinolo D, Volmer DA. (2015). Seven new microcystin variants discovered from a native Microcystis aeruginosa strain - unambiguous assignment of product ions by tandem mass spectrometry. Rapid Commun Mass Spectrom. 2015 Jan;29 (2):220-4. Available from: http://dx. doi. org/10. 1002/rcm. 7098

[34]. Quiblier C, Wood S, Echenique-Subiabre I, Heath M, Villeneuve A, Humbert J-F. (2013). A review of current knowledge on toxic benthic freshwater cyanobacteria--ecology, toxin production and risk management. Water Res. 2013 Oct 01;47 (15):5464-79. Available from: https://doi. org/10. 1016/j. watres. 2013. 06. 042.

[35]. Rapala, J., Lahti, K., Sivonen, K., & Niemelä, S. I. (1994). Biodegradability and adsorption on lake sediments of cyanobacterial hepatotoxins and anatoxin-a. Letters in Applied Microbiology, 19 (6), 423-428.

[36]. Senogles, P., Shaw, G., Smith, M., Norris, R., Chiswell, R., Mueller, J., & Eaglesham, G. (2000). Degradation of the cyanobacterial toxin cylindrospermopsin, from Cylindrospermopsis raciborskii, by chlorination. Toxicon, 38 (9), 1203-1213.

[37]. Shen, Q., Zhu, J., Cheng, L., Zhang, J., Zhang, Z., & Xu, X. (2011). Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. Desalination, 271 (1), 236-240. https://doi. org/10. 1016/j. desal. 2010. 12. 039

[38]. Svirčev, Z., Drobac, D., Tokodi, N., Mijović, B., Codd, G. A., & Meriluoto, J. (2017). Toxicology of microcystins with reference to cases of human intoxications and epidemiological investigations of exposures to cyanobacteria and cyanotoxins. Archives of toxicology, 91, 621-650.

[39]. Tsuji K, Naito S, Kondo F, Ishikawa N, Watanabe MF (1994). Environ Sci Technol 28:173 A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment 1713

[40]. Westrick, J. A., Szlag, D. C., Southwell, B. J., & Sinclair, J. (2010). A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment. Analytical and bioanalytical chemistry, 397, 1705-1714

[41]. Wood, S. A., Hamilton, D. P., Paul, W. J., Safi, K. A., & Williamson, W. M. (2009). New Zealand Guidelines for cyanobacteria in recreational fresh waters: interim guidelines.

[42]. World Health Organization. (2015). Management of cyanobacteria in drinking-water supplies: Information for regulators and water suppliers (No. WHO/FWC/WSH/15. 03). World Health Organization

[43]. Ye, W., Tan, J., Liu, X., Lin, S., Pan, J., Li, D., & Yang, H. (2011). Temporal variability of cyanobacterial populations in the water and sediment samples of Lake Taihu as determined by DGGE and real-time PCR. Harmful Algae, 10 (5), 472-479. https://doi. org/10. 1016/j. hal. 2011. 03. 002

[44]. Yoo, R. S. (1995). Cyanobacterial (blue-green algal) toxins: a resource guide. American Water Works Association.

Chapter 8

THE IMPORTANCE OF ETHNOBOTANICAL STUDY IN INDIA

RAIMA GUHA

Department of Botany, Scottish Church College, University of Calcutta, West Bengal, India
Corresponding author E-mail id: raimaguha21@gmail.com

ABSTRACT

Ethnobotany, a branch of science, focuses on the relationship between people and plants. People are dependent on plants from the very past for their various uses such as food, fodder, medicine and other useful products. Thus, ethnobotanical studies embrace various relationships between humans and plants, including their healthful, religious, indigenous beliefs and utility. India is a vast country with diverse topographics, climates, vegetations, people. In general, knowledge acquired from ethnobotanical study of various medicinal plants in India have led to new drug development. This chapter focuses on Ethnobotanical study in India and its importance, particularly, its role in study of medicinal plants and conservation of natural resources.

KEYWORDS: Ethnobotany, Indigenous People, Traditional Knowledge, Tribal Communities, Medicinal Plants, Folk Medicine.

INTRODUCTION

Plants have been an intrinsic part of human life since time immemorial. People from all cultures have relied on them for their basic needs such as food, shelter, and medicines. It is a fact that plant knowledge has been shared and expanded upon through the ages by nomadic tribes and their neighbouring communities. Ethnobotany, which is the study of relationships between plants and people, is a multidisciplinary science that has been practiced by all cultures for generations.

The relationship between plants and human is not just limited to their use for food, shelter, and clothing. It also involves their use for religious ceremonies, health care, ornamentation, and other aspects of life. Ethnobotany focuses on how plants have been used, managed, and perceived in human societies. This includes plants used for medicine, cosmetics, dyeing, textiles, clothing, building, currency, tools, rituals and social life.

It cannot be overstated how important plants are to human life. They play a crucial role in regulating the concentration of gases in the air and transforming sunlight into food energy, which is the foundation of all other forms of life. Indigenous people, who have extensive knowledge of medicinal plants, are invaluable resources for retrieving this information, particularly for modern medicine.

ETHNOBOTANY CONCEPT

Ethnobotany combines two terms "ethano" which mans study of human or folks and "botany" which means study of plant species (Choudhary *et al.,* 2008). Ethnobotany is the study area dealing with relationships between people and plants. It mainly focuses on the study of those plants that help in local's traditional knowledge and cultural practices.

The term "Ethnobotany" was first used by J. W. Harshberger in 1895 to include in the study of "Plants used by primitive and aboriginal people".

Schultes (1962) defined ethno botany as "the study of the relationships between the people of a primitive society and plants".

Jain (1987) explained it as the total natural and traditional relationship and interaction between man and his surrounding plant wealth.

Ethnobotany is now recognized worldwide as the total direct or natural relationship between human and plants and includes the utilization of plants by both tribals and non-tribals without any implication of primitive or developed societies.

ETHNOBOTANY IN INDIA

India possesses an incredibly vast trove of ethnobotanical knowledge. With 227 unique ethnic groups residing in 500 different regions, India hosts an impressive 7500 varieties of medicinal plants. A rich source of curative properties of 99 plants can be traced back to the Vedic period between 3500 and 1800 BC. The Indian medical system's cornerstone texts, Charak and Sushruta, emerged during this time. With 20,000 angiosperm species and numerous social groups with historical links, India is one of the nations with the most abundant ethnobotanical data.

Though Harshberger (1895) provided the idea of ethnobotany, India had already laid the groundwork for this discipline. Dr. E. K. Janaki Ammal started organized fieldwork and other Ethnobotany research at the BSI (Botanical Survey of India). The founder of ethnobotany, Dr. S. K. Jain, conducted ample of field researches among tribal populations in the central part of India. He developed ethnobotany methods, especially for the Indian context.

Approximately 28,000 plant species are used in human medicine, with about 25,000 of them producing plant-based formulations used by agricultural and ethnic groups in India (Pandey *et al.,* 2013). The Jantia community in India uses medicinal plants in highly effective ways, as reported by Sajem and Gosai (Sajem, *et al.,* 2006). There are 39 different medicinal plant species, divided into 27 different families, which are claimed to have medicinal properties in India. As one of the twelve biodiversity hotspots in the world, India is home to over 45000 plant species, making it a significant biodiversity hotspot. More than 20,000 plants are believed to have medicinal worth, but only 7,000-7,500 species have been used by traditional communities (Mao *et al.,* 2009).

IMPORTANCE OF ETHNOBOTANICAL STUDY

- Ethnobotanical knowledge provides information on the traditional uses of plant wealth that can be utilized to promote integrated tribal development. Ethnobotanical studies help to identify certain unknown useful plants and discover new uses of many known plants that lead to the development of new sources of some plant products and agro-based industries such as food processing, extraction of oils (both edible and non-edible), resins, gum, fibres and floss, tannin and dye extraction, which can contribute to the betterment of tribal communities.
- With the opening of various new prospects of ethnobotany, the scope of this natural science has now greatly increased. It now has both theoretical and practical contributions towards understanding the plant and human relationship and knowledge of tribal people in agriculture, medicine, health and industry.
- The tribals rely mostly on forest flora to meet their daily needs along with primary health care requirements. They gather information and utilize numerous wild plants for fibres, food, tannins, dyes, gums, oils, and medicines from the surrounding vegetation in their vicinity.

- The agricultural practices are not advanced technologically and most of the tribes in the northeastern part of India widely resort to shifting cultivation widely known as jhuming. This involves clearing of forest trees, shrubs and undergrowth in limited area and turning of soil to sow crops.
- Tribals have known the use of many plant species which are not known to modern society. The botanists must gatheri nformation about the traditional uses of such wild plants from them and the anthropologists should deal with cultural aspects of the life of tribal people.

ETHNOBOTANY IN STUDY OF MEDICINAL PLANTS AND DRUG DEVELOPMENT

Table 1: Medicinal plants of ethnobotanical importance used by tribals (Singh and Pandey, 1998)

Sl. No.	Plant Name	Tribe	Uses
1.	*Abelmoschus moschatus*	Bhil	Root and Root bark for dysentery and abdominal pain
2.	*Acacia leucophloea*	Kathodia	Decoction of stem bark powder for avoiding abortion
3.	*Aegle marmelos*	Garasia	Decoction of roots in fever and diabetes
4.	*Azadirachta indica*	Meena	Leaves are used in case of snake bite and nose bleeding
5.	*Butea monosperma*	Garasia	Decoction of flowers used as coolant and in swelling
7.	*Diospyros melaxylon*	Garasia and Bhil	Fruits and flower powder used in frequent urination and heart diseases
8.	*Pterocarpus marsupium*	Bhil	Bhil tribe Decoction of stem bark used in anaemia

- Herbal medicines have been used in India for centuries. India has a diverse ethnic groups and rich biodiversity. India has a rich history of medicinal phototherapy for the treatment of various diseases and promotion of health. The branch of ethnobotany dealing with the traditional systems of medicine or folklore medicines is known as medico-ethno botany.
- Tribal communities use ethno medicinal plants for the treatment of diseases and disorders like dysentery, diarrhea, headache, fever, cough, cold, asthma, skin diseases, burns and blisters, piles, jaundice, rheumatism and gout, ophthalmic diseases, toothache, cuts and wounds, bone fracture, helminthic or worm infection, snake bite, etc.
- Since past few decades, a succession of the so-called Wonder drugs e. g. quinine, reserpine, colchicine, digitoxin, artemisinin, taxol etc. have been discovered from plants with rich ethnobotanical lore in tribal communities. The isolation of these alkaloids from plants heralded a new era in the use of plant products in modern medicines.
- The tranquilizers rescinnamine and reserpine which have been isolated from the roots of *Rauwolfia serpentine* has been in use in India for about thousand years in folk medicine for the treatment of fever, snake bite, high blood pressure, and epilepsy.
- *Catharanthus roseus* (Sadaa bahar) yielded two important drugs, namely Vincristine and Vinblastine that are known to be effective in leukemia (blood cancer).
- The efficacies of a number of phytopharmaceuticals derived from plants such as atropine (pupil dilator), berberine (used in gastrointestinal disorders), caffeine (a stimulant), digitoxin (a cardiac tonic), ephedrine (anti-asthmatic), morphine (analgesic), quinine (antimalarial), reserpine (tranquilizer), Vinblastine and Vincristine (antileukemic) with rich folk-lore have been discovered.

- The recent discovery of certain bioactive compounds such as Gossypol (a male contraceptive from *Gossypium* spp), hypericine (antiviral from *Hypericum perforatum*), taxol (anticancer drug obtained from *Taxus brevifolia*).
- The primitive societies in India have depended on herbal medicines for centuries. In fact, all traditional systems of medicine have their roots in folk medicines or ethno medicines. The knowledge of ethnobotany plays an important role in the primary health care and economy of the tribals and aboriginal populations of our country. It has the potential for discovering new herbal drugs.

ROLE OF ETHNOBOTANY IN THE CONSERVATION OF NATURAL RESOURCES

The ethnobotanical studies are vital in revealing the inherent cultures in a community and must take into account the various beneficial species present in the system. The native and indigenous knowledge is an extremely valuable ecological resource and should be preserved at all costs. Unfortunately, this local knowledge is often lost due to the modernization process of people. Deforestation, population growth, and other environmental challenges have resulted in rapid loss of diversity and destruction of the natural system. However, if vast areas of tropical forests and natural systems are preserved in their system, then likely useful foods, medicines, and materials available from plant diversity can be conserved. It is imperative that native indigenous peoples take charge of conserving their own culture.

The study must focus on identifying and documenting vulnerable species, especially those used for medicinal and religious purposes. The knowledge on the thoughtful use of plants is a dynamic and ever-evolving process, and new knowledge is constantly being obtained. The potential economic benefits from the thoughtful utilization of tropical forest products instead of solid timber products must be taken into account. The leaves, root, stem, fruits, and seeds of plants have thoughtful benefits and can improve the condition of people. The non-timber forest products are a rescue against the tough conditions of a country. It is high time we recognize the significance of ethnobotanical studies and take necessary steps to conserve our natural resources.

CONCLUSION

Ethnobotanical research is an essential link between the medicine of the past and present, utilizing plants and traditional societies. It is a vital tool for the development of the pharmaceutical and healthcare industry. In addition to its traditional roles in economic botany and exploration of human cognition, ethnobotanical research can be used in current areas of study like biodiversity prospecting and vegetation management. It is firmly believed that, in the future, ethnobotany will play an increasingly critical role in sustainable development and biodiversity conservation.

ACKNOWLEDGEMENT

I would like to thank my University Professors for providing necessary information and guidelines and suggesting me important research papers, articles and journals that are required in formulating this chapter.

REFERENCES

[1]. Ansari, J. A., & Inamdar, N. N. (2010). The promise of traditional medicines. International Journal of Pharmacology, 6 (6), 808-812.

[2]. Bhodiwal, S., Pathan, S., & Barupal, T. (2022). A Review: Ethnobotany of Various Plants in Respect to Health. International Journal of Multidisciplinary Research and Growth Evolution, 3 (2), 149-152.

[3]. Chauhan, K. (2020). Role of ethnobotany on Indian society: a review. Journal of Arts, Culture, Philosophy, Religion, Language and Literature, 4 (2), 109-111.

[4]. Chavda, N., Rathore, R., Solanki, H. (2022). An Overview of Historical Background Of Ethnobotany And Indigenous Culture Of India. International Journal of Creative Research Thoughts, 10 (4), 738-751.

[5]. Chhetri, D. R., Basnet, D., Chiu, P. F., Kalikotay, S., Chhetri, G., & Parajuli, S. (2005). Current status of ethnomedicinal plants in the Darjeeling Himalaya. Current science, 89 (2), 264-268.

[6]. Choudhary, K., Singh, M., & Pillai, U. (2008). Ethnobotanical survey of Rajasthan-An update. American-Eurasian Journal of Botany, 1 (2), 38-45.

[7]. Deepak, A., & Anshu, S. (2008). Indigenous herbal medicines: Tribal formulationsand traditional herbal practices. Jaipur: Aavishkar Publishers Distributor.

[8]. Doss, A. (2009). Preliminary phytochemical screening of some Indian medicinal plants. Ancient science of life, 29 (2), 12-16.

[9]. Fleming, J. (1812). A Catalogue of Indian Medicinal Plants and Drugs: with Their Names in the Hindustani and Sanscrit Languages. London: J. Cuthell.

[10]. Harshberger, J. W. (1896). The purpose of ethnobotany. Botanical Gazette, 21 (3),146-156.

[11]. Jain S. K. (1996). Ethnobiology in Human Welfare, India. New Dehli: Deep publication.

[12]. Jain, S. K. (1987). Ethnobotany, its scope and various sub-disciplines. A manual of ethnobotany. (pp. 1-11). Jodhpur: Scientific Publishers.

[13]. Jain, S. K. (1991). Dictionary of Indian Folk medicine and ethno botany. New Delhi: Deep publication.

[14]. Katara, K., Chaudhari, K., Pandya, H., Maitreya, B. (2023). The Review on Ethno-botanical Concept, History and Traditional Knowledge of Indigenous Communities of India and its Threats. International Association of Biologicals and Computational Digest, 2 (1), 71-74.

[15]. Majumdar, K., & Datta, B. K. (2007). A study on ethnomedicinal usage of plants among the folklore herbalists and Tripuri medical practitioners: Part-II. Natural Product Radiance, 6 (1), 66-73.

[16]. Mao, A. A., Hyniewta, T. M., and Sanjappa, M. (2009). Plant Wealth of North East India with reference to Ethnobotany. Indian Journal of Traditional Knowledge, 8, 96-103.

[17]. Mukherjee, P. K., and Wahile, A. (2006). Integrated approaches towards drug development from Ayurveda and other Indian system of medicines. Journal of Ethnopharmacology, 103 (1),25-35.

[18]. Pandey, M. M., Rastogi, S., & Rawat, A. K. S. (2013). Indian traditional ayurvedic system of medicine and nutritional supplementation. Evidence-Based Complementary and Alternative Medicine, 2013,1-12.

[19]. Panigrahi, S., Rout, S., & Sahoo, G. (2021). Ethnobotany: A strategy for conservation of plant. Annals of the Romanian Society for Cell Biology, 25 (6), 1370-1377.

[20]. Potterat, O., & Hostettmann, K. (1995). Plant sources of natural drugs and compounds. Encyclopedia of environmental biology, 3, 139-153.

[21]. Sajem, A. L., & Gosai, K. (2006). Traditional use of medicinal plants by the Jaintia tribes in North Cachar Hills district of Assam, Northeast India. Journal of ethnobiology and ethnomedicine, 2 (1), 1-7.

[22]. Schultes (1962). The study of the relationship which exists between people of primitive societies and their plant environment.

[23]. Sen, S., & Chakraborty, R. (2015). Toward the integration and advancement of herbal medicine: a focus on traditional Indian medicine. Botanics: Targets and Therapy, 5, 33-44.

[24]. Sen, S., Chakraborty, R., De, B., & Devanna, N. (2011). An ethnobotanical survey of medicinal plants used by ethnic people in West and South district of Tripura, India. Journal of Forestry Research, 22 (3), 417-426.

[25]. Singh V. and Pandey R. P. (1989). Ethnobotany of Rajasthan, India. Jodhpur: Scientific Publishers.

[26]. https://www.biologydiscussion.com/botany/ethno-botany-definitions-deveopment-and-importance/

Chapter
9

EFFECTS OF PESTICIDE ON PLANTS

DARSHANA PATIL[1], MINAL TRIVEDI*[2] AND AVINASH PATIL[2]

[1]Smt. C. H. M. College, Ulhasnagar, Thane
[2]B. K. Birla College of Arts, Science & Commerce (Autonomous), Kalyan, Thane
*Corresponding author E-mail: minal3999@gmail.com

ABSTRACT
With growing population there is need to increase the crop yield. The crop yield can get reduced due to pests. Agrichemicals especially, pesticides are indiscriminately used for control of pests on plants. These chemicals like insecticides, rodenticides, herbicides etc. persist in the environmentfor longer time creating hazard to the plant, human and animal health. This chapter reviews effect of pesticidesapplication on the plant from germination till its full growth that alters its biochemical parameters. Further use of pesticide degrading bacteria represents a good alternative to get rid of pesticides residue.
KEYWORDS: Agriculture, Growth, Pesticide.

INTRODUCTION

With the growing global populationthere is need to increase the agricultural yield by boosting the growth of plants. The plant growth can be enhanced by adding fertilizers but many times the plant growth deterioratesdue to plant disease or the pests. Pests is any organisms that causes an economic loss or damage to the plants. To have control over the pests, plants are treated with pesticides which are used since 2000BC (Banaszkiewicz, T., 2010). The use of poisonous plants as pesticides has been mentioned in Rig Veda, one of the ancient Indian scriptures (Abubakar *et al.,* 2020). Sulphur dustings were the first known pesticide used in Mesopotamia. DDT (dichloro diphenyl trichloroethane) and 2-4 D (2, 4 dichlorophenoxy acetic acid) were the pesticides used during the second world war (Smith *et al.,* 1975).

The pesticides are classified based upon the types of pests killed or controlled. These can be categorisedas fungicides, weedicides/herbicides, nematicides, rodenticides, insecticides, algicides (Abubakar *et al.,* 2020) (Figure 1).

In order toeliminate the fungal plant diseases fungicides liketillex, agrosan (mercury-based compounds), dithanes (carbamates), vitavax (oxanthins), Bordeaux mixture & benzimidazole is used (Ivic 2010). Curative and eradicative effects of fungicides. These fungicides do have toxic effect on zooplanktons. Neem oil consists of Azadirachtin and Nimbinwhich are known to have antifungal properties (Saha *et al.,* 2010). Nematicidesare used to kill the nematodes attacking the plants. *Purpureocillium lilacinum* is known to kill *Meloidegyne incognitia*, it basically produces enzymes like chitinaseand proteases that weaken the egg shell of nematodes. An acetylcholine esterase inhibitor viz. Aldirab is used to control nematodes attacking tobacco plants. Other nematicides includemethyl bromide, ethylene dibromide and chloropicrin. Heat treatment like soil sterilization too helps in having control over nematodes (Liong *et al.,* 2021). Rodents also impact the plant yield so rodenticides are used to have control over them. Warfarin, Zinc phosphide inhibit the vitamin K cycle in rats. Strychnine causes asphyxia in rats. Other rodenticides includechloralose, copperacetate and arsenic trioxide (Murphy, 2002).

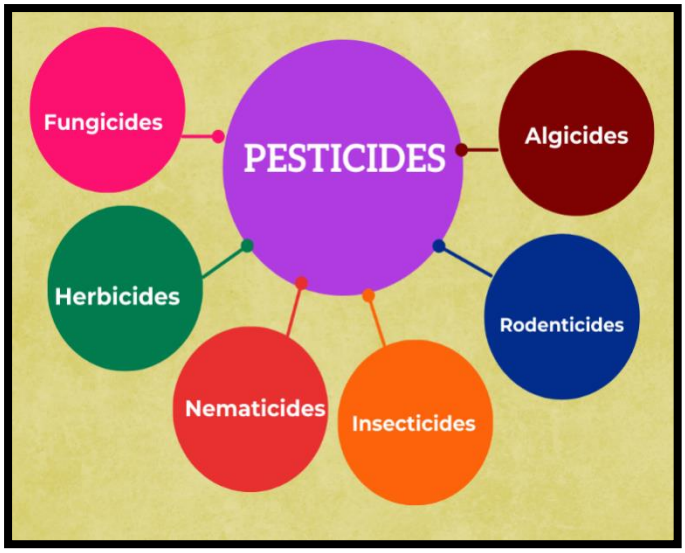


Fig. 1: Different categories of pesticides

Many times, along with plants unwanted plant or weeds grow, tokill them herbicides are being used. Herbicides used are auxin derivatives (e. g., 2,4-D, and 2, 4, 5-T), carbamates (e. g., thiocarbamates, phenyl carbamates) and triazines (e. g., atrazine, simazine). Atrazine is another well-known herbicide used but it's a teratogen (Kortekamp, 2011). Insects are another group of organisms impacting the plant health. Neem leaves or oil is a larvicide. Sporeine was first developed in Germany. Insecticide inhibits the exoskeleton development or chitin synthesis. Synthetic insecticides are organochlorines, organophosphates, carbamates and pyrethroids, Ethylene dibromide (EDB) is a volatile liquid (fumigant) used in controlling insect pests in stored grains and fruits. To eliminate the algal growth in wateralgicides like toluene, Cupricsulphate or Bluestone are used. They inhibit photosynthesis and electron transport chain (Gupta *et al.,* 2019).

RESIDUE OF PESTICIDES DETECTED IN PLANTS

Indiscriminate use of pesticides has ledto greater levels of residue in the foods. Even if they are present in smaller amount, they are known to impact the human health. Shinde *et al.,* . (2012) studied that Cypermethrin were applied in dosage of, 50, 75, and 100 ppm on okra crops and the residue were determined at regular interval upto21 days after application. The results indicate that the residue below the detectable level were found after 17 days. Upto 196ppm Dieldrin, 298ppm Disulfoton, 110ppm Endosulfan sulfate, 681ppm Parathion was detected in Malus domestica (Latif *et al.,* .). Studies by Dhas and Srivastav (2010) showed the initial deposit of Carbaryl on brinjal fruits were of 11. 47 ppm. Among the pesticides, organochlorine pesticides (OCPs) have been widely used across the world that are non-volatile compounds. They persistfor longer time in the ct the environment and impact drinking water systems and human health. Their exposure has been reported to cause birth deformities, neurological impairment, reproductive problems, and cancer (Fosu-Mensah *et al.,* 2016).

EFFECT OF PESTICIDES ON PLANT GROWTH

Spraying pesticides has an impact on different biochemical parameters of plant. Table 1 summarizes different studies done on effect of pesticide on plants.

Table 1: Summary of effect of pesticides on plant growth

Pesticide	Plant under study	Mode of application	Dosage	Plant part analysed	Research study findings	Reference
Chlorpyrifos	*Vigna radiata L*	Foliar	0–1. 5 mM	Leaves	0. 6 and 1. 5 mM were more toxic and decreased nitrate, NR activity, soluble sugar, and protein content	Parveen *et al.,* . (2018)
Chlorpyriphos Methyl parathion, endosulfan, imidacloprid, and deltamethrin	*Oryza sativa L*	Foliar	0. 0025-0. 10mM	Leaves	Increased quantities of reducing sugars, proteins and amino acids, but lower amounts of total phenols in leaf sheaths and blades of methyl parathion-, deltamethrin-, and quinalphos-treated plants Chlorpyriphos and endosulfan did not influence significantly	Suri and Singh (2011)
Chitosan .	*Abelmoschusesculentus L.*	Foliar application	0–125 ppm	Fruits	Number of fruits/plants, fruit size, etc. increased	Mondal *et al.,* . (2013)
Amide	*Z. mays L.*	Seedling	74. 4 µM L-1	Root	Increase in oxidative stress seen in the plant	Liu *et al.,* . (2012)
Imidazolinone	*Nicotiana tabacum L.*		0. 12 mM	Leaves	Increase in oxidative stress seen in the plant	Kaya and Doganlar (2016)
Isoproturon	*P. sativum*	Leaves	10 mM	Leaves	Increase in H_2O_2 activity	Singh *et al.,* . (2016)
Acetochlor	*Vitis vinifera L*	Soil	22460 g/ha	Leaves	Decrease in SOD& CAT activity	Tan *et al.,* . (2012)
Chlorotoluron	*Triticum aestivum L.*	Soil	0–25 mg/kg	Leaves	Chlorophyll content decreased even at 5 mg/kg.	Song, *et al.,* . (2007)
2, 4-DCP (2,4-dichlorophenols)	*Triticum aestivum L*	Soil	0–5 mg/ kg	Leaves	Inhibition in SOD and CAT activity seen	Michalowicz *et al.,* . (2009)
Paraquat	*Cucurbita maxima L.*	Foliar Spray	50–1000 mM	Leaves	No SOD response to oxidative stress and lowered lipid peroxidation seen	Yoon *et al.,* . (2011)

PESTICIDE DEGRADING MICROBES

With the above studies its evident that pesticides have impact on the plants too. In order to eliminate such impacts microbes can be a good alternate to combat with the ill-effects of pesticides. There are different bacteria that contain enzymes which help them to degrade the pesticides. Table 2 summarizes different organisms, their enzymes that have ability to degrade the pesticides. (Ortiz-Hernández *et al.*, 2013).

Table 2: Enzymes present in organisms degrading pesticides

Organism	Enzyme	Pesticide
Ralstonia eutropa	TfdA	2,4-dichlorophenoxyacetic acid
Nocardioides spp.	TrzN	Chloro-S-trazina
Pseudomonas spp.	AtzA	Chloro-S-trazina
Mycobacterium spp., *Arthrobacter* spp.	Monooxygenases	Endosulfan, aldrin, malathion, DDT,
Pseudomonas spp., *Agrobacterium* spp	Oxidoreductase	Gylphosate
Ralstonia eutropa	TfdA	Pyridyl-oxyacetic acid
Pseudomonas putida	Dioxygenases	Trifluralin

CONCLUSION

Pesticides are viable option to control the pests attacking the plants but their indeterminate use has posed great threat to plants. The impact of these pesticides needs to be studied well before applying to the crops. Further research is needed to see the persistence of pesticides in cropsand its impact on the soil micro-flora indirectly affecting the ecosystem. Microbes degrading pesticides represent a good option to get rid of pesticides that persists for longer time in the environment. Use of suitable genetically modified microbes can enhance this degradation process of pesticidesMore cheaper methods like use of biopesticide should be encouraged to reduce the adverse effect and persistence of pesticides on plants.

REFERENCES

[1]. Abubakar, Y., Tijjani, H., Egbuna, C., Adetunji, C. O., Kala, S., Kryeziu, T. L., & Patrick-Iwuanyanwu, K. C. (2020). Pesticides, history, and classification. In Natural remedies for pest, disease and weed control (pp. 29-42). Academic Press.

[2]. Banaszkiewicz, T. (2010). Evolution of pesticide use. Contemporary Problems of Management and Environmental Protection, 5, 7-18.

[3]. Dhas, S., & Srivastava, M. (2010). An assessment of carbaryl residues on brinjal crop in an agricultural field in Bikaner, Rajasthan (India). Asian Journal of Agricultural Sciences, 2 (1), 15-17.

[4]. Fosu-Mensah, B. Y., Okoffo, E. D., Darko, G., & Gordon, C. (2016). Organophosphorus pesticide residues in soils and drinking water sources from cocoa producing areas in Ghana. Environmental Systems Research, 5, 1-12.

[5]. Gupta, R. C., Mukherjee, I. R. M., Malik, J. K., Doss, R. B., Dettbarn, W. D., & Milatovic, D. (2019). Insecticides. In Biomarkers in toxicology (pp. 455-475). Academic Press.

[6]. Ivic, D. (2010). Curative and eradicative effects of fungicides. Fungicides, 3-22.

[7]. Kaya, A., &Doganlar, Z. B. (2016). Exogenous jasmonic acid induces stress tolerance in tobacco (*Nicotiana tabacum*) exposed to imazapic. Ecotoxicology and environmental safety, 124, 470-479.

[8]. Kortekamp, A. (Ed.). (2011). Herbicides and environment. BoD–Books on Demand.

[9]. Leong, S. S., Leong, S. C. T., Pau, C. G., & Beattie, G. A. C. (2021). In vitro bioassay of *Purpureocillium lilacinum* and *Bacillus thuringiensis* for control of Meloidogyne incognita on black pepper (*Piper nigrum* L.) in Sarawak, Malaysia, Northern Borneo. Journal of the Entomological Research Society, 23 (1), 41-59.

[10]. Liu, X., Xiang, S., Zong, T., Ma, G., Wu, L., Liu, K., & Bai, L. (2012). Herbicide resistance in China: a quantitative review. Weed Science, 67 (6), 605-612.

[11]. Michałowicz, J., Posmyk, M., & Duda, W. (2009). Chlorophenols induce lipid peroxidation and change antioxidant parameters in the leaves of wheat (*Triticum aestivum* L.). Journal of plant physiology, 166 (6), 559-568.

[12]. Mondal, M. M. A., Malek, M. A., Puteh, A. B., & Ismail, M. R. (2013). Foliar application of chitosan on growth and yield attributes of mungbean (*Vigna radiata* (L.) Wilczek). Bangladesh Journal of Botany, 42 (1), 179-183.

[13]. Murphy, M. J. (2002). Rodenticides. Veterinary Clinics: Small Animal Practice, 32 (2), 469-484.

[14]. Ortiz-Hernández, M. L., Sanchez-Salinas, E., Godínez, M. L. C., González, E. D., & URSINO, E. C. P. (2013). Mechanisms and strategies for pesticide biodegradation: opportunity for waste, soils and water cleaning. Revista Internacional de Contaminación Ambiental, 29, 85-104.

[15]. Parween, T., Jan, S., & Fatma, T. (2018). Variation in elemental composition as influenced by chlorpyrifos application in mung bean (*Vigna radiata* L.). Saudi Journal of Biological Sciences, 25 (7), 1439-1445.

[16]. Saha, S., Walia, S., & Parmar, B. S. (2011). Exploring the diversity of neem bioactives as eco-benign pesticides: a reappraisal. Toxicological & Environmental Chemistry, 93 (8), 1508-1546.

[17]. Shinde, L. P., Kolhatkar, D. G., Baig, M. M. V., & Chandra, S. (2012). Study of cypermethrin residue in okra leaves and fruits assessed by GC. International Journal of Research in Pharmacy and Chemistry, 2, 273-276.

[18]. Singh, R. J. (2012). Weed management in irrigated wheat (*Triticum aestivum*) with special reference to buttercup weed (*Ranunculus* spp) in north-west Himalayas. Indian Journal of Agricultural Sciences, 82 (8), 706-710.

[19]. Smith, A. E., & Secoy, D. M. (1975). Forerunners of pesticides in classical Greece and Rome. Journal of Agricultural and Food Chemistry, 23 (6), 1050-1055.

[20]. Song, N. H., Le Yin, X., Chen, G. F., & Yang, H. (2007). Biological responses of wheat (*Triticum aestivum*) plants to the herbicide chlorotoluron in soils. Chemosphere, 68 (9), 1779-1787.

[21]. Tan, W., Li, Q., & Zhai, H. (2012). Photosynthesis and growth responses of grapevine to acetochlor and fluoroglycofen. Pesticide biochemistry and physiology, 103 (3), 210-218.

[22]. Yoon, J. Y., San Shin, J., Shin, D. Y., Hyun, K. H., Burgos, N. R., Lee, S., & Kuk, Y. I. (2011). Tolerance to paraquat-mediated oxidative and environmental stresses in squash (*Cucurbita* spp.) leaves of various ages. Pesticide biochemistry and physiology, 99 (1), 65-76.

Chapter 10

APPLICATION OF NANOPARTICLES AS NANOFERTILIZER IN CROP YIELD IMPROVEMENT

CHARUL SOMANI, FARHAT ZABI AND ANJANA VAISHNAV

Department of Science, Smt. SDM PG Girls College, Bhilwara -311001 Rajasthan

ABSTRACT

Today's agricultural zones are overlooking a wide range of challenges such as crop yield stagnation, low nutrient use efficiency, declining soil organic matter, multi-nutrient deficiencies, cultivable land contracts, water availability, and labor curtailment due to emigration from farming [1,2]. According to data collected by the UN Food and Agriculture Organization, the destruction and degradation of land and water pose serious obstacles to producing enough food and other agricultural products to sustain livelihoods and fulfill the wants of the world's ever-increasing community [3]. Nanotechnology, which produces ultra-small particles with remarkable qualities such as surface area to volume size ratio and increased optoelectronic and physicochemical capabilities compared to their bulk equivalents [4]., is currently emerging as a viable technique to boost plant growth and development. [5-8].

KEYWORDS: Nanofertilizer, Agriculture, Physicochemical.

INTRODUCTION

Today's agricultural zones are overlooking a wide range of challenges such as crop yield stagnation, low nutrient use efficiency, declining soil organic matter, multi-nutrient deficiencies, cultivable land contracts, water availability, and labor curtailment due to emigration from farming [1,2]. According to data collected by the UN Food and Agriculture Organization, the destruction and degradation of land and water pose serious obstacles to producing enough food and other agricultural products to sustain livelihoods and fulfill the wants of the world's ever-increasing community [3]. Nanotechnology, which produces ultra-small particles with remarkable qualities such as surface area to volume size ratio and increased optoelectronic and physicochemical capabilities compared to their bulk equivalents [4], is currently emerging as a viable technique to boost plant growth and development [5-8].

Agriculture development will depend on farmers utilizing technological advances to efficiently use water, fertilizer, and other inputs. Accurate farming makes agriculture more sustainable by lowering waste and energy demand. Nanotechnology and its derivatives are being tested in agriculture for a variety of applications, including increasing crop productivity and lowering pesticide applications. Increased crop output can be achieved through the use of precise agricultural techniques that do not impact the soil or water. Preventing the loss of nitrogen caused by leaching, discharges, and soil microbes is something it can do. Post-harvest processing of agricultural products for extended shelf-life; nanoscale sensors for sensing nutrients, pesticides, and contaminants; Nanoscale pesticides for effective plant disease control; smart and targeted biomolecule and nutrient delivery; agronomic fortifications; water purification, nutrient management [9-12].

ROLE OF FERTILIZER IN PLANT GROWTH

Fertilizers are essential nutrients for plants to achieve optimal productivity. Farmers typically apply fertilizers through the soil, either through surface transmissions, sub-surface placement, or mixing with

irrigation water. The ecosystem is polluted by a significant proportion of fertilizers applied using these methods that are lost to the atmosphere or surface water bodies [13,14]. For example, excess nitrogen is lost within denitrification as NH_3 or emission as N_2O or NO, or within NO_3 leaching or runoff to water bodies. In contrast, excess phosphorus enhances "fixed" in soil, where it produces synthesized connections with other elements such as Ca-P, Mg-P, Al-P, Fe-P, and Zn-P, and becomes unavailable for uptake by the plants. Nitrogen and phosphorus compounds are absorbed by rain into waterways like rivers, lakes, and the sea, resulting in dangerous pollution problems. Fertilizer use is on the rise, along with the growth of the global population [15]. Farmers are currently utilizing nearly 85% of the world's total mined phosphorus as fertilizer, but the plants can only absorb approximately 42% of the applied phosphorus. The world's phosphorus supply could run out within the next 80 years if this scenario persists, which would impact agricultural productivity. The decline in cropland in metropolitan-influenced counties in the United States was 77% from 1978 to 1987, according to trends [16,17]. Farmers use more chemical fertilizers to meet food demand, which ultimately affects soil and environmental health and reduces natural resources. Using hydroponic techniques, crops can be grown under artificial conditions, but the cost of energy and dollars is approximately 10 times that of conventional agriculture. Therefore, systems are neither affordable nor sustainable for the future. The development of sustainable strategies that lead to more nutritious and enhanced crop production by minimizing the use of resources and fertilizers is necessary. In contrast to conventional fertilizer use, which involves 80-140 or more kilograms of inputs per hectare under intensive production systems, nanotechnology focuses on the use of smaller quantities. Moreover, nanoscale fertilizers may have the potential to minimize nutrient losses through leaching and avoid rapid changes in their chemical nature, thus enhancing nutrient use efficiency and addressing fertilizer environmental concerns. The definition of 'nanofertilizer' is currently under discussion. In the literature related to nanotechnology application in agriculture, nanofertilizer is used for both materials of a physical diameter between 1 and 100 nm in at least one dimension (e. g., ZnO nanoparticles), and those existing at the bulk scale, with more than 100 nm in size, but that has been modified with nanoscale materials (e. g., bulk fertilizer coated with nanoparticles). In this chapter, the term 'nanofertilizer' refers to both real nanomaterials and bulk materials that are nano-enabled and used as fertilizers. Due to their unique properties, nanoparticles may influence the plant's metabolic activities to different degrees, compared to conventional materials, and have the potential to mobilize native nutrients such as phosphorus in the rhizosphere [18, 19]. A hypothesized nanotechnology-based agriculture input is illustrated in Figure 1.

In the following sections, recent literature relevant to nanoscale material nanoparticles/ nanocomposites used for plant nutrition as nanofertilizers is reviewed. The discussion is presented systematically, to allow a better understanding of both fundamental and applied aspects of nanofertilizers for sustainable and precision agriculture.

NANOFERTILIZERS

Nanofertilizers are nutrient fertilizers that are composed of nanostructured formulations that can be delivered to plants, allowing for efficient uptake or slow release ofactive ingredients. The application of conventional bulk fertilizers requires larger amounts due to their low plant uptake efficiency. Two main challenges of the low nutrient uptake efficiency for nitrogen and phosphorus-based fertilizers are the rapid changes into chemical forms that the plants do not take up, and runoff, leaching, or atmospheric losses.

Fig. 1: Nanotechnology based Agriculture

The resultant effects are the emission of harmful greenhouse gases (such as certain oxides of nitrogen), and eutrophication, with negative consequences for soil and environmental health. Therefore, it is critical to develop smart fertilizers that are more readily uptake by the plants. Nanotechnology is one possible route for sustainably and precisely attaining this objective, for this reason, scientists are actively researching a range of metal and metal oxide nanoparticles for use in plant science and agriculture. The environmental health and safety aspects of nanotechnology must also be taken into account, and it is crucial to determine the toxicity/biocompatibility of nanofertilizers [20-22]. Since nanoscale particles are smaller in dimension compared to bulk particles, the plants can absorb them with different dynamics than bulk particles or ionic salts, which presents an added advantage [23-26]. To assess their potential impact on plant growth, development, and productivity, severalinorganics, organic, and composite nanomaterials have been tested on various plants. A summary of the nanoparticles used as nutrients/fertilizers and validated on agriculturally important crops is presented in Table 1. Since, the effects of nanoscale materials and corresponding plant responses depend on various factors related to nanoscale properties, soil, and environment, the table included the information on the type of nanoparticles, nanoscale property, mode of nanoparticle delivery, tested plants, and studied responses. In the following sub-sections, we discuss specific examples of nanoparticles used as nanofertilizers or nanonutrients.

METHODICAL ANALYSIS

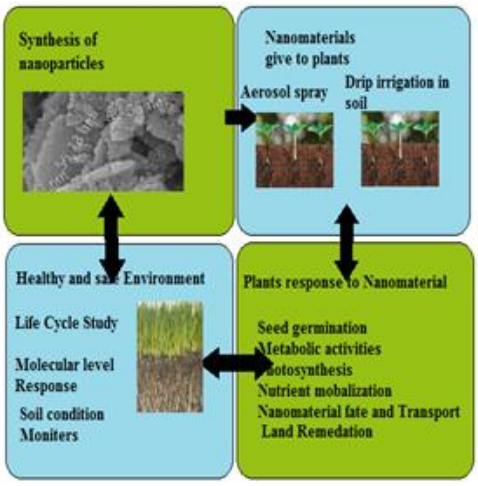


Fig. 1: Methodical analysis of nanoparticles in agriculture

Table 1: Type of nanoparticle used as in crop and effect on plant growth

Type of NP	Concentration (ppm)	Treatment planning method in plants	Plant	Observation
ESSENTIAL PLANT NUTRIENT				
Carbon based NPs	5-500	Nutrient media and Foliar uptake; Seed treatment	Tomato [27]; Tobacco [30]	1. Progressing upregulation of stress-related genes. 2. Risen root elongation. 3. Enhancing crop yield and seed property. 4. Reduce heavy metal toxicity.
Nitrogen Urea HA	50 Kg/ha	Soil exposure	Rice [43]	1. A gradual release of nitrogen 2. Enriched rice yield
Phosphorous $CaPO_4$, CMC –HA, Phosphorite Zn induced P	10-100	Soil and foliar applications	Cotton [45], Pearlmillets [46], Beans [47], Wheat, Rye, Pea, Barley, Corn, Buckwheat, Radish, Cucumber [50]	1. Protect toward oxidative pressure 2. Mobilize native P and improve uptake 3. Improves plant growth and yield
Magnesium MgO	15	Foliar	Clusterbean [51]	1. Advancing biomass, chlorophyll content & phenological growth
Manganese	100 -1200	Foliar & seed treatment	Corn [52], Tomato [27]	1. Improved seedling germination, plant biomass, and biochemical activities
Zinc ZnO	10 - 2000	Foliar application Seed application	Peanut [53] Beans [54] Tomato [27]	1. Accretion of yield potential and plant growth. 2. Enhance plant hormone level and plant growth 3. Help to decrease drought intensity and improve agronomic support Enhance shoot length, root length, root and shoot dry mass, leaf area and number of roots, plant biomass, root and shoot growth

Type of NP	Concentration (ppm)	Treatment planning method in plants	Plant	Observation
Iron Iron Oxide	1. 5-4000	Foliar Spray	Wheat [60], Watermelon [61], Clover [63], Soybean [64], Rice [43], Tomato [27]	1. Enhance photosynthesis rate, chlorophyll content, biomass, grain yield & nutritional quality 2. Improving plant growth 3. Enhance nutrient absorption by increase microbial enzyme activity in the rhizosphere chlorophyll content, root length, leaf length, and stem length
NON-ESSENTIAL PLANT NUTRIENT				
Titanium TiO2	200-600	Seed, soil and foliar exposure	Spinach [67], *Lemna minor* [70], Tomato [27], Wheat [71], Watermelon [61]	1. Raised plant biomass and photosynthetic movement. 2. Increased biochemical enzyme activity and light absorption by chloroplast, carbon fixation 3. Enhanced germination rate. Increased nitrogen metabolism
Cerium CeO	0. 1-250	Irrigation; Seed/root	Tomato [27], Wheat [60	1. Cultivated plant growth and yield 2. Enhanced physiological and Molecular response 3. Increase stress threshold enzyme activity
Silver Ag	1 -10	Hydroponics, Soil	Poplars [82], *Arabidopsis thaliana* [79]	1. Influence Phyto-stimulatory effect 2. Increase nutrient consumption by improving microbial activity in the rhizosphere.
Silica Si SiO SiO_2	5-800	Soil irrigation, Seed & Root exposure	Tomato [27], Wheat,	1. Help overcome from salinity stress and Improve plant growth. 2. Enhance germination and growth. 3. Enrichment in total protein and chlorophyll content. 4. Raised seedling growth and quality.
Cobalt Ferrite	1 – 1000	Root exposure	Tomato [27]	1. Encourage root growth
Indium In_2O_3	250	Seed/Root	*Arabidopsis thaliana* [79]	Improved physiological and molecular response

The influence of nanomaterials on plants depends greatly on the intrinsic properties, and extrinsic interactions, of the nanoparticles. It's possible that this is one of the reasons why the literature has shown contrasting results from the same class of particles. For example, exposure to TiO2 nanoparticles to corn seeds delayed germination [47-48], whereas they show a nonsignificant effect on rice seed germination, and improved seed germination of wheat.

In the following sections, we discuss some of the factors needed to be examined, while comparing a nanoparticle type and its influence on plants.

SYNTHESIS OF NANOPARTICLES/NANOFERTILIZER.

Nanomaterials are frequently being synthesized by both 'wet' methods such as sol-gel, hydrothermal, homogeneous precipitation, biosynthesis using enzyme and protein template and reversed micelles methods [49-50]. and 'dry' synthesis strategy like aerosol-based processes, ranging from single element nanoparticles, oxide semiconductors, other metal oxides, metal alloys, polymers, doped and composite nanoparticles. Nanoparticles to be used as fertilizers require a synthesis approach capable of producing mass scale particles with controlled physicochemical properties at a low cost [51].

NANOPARTICLES DELIVERY, UPTAKE, TRANSLOCATION, AND BIODISTRIBUTION.

In general, there are three methods for delivering agrochemicals to plants - seed treatment, soil amendment, or foliar spray. Engineered nanoparticles have different results when particles are mixed in the soil particulate exposure and localized concentration are much higher than indirect exposure during foliar spray or translocation to fruiting roots that lead to drinking & contributes a very small amount [52-53]. The major result for foliar applications is that they require high leaf area index, low exposure dose, potential multiple application, and application time depending on the season to avoid nutrient loss. Subsequent transport of nanoparticles from shoot to root is achieved by convective systems - the phloem transport pathway, a bidirectional route along the photosynthate gradient. Cellular transport of nanoparticles is performed by both the apoplast and symplast pathways. The apoplast pathway favors the transport of larger particles (~ 200 nm), while the simplistic pathway favors smaller (<50 nm) particles.

FUTURE PREPECTIVES

Due to the unique physicochemical properties of nanostructures, their use as agrochemicals (fertilizers or pesticides) is continuously being explored for plant growth and protection. Recently funded projects and future research calls appear to be more focused on designing safe nanometer materials for effective reactions while being environmentally friendly. Nanotechnology research in agriculture is still under development but is developing rapidly. However, before nano-fertilizers can be used in the field for common agricultural practice, there is a need for a better understanding of their methods of operation according to the regulatory framework that ensures the safe use of such agrochemicals.

The United States Food and Drug Administration has already issued guidelines for the use of nanometry in animal feeds [51] manufacturers are also adding engineered nanoparticles to foods, personal care, and other consumer products. Examples include silica Nanoparticles in baby formulas, titanium dioxide nanoparticles in powdered donuts and other nanomaterials in paints, plastics, paper fibers, pharmaceuticals and tubes of toothpaste [52-53].

REFERENCES

[1]. http://www.fao.org/fileadmin/templates/wsfs/docs/Issues_papers/HLEF2050_Global_Agricultu re. pdf.

[2]. Godfray, H. C. J; Beddington, J. R; Crute, I. R; Haddad, L; Lawrence, D; Muir, J. F; Pretty, J; Robinson, S; Thomas, S. M; Toulmin, C. (2010). Food security: The challenge of feeding 9 billion people. Science, 2010, 327, 812-818.

[3]. Nations, U. (2017). http://www. un. org/en/development/desa/news/population/2015-report. html (March 1, 2017),

[4]. Initiative, N. N. (2017). http://www. nano. gov/ (March 1, 2017),

[5]. USDA-NIFA (2017). https://nifa. usda. gov/program/nanotechnology-program (March 1, 2017),

[6]. Tarafdar, J; Sharma, S; Raliya, R. (2013). Nanotechnology: Interdisciplinary science of applications. African J. Biotechnol. 2013, 12.

[7]. Raliya, R; Tarafdar, J; Gulecha, K; Choudhary, K; Ram, R; Mal, P; Saran, R. (2013). Scope of nanoscience and nanotechnology in agriculture. J. Appl. Biol. Biotechnol., 2013, 1, 041-044.

[8]. Gogos, A; Knauer, K; Bucheli, T. D. (2012). Nanomaterials in plant protection and fertilization: Current state, foreseen applications, and research priorities. J. Agric. Food Chem., 2012, 60, 9781-9792.

[9]. Chhowalla, M. (2017). Slow release nanofertilizers for bumper crops. ACS Central Science, 2017, 3, 156.

[10]. Dimkpa, C. O; Bindraban, P. S. (2017). Nanofertilizers: New products for the industry? J. Agric. Food Chem., 2017

[11]. Nair, R; Varghese, S. H; Nair, B. G; Maekawa, T; Yoshida, Y; Kumar, D. S. (2010). Nanoparticulate material delivery to plants. Plant Sci., 2010, 179, 154-163

[12]. Saharan, V; Khatik, R; Kumari, M; Raliya, R; Nallamuthu, I; Pal, A. (2014). International Conference on Advances in Biotechnology (BioTech). Proceedings, 2014; Global Science and Technology Forum 2014; p 23.

[13]. Tilman, D; Cassman, K. G; Matson, P. A; Naylor, R; Polasky, S. (2002). Agricultural sustainability and intensive production practices. Nature, 2002, 418, 671-677.

[14]. Carpenter, S. R; Caraco, N. F; Correll, D. L; Howarth, R. W; Sharpley, A. N; Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl., 1998, 8, 559-568.

[15]. Tilman, D; Cassman, K. G; Matson, P. A; Naylor, R; Polasky, S. (2002). Agricultural sustainability and intensive production practices. Nature, 2002, 418, 671-677.

[16]. Carpenter, S. R; Caraco, N. F; Correll, D. L; Howarth, R. W; Sharpley, A. N; Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl., 1998, 8, 559- 568

[17]. http://web. mit. edu/12. 000/www/m2016/finalwebsite/solutions/phosphorus. html (March 1, 2017),

[18]. Dawson, C. J; Hilton, J. (2011). Fertiliser availability in a resource-limited world: Production and recycling of nitrogen and phosphorus. Food Policy, 2011, 36,S14-S22.

[19]. USGIS http://www. usgs. gov/climate_landuse/. (March 1, 2017),

[20]. Greene, R. P; Harlin, J. M. (1995). Threat to high market value agricultural lands from urban encroachment: A national and regional perspecitve. Social Sci. J., 1995, 32, 137-155.

[21]. Pimentel, D; Wilson, A. (2004). World population agriculture and malnutrition. World Watch, 2004, 22- 25.

[22]. Saharan, V; Kumaraswamy, R; Choudhary, R. C; Kumari, S; Pal, A; Raliya, R; Biswas, P. (2016). Cu-chitosan nanoparticle mediated sustainable approach to enhance seedling growth in maize by mobilizing reserved food. J. Agric. Food Chemi., 2016, 64, 6148-6155.

[23]. Zahra, Z; Arshad, M; Rafique, R; Mahmood, A; Habib, A; Qazi, I. A; Khan, S. A. (2015). Metallic nanoparticle (tio_2 and fe_3o_4) application modifies rhizosphere phosphorus availability and uptake by lactuca sativa. J. Agric. Food Chemi., 2015, 63, 6876-6882.

[24]. Suttiponparnit, K; Jiang, J; Sahu, M; Suvachittanont, S; Charinpanitkul, T; Biswas, P. (2010). Role of

surface area, primary particle size, and crystal phase on titanium dioxide nanoparticle dispersion properties. Nanoscale Res. Lett., 2010, 6, 1.

[25]. Biswas, P; Wu, C. -Y. (2005). Nanoparticles and the environment. J. Air Waste Manag. Assoc., 2005, 55, 708-746.

[26]. Wiesner, M. R; Lowry, G. V; Alvarez, P; Dionysiou, D; Biswas, P. (2006). Assessing the risks of manufactured nanomaterials. Environ. Sci. Technol., 2006, 40, 4336-4345.

[27]. Lahiani, M. H; Chen, J; Irin, F; Puretzky, A. A; Green, M. J; Khodakovskaya, M. V. (2015). Interaction of carbon nanohorns with plants: Uptake and biological effects. Carbon, 2015, 81,607-619.

[28]. Khodakovskaya, M. V; de Silva, K; Biris, A. S; Dervishi, E; Villagarcia, H. (2012). Carbon nanotubes induce growth enhancement of tobacco cells. ACS Nano, 2012, 6,2128-2135.

[29]. Raliya, R; Tarafdar, J. C; Biswas, P. (2016). Enhancing the mobilization of native phosphorus in the mung bean rhizosphere using zno nanoparticles synthesized by soil fungi. J. Agric. Food Chemi.,2016, 64,3111-3118.

[30]. Yousefzadeh S., Sabaghnia N. (2016). Nano-iron fertilizer effects on some plant traits of dragonhead (*Dracocephalummoldavica)* under different sowing densities. Acta Agric. Slov. 2016;107:429–437.

[31]. Raliya,R;Tarafdar,J;Singh,S;Gautam,R;Choudhary,K;Maurino,V. G;Saharan,V. (2014). MgO nanoparticles biosynthesis and its effect on chlorophyll contents in the leaves of clusterbean (Cyamopsis tetragonoloba.). Adv. Sci. Eng. Med., 2014, 6, 538-545.

[32]. Pradhan, S; Patra, P; Mitra, S; Dey, K. K; Jain, S; Sarkar, S; Roy, S; Palit, P; Goswami, A. (2014). Manganese nanoparticles: Impact on non-nodulated plant as a potent enhancer in nitrogen metabolism and toxicity study both in vivo and in vitro. J. Agric. Food Chemi., 2014, 62, 8777-8785.

[33]. Sheykhbaglou, R; Sedghi, M; Shishevan, M. T; Sharifi, R. S. (2010). Effects of nano-iron oxide particles on agronomic traits of soybean. Notulae Scientia Biologicae, 2010, 2, 112.

[34]. Giordani, T; Fabrizi, A; Guidi, L; Natali, L; Giunti, G; Ravasi, F; Cavallini, A; Pardossi, A. (2012). Response of tomato plants exposed to treatment with nanoparticles. EQA-International J. Environ. Quality, 2012, 8, 27-38.

[35]. Laurent, S; Forge, D; Port, M; Roch, A; Robic, C; Vander Elst, L; Muller, R. N. (2008). Magnetic iron oxide nanoparticles: Synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chemi. Rev., 2008, 108, 2064-2110.

[36]. Li, J; Hu, J; Ma, C; Wang, Y; Wu, C; Huang, J; Xing, B. (2016). Uptake, translocation and physiological effects of magnetic iron oxide (γ-Fe_2O_3) nanoparticles in corn (Zea mays.). Chemosphere, 2016, 159, 326-334.

[37]. Zhu, H; Han, J; Xiao, J. Q; Jin, Y. (2008). Uptake, translocation, and accumulation of manufactured iron oxide nanoparticles by pumpkin plants. J. Environ. Monit.,2008, 10, 713-717.

[38]. Alidoust, D; Isoda, A. (2014). Phytotoxicity assessment of γ-Fe_2O_3 nanoparticles on root elongation and growth of rice plant. Environ. Earth Sci., 2014, 71, 5173-5182.

[39]. Rui, M; Ma, C; Hao, Y; Guo, J; Rui, Y; Tang, X; Zhao, Q; Fan, X; Zhang, Z; Hou, T. (2016). Iron oxide nanoparticles as a potential iron fertilizer for peanut (Arachis hypogaea). Front. Plant Sci., 2016, 7. 815.

[40]. Raliya, R. (2012). Appliance of nanoparticles on plantsystem and associated rhizospheric microflora. Ph. D Thesis, J. N. Vyas University Jodhpur, 2012. Pp 199.

[41]. Yang, F; Hong, F; You, W; Liu, C; Gao, F; Wu, C; Yang, P. (2006). Influence of nano-anatase tio2 on thenitrogen metabolism of growing spinach. Biol. Trace Element Res., 2006, 110, 179-190.

[42]. Hong, F; Yang, F; Liu, C; Gao, Q; Wan, Z; Gu, F; Wu, C; Ma, Z; Zhou, J; Yang, P. (2005). Influences of nano-TiO_2 on the chloroplast aging of spinach under light. Biol. Trace Element Res., 2005, 104,249-260.

[43]. Feizi H; Moghaddam, P. R; Shahtahmassebi, N; Fotovat, A. (2012). Impact of bulk and nanosized titanium dioxide (TiO_2) on wheat seed germination and seedling growth. Biol. Trace Element Res., 2012, 146, 101-106.

[44]. Liang, Y; Nikolic, M; Bélanger, R; Gong, H; Song, A. (2015). Springer: 2015; pp 123-142.

[45]. Wang, J; Koo, Y; Alexander, A; Yang, Y; Westerhof, S; Zhang, Q; Schnoor, J. L; Colvin, V. L;Braam, J; Alvarez, P. J. (2013). Phytostimulation of poplars and arabidopsis exposed to silvernanoparticles and ag^+ at sublethal concentrations. Environ. Sci. Technol., 2013, 47, 5442-5449.

[46]. Sun, D; Hussain, H. I; Yi, Z; Rookes, J. E; Kong, L; Cahill, D. M. (2016). Mesoporous silica nanoparticlesenhance seedling growth and photosynthesis in wheat and lupin. Chemosphere, 2016, 152, 81- 91.

[47]. Ruffini Castiglione, M; Giorgetti, L; Geri, C; Cremonini, R. (2011). The effects of nano-TiO2 on seed germination, development and mitosis of root tip cells of vicianarbonensis l. And zea mays L. J. Nanopart. Res., 2011, 13, 2443-2449.

[48]. Boonyanitipong, P; Kositsup, B; Kumar, P; Baruah, S; Dutta, J. (2011). Toxicity ofzno and tio2 nanoparticles on germinating rice seed *Oryza sativa* L. Int. J. Biosci., Biochem. Bioinfo., 2011, 1, 282.

[49]. Kaul, R; Kumar, P; Burman, U; Joshi, P; Agrawal, A; Raliya, R; Tarafdar, J. (2012). Magnesium and iron nanoparticles production using microorganisms and various salts. Mater. Sci. -Poland, 2012, 30, 254-258.

[50]. Raliya, R; Rathore, I; Tarafdar, J. (2013). Development of microbial nanofactory for zinc, magnesium, and titanium nanoparticles production using soil fungi. J. Bionanosci., 2013, 7, 590-596.

[51]. Jiang, J;Chen, D. -R; Biswas, P. (2007). Synthesis of nanoparticles in a flame aerosol reactor with independent and strict control of their size, crystal phase and morphology. Nanotechnol, 2007, 18, 285603.

[52]. Torney, F; Trewyn, B. G; Lin, V. S. -Y; Wang, K. (2007). Mesoporous silica nanoparticles deliver DNA and chemicals into plants. Nat. Nanotechnol., 2007, 2, 295-300.

[53]. Monreal, C; DeRosa, M; Mallubhotla, S; Bindraban, P; Dimkpa, C. (2016). Nanotechnologies fornincreasing the crop use efficiency of fertilizer-micronutrients. Biol. Fert. Soils, 2016, 52, 423-437

Chapter 11

RECENT TRENDS IN BIOTECHNOLOGY: NANOTECHNOLOGY

PRATIKSHA S. JADHAV*, RIYAJ R. INAMDAR, ANURADHA A. KAMBLE AND NARAYAN. M. GHANGAONKAR

Department of Botany, PG and Research Center,
Chandmal Tarachand Bora Collage, Shirur, Pune-412210.
Corresponding author E-mail: pratikshajadhav0601@gmail.com

ABSTRACT

Biotechnology is the foundation of biological sciences and has wide applications in engineering, technology, medicine and other fields. It uses organisms and biological processes to solve global problems, from disease control to environmental protection. Additionally, the integration of nanotechnology has created interest, especially in the pharmaceutical and biomedical fields. The integration of nanotechnology and biotechnology, along with the integration of information technology and artificial intelligence, will definitely change the field of science. In this context, nanobiotechnology has emerged as an important field in which nanoprinciples and techniques are used to understand and control biological systems and create nanoscale devices using nanomaterials. Recent advances in nanotechnology are transforming important areas of agriculture, especially in the production of specialty nanopesticides and nanofertilizers, has attracted international attention. The world's population is estimated to reach 8. 5 billion by 2030, and food needs to be produced for approximately 9 billion people by 2050. Recent trends in nanotechnology have the potential to provide sustainable solutions for food production and precision agriculture. Nanoparticles, nanowires, nanotubes and nanocrystals have a variety of thermal, electrical, optical and chemical properties that provide high sensitivity, rapid response and low detection limits in many agricultural applications, ultimately curing pests and diseases. In addition, the impact of nanotechnology spreads to daily life and provides many benefits. However, increasing human exposure to nanoparticles has raised health and environmental concerns. This has led to the emergence of disciplines such as nanotoxicology, which focuses on evaluating the adverse effects of nanoparticles on health and investigating the benefits and risks of nanomaterials in medical use. Benefits of medical devices include better drug delivery, pain relief, pain management, tissue repair, and cancer diagnosis. However, the lack of reliable data reflects ongoing concerns about the impact of nanomaterials on human health. In conclusion, this article highlights the important role that the evolution of biotechnology and nanotechnology plays in solving global problems in various fields. discussed the emergence of nanobiotechnology and its applications in agriculture and medicine, which are expected to accelerate in the next decade. This chapter also highlights the need for rigorous research to exploit the benefits of nanotechnology while minimizing health and environmental risks and reviewed biotechnology is the driving force behind civilization; It offers new solutions to global challenges related to energy, waste, conservation finance and environmental protection. Their practices continue to evolve, becoming more effective and environmentally responsible in the future.

KEYWORDS: Biotechnology, Nanotechnology, Applications, Sustainability

INTRODUCTION

One of the most important fields of biology is biotechnology. It involves the use of living things biological processes, and other important applications in various industries such as engineering, technology, medicine, and other that require biological materials. Biotechnology has many applications, and use as worldwide, almost every industry uses this technology. Bioremediation using bacteria to clean water, biotechnology in conservation such as PTAse (an enzyme that breaks down plastic), genetic engineering and cloning, to name just a few of the innovations in biotechnology. A global challenge has led to the development and use of biotechnology, which it is hoped will bring new solutions to the world's major problems, including diseases, food shortages and damage to the environment (Chen *et al.,* 2017).

The widespread integration of nanotechnology across various sectors has sparked significant interest and potential applications, particularly in chemistry and biomedicine. These fields are pivotal for identifying novel molecules with potential human benefits. Nanotechnology has facilitated the advancement of techniques, both by adapting existing methods and introducing novel ones.

Researchers in academia and industry in disciplines such as biochemistry, chemical engineering, molecul ar biology, and genetics are increasingly aware of the advantages of using nanobiotechnology tools in res earch.

This technology supports international collaboration by enabling international research centers to exchan ge ideas and intensifying international research cooperation to understand the use of nanotechnology for biological diseases (Das *et al.,* 2016). This thematic issue aims to provide essential insights to support emerging research and innovations in the realm of nanobiotechnology. It seeks to harness recent trends in nanobiotechnological processes, fostering the development of these converging technologies to promote sustainable economic growth.

Nanobiotechnology is defined as the field that uses nanoscale principles and technologies to understand and modify biological systems (living or non-living) and uses biological elements and materials to create new devices and systems at the nanoscale. The convergence of nanotechnology and biotechnology, as well as information technology and cognitive science, is expected to accelerate in the next decade (Mihail *et al.,* 2003).

RECENT DEVELOPMENT IN NANO TECHNOLOGY ARE CHANGING AGRICULTURE

The application and benefits of nanotechnology in agriculture are attracting worldwide attention, especially in the production of specialized nano pesticides and nanofertilizers. According to UN reports and recent reports, the world population is expected to reach 8. 5 billion by 2030 and the world needs to produce less than 50% of food to feed nearly 9 billion people by 2050 (Wiens *et al.,* 2016). Recent trends in nanotechnology and nanomaterial-based systems can provide sustainable services in food management and precision agriculture. Nanoparticles, nanowires, nanotubes and/or nanocrystals have thermal, electrical, optical and chemical properties (Sumriddetchkajorn *et al.,* 2013). This material can be used to develop high sensitivity, fast response time, and low detection limits for different analytes and multiple analyzers. Therefore, farming can be made more efficientby using modern practices that better control pests and diseases (Yao *et al.,* 2014 & Kaur *et al.,* 2011). For instansce, nanotechnology has many applications in the development of plant protection and food products (Figure 1). Various types of hydrogel and nanoclay polymer composites have been used to increase soil moisture and improve soil water retention (Vundavalli *et al.,* 2015). Recent trends in nanotechnology and nanomaterial-based systems can provide sustainable services in food management and precision agriculture. Nanoparticles, nanowires, nanotubes and/or nanocrystals have thermal, electrical, optical and chemical properties. This information can be used to develop high sensitivity, fast response time, and low detection limits for

different analytes and multiple analyzers. Therefore, farming can be made more efficientby using modern practices that better control pests and diseases.

Nowadays, nanotechnology affects people's daily lives. The potential benefits are many. However, due to increased human exposure to nanoparticles, there are potential health and environmentalconcerns. These concerns have led to the emergence of other disciplines, including nanotoxicology and nanomedicine. Nanotoxicology is the study of the potential adverse health effects of nanoparticles (Oberdorster *et al.,* 2005). Nanomedicine includes subfields such as tissue engineering, biomaterials, biosensors, and bioimaging and is designed to study the benefits and risks of using nanomaterials in medicine and medical devices. Some of the benefits of medical devices include improved drug delivery, anti-inflammatory properties of medical devices, pain reduction, better tissue repair, and detection of cancer cells. However, due to the lack of reliable data, its potential impact on human health is still a major concern (Egusquiaguirre *et al.,* 2012, Gu *et al.,* 2013).

BIOTECHNOLOGY AND SUSTAINABILITY

Biotechnology has become a major player in increasing sustainability across sectors. His practice fosters innovation in environmentally friendly processes and products, with a particular focus on the development of biofuels, biodegradable materials and environmentally friendly production methods.

Biofuels: Biotechnology is at the forefront of creating profitable options. Fossil fuels. This involves the use of renewable resources such as algae, sugarcane and agricultural residues to produce biofuels such as biodiesel and bioethanol. These biofuels provide green energy options, reduce carbon emissions and reduce dependence on finite fossil fuels. (Ragauskas *et al.,* 2006 & Singh *et al.,* 2011).

Biodegradable Materials: The production of biodegradable materials is another important aspect of biotechnology for sustainable development. Biodegradable plastics and polymers are made using biological processes and materials. These materials break down naturally in the environment, reducing plastic pollution and the burden on landfills (Zhang *et al.,* 2015, Vert, 2005).

Waste reduction and recycling: Biotechnology is used to reduce waste and recycle. Bacteria can be used to break down and digest organic waste, converting it into useful products or energy. This reduces waste in landfills and minimizes the release of hazardous substances into the environment (Zhu *et al.,* 2016, Ucisik & Henze, 2008).

Permaculture: Biotechnology has revolutionized agriculture by producing genetically modified (GM) seeds that are resistant to pests, diseases and harsh environments. This will increase crop yields, reduce the need for pesticides and increase resource efficiency, contributing to sustainable food production (Pellegrino *et al.,* 2018, James, 2014).

Water Purification: Biotechnology is used to develop clean and hygienic water purification processes. Using microbial-based bacteria to remove contaminants from water provides a greener way to clean water supplies (Verlicchi *et al.,* 2012).

Renewable Energy: Biotechnology is the production of renewable energy (such as biohydrogen, biogas and microbial fuel cells). This technology uses microorganisms to produce clean energy from organic materials, reducing carbon monoxide emissions and relying on non-renewable energy sources (Logan *et al.,* 2009).

Environmental bioremediation: Biotechnology plays an important role in environmental bioremediation by using bacteria to clean polluted areas. This approach helps restore ecosystems affected by pollution and harmful substances (Rai *et al.,* 2016).

Carbon Capture and Utilization (CCU): Biotechnology is exploring the potential for carbon capture and utilization, using bacteria to transform carbon dioxide (CO2) emissions into useful products, mitigating climate change, and converting carbon. promoting culture (Singh *et al.,* 2018).

Sustainable Production: Biotechnology enables the development of environmentally friendly production processes in many industries, from textiles to pharmaceuticals. Microbial fermentation, for example, can replace chemical compounds and reduce waste and energy. (Shirkavand *et al.,* 2020).

Circular Economy: Biotechnology follows the principles of the circular economy by promoting the recycling and reuse of biological materials. This minimizes waste and increases safety by conserving resources (Bocken *et al.,* 2016).

CONCLUSION

This research paper highlights the important role of biotechnology and nanotechnology in solving various global challenges while promoting sustainability across sectors. It addresses the use of this technology in agriculture, medicine and environmental protection, focusing on innovations such as nanopesticides, biodegradable materials and renewable energy. But it also highlights the need to investigate the potential health and environmental risks associated with increased exposure to nanoparticles. Overall, this article highlights the revolutionary potential of technology in driving a safer and more environmentally friendly future.

REFERENCES

[1]. Austin, H. P., Allen, M. D., Donohoe, B. S., Rorrer, N. A., Kearns, F. L., Silveira, R. L., & Beckham, G. T. (2018). Characterization and engineering of a plastic-degrading PETase. Nature, 558 (7708), 165-170.

[2]. Bocken, N. M., (2016). A literature and practice review to develop sustainable business model archetypes. Journal of Cleaner Production, 135, 1218-1233.

[3]. Chen X., Schluesener HJ., Nanosilver: (2008). A nanoproduct in medical application. Toxicol Lett; 176: 1–12.

[4]. Chen, H., Seviour, T., &Gu, J. D., (2017). Applying Microbiology and Biotechnology in Bioremediation of Contaminated Waters and Soils. In Biotechnology of Microbial Enzymes. Elsevier., pp. 73-106.

[5]. Das, R. K., & Sharma, B. S., (2016). Nanotechnology in Medicine and Antibacterial Effect of Silver Nanoparticles. In Nanotechnolog., 1-26.

[6]. Egusquiaguirre SP., Igartua M., Hernandez RM., (2012). Nanoparticle delivery systems for cancer therapy: advances in clinical and preclinical research. Clin Transl Oncol,. 14: 83–93.

[7]. Gu Z., Aimetti AA., Wang Q., (2013). Injectable nano-network for glucose-mediated insulin delivery. ACS Nano ; 7: 4194 - 4201.

[8]. James, C. (2014). Global status of commercialized biotech/GM crops: 2014. ISAAA Brief, 49, 22-23.

[9]. Kaur N and Kumar S., (2011). Colorimetric metal ion sensors. Tetrahedron 67:9233-9264

[10]. Logan, B. E., (2009). Exoelectrogenic bacteria that power microbial fuel cells. Nature Reviews Microbiology, 7 (5), 375-381.

[11]. Marra, A., & Bozzi, A., (2019). Advances in Cloning and Genetic Engineering. In Advances in Genetics Research. Nova Science Publishers, Vol. 21, pp. 63-86.

[12]. Mihail C. Roco., (2003). Nanotechnology: convergence with modern biology and medicine. Current Opinion in Biotechnology,Vol 14, Issue 3, Pages 337-346.

[13]. Narancic, T., & O'Connor, K. E. (2017). Microbial biotechnology addressing the plastic waste disaster. Microbial Biotechnology, 10 (5), 1232–1235.

[14]. National Center for Biotechnology Information (NCBI). (2010). Biotechnology: Past, Present, and Future.

[15]. Oberdorster G., Maynard A., Donaldson K., (2005). Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy. Part Fibre Toxicol,2: 1- 35.

[16]. Pellegrino, E., (2018). A meta-analysis on the impact of genetically modified crops. PLoS ONE, 13 (3), e0192474.

[17]. Ragauskas., A. J., (2006). The path forward for biofuels and biomaterials. Science, 311 (5760), 484-489.

[18]. Rai, P. K., (2016). Role of biotechnology in bioremediation of contaminated environment: A review. Environmental Science and Pollution Research, 23 (14), 13711-13731.

[19]. Shirkavand, E., and Baroutian, S., (2020). A critical review on the application of chemical and biological pretreatment methods for second-generation lignocellulosic biorefineries. Bioresource Technology Reports, 9, 100344.

[20]. Singh, A., & Pant, D., (2011). A sustainable approach for the utilization of waste bread for bioethanol production. Energy & Environmental Science, 4 (9), 3680-3686.

[21]. Singh, A., (2018). Sustainable synthesis of nanoparticles: An environmental perspective. Nanoscale Advances, 1 (9), 3640-3646.

[22]. Sumriddetchkajorn S., (2013). How optics and photonics is simply applied in agriculture?, Ed, pp 888311-888311-888317.

[23]. Ucisik, A. S., & Henze, M., (2008). Biodegradation of linear alkylbenzene sulfonate (LAS) in a biofilm reactor: model development and practical implications. Water Research, 42 (11-12), 2809-2820.

[24]. Verlicchi, P., Al Aukidy, M., and Zambello, E. (2012). Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review. Science of the Total Environment, 429, 123-155.

[25]. Verma, J., & Bhatia, S. (2020). Biotechnology and its applications in agricultural science. Environmental Sustainability, 3 (2), 135–143.

[26]. Vert, M., (2005). Aliphatic polyesters: great degradable polymers that cannot do everything. Biomacromolecules, 6 (2), 538-546.

[27]. Vundavalli R., Vundavalli S., Nakka M and Rao DS., (2015). Biodegradable nano-hydrogels in agricultural farming - alternative source for water resources. Procedia Materials Science 10:548-554.

[28]. Wiens JA., (2016). Population growth, in Ecological Challenges and Conservation Conundrums. John Wiley & Sons, Ltd, pp 105-108.

[29]. World Economic Forum. (2021). Biotechnology and the Fourth Industrial Revolution.

[30]. Yao J., Yang M and Duan Y., (2014). Chemistry, biology, and medicine of fluorescent nanomaterials and related systems: new insights into biosensing, bioimaging, genomics, diagnostics, and therapy. Chemical Reviews 114:6130-6178.

[31]. Zhang, M., (2015). Biodegradable polymers derived from renewable resources. Progress in Polymer Science, 60, 37-59.

[32]. Zhu, Y., (2016). Comprehensive review of COD, nitrogen and phosphorus removal in membrane bioreactor: The current state of the art. Bioresource Technology, 216, 117-125.

Chapter
12

STUDY OF TOXICITY AND CYTOTOXICITY OF PROMINENT HEAVY METALS ON HUMAN HEALTH

ANURADHA A. KAMBLE*, RIYAJ R. INAMDAR, PRATIKSHA S. JADHAV, NARAYAN M. GHANGAONKAR AND RANGNATH K. AHER

Department of Botany, New Arts, Commerce and Science College Parner, Ahemadnagar.
Department of Botany, Chandmal Tarachand Bora college Shirur, Pune.
*Corresponding author E-mail: kamble.anuradha12345@gmail.com

ABSTRACT

Several substances can harm cells, with heavy metals like mercury, lead, chromium, cadmium, and arsenic posing significant risks. Industrial activities and human actions have heightened exposure, impacting water, air, and food quality. Human health is affected, with gender playing a role in the varying toxic effects. The focus is on understanding the cytotoxicity of these metals and their dangerous impact on human well-being. Some heavy metals, such as arsenic, mercury, chromium, and lead, pose serious health risks even at low levels of exposure. Arsenic, found in various sources including rice and water, is a known carcinogen. Mercury affects the brain and various organs, while chromium is linked to DNA damage and carcinogenicity. Lead, a prevalent environmental contaminant, impacts multiple bodily systems, including the nervous and hematopoietic systems. Its toxicity is associated with neuropsychiatric effects. The understanding of the cytotoxic effects of these metals is crucial for assessing their impact on human health. Accordingly, the present study aimed to Heavy metals and their cytotoxicity.

KEYWORDS: Heavy Metals, Toxicity, Cytotoxicity, Carcinogen, Pollutants, Human Health

INTRODUCTION

Various substances possess varying degrees of toxicity, making it imperative for scientists and healthcare practitioners to comprehensively understand their effects on organisms and the extent of harm they can cause. Cell cytotoxicity refers to the capacity of specific chemicals or mediator cells to induce the destruction of living cells. This phenomenon holds significant implications, particularly concerning the healing process, as the inadvertent elimination of healthy cells surrounding the wound site can impede the overall recovery trajectory. Cytotoxicity represents the overarching characteristic of being detrimental to cells, and can arise from various sources such as chemical stimuli or exposure to neighbouring cells. Toxicity is the inherent property of a substance, such as a medication, to exhibit poisonous or harmful qualities. It is crucial to emphasize that the level of toxicity is intricately tied to the dosage administered. The industrial activities of the previous century have led to significant escalations in human exposure to heavy metals. Specifically, mercury (Hg), lead (Pb), chromium (Cr) and arsenic (As), have emerged as the most prevalent heavy metals responsible for inducing cases of human poisoningand they can cause irreversible damage. (Mahdi *et al.,* 2021) Heavy metal exposure has increased as a result of anthropogenic, industrial, and agricultural activity as well as modern industrialisation, all of which have negative impacts on human health. The global issue of harmful metal pollution in water and air has an impact on

the lives of millions of individuals across the globe. The presence of heavy metals in food poses a significant challenge to the well-being of both humans and animals. In this context, the concentration of heavy metals in food, air, and water resources is evaluated (Mousavi *et al.,* 2013; Ghorani-Azam *et al.,* 2016; Luo *et al.,* 2020). Metals, like various other environmental pollutants such as soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crop, and many others. Consequently, human exposure to these metals is an inescapable reality, and a number of research studies have documented variations in the toxic effects of these metals based on gender. (Vahter *et al.,* 2007; Tchounwou *et al.,* 2012, Morais *et al.,* 2012). The aim of to provide updated knowledge regarding the cytotoxicity of some heavy metals on human health, as well as their negative impact on human health.

HEAVY METALS AND THEIR TOXICITY

Metallic elements, such as mercury, arsenic, and lead, Chromium, Mercury, possess the capacity to induce harmful effects even at minimal levels of exposure. Holding a paramount position on the register of hazardous substances, the subsequent segments offer a comprehensive understanding of the intricate mechanisms by which these metallic elements manifest their toxic impacts within the biological systems of living organisms.

ARSENIC

Arsenic, a naturally occurring metalloid, is widely dispersed throughout the environment. Despite its status as the 20th most prevalent element in the earth's crust, it claims the top spot on the list of hazardous substances that pose a significant risk to public health. (Hughes *et al.,* 1988). This element is notably present in significant levels within various seafood, make available it easily accessible through dietary means. Notably, its presence in rice, a staple food globally, presents a heightened accessibility compared to other sources. Consequently, this phenomenon poses a heightened concern for infants, particularly those reliant on rice-based meals, such as baby foods. Following World Health Organization (WHO) protocols, a safer threshold of 200 μg/kg for white rice and a maximum allowance of 400 μg/kg for brown rice has been established. Being classified as a Group I carcinogen, its pollution of drinking water stands as a significant global environmental crisis (Kulshresth *et al.,* 2014). The toxicity linked to water contaminated with arsenic has been documented across various countries, including Bangladesh, India, China, and others. Approximately 200 million individuals are estimated to be primarily exposed through drinking water containing levels surpassing the recommended threshold (Naujokas *et al.,* 2013, Ramos-Chavaz *et al.,* 2015).

CARCINOGENIC HEALTH EFFECTS

Prolonged arsenic exposure impacts various bodily systems including the gastrointestinal tract, circulatory system, skin, liver, lungs, kidneys, nervous system, and heart. Epidemiological evidence strongly supports the notion that exposure to inorganic arsenic elevates the likelihood of cancer. Among workers exposed via inhalation, the primary carcinogenic consequence is an elevated susceptibility to lung cancer (Enterline PE *et al.,* 1987, Lee-Feldstein *et al.,* 1986) In addition to skin cancer, exposure to arsenic has been reported to increase the risk of several internal cancers (primarily liver, kidney, lung, colon, and bladder). Reported by (Tchounwou PB *et al.,* 1999)

MERCURY (Hg)

Mercury is a toxic heavy metal It is a natural constituent of the earth's crust Human activities have drastically altered the bio-geo/chemical cycle and balance of mercury (Dwayne *et al.,* 2002) Mercury is a stable and persistent environmental contaminant since it cannot be degraded or destroyed. Excessive

accumulation of mercury in soils and sediments is a prevalent concern, particularly due to its potential implications for marine ecosystems and human consumers of seafood. Elevated levels of mercury within the marine environment can significantly impact marine organisms, thereby posing a significant risk to public health through the consumption of contaminated seafood.

CARCINOGENIC HEALTH EFFECTS OF MERCURY

Mercury primarily targets the brain, although its effects can extend to various organs, causing impairment of nerves, kidneys, and muscles. It disrupts the membrane potential and interferes with intracellular calcium homeostasis. The strong stability constants lead to the binding of mercury to readily available thiols. (Partik 2002) metallic mercury vapours at higher levels for shorter periods of time can lead to vomiting, diarrhoea, nausea, skin rashes, increased heart rate or blood pressure and lung damage. Diagnosing cases of organic mercury poisoning can be challenging, as the symptoms, including but not limited to depression, memory issues, tremors, fatigue, headaches, and hair loss, often overlap with those of other conditions (Martin and Griswold 2009) (Chen R. *et al.,* 2019) investigated the impact of mercury (Hg) exposure on non-alcoholic fatty liver disease among a cohort of 6,389 adolescents aged 12–17 years. The study found that Hg tends to accumulate primarily in the kidneys and can have adverse effects, particularly within the proximal tubules. The median blood Hg level was recorded at 0. 73 ± 0. 91 μg/L, with the observation of a mild elevation in alanine aminotransferase (ALT) levels (Chen R. *et al.,* 2019).

CHROMIUM (Cr)

Chromium is a type of chemical element identified by the symbol Cr and possessing an atomic number of 24. It falls into the first position within group 6 of the periodic table. This element is characterized by its steely-grey appearance, possessing a lustrous and hard texture, and being classified as a brittle transition metal.

The accumulation of chromium (Cr) within bodily organs has been linked to potential implications for human health. Chromium exhibits various oxidation states that span from -2 to +6. Among these states, the trivalent and hexavalent forms are the most commonly found and stable. (Shekhawat *et al.,* 2015) Chromium (VI) has been linked to a spectrum of illnesses and medical conditions. On the other hand, Chromium (III) is essential in minute quantities for inherent lipid and protein metabolism, and it also acts as a critical component in facilitating insulin function. (Cefalu and Hu, 2004; Achmad *et al.,* 2017; Vincent, 2017; Vincent, 2019). DNA damage, genomic instability, and the generation of reactive oxygen species (ROS) are recognized as established mechanisms of chromium (Cr) toxicity and its potential to cause cancer. Both chromium (VI) and chromium (III) are capable of inducing ROS. (Pavesi and Moreira 2020). The carcinogenic effects of chromium are associated with subsequent DNA damage, leading to the disruption of transcription regulation. Moreover, this process disrupts chromatin architecture, resulting in alterations in chromatin accessibility, as well as local and genome-wide nucleosome position shifts. (Schnekenburger *et al.,* 2007). DNA repair systems are lesion-specific, several of them are likely activated in response to the wide range of DNA lesions induced by Cr (VI). Deficiencies in these repair systems can be associated with both the onset and the progression of cancer, as an increased frequency of mutations can result in the activation of oncogenes and inactivation of tumor suppressor genes. (Urbano *et al.,* 2012) Single-strand breaks (SSBs) and double-strand breaks (DSBs) were identified in fast-growing cells like cancer cells, arising from the failure of the replication fork during the process of DNA replication. This failure can result in the interruption of the cell cycle and programmed cell death (apoptosis) through the activation of the p53 protein (Lee *et al.,* 2016; Wilhelm *et al.,* 2020)

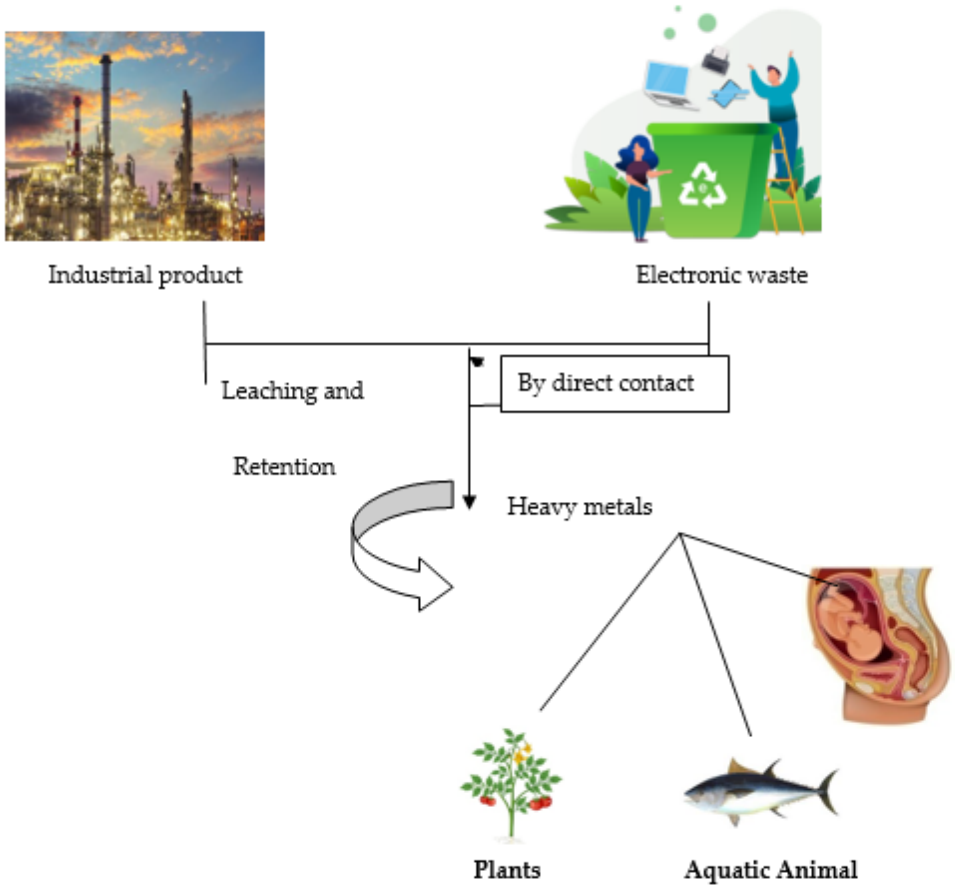
LEAD

Lead is a prevalent environmental contaminant, with exposure predominantly occurring in occupational settings such as lead-acid battery or pipe production, metal recycling, and foundries. (Woolf *et al.*, 2007). Lead toxicity can arise from the consumption of fruits and vegetables grown in soils contaminated with elevated lead levels, often originating from pipes, lead paint, and remnants of emissions from leaded gasoline, predominantly before the Environment Protection Agency's regulatory interventions around 1980. Educating the public about the primary sources of lead poisoning is imperative to prevent domestic lead exposure among the general population.

CYTOTOXICITY

Blood led levels ranging from 25 to 60 µg/dL are associated with a spectrum of neuropsychiatric manifestations, including delayed reaction times, irritability, and difficulties in concentration. Additionally, these levels have been observed to impede motor nerve conduction and may induce symptoms such as slowed cognitive processing and headaches. (Ab Latif *et al.*, 2015). Lead exhibits a multifaceted toxic profile, impacting various bodily systems including the gastrointestinal tract, cardiovascular system, central and peripheral nervous systems, immune system, and reproductive system. Despite this, the specific effects of lead on the hematopoietic system remain relatively understudied. Thus, the current research was structured to investigate the influence of lead exposure on the incidence of acute promyelocytic leukemia (APL) using human leukemia (HL-60) cells as a model. Furthermore, the study sought to ascertain the potential involvement of oxidative stress in the mechanism underlying lead nitrate-induced cytotoxicity in this particular cellular model (Clement *et al.*, 2010).

Heavy Metal Toxicity: Abnormal Growth and Development



CONCLUSION

In this way an attempt has been made to identify Hazardous effects of heavy metals, such as arsenic, mercury, chromium, and lead on Human health. The biggest threat of exposure of these heavy metals is cause of increasing cancer amongst the people in the society. Therefore, it is important to initiate corrective measures related to negative effects of arsenic, mercury, chromium, and lead on human health.

REFERENCES

[1]. Ab Latif Wani, Anjum Ara, Jawed Ahmad Usmani (2015) Lead toxicity: a review Interdiscip Toxicol 8 (2): 55–64

[2]. Achmad, R. T., Budiawan, B., and Ibrahim Auerkari, E. (2017). Effects of chromium on human body. Annu. Res. Rev. 13, 1–8.

[3]. Cefalu, W. T., and Hu, F. B. (2004). Role of chromium in human health and in diabetes. Diabetes Care 27 (11), 2741–2751.

[4]. Chen, R., Xu, Y., Xu, C., Shu, Y., Ma, S., Lu, C. (2019). Associations between mercury exposure and the risk of nonalcoholic fatty liver disease (NAFLD) in US adolescents. Environ. Sci. Pollut. Res. 26 (30), 31384–31391.

[5]. Clement Yedjou, Linden Haynes, Waneene Dorsey, Robert MCMurray and Paul B. Tchounwou (2010) Lead-Induced Cytotoxicity and Oxidative Stress in Human Leukemia (HL-60) Cells Arch Environ Contam Toxicol. 44 (3): 417-420

[6]. Dwayne J. Sutton, Paul B. Tchounwou, Nanuli Ninashvili and Elaine Shen (2002) Mercury Induces Cytotoxicity and Transcriptionally Activates Stress Genes in Human Liver Carcinoma (HepG2) Cells Int. J. Mol. Sci. 3 (9), 965-984

[7]. Enterline PE, Henderson VL, Marsh GM (1987). Exposure to arsenic and respiratory cancer: a reanalysis. Am J Epidemiol 125: 929–938.

[8]. Ghorani-Azam, A., Riahi-Zanjani, B., and Balali-Mood, M. (2016). Effects of air pollution on human health and practical measures for prevention in Iran. J. Res. Med. Sci., 21, 65.

[9]. Hershko C, Link G, Ioav C. (1998). Pathophysiology of iron overload. Ann N Y Acad Sci 850: 191–201.

[10]. Kulshrestha, A; Jarouliya, U; Prasad, G. B. K. S; Flora, S. J. S; Bisen, P. S. (2014). Arsenic-induced abnormalities in glucose metabolism: Biochemical basis and potential therapeutic and nutritional interventions. World J. Transl. Med. 2014, 3, 96–111.

[11]. Lee, J. -K., Choi, Y. -L., Kwon, M., and Park, P. J. (2016). Mechanisms and consequences of cancer genome instability: lessons from genome sequencing studies. Annu. Rev. Pathol. 11, 283–312. doi:10. 1146/annurev-pathol-012615-044446

[12]. Lee-Feldstein A (1986). Cumulative exposure to arsenic and its relationship to respiratory cancer among copper smelter employee. J Occup Med 28: 296–302.

[13]. Luo, L., Wang, B., Jiang, J., Huang, Q., Yu, Z., Li, H. (2020). Heavy metal contaminations in herbal medicines: determination.comprehensive risk assessments. Front. Pharmacol. 11, 595335.

[14]. Mahdi Balali-Mood, Kobra Naseri , Zoya Tahergorabi, Mohammad Reza Khazdair (2021) Toxic for Animals Humans Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic, Front. Pharmacol Sec. Predictive Volume 12

[15]. Martin S, Griswold W. (2009). Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens. 2009; (15):1–6

[16]. Mazumder DN, Haque R, Ghosh N, De BK, Santra A, Chakraborty D, Smith A (1998). Arsenic levels in drinking water and the prevalence of skin lesions in West Bengal, India. Int J Epidemiol 27: 871–877.

[17]. Moitra, S., Blanc, P. D., and Sahu, S. (2013). Adverse respiratory effects associated with cadmium exposure in small-scale jewellery workshops in India. Thorax 68 (6), 565–570.

[18]. Morais S, Costa FG, Pereira ML. (2012). Heavy metals and human health, in Environmental health – emerging issues and practice (Oosthuizen J ed), InTech pp. 227–246

[19]. Naujokas, M; Anderson, B; Ahsan, H; Aposhian, H. V; Graziano, J. H; Thompson, C; Suk, W. A. (2013) The broad scope of health effects from chronic arsenic exposure: Update on a worldwide public health problem. Environ. Health Perspect. 121, 295–302.

[20]. Patrick L. (2002) Mercury toxicity and antioxidants: Part 1: role of glutathione and alpha-lipoic acid in the treatment of mercury toxicity. Altern Med Rev. 7 (6):456–471.

[21]. Ramos-Chavaz, L. A; Rendon-Lopez, C. R. R; Zepeda, A; Silva-Adaya, D; Razo, L. M. D; Gonsebatt, M. E. (2015) Neurological effects of inorganic arsenic exposure: Altered cysteine/glutamate transport, NMDA expression and spatial memory impairment. Front. Cell. Neurosci. 9, 1–12.

[22]. Sharma, B; Singh, S; Siddiqi, N. J. (2014) Biomedical implications of heavy metal induced imbalances in redox systems. BioMed Res. Int. 640754.

[23]. Shekhawat, K., Chatterjee, S., and Joshi, B. (2015). Chromium toxicity and its health hazards. Int. J. Adv. Res. 3 (7), 167–172.

[24]. Tchounwou PB, Wilson B, Ishaque A (1999). Important considerations in the development of public health advisories for arsenic and arseniccontaining Compounds in drinking water. Rev Environ Health 14 (4): 211–229.

[25]. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., and Sutton, D. J. (2012). Heavy metal toxicity and the environment. Mol. Clin. Environ. Toxicol. 101, 133–164.

[26]. Urbano, A. M., Ferreira, L. M. R., and Alpoim, M. C. (2012). Molecular and cellular mechanisms of hexavalent chromium-induced lung cancer: an updated perspective. Curr. Drug. Metab. 13 (3), 284–305.

[27]. Vahter, M., Åkesson, A., Lidén, C., Ceccatelli, S., and Berglund, M. (2007). Gender differences in the disposition and toxicity of metals. Environ. Res. 104 (1), 85–95.

[28]. Vincent, J. B. (2017). New evidence against chromium as an essential trace element. J. Nutr. 147 (12), 2212–2219.

[29]. Vincent, J. B. (2019). Effects of chromium supplementation on body composition, human and animal health, and insulin and glucose metabolism. Curr. Opin. Clin. Nutr. Metab. Care 22 (6), 483–489.

[30]. Wilhelm, T., Said, M., and Naim, V. (2020). DNA replication stress and chromosomal instability: dangerous liaisons. Genes (Basel) 11 (6), 642.

[31]. Woolf AD, Goldman R, Bellinger DC. (2007) Update on the clinical management of childhood lead poisoning. Pediatr Clin North Am. 54:271–294.

Chapter 13

SUSTAINABLE ORGANIC FARMING: A FUTURE PROSPECTUS IN INDIA

GUNMALA GUGALIA

Principal, SDM PG Girls College, Bhilwara (Rajasthan)
Corresponding author E-mail: gunmala24@gmail.com

ABSTRACT

The increasing global demand for sustainable agriculture practices and the need to manage biomass waste efficiently have led to the development of organic fertilizers from biomass waste in granular form. This review paper provides an overview of the current state of research on developing sustainable organic fertilizer from biomass waste, focusing on its production methods, nutrient content, agronomic effectiveness, and environmental benefits. The potential challenges and future prospects of utilizing granular organic fertilizers derived from biomass waste are also discussed. The findings highlight the promising role of these fertilizers in improving soil health, enhancing crop productivity, and contributing to a more sustainable agricultural system.

KEYWORDS: Sustainable Agriculture, Organic Fertilizer, Soil Health.

INTRODUCTION

Traditional agricultural techniques, which have been used for many centuries, have a significant historical influence on India's organic farming industry. Using natural resources and methods to grow crops without damaging the environment has always been a focus of traditional Indian farming. Because of growing public concern about the negative impacts of conventional agricultural practices on the environment and human health, the organic farming movement has gained traction in India in recent years. The government has launched a number of measures to encourage organic farming since it understands how important it is. The creation of organic agricultural zones, the provision of financial aid to farmers for the purchase of organic inputs, and the development of organic certification schemes are a few examples.

In addition, a number of non-governmental organizations have been actively promoting organic farming in India by attempting to inform farmers about the advantages of sustainable agriculture and by offering instruction on organic farming methods. Despite these initiatives, organic farming in India still confronts several difficulties, such as a lack of infrastructure, restricted market access, and expensive organic inputs. With a focus on biofertilizers and vermicomposting, this study examines the various facets of organic farming in India in order to better understand the advantages, difficulties, and future prospects of this sustainable farming method.

MATERIAL AND METHOD

This review study was undertaken by the researcher with the goal of locating current writing on organic farming in India. The databases used to find and identify journal articles with high-impact outcomes included Scopus, Web of Science, EBSCO, ProQuest, Science Direct, Google Scholar, Semantic Scholar, and ResearchGate. The researcher used terms like "benefits," "significance," "organic farming," and "India" to start finding and identifying papers, and this produced 16,700 search results. In order to identify the

pertinent publications required for this paper, the researcher also used a critical screening approach that focused on inclusion/exclusion criteria. Forty articles were chosen after carefully examining the paper titles and abstracts.

The 40 papers were then further evaluated in accordance with predetermined standards and limitations. Studies exhibiting a theoretical interpretation of organic farming, examining the advantages of organic farming, and addressing the advantages of organic farming in India were among the studies that met the inclusion requirements. 12 articles were excluded as a result of this. Twenty of the remaining 28 papers were chosen for examination after the remaining 28 were subjected to inclusion/exclusion criteria and full-text analysis.

According to a number of studies, excessive traditional agriculture can contaminate the entire food supply chain, necessitating the adoption of healthier foods produced using eco-friendly methods that are very authentic—hence the term "organic farming. " According to the International Federation of Organic Agriculture Movements (IFOAM), "organic farming" is an agricultural practice that makes use of bio-fertilizers and pesticides with an ecological foundation that are largely derived from plant and animal waste and organic manure [1]. In contrast to conventional farming, which mostly relies on artificial pesticides and chemical fertilizers, organic farming emphasizes the use of natural methods to develop plants and raise animals. According to Elayaraja [2]., organic farming may assure that eco-friendly and genuine food and goods are produced and consumed, reflecting green farming techniques.

Dey [3]. emphasizes how biological input is used in organic farming to maintain and control soil fertility and ecological equilibrium, reduce waste and pollution, and preserve human health.

SIGNIFICANCE OF ORGANIC FARMING

The concept "sustainability" has gained popularity across various industries, with organic farming being a promoter of agriculture. In the 21st century, a sustainable way of life is gradually taking the stage. Organic farming strives to have a good effect on the environment and human health. According to Elayaraja [2]., switching to organic farming is essential if you want to stay away from pesticides and fertilisers made of chemicals. The procedure has a focus on using natural approaches to eradicate weeds and pests. Chemicals may also leave behind residues in items and foods that could have disastrous impacts on the environment and our health. Additionally, organic farming can be used to benefit the environment, as Kumari [4]. claims. The larger worldwide problem of climate change illustrates the danger posed to our environment and calls for actions to keep nature rich and pure, such as organic farming in the agriculture sector. In comparison to conventional production methods, ecological production techniques considerably support the expansion of biodiversity. Moreover, Karunakaran [5,4]. emphasizes that organic farming, as opposed to conventional farming, could enhance the nutritional value of food and its derivatives. According to a recent study, organic components have much greater quantities of antioxidants and other crucial substances, such anti-inflammatory effects, that are beneficial to consumers [6].

Additionally, organic farming helps local farmers gain more authority and safeguards their environment from dangerous chemicals [7]. Because there is a market for organic foods, farmers who grow them can provide it and profit from it. In this regard, buying organic food ensures that the production process as a whole won't impact the surrounding areas or the local residents. But avoiding products made from genetically modified organisms (GMOs) may be possible with organic farming [4, 6]. Instead of utilizing GMOs, organic farming practices are used, reducing the risk of adverse health and environmental effects.

As a result, organic farming benefits both people and the environment more. It should therefore be broadly embraced to promote sustainable living.

TECHNIQUES OF ORGANIC FARMING

If chemical-based insecticides and fertilizers are avoided, organic farming can take many different forms. Organic farming techniques combine modern scientific technology with the currently used conventional farming methods that are centered on natural bioprocesses. Numerous research explores organic farming practices, with a particular emphasis on crop rotation and intercropping, integrated pest management, vermicomposting, organic soil fertility (NPK), biological fertilizers, bio-pesticides, organic manure, and waste management, among other things.

CROP ROTATION AND INTERCROPPING

Since organic farming depends on the biology and health of the soil, techniques like crop rotation, intercropping, and mixed cropping may be useful in enhancing soil life by enhancing soil characteristics and related bioactivities. Crop rotation, according to Soni [8]., is the practice of growing different types of crops on various farmlands such that no one crop is successively planted in the same spot. It is a good idea to preserve and improve the soil's composition and nutrient levels while also thwarting pests that are carried by the soil. Additionally, intercropping is the practice of growing many crops at once in the same space [9,8]. Intercropping, according to Yadav [10]., enables farmers to grow at least one high-value crop while utilizing crop combinations to control weeds and reduce soil erosion.

INTEGRATED PEST MANAGEMENT (IPM)

The goal of integrated pest management is to keep the pest population below the level that could cause irreparable damage to the economy. Integrated pest management, according to the Department of Agriculture [11]., comprises holistically merging multiple acceptable control strategies, making sure they are ecologically oriented, and including biological and cultural pest management. Crop rotation, a schedule for planting and harvesting, and the creation of habitats with resources for beneficial creatures are some examples of these techniques.

NATURAL SOIL FERTILITY

Yadav states that organic soil fertility involves "the use of natural materials and exploitation of biological processes to provide necessary nutrients to soils". Utilisingbiofertilizers, organic manure, and vermicomposting are some of the methods that can increase and improve soil fertility organically [10].

BIO-FERTILIZERS

The definition of biofertilizers by Soni [8]. and Yadav [10]. is "preparations comprising latent cells or living cells of effective strains of microorganisms that enhance crops' absorption of nutrients by their relationship with one another in the root system when applied through soil or seed. " Different types of microorganisms, including fungi, bacteria, and algae, are included in biofertilizers. They play a crucial role in the soil's microbial processes that increase the amount of nutrients available in a way that plants can easily absorb.

ORGANIC MANURE

Natural resources are referred to as organic manures and are used by farmers to provide crop plants with nutrients [3]. There are several types of organic manure, such as green manures, farmyard manures, vermicompost, biological wastes, compost manures, and oil cakes, among others. Improved organic matter, increased soil water-holding capacity, and improved drainage are all a result of using organic manures.

VERMICOMPOSTING

Vermicomposting is a crucial technique that can enhance soil fertility in terms of its physical, biological, and chemical composition. Vermicomposting is defined by Olle [12]. and Pathania [9]. as "the process that uses earthworms to convert organic materials into humus-like material. " Vermicompost is a practical method to improve the nutrient composition of soil, increase productivity, and strengthen soil structure since it has a greater nutrient profile than standard compost, according to numerous research.

BIOPESTICIDE

Biopesticides are biological agents that emit toxins harmful to pests invading plant crops, according to Das [1]. and Dey [3]. For instance, secondary metabolites like phenolics, terpenoids, and alkaloids aid in the battle against and death of worms, nematodes, insects, and other pests. The biopesticides nicotine, pyrethrum, margosa, and neem are a few examples [3].

BIOCOMPOST

According to Kumari [4]., certain soil qualities depend on waste management practices including composting and recycling of organic waste. By using techniques like anaerobic digestion, composting, and thermos-chemical treatments, organic farming offers a way to manage home and agricultural waste efficiently while using fewer conventional chemical pesticides, fertilizers, and other energy sources. Management of organic waste enhances biological activity and pore structure, which benefits the ecosystem.

THE SITUATION OF ORGANIC AGRICULTURE IN INDIA

More than 72. 3 million hectares of land were cultivated organically in 2019 [5]., indicating that organic farming is continuously increasing in popularity around the world. With more than 2. 3 million hectares of organic farming in 2019 [5]., an increase from the 41,000 hectares of organic land in 2002 [1]., India is one of the world's top producers of organic food. Following the establishment of the National Programme for Organic Production (NPOP) in 2001 under the Agricultural and Processed Food Products Export Development Authority (APEDA), of the Ministry of Commerce and Industry [5]., India recorded organic production of 14,000 tonnes in 2002, of which only 85% were for export.

It received a low score given that the product was intended for export, mostly because of a number of difficulties, including insufficient biomass, inconsistencies in government policies to assist organic farming, a lack of knowledge, insufficient funding, a low yield, etc. [5]. The National Mission for Sustainable Agriculture was established to support organic farming later in 2005 after the Indian government passed its first organic farming legislation [11,13]. Large areas in Madhya Pradesh, Rajasthan, Maharashtra, Gujarat, Karnataka, Odisha, Sikkim, and Uttar Pradesh are now certified as organic due to the policies, institutions, and programmes that have been introduced, which have significantly increased organic farming in India [5]. Large areas in Madhya Pradesh, Rajasthan, Maharashtra, Gujarat, Karnataka, Odisha, Sikkim, and Uttar Pradesh are now certified as organic due to the policies, institutions, and programmes that have been introduced, which have significantly increased organic farming in India [5].

ADVANTAGE OF ORGANIC FARMING

CROP PRODUCTIVITY

Vermicomposting and bio-fertilizers have received special attention in research exploring the impact of organic farming on crop productivity. Vermicomposting has a positive correlation with crop yield and income, according to Cidón [14]. It comes about as a result of vermicomposting's advantages, which reduce nitrogen concentration and result in increased and stabilized output, higher farm income, and

lower costs for buying and utilizing nitrogen fertilizers [14,15,16]. When compared to artificial fertilizers that leave behind nitrate residues, which are frequently linked to negative health effects for people, vermicomposting improves the nutrient content naturally, which is vital in increasing crop plant yields.

Vermicompost is a high-quality manure that contains phosphorus, nitrogen, calcium, potassium, magnesium, and other vital nutrients that crop plants need. It also contains micronutrients like zinc, iron, manganese, and copper in sufficient proportions that may increase crop output [16]. The nutrient composition of vermicompost, according to Kumar [15]., is different from the waste material used in vermicompost processing. Similar to this, the type of earthworm species used in vermicomposting may affect the product's quality [15]. In general, vermicompost has a substantially greater nutrient profile than regular compost, which reduces the need for synthetic fertilizer [7].

Generally, using vermicompost in soil provides sufficient levels of antibiotics, amino acids, enzymes, and hormones that are essential in boosting the growth and development of plants, rendering stable and sustainable crop production. The incorporation of nutrient management practices into microbial inoculants (biofertilizers) increases crop productivity [17]. Recent research has demonstrated the critical function that biofertilizers play in controlling the dynamics of organic matter decomposition and the availability of plant nutrients like phosphorus (P), nitrogen (N), and sulfur (S) [17]. This is due to the fact that biofertilizers effectively and sustainably start microbial processes in the soil, which makes them useful for crop production [7].

Similar to this, the use of advantageous microorganisms as biofertilizers ensures sustainable crop production while minimizing reliance on inorganic fertilizers and the environmental impact. Additionally, the application of biofertilizers to the soil, seeds, and roots of plants can increase microbial activity, enhancing target plants' ability to absorb nutrients and increasing crop productivity [18]. In a related study, Gurjar [16]. makes the claim that enhanced agricultural yield is reflected in improved plant growth and development. Farmers can sustainably produce a huge amount that is enough for both consumption and selling. Chemical fertilizers, on the other hand, can be used to increase agricultural productivity, but they may have negative consequences on consumers and the environment.

PRODUCT QUALITY

When addressing various physiological processes and outcomes in crop plants, crop product quality is an important factor to take into account. This includes aspects like texture, taste, appearance, nutritional value, and safety. Vermicomposting, as demonstrated by recent research, is associated with increased product quality in process modifications, improved product durability and storage, and improved physiological properties of the product, all of which are expected by many consumers [15,12]. In this regard, vermicomposting necessitates ongoing testing and empirical data to guarantee consistent outcomes. In a similar vein, vermicompost provides crops with important nutrients that are crucial for enhancing the quality of agricultural output since they are easily assimilated by plants and allow for effective flowering with few flaws. Improved nutrient content is related to vermicomposting.

It enhances the pH of juice as well as the micro- and macronutrients, protein, and carbohydrates [12]. Nevertheless, Olle [12] discovered that because vermicomposting contains a lot of nutrients, it is associated with greater consumer health. Plants that are growing properly reach their full potential and contribute vital elements that make the finished products advantageous to both consumers and the environment. Comparative studies have shown that biofertilizers are essential for decomposing complex nutrients, allowing plants to easily access nutrients that guarantee optimal growth and development of products [19]. Furthermore, Kanthesh [17] emphasizes that biofertilizers inhibit microorganisms that

could degrade goods' quality, guaranteeing that they are safe and healthy for ingestion and re-cultivation.

CHALLENGES OF ORGANIC FARMING IN INDIA

Yet, there are still a number of obstacles in India even with the country's broad embrace of organic farming. This section discusses a number of pressing issues that recent studies have brought to light.

LACK OF DOMESTIC MARKET AND IMPORT POLICIES

India's present organic agricultural policy, according to Pathania [9], places a high priority on export-oriented production and pays little attention to developing policies for domestic and import markets. Because there is no regulation on labeling requirements for organic production and logos, it is quite likely that consumers and farmers will not be able to tell organic products apart from conventional ones. Thus, although customers are prepared to pay more for organic items, dishonest practices impede legitimate parties from realizing premiums.

A DROP IN CROP PRODUCTION

According to Elayaraja's [2] research, farmers making the switch to organic farming frequently face lower yields in the initial stages of production. Furthermore, it is unclear how long it will take crops grown organically to become sustainable, which makes farming unprofitable and raises cultivation expenses.

LACK OF ORGANIC SEEDS TO MAINTAIN ORGANIC FARMING

Because native types are suited to react to chemicals and fertilizers, concurrently fertilizer-sensitive and genetic planting materials and seeds put them at risk [2]. Therefore, it prevents farmers from implementing organic farming by creating notable disparities in the supply of high-quality organic seeds. All parties interested in organic farming in India will need to work together to find solutions to these problems.

To support farmers adapt to the consequences of climate change, this might entail creating regulations that support the infrastructure and services needed by organic farmers, raising knowledge of the advantages of organic farming, and funding research and technology.

For instance, through collaborating with seed businesses and offering financial assistance to farmers that utilize them, the government might promote the development and dissemination of organic seeds. Additionally, encouraging the use of composting and organic fertilizers can assist lessen reliance on chemical fertilizers and improve soil fertility, both of which can eventually raise crop yields. In the end, addressing these obstacles will contribute to ensuring the sustainability and long-term viability of organic farming in India.

ORGANIC FARMING FUTURE IN INDIA

India is one of the world's most fertile land-rich countries, with a net agricultural area of 140. 1 million hectares [5]. Alongside the broader agricultural sector, which provides 20–30% of all household income in the nation, it is the main source of economic subsistence [11]. In India, organic farming is still performed traditionally, but with the introduction of new methods and rapid population increase, conventional farming became widely adopted as a solution to the food crisis. The rising understanding of the chemical's effects on soil health and food safety and quality issues, however, is the reason behind the increased demand for organic produce [13].

DISCUSSION

Thirty percent of India's total revenue comes from the agricultural sector, which is an essential part of the country's economy [14]. Although organic farming has long been practiced in India, the modern form of the industry has lately been more well-known due to growing concerns about the quality and safety of

food. This paper highlights the many potential advantages of organic farming for the nation, including meeting the rising need for organic produce, fostering sustainable food security, preserving healthy and sustainable ecosystems, enhancing social health, and striking a balance between environmental preservation and livelihood. But in some locations, there is disagreement regarding the viability and efficacy of organic farming, which needs to be resolved to encourage its widespread use in India.

The authors can propose a course of action based on the facts gathered in this study in order to further the conversation. For instance, comparing organic and conventional agricultural practices in various Indian locations might provide light on the unique opportunities and problems that organic agriculture faces. Studies of this kind can also clarify the possible advantages and disadvantages of converting to organic farming, as well as the social and economic aspects that influence the adoption and efficacy of such methods.

Comprehensive regulations and initiatives, including money for R&D, infrastructure, and market access, are required to encourage the adoption of organic agricultural methods in India. To assist farmers and increase consumer access to their products, India must build a strong supply chain and facilities for organic farming. India can fully realize the promise of organic agriculture to provide sustainable food security and boost the nation's economy by tackling the debates around the practice and concentrating on creating efficient regulations and programes.

Organic farming is controversial even though it has a lot of potential to address important problems like environmental sustainability and food security in India. Some farmers and others contend that because organic farming may result in reduced crop yields and financial losses, it is not viable or feasible to practice on a wide scale. Some people are worried about the increased expenses linked to using organic agricultural methods, such as the need for certification and the usage of organic inputs.

But according to the data in this article, Indian farmers may find organic farming to be a profitable and feasible alternative. Organic farming has been demonstrated to raise crop quality and nutritional content, decrease the need for toxic pesticides and fertilizers, and improve soil health, even if it may initially involve more work and money. Organic farming is also more resistant to climate change and extreme weather, which is why farmers in areas that frequently experience droughts or floods are finding it to be a more appealing option.

CONCLUSION

India's reliance on agriculture to support livelihoods and the nation's economy emphasizes the necessity of implementing sustainable agricultural methods that advance environmental preservation, social well-being, and economic expansion. The natural and biological methods of organic farming are essential for achieving this equilibrium between the natural world and way of life while boosting output and product quality. Organic farming has several advantages in India, but there are a number of obstacles preventing its widespread implementation. To overcome the difficulties, these issues—which range from insufficient legislative frameworks to restricted availability of organic inputs and markets—must be resolved. Stakeholders and governments need to work together and be proactive in order to remove these obstacles. . . This could involve supplying funds for the study and advancement of organic agricultural methods, granting access to organic inputs and seeds, and enhancing the infrastructure of the market to make it easier to sell and distribute organic goods. Extension programmes and community outreach are two otherways that education and outreach initiatives can encourage the adoption of organic farming by educating farmers and consumers about its advantages. Policies that promote organic farming should seek to level the playing field for farmers, guarantee a fair price for organic produce, and offer incentives

for farmers to follow sustainable practises in order to develop a comprehensive and integrated regulatory framework. In addition, governments ought to give top priority to the preservation of natural resources, biodiversity, and organic farming's traditional expertise.

REFERENCES

[1]. Das, S., Chatterjee, A., Pal, T. K. (2020). "Organic farming in India: a vision towards a healthy nation," Food Quality and Safety, vol. 4, no. 2, pp. 69-76, 2020. https://doi. org/10. 1093/fqsafe/fyaa018

[2]. Eayaraja, M., Vijai, C. (2020). "Organic farming in India: Benefits and Challenges," European Journal of Molecular & Clinical Medicine, vol. 7, no. 1, pp. 3021-3029, 2020.

[3]. Dey, S., Achar, S., Dey, A. (2021). "Organic farming: concept, principles, benefits and prospects in India," Agriculture Letters, vol. 2 no. 5, pp. 24-26, 2021.

[4]. Kumari, S. V., Raj, S. (2020). "Organic Farming: Path for Sustainable Ecosystem, Discussion Paper 17," National Institute of Agricultural Extension Management (MANAGE), pp. 1-102, 2020.

[5]. Karunakaran, N. (2021). "Status, benefits and future prospects of organic farming in India: A review". Journal of Management Research and Analysis, vol. 8, no. 3, pp. 103-111, 2021. https://doi. org/10. 18231/j. jmra. 2021. 022

[6]. Madhavi, R., Vijaya, G. S., Malathi, H. (2021). "A Paper on Sustainable Organic Farming in India," International Journal of Modern Agriculture, vol. 10, no. 2, pp. 1080-1088, 2021.

[7]. Kumara, K. T. M., Singh, D. R., Praveen, K. V. (2015). "Economic Benefits from Adoption of Organic Farming in India," Economic Affairs, vol. 60, no. 3, pp. 569, 2015. https://doi. org/10. 5958/0976-4666. 2015. 00080. 7

[8]. Soni, R., Gupta, R., Agarwal, P., Mishra, R. (2022). "Organic farming: A sustainable agricultural practice," Vantage: Journal of Thematic Analysis, vol. 3 no. 1, pp. 21-44, 2022. https://doi. org/10. 52253/vjta. 2022. v03i01. 03

[9]. Pathania, N. (2020). "Organic Farming: Its Objectives, Principles, Types, Techniques, Favourable Circumstances & Downsides," vol. 1 no. 1, pp. 50-55, 2020.

[10]. Yadav, S. K., Babu, S., Yadav, M. K., Singh, K., Yadav, G. S., & Pal, S. (2013). "A Review of Organic Farming for Sustainable Agriculture in Northern India," International Journal of Agronomy, pp. 1–8, 2013.

[11]. Department of Agriculture and Cooperation, Govt of India, "Organic Agriculture (Concept, Scenario, Principals and Practices)," National Centre of Organic Farming, (2017). Available at: https://www. jaivikkheti. in/DMS/Organic%20 Agriculture. pdf

[12]. Olle, M. (2019). "Review: vermicompost, its importance and benefit in agriculture," Journal of Agricultural Science. 2, pp. 93-98, 2019. https://doi. org/10. 15159/jas. 19. 19

[13]. Manida, M. (2021). "Organic Farming – Current Status and Opportunities for Future Development," Agriculture and Food: E-Newsletter, vol. 3 no. 5, pp. 14-18, 2021.

[14]. Cidón, C. F., Figueiró, P. S., Schreiber, D. (2021). "Benefits of Organic Agriculture under the Perspective of the Bioeconomy: A Systematic Review," sustainability, 13 (12), pp. 1-19, 2021. https://doi. org/10. 3390/su13126852

[15]. Gurjar, S. (2022). "Organic Farming in Sikkim -A Sustainable Nexus between Crop Yield and Crop Productivity," Indian Journal of Organic Farming, vol. 1 no. 1, pp. 33-65, 2022.

[16]. Kumar, A., Prakash, C. H. B., Brar, N. S., Kumar, B. ' (2018). "Potential of Vermicompost for Sustainable Crop Production and Soil Health Improvement in Different Cropping Systems,"

International Journal of Current Microbiology and Applied Sciences, vol. 7 no. 10, pp. 1042–1055, 2018. https://doi. org/10. 20546/ijcmas. 2018. 71 0. 116

[17]. Kanthesh M. Basalingappa, Raghu Nataraj. (2018). Gopenathfertility," Academia Journal of Agricultural Research, vol. 6 no. 8, pp. 299-306, 2018. https://doi. org/10. 15413/ajar. 2018. 0130

[18]. Yadav, K. K., Sarkar, S. (2018). "Biofertilizers, Impact on Soil Fertility and Crop Productivity under Sustainable Agriculture," Environment and Ecology. 37 (1), pp. 89-93, 2018.

[19]. Kumar, S., Diksha, Sindhu, S. S., Kumar, R. (2022). "Biofertilizers: An ecofriendly technology for nutrient recycling and environmental sustainability," Current Research in Microbial Sciences, vol. 3, pp. 100094, 2022. https://doi. org/10. 1016/j. crmicr. 2021. 100094

[20]. Pavani, P., Kumar, P. A. D., Bharath, U. (2022). "Futuristic Agriculture (Organic Farming) in India: A Review," Acta Scientific Agriculture, vol. 6 no. 7, pp. 25-31, 2022. https://doi. org/10. 31080/asag. 2022. 06. 1157

Chapter
14

THE THREAT OF HEAVY METALS: UNRAVELLING THEIR TOXICITY AND HEALTH CONSEQUENCES

ARCHANA JUYAL*, SNEHALATHA AND NUKALA NAGA PAVANI SAI SRINIDHI

Department of Chemistry, St. Pious X Degree & PG College for Women,
Hyderabad, Telangana, India
*Corresponding author E-mail: chemarchana23@gmail.com

ABSTRACT

Heavy metals pose significant environmental and public health concerns, involving aspects of environmental science, occupational safety, nutrition, and human health. These Heavy metals have multiple applications in industrial, domestic, agricultural, medical, and technological areas whichled to their wide distribution in the environment and resulted in serious concern over their effects onhuman health and environment. Exposure to these metals at concentrations exceeding a certain threshold can lead to acute and chronic poisoning effects. Major sources include industries, mining, combustion byproducts and contaminated food and water. Their toxicity depends on factors like dose, exposure type, and the specific metal. The metal toxicity can result in issues like oxidative stress, ROS (Reactive oxygen species) production, enzyme site interference, DNA damage, and neurological effects. These metals are a matter of concern due to their bioaccumulative, non-biodegradable, low threshold, and multisystem impact nature. This review simplifies the sources, cell disruption pathways, and health effects of heavy metals, emphasising the need for a holistic approach to tackle the issue.

KEYWORDS: Heavy Metals; Oxidative Stress; Carcinogens; ROS; Acute and Chronic Effects.

INTRODUCTION

Metals are natural materials that are found in the earth's crust. They are malleable, lustrous, andhave high electrical conductivity. Metals have the ability to lose an electron involuntarily and form cations. A metal's distribution is controlled by its different environmental factors and also by its properties. On the other hand, heavy metals can be described as materials with more than 5g/cm^3 specific density. Heavy metals when present in low concentrations help in contributing to various biochemical and physiological functions but ironically, they are also a major contributor to environmental pollution when present in high concentrations, and their increasing toxicity is now amajor problem all over the world.

This chapter's objective is to discuss various heavy metals, their toxic mechanisms, and their health effects.

HEAVY METALS

Heavy metals play a significant role in various domains such as industries, agriculture, medicine, and technology, and through these human activities, they enter the food chain by natural means. Themost commonly found heavy metals are Arsenic, lead, mercury, chromium, cadmium, iron, etc. These heavy metals due to oxidation-reduction properties often escape mechanisms like homeostasis and bind to protein sites, causing cell malfunction.

Arsenic (^{33}As)

Environmental Occurrence, Uses, and Human Exposure

Arsenic is the 12th most abundant semimetal having toxic and carcinogenic properties. It mainly appears as trivalent arsenite and pentavalent arsenate, along side methylated forms. Arsenic is present in the form of oxides, sulphides, and common metal salts (Fe, Na, Ca, Cu), prevalently as arsenite and arsenate compounds. Exposure to arsenical pesticides, natural mineral deposits, disposed arsenical chemicals, and deliberate consumption may lead to lethal effects on the environment and living creatures. It's used in agriculture and medicine which impacts people globally. Arsenic pollution arises from natural events and human activities. Exposure happens via, ingestion, inhalation, dermal contact, and occasionally, the parenteral route.

Mechanism of toxicity

Most cases of human toxicity from arsenic occur due to exposure to inorganic arsenic. Inorganic trivalent arsenite [As (III)]. is 2–10 times more toxic than pentavalent arsenate [As (V)]. Human beings along with microorganisms like algae, fungi, and bacteria, carry out a biotransformation process in which iAs (inorganic Arsenic species) are enzymatically (methyl transferase) converted toMMA (monomethyl arsonic acid) and DMA (dimethyl arsinic acid). In this detoxification process, MMA (III) is not excreted (remains as an intermediate product) which is found to be carcinogenic while MMA (V) and DMA (V) are excreted acting as the bioindicators for chronic arsenic exposure.

iAs (V) →iAs (III) → MMA (V) →MMA (III) → DMA (V)

Health effects

Arsenic is highly carcinogenic and can cause cancer of the lungs, liver, skin, and bladder. Exposure to the toxicity of Arsenic can be explained in 3 levels: Lower, Chronic, and Long-term (Figure 1 shows the health effects of Arsenic).

Fig. 1: Arsenic toxicity

Lead (^{82}Pb)

Environmental Occurrence, Uses and Human Exposure

Lead is the 36th most abundant rare bluish-grey metal and causes wide spread environmental contamination and health problems. Human activities like burning fossil fuels, mining, and

manufacturing release significant amounts of lead into the environment. Despite its toxicity, lead has many industrial, agricultural, and domestic uses. Its sources include asoline, lead bullets, plumbing pipes, toys, and faucets (other sources mentioned in Figure 2). It reaches plants and humans through soil fixation. Uniquely, it does not have a biological function, rather it suppresses the overall growth of the plant by damaging the chlorophyll and photosynthetic process. Lead exposure primarily happens through inhaling contaminated dust or ingesting tainted food, water, and paint

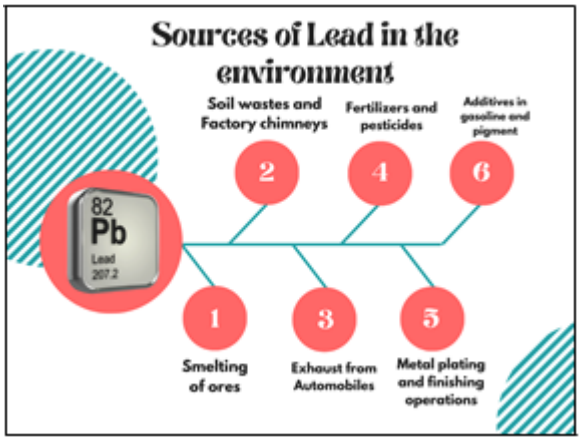


Fig. 2: Sources of Lead

Mechanism of toxicity

Studies show that lead's toxic mechanism involves mimicking and inhibiting calcium, incorporating it into the skeleton, competing for binding sites, and inhibiting enzymatic activity. One of the toxic mechanisms Lead causes is oxidative stress; an imbalance between the presence of Reactive Oxygen Species (ROS) and the generation of Antioxidants which neutralise the free radicals induced from ROS. This is because the lead influences the increase in the level of ROS and decrease in the production of Antioxidants such as Glutathione. Conventionally, Glutathione neutralises Peroxide (H_2O_2) by converting GSH (A reduced form of Glutathione) to GSSG (oxidised form) by oxidation-reduction process, giving out an H_2O molecule. This gives the normal concentration of GSH to be 90% of the total Glutathione and oxidised form (GSSG) accounts for 10% under normal conditions. Under Oxidative Stress caused by Lead Toxicity, the concentration of GSSG exceeds GSH.

$GSH+H2O2 \rightarrow GSSG+H2O$

Anotherform of Lead Toxicity is Lipid Peroxidation which ultimately causes damage to cells, proteins, nucleic acids, and lipid membranes at the structural and cellular level.

Lead ions can also replace several monovalent and bivalent cations, ultimately disturbing biological functions such as cell adhesion, cell signalling, protein folding, apoptosis, neurotransmitter release, etc.

Health effects

The Central nervous system and gastrointestinal tract are common areas of Lead infections found inboth adults and children alike and this metal poisoning is one of the classic diseases. Drinking watermay be one of the common areas of disease if lead and its compounds are carried in the pipes. Lead is also considered as a carcinogen. Lead toxicity and poisoning can be cured with proper precautionary tools. The levels of Lead toxicity can be Acute and Chronic exposure. Additionally, elevated Lead levels in the blood (>10µg/dl) can cause cellular and neurological effects.

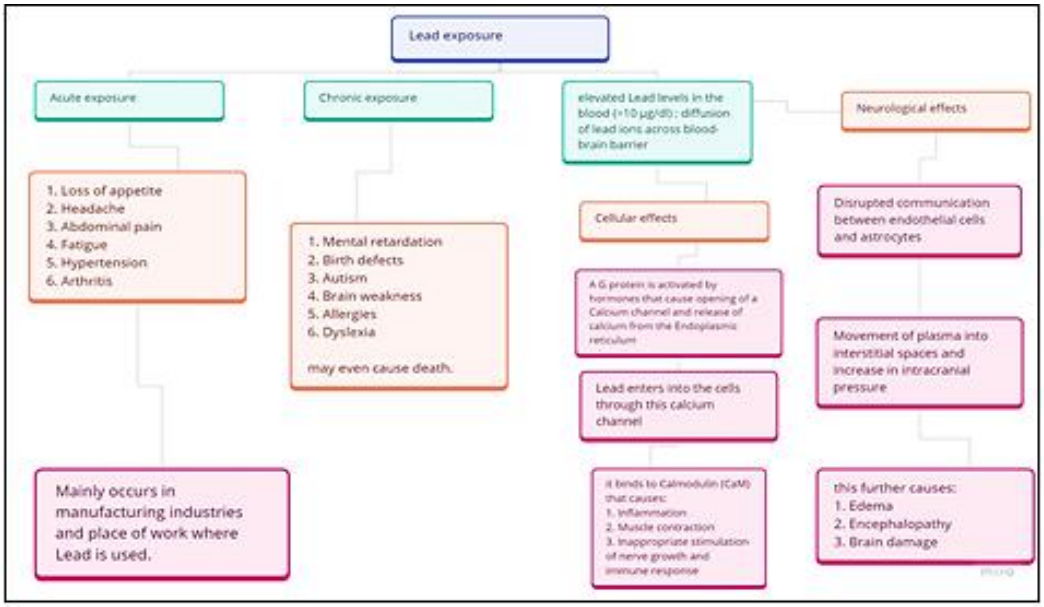


Fig. 3: Exposure of Lead

Mercury (^{80}Hg)

Environmental Occurrence, Uses and Human Exposure

Mercury, a transition element, has elemental, inorganic, and organic forms with distinct toxicities. Elemental mercury, at room temperature, has high vapour pressure, released into the environment. It also exists in mercurousor mercuric cation states. Mercury isused in the electrical industry, dentistry, pharmaceutical preservation, industrial processes, and wood preservation. It primarily comes from agriculture, municipal and industrial waste water, and mining. In soil and water, it's convertedby microorganisms into highly toxic methyl mercury.

Mechanism of Toxicity

Methyl mercury, an eurotoxic compound causes mitochondrial damage, lipid peroxidation and microtubule destruction. Mercury's target organ is the brain, however, it also affects the kidneys, nerves and muscles. When methyl mercury undergoes a reaction by binding with sulfhydryl group it can alter the cellular function and structure by damaging the tertiary and quaternary proteins. It alsocan interfere with transcription and translation processes and can eradicate endoplasmic reticulum and ribosomes. Cell membranes are permeable to organic mercury because of their lipophilic nature.

Health effects

Mercury poisoning is also known as acrodynia or pink disease. Mercury vapours cause bronchitis, asthma and temporary respiratory problems. Mercury Chloride and methyl mercury are considered carcinogens, although our nervous system is sensitive to all kinds of mercury. Increased levels of Mercury can cause damage to the foetus, kidneys and brain by causing memory problems, depression and irritability. Shorter time exposure can lead to vomiting, nausea, diarrhoea, skinrashes and tachycardia.

Cadmium (^{48}Cd)

Environmental Occurrence, Uses and Human Exposure

Cadmium, a widespread heavy metal in Earth's crust, mainly accumulates in sedimentary rocks and marine phosphate. It ranks 7th among the most toxic heavy metals and is highly bioaccumulative. Cadmium is commonly used in rechargeable batteries and alloy production. Cadmium, a componentin tobacco smoke, leads to acute and chronic intoxication through inhalation and ingestion. Plants absorb

cadmium from the soil, contaminating fruits and vegetables. Inhalation and ingestion are the primary exposure routes. While cadmium emissions have decreased, it remains a concern for workers. Smokers face higher cadmium exposure as tobacco plants uptake cadmium from the soil, while non-smokers get lower exposure through food.

Mechanism ofToxicity

Cadmium causes damage to cells primarily through the generation of ROS, which causes single-strand DNA damage and disrupts the synthesis of nucleic acids and proteins.

Health effects

Cadmium can be fatal if inhaled or ingested. Acute ingestion of cadmium causes abdominal pain, burning sensation, nausea, vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness, and convulsions. On the other hand, Chronic exposure to cadmium has a depressive effect on levels of norepinephrine, serotonin, and acetylcholine. Cadmium is highly toxic to thekidney and it accumulates in the proximal tubular cells in higher concentrations. Cadmium cancause bone mineralization.

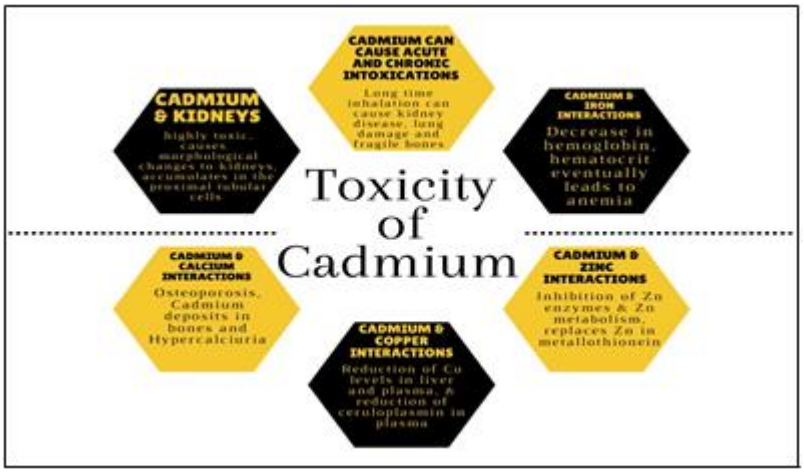


Fig. 4: Interactions of Cadmium

Chromium (^{24}Cr)

Environmental Occurrence, Uses, and Human Exposure

Chromium, Earth's 7th most abundant element, has various oxidation states. Cr (III) in ores like ferrochromite is extracted from natural sources like coal, oil, petroleum, refractory material, and oil drilling. It threatens biological species when used in metallurgy, electroplating, paint production, and tanneries. While Cr (III) is immobile and not a ground water contaminant, oxidation to Cr (IV) with excess oxygen makes it highly toxic and contaminates groundwater. Cr (VI) is a Group 1 human carcinogen. Industrial emissions, mainly from metallurgy, refractories, and chemicals, increase environmental chromium, harming farmland and crops. Chromium toxicity affects iron-containing plant enzymes like catalase and cytochrome oxidase.

Mechanism of toxicity

Cr (VI) compounds are potent oxidizers, more toxic than Cr (III). The key to this difference is Cr (III)'s limited membrane permeability compared to Cr (VI). Cr (VI) easily enters cells, while Cr (III) is poorly absorbed, making it less toxic. Reduction of Cr (VI) away from the target site is considered as a detoxification process whereas the enhancement of toxicity can be seen during reduction in or near the nucleus of the target organ. Cr being a strong oxidising agent undergoes reduction to release tetravalent (Cr^{4+}) and pentavalent (Cr^{5+}) Chromium. If the reduction occurs a way from the target, Cr (V) is stabilised by detoxification through Gluta thione. Near the target region, intracellular reduction of Cr (IV) occurs

which helps in the activation of Cr. Reactions with ascorbate and thiols influence the increase of ROS (H_2O_2, O_2^{2-}, OH-) and the oxidative stressresults, ultimately leading to DNA and Protein damage.

Health effects

Chromium compounds can result in the formation of Ulcers that do not heal quickly. Nasal septumulcers are very common in the case of chromate workers. High chromium exposure can result ininhibition of erythrocyte glutathione reductase which makes the reduction of methemoglobin to haemoglobin difficult. Through some in vitro and in vivo experiments, it was found that chromate compounds can create DNA damage that leads to the formation of chromosomal aberrations, sister chromatid exchanges, and alterations in the replication and transcription of DNA.

Aluminium (^{13}Al)

Environmental Occurrence, Uses, and Human Exposure

Aluminium, the 3rd most abundant element, is widespread in air, water, and soil, primarily in the 3^+ oxidation state. It turns highly toxic in acidic conditions (pH<5), due to soil acidification from acid rain, leaching silicon and forming unstable aluminium oxyhydroxides like gibbsite and boehmite. These release phytotoxic Al^{3+} ions, causing cellular changes, chlorosis, and foliar necrosis, resulting in forest drying, plant damage, and crop reduction. In gill-breathing aquatic organisms, aluminium interferes with vital gill enzymes, disrupting osmoregulation. It also inhibits enzymes like hexokinase, phosphodiesterase, and alkaline phosphatase, affecting metabolism and health. Human exposure occurs through inhalation, ingestion, and dermal contact, mainly via water, food, beverages, and drugs.

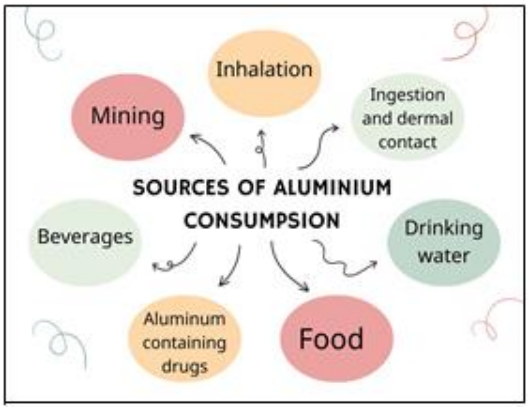


Fig. 5: Aluminium consumption

Mechanism of toxicity

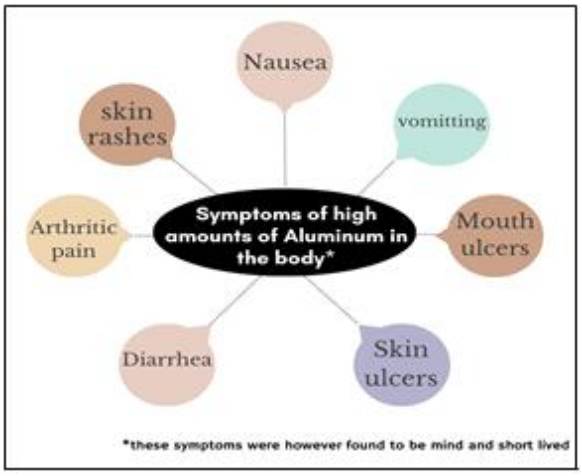


Fig. 6: Symptoms of high amounts of Aluminium

Aluminium interacts with plasma membranes in apoplastic and symplastic targets. Its ionic form replaces Mg^{2+} and Fe^{3+} causing disruption in intercellular communication, cellular growth, and secretory functions. Neuron change by Aluminium was found to be similar to the degenerativelesions of Alzheimer's patients. The neurotoxic effects extend to problems such as neuronal atrophy in different parts of the brain.

Health effects

Aluminium toxicity has dangerous effects on the nervous system and can cause loss of memory, loss of coordination, and balance. Renal dysfunction leads to Aluminium accumulation causing bone (adynamic bone disease) and osteomalacia. Someother complications include lung problems, anaemia, nervous system problems, etc. Symptoms of high amounts of Aluminium are listed in Figure 6.

Iron (^{26}Fe)

Environmental Occurrence, Uses, and Human Exposure

It is the 2nd most abundant heavy metal which has vital effects on the growth and survival of several living creatures. It is present in cytochromes, catalase, and proteins like Haemoglobin and Myoglobin. In mining processes, the Iron pyrites (FeS_2) undergo oxidation to produce Ferric ions and Sulfuric acid. This Redox property of Ferrous (Fe^{2+}) and Ferric (fe^{3+}) ions is extremely common.

$2FeS_2+7O_2 \rightarrow 2FeSO_4+H_2SO_4$ (Ferrous)

$4FeSO_4+O_2+10H_2O \rightarrow 4Fe(OH)_3+4H_2SO_4$ (Ferric)

In the deep ocean, Fe levels are around 33. 5×10-9 mg/L, while freshwater has as little as 5µg/L. Groundwater has high iron levels, up to 20 mg/L, affecting drinking water. Iron threatens aquaticlife directly and indirectly, impacting periphyton, invertebrates, and fish. Iron toxicity, with a 1mg/L total iron concentration, inhibits aquatic plant growth, like rice, causing root uptake of Fe2+, leaf translocation, leaf bronzing, yield loss, and, when coupled with Zinc deficiency, macronutrient disorders.

Mechanism of toxicity

Failure of Iron binding to protein releases harmful free radicals thereby affecting the concentration of Iron in mammalian cells and biological fluids, ultimately leading to corrosive effects in the gastroin testinal tract and lipid peroxidation. The free iron disrupts oxidative phosphorylation releasing H+ ions and increasing metabolic acidity; these Hydrogen free radicals then attack the DNA causing cellular damage and mutation. Iron toxicity severely affects cellular organelles like mitochondria, microsomes, and lysosomes.

Health effects

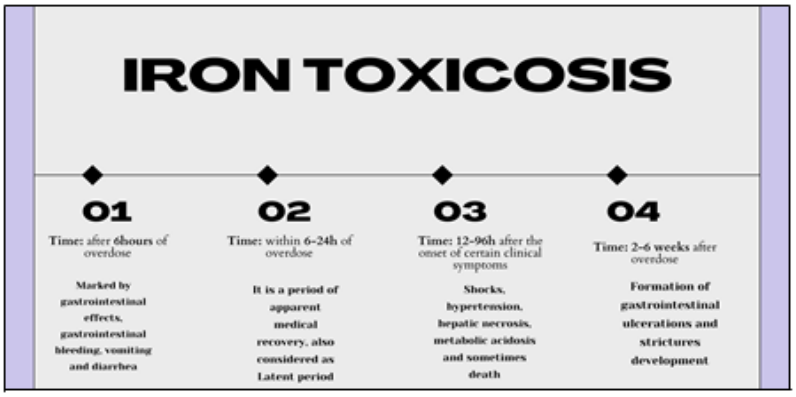


Fig. 7: Iron Toxicosis

Children are exposed to iron toxicity as they are exposed to high iron-containing products. Irontoxicity occurs in 4 stages (Figure 7 shows the different stages and consequences). Additionally, workers exposed

to asbestos (containing 30% iron) have a high chance of asbestosis, which is the most important cause of lung cancer.

Iron toxicity causes an increase in the concentration of free radicals such as peroxide and superoxide, which influences iron release from ferritin. This consequently leads to Hydroxyl production in a process explained in Figure 8.

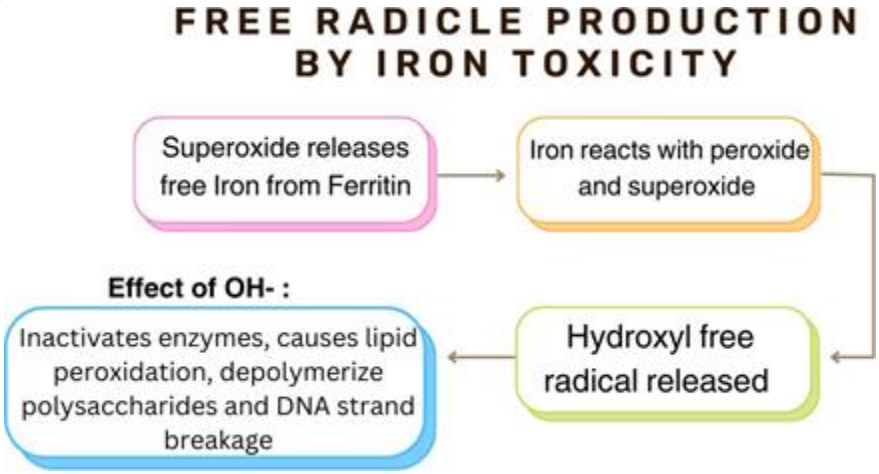


Fig. 8: Free Radicle Production by Iron Toxicity

CONCLUSIONS

In this chapter, were viewed some of the heavy metals, i. e. arsenic, lead, mercury, cadmium, chromium, aluminium and iron, their toxicity and health effects. The mechanisms and effects arespecific, varying from element to element and also their oxidation states. For example, mercurytargets the nervous system while cadmium is particularly harmful to the kidneys. The extent of poisoning depends on genetics, individual health, and concentration. We must look for a way to reduce occupational exposure with engineering methods and monitor intervention to prevent additional exposure. Chelation therapy is a method to subside the high levels although prevention isconsidered ideal.

REFERENCES

[1]. Monisha Jaishankar, Tenzin Tseten, Naresh Anbalagan, Blessy B. Mathew, Krishnamurthy N. Beeregowda (2014): Toxicity, mechanism and health effects of some heavy metals, Interdiscip Toxicol. 2014; Vol. 7 (2): 60–72.

[2]. Paul B. Tchounwou, Clement G. Yedjou, Anita K. Patlolla, and Dwayne J. Sutton; Heavy Metal Toxicity and the Environment, Experientia Supplementum, Volume 101: 143-164.

[3]. Fergusson JE (1990): The heavy elements: chemistry, environmental impact and Health effects. Pergamon, Oxford

[4]. Duffus JH (2002): Heavy metals—ameaningless term? Pure Appl Chem 74: 793–807

[5]. Bradl H (2002): Heavy metals in the environment: origin, interaction and remediation, vol 6. Academic, London

[6]. Goyer RA (2001): Toxic effects of metals. In: Klaassen CD (ed) Cassarett and Doull's toxicology: the basic science of poisons. McGraw-Hill, NewYork, NY, pp811–867

[7]. Bernard A. (2008): Cadmium & its adverse effects on human health. Indian J Med Res 128 (4): 557–64.

[8]. Chandra P, Kulshreshtha K. (2004). Chromium accumulation and toxicity in aquatic vascular plants. Botanical Rev 70 (3) : 313–327.

[9]. Patlolla A, Barnes C, Yedjou C, Velma V, Tchounwou PB (2009) Oxidative stress, DNA damage and

antioxidant enzyme activity induced by hexavalent chromium in Sprague Dawleyrats. Environ Toxicol24: 66–73

[10]. Goyer RA. (1990). Lead toxicity: from overt to subclinical to subtle health effects. Environ Health Perspect 86: 177–181.

[11]. Jaishankar M, Mathew BB, Shah MS, Gowda KRS. (2014). Biosorption of few heavy metal ions using agricultural wastes. Journal of Environment Pollution and Human Health, 2 (1): 1–6.

[12]. Mala Das Sharma, Archana Juyal, Karuna Mantha and Subrata Das Sharma Astudent-centric research and education programme on heavy metal pollution of water bodies from selected Indian cities, Current Science, Vol. 111, NO. 8.

[13]. Das Sharma, M., Juyal, A., Karuna, M. and Das Sharma, S. (2015). Spectrophotometer-based student education program on health hazard assessment due to Cr(VI) and Pb contamination in surface and groundwaters of Hyderabad City, India, Pollution, 1 (2): 139-149, Spring2015.

[14]. Khlifi R, Hamza-Chaffai A. (2010). Head and neck cancer due to heavy metal exposure via tobacco smoking and professional exposure: Areview. Toxicol Appl Pharmacol 248: 71–88.

[15]. Flora SJS, Mittal M, Mehta A. (2008). Heavy metal-induced oxidative stress & its possible reversa lby chelation therapy. Indian J Med Res128: 501–523.

[16]. Mazumder G. (2008). Chronic arsenic toxicity & human health. Indian J Med Res128 (4): 436–447.

[17]. Morais S, Costa FG, Pereira ML. (2012). Heavy metals and human health, in Environmental health–emerging issues and practice (OosthuizenJ ed), pp. 227–246, InTech.

[18]. Patrick L. (2003). Toxic metals and antioxidants: Part II. The role of antioxidants in arsenic and cadmium toxicity. Altern Med Rev 8 (2): 106–128.

Chapter 15

A REVIEW ON NON-EDIBLE OILS AS BASE STOCK FOR THE LUBRICANTS

CH. SNEHALATHA* AND ARCHANA JUYAL

Department of Chemistry, St. Pious X Degree & PG College for Women,
Hyderabad, Teleangana, India
*Corresponding author E-mail: snehareddych@gmail.com

ABSTRACT

As the stock of fossil fuels diminishes, throughout the world and demands for energy-based comforts and mobility ever increasing, there is a need to increase bio lubricant production. Bio lubricant is an alternative lubricant different from mineral oil lubricant as it is prepared from non-conventional energy resources and is nontoxic, biodegradable, and eco-friendly. India has great potential for the production of lubricants from non-edible oilseeds. From about 100 varieties of oil seeds, only 13-14 varieties have been tapped so far. The promising non-edible sources in India are *Pongamia pinnata* (Karanja), *Melia Azadirachta* (Neem), Rice Bran oil (*Oryza sativa*) and *Jatropha curcus*.

This review paper assesses and integrates the biological, chemical, and genetic attributes of the plant and describes the different tree-borne oilseeds in India, extraction of oil from tree-borne oilseeds, properties, composition, and future potential of bio lubricant. Non-edible oils and their chemically modified derivatives can be produced at a relatively cheaper cost than similar oils marketed in the developed world and can be introduced in India with immense environmental and performance benefits, particularly in applications involving high environmental contamination safety and public health.

KEYWORDS: Biolubricant, Eco-friendly, Biodegradable.

INTRODUCTION

A lubricant is a substance introduced between two moving surfaces to reduce the friction and wear between them. Lubricants contain 90% base oil and 10% additive Petroleum-based lubricants comprise a very high percentage of the liquid lubricants which continue to be the predominant form of lubrication for machineries. Over 95% of the lubricants in use today are based on petroleum-based oil. currently, 50% of all lubricants sold worldwide end up in the environment via total loss applications, volatility, spills, or major accidents. In view of its high ecological toxicity and low biodegradability, it poses a considerable threat to the environment. Concerns over the discharge and accumulation of lubricants and fuels on land, water, and air led to the framing of policies discouraging the use of conventional petroleum-based lubricants in several applications and encouraging their replacement with rapidly biodegradable lubricants.

The triacylglycerol structure of vegetable oils makes it an excellent candidate for its potential use as a base stock for lubricants. It is generally recognized that mineral oil lubricants represent a potential danger in many applications because they are not readily biodegradable and are toxic. The need for biodegradable and nontoxic lubricants has been recognized especially in applications where they come in contact with soil ground water. The term biodegradable is defined as the ability of a substance to be decomposed by the action of microorganisms. Some of the important properties necessary for a

satisfactory lubricant performance are viscosity, low volatility, superior stability, compatibility etc. low volatility under operating conditions: Volatility characteristics are essentially inherent in the choice of base stock oil for a particular type of service. Viscosity gives an indication of the volatility of a lubricant: in general, the lower its viscosity the higher its volatility. Satisfactory viscosity characteristics in the temperature range of use. The viscosity of engine oil is one of its most important and most evident properties. Chemical additives, fuel dilution, contaminants from within and outside of the engine, wax in the oil, oil oxidation, volatilization, and many other materials found in or added to the oil affect the viscosity in advantageous or disadvantageous ways. Superior stability or ability to maintain desirable characteristics for a reasonable period of use: The factors, which affect the lubricant stability are temperature, oxygen, contamination with water, unburned fuel fragments, and corrosive acids, which limit the useful life of a lubricant. All lubricating oils react with oxygen in the air, eventually forming acid or sludge products. These products could cause surface corrosion or blocking of oil lines. There are numerous laboratory tests for oxidation stability. All tests depend on artificially accelerated oxidation, by heating the oil and by blowing air or oxygen through it, in some cases in the presence of a catalyst. This is the area where additives have made a major contribution in improving the performance characteristics and extending the useful life of lubricants compatibility with material parts in the system: Compatibility of lubricants with bearings, seals, clutch plates, etc. may also be partially associated with the base oil. However, additive chemistry can have a major influence on such characteristics.

Lubricating oils find applications in engines, industrial uses, greases, and automotive transmissions. The major uses of these oils are in engines (55 percent), industry (27 percent), processes (9 percent), greases (5 percent), and automotive transmissions (4 percent). Vegetable oils or the derived lubricants are primarily triglyceride esters or their modifications derived from plants. Use of the vegetable oil-derived lubricant base oils is preferred for certain specific applications. Commonly employed include high oleic canola, castor, palm, sunflower, tall and rapeseed oils from vegetable sources, and tallow fat from animal sources. Vegetable oils are often hydrolyzed to yield the acids which are then subsequently combined selectively with other alcohols to form specialist synthetic esters. Other naturally derived lubricants include lanolin, a wool grease which itself is a natural water repellent. Vegetable oils are rapidly replacing petroleum-based lubricants. This is an invention of history because such oils were used for these purposes before the advent of hydrocarbon lubricants.

Today's demand for lubricants is so large and products based on vegetable oilsmake only a small contribution of 3-5% of the total lubricant requirement. Nevertheless, there is a growing demand for vegetable oil-based products particularly in situations where there is a rapid loss of lubricants e. g with chain–saws where the chain lubricant is lost on to forest floor and in outboard engines (particularly on inland lakes and seas) where lubricants are spilled into the water. Under these conditions, the shorter life of the vegetable oil-derived lubricants is not a serious disadvantage and this is more than balanced by ecological factors.

Pour point Characteristics of oil: The temperature at which the oilno longer flows is called the pour point. The pour point depends on the viscosity and chemical structure of the oil. In paraffinic oils, stiffening is caused by the wax in the oil, which is distinguishable as crystals. As the temperature of the oil is gradually lowered, there is a corresponding increase in the size of crystals, eventually forming a flow-preventing network within the oil. Naphthenic oils remain fluid at lower temperatures than paraffinic oils. Fully synthetic oils do not contain wax and their low-temperature properties are excellent. The pour point can be improved by using an additive that prevents the growth and interconnection of wax crystals.

The pour point indicates approximately the cold start properties of oil. However, it is important to know the true oil viscosity at the starting temperature.

Vegetable oils, modified vegetable oils, and synthetic esters are the most common base stocks for biodegradable lubricants. Synthetic esters represent a fairly recent development in the lubrication market. Synthetic esters offer improved performance compared with all other lubricants. The polar groups present also make vegetable oils better solvents for sludge and dirt removal, which would be otherwise deposited on the surface being lubricated. Because of these properties, reduced amounts of additives like friction modifiers, antiwear agents, and dispersants are required to formulate vegetable oil-based lubricants.

Vegetable oils are obtained from natural and renewable sources, therefore their chemical composition varies somewhat from one crop to another. They have some undesirable characteristics like poor cold-temperature properties and oxidation stability compared to petroleum-based oil, and special additives are needed to overcome these problems. Vegetable oils have many good natural properties including good lubricity, good resistance to shear, a high flash point, and a high viscosity index. Vegetable oils vary in price but, in general, are about twice as expensive as petroleum-based oils. The major drawback of vegetable oil-based lubricants is the poor thermal and oxidative stability due to the presence of unsaturated linkages in the carbon chain. Hence, they find use in applications where high temperatures are not encountered. Later developments resulted in the use of nonedible oils as lubricating base fluids. The lubricant basenon-edible vegetable oil, has the requisite potential to provide the desirable physiochemical characteristics. Hence the present investigation to pertainsstudy on nonedible oils Karanja, Jatropha, Neem, and Ricebran oilsfor the preparation of lubricant base stocks focusing mainly onviscosity, low-temperature properties, andtheir physical-chemical properties.

NON-EDIBLE TREE BORNE OILSEEDS

National Oilseeds and vegetable oils development (NOVOD) board is promoting, Karanja, Neem, Jatropha, Rice bran, etc, and many other tree-borne oilseeds, as India stands at the sixth place in the world in energy needs and overall demand of crude oil which is expected to rise annually by 6. 2%upto 2013

KARANJA (*Pongamia glabra*) *Pongamia glabra* is from the family Leguminaceae is and widely distributed in dry tropical Asia. Major producing countries are India (annual production of 60 MT), the Philippines, and the East Indies. It has high oleic acid content which is required for desirable bio lubricant and is non-edible oil. The oil content extracted byvarious authors ranges between 30. 0 to 33%. The fatty acid compositions of karanja oil determined by EMS is given in Table 1.

NEEM OIL (*Mellia azadirachta*) The Neem tree occurs in all parts of India, representing a large scattered source of oilseeds. Neem is of the Meliaceae family. The other names of neem are Margosa, Veppam, Vepun, Nimba, Vepa (Telgu), etc. The major fatty acid composition of neem oil is given in Table 1. Neem oil is unusual in containing non-lipid associates often loosely termed as "bitter" and organic sulphur compounds that impart a pungent, disagreeable odor

JATROPHA (*Jatropha curcas* L.) belonging to the Euphorbiaceae family, is mostly foundin tropical and subtropical regions of the world. Various parts of the plant finduse for a wide range of applications. Recent interest includes the use of seed oil asraw material for lubricant

RICE BRAN OIL (*Oryza sativa*) is from the family Graminaceae. Major producing regions are Asia, Africa, and America. Rice bran is a by-product of the pearling process of rice and comprises the pericarp, aleurone layer, embryo, and some endosperm. Crude rice bran oil is a non-edible oil. In India its production is 30MT. Its fatty acid composition is given in Table 1.

Table 1: Fatty Acid Composition of Non edible oils

Characteritics	Karaja oil	Neem Oil	Jatropha Oil	Rice Bran Oil
Saturated Acids				
C12	1. 6	-	-	-
C14	7. 9	-	-	0. 4
C16	4. 0	14	15. 8	17. 0
C18	2. 0	19	7. 3	2. 7
Unsaturated FattyAcids				
C18:1	62	49	43	45. 5
C18:2	12	9. 5	32	27. 7
C18:3	5	-	0. 2	-

The non-edible oils currently available as starting materials in India Include Neem oil, Karanja oil, Rice bran oil, Castor oil, Linseed oil, and Mahua oil. Vegetable oils are long-chain fatty acid triesters of glycerol. The fatty acid may differ in saturation and chain length, which provide most of the desirable lubricant properties such as good boundary lubrication, high viscosity index, high flash point, and low volatility Table 2. In India [40-42]. large quantities of low-costvegetable oils of forest and wasteland origin are available which can be converted easily by such means as hydrogenation, transesterification, acetylation and alkylation into lubricant base fluids of moderate to high Thermo oxidative stability, low-temperature flow properties, superior viscosity-temperature and lubricity characteristics. These products are non-toxic and 90-100% biodegradable. The purchasing cost of finished base fluids may be up to 2. 5 times that of highly refined hydrocracked VHVI oils. Most of these formulated oils may require noantiwear additives or viscosity index improvers, and only relatively small quantities of dispersants and emulsifiers. The overall performance could turn out to be superior to the conventional petroleum-based oils. Apart from a cleaner environment, these oils are expected to provide energy efficiency, fuel economy, longer service life, and better health and safety. Vegetable oils were transesterified by reacting with ethyl hexanol, which has been treated earlier with sodium. The temperature was kept near the boiling point of alcohol and the reaction was refluxed. The excess ethyl hexanol was distilled under a vacuum. The lower layer was acidified to a pH of 4-5 and withdrawn. The upper oil layer dissolved in toluene was refluxed with a Dean and Stark trap to remove water. The toluene was distilled off yielding the ester. The ester was percolated over Fuller's earth to remove organic acidity and obtain the straw yellow product. Performance evaluations of various lube oil formulations were conducted to find out their suitability (Table 2). The main characteristics for evaluation were oxidation stability, Thermal stability, corrosion, deposit forming tendency on the hot metal surface, lubricity Kinematic Viscosity, Flash point, Acid Value, oxidation, lubricity, etc

The study indicates that the formulations meet the requirements of biodegradability also. Vegetable oils and its esters are well known to be biodegradable. It is possible to formulate automotive and industrial lube oil from vegetable oil esters for applications such as Engine Oils, Two Stroke Oils, Compressor Oils, Aviation Oil, Metal Working Fluids, Insulating Oils, Gear Oils, Hydraulic Oils, and refrigeration oils, etc. Trends in gear oil and transmission oils are currently undergoing significant change. Most passenger cars, buses, and goods transport vehicles sold in the USA incorporate automatic transmission. The trends towards the use of alternative refrigerants as replacements for ozone-depleting CFCs, improved heat transfer, filled-for-life refrigeration lubricants and maximization of operational efficiency has made polyol esters and diesters attractive replacement for conventional low-temperature petroleum-based

lubricants. The loss of hydraulic fluids used in agricultural machinery, earthmoving machinery, tunneling machinery, snow crawlers, and deck machinery on ships, waste trucks, and road cleaners is uncontrollable and contributes severely to soil contamination because of the toxicity of conventionally used petroleum-based and synthetic hydrocarbon-based fluids and even Phosphoesters.

Table 2: Typical Specifications and Characteristics of Four Bio-Lubes

Characteristics	Karanja Oil	Neem Oil	Jatropha Oil	Rice bran OiI
Kinematic Viscosity, cSt 40^0 C 100^0 C	 43. 42 8. 35	 68. 04 10. 15	 138 18	 23. 75 6. 06
Visocity Index	172	134	119	222
Pour point	-9	9	-9	3
Iodine value	78	62		108
Acid value	22	23	20	86
Saponification Value	176	169	182	183

CONCLUSION

The study of Fattyacid composition and viscosity, high viscosity index and low pour point of all nonediable oils conforming that these oils are suitable for the biodegradable lubricants. A Contaminated environment is expensive. Conventional mineral oil-based lubricants are extremely harmful to the biosphere when they get into the environment. Due to poor degradability mineral oils remain in the ecosystem for a long time. Even in the case of high dilution, the effect will be fatal (eco-toxicological effect). A higher amount will be required for the elimination of contaminated ecosystems clearly. Eco-friendly hydraulic oil, refrigerator oil, gear oil, motor oil, two-stroke engine oils, lubricants for food processing and water management and disposal operations, and eco-friendly greases for both general purpose and multipurpose should be widely used. Eco-friendly biodegradable lubricants have to be immediately introduced in the market to replace the mineral oil and other non-biodegradable products currently in use in these countries to check the rampant pollution caused by these lubricants. Edible oils are in use in developed nations such as the USA and European nations but in developing countries, the production of edible oils is not sufficient. In a country like India, there are many plant species whose seeds remain unutilized and underutilized and have been tried for biodiesel production. Non-edible oil seeds are the potential feedstock for the production of bio-lubricants in India.

REFERENCES

[1]. Stability of vegetable based oils used in the formulation of eco-friendly lubricants – a review, EgyptJ. Petrol., 29 (3) (2020). pp. 251-256, 10. 1016/j. ejpe. 2020. 09. 003

[2]. F. J. Owuna, M. U. Dabai, M. A. Sokoto, S. M. Dangoggo, B. U. Bagudo, U. BirninYauri, L. G. Hassan, I. Sada, A. L. Abubakar, M. Jibrin. (2019). Chemical modification of vegetable oils for the production of biolubricants using trimethylolpropane: a review, EgyptJ. Petrol., 29 , 10. 1016/j. ejpe. 2019. 11. 004

[3]. National Oilseeds and Vegetable Oils Development Board, Ministry of Agriculture, Govt. of India 6th May, (2008).

[4]. Azam A. M., and Nahar N. M., (2005). Biomass and Bioenergy. 2005 Article in press.

[5]. Katwal RPS, Soni PL. (2003). Indian Forester 2003; 129 (8):939-49.

[6]. Eckey, E. W. (1954). Vegetable Fats and Oils, Reinhold Publishing Corp, 1954 p 559.

[7]. Rumkini, C., Food Chemistry, Vol26, No. :2, p. 119-124.

[8]. Altin R, Catinkaya s, YucesuHS. (2001). Energy Convers Manage 2001; 42: 529-38

[9]. Shubkin RL (Ed.) (1993). Synthetic Lubricants and High-Performance Functional Fluids. Marcel Dekker: New York, 1993.

[10]. Zehler GR. (2001). Performance tiering of biodegradable ׀ hydraulic fluids. Lubricants World 2001; 1 Sept: 22-26

[11]. O. N. Anand and Vijay Kumar Chhibber. (2006). Vegetable oil derivatives: environment-friendly lubricants and fuels . J. Synthetic Lubrication 2006; 23:91-107.

[12]. Esa Uosukainen., Yu-Yen, L., Lamsa, M., Tevakangas, T. and Pekka, L. (1998). J. Am Oil. Chem. Soc.,75, 1157.

[13]. Pavlovicova, A. and Cvengros, J. (1999). Petroleum and Coal41: 99.

[14]. Schlosberg, R H., Chu, J. W., Knudsen, G. A. and Suciu, E. N. (2001). Lubrication Engineering, 56 (7), 21.

[15]. Bongardt, F., Bossmann, B., Westfechtel, A. and Giede, W., Ger. Offen. DE 4,444,137, (1996).

[16]. Lamsa, M. (1995). in Proceedings of 4th Scandinavian International Conference on Fluid Power, September 26.

[17]. Lamsa, M. (1995). Finnish PatentFI 95,367 and PCT FI 95/00477.

[18]. Cooley, S. D. and M. Slovinsky. (1961). U. S. Patent No. 2,991,297.

[19]. Kaimai, T. and Morishima, Y. (2004). JP Patent No. 315,553.

[20]. Talis Paeglis., Pavels Karabesko., Inese Mierina., Rasma Serzane., Maija Strele., Velta Tupereina., Mara Jure Jelgava, 05, 28-29, (2009).

[21]. Gryglewicz, s., Piechocki, W. and Gryglewicz, G. (2003). Bioresource Technology, 87, 35.

[22]. Randles, S. J. (1999). Refrigeration Lubes., in Synthtic Lubricants and High-Performance Functional Fluids, M. Dekker, 2nd edn, New York, 77, 63.

[23]. R. M. Mortier and S. T. Orszulik. (1997). Chemistry and Technology of Lubricants, Blackie Academic and Prof Leleu, G, P. Bedague, and b. Silion., U. S. Patent N. o. 4,061,581.

[24]. Leleu, G., Bedague, P. and Silion, B. (1997). U. S. Patent No. 4,061,581.

[25]. Mattei, L., Pacor, P. and Piccone, A. (1995). Synth. Lubr. 26, 49.

[26]. Linko, Y. -Y., Tervakangas, T., Lamsa, M. and Linko, P. (1997). Biotechnology Techniques 11 (12), 889.

[27]. Osada, F., Kobyashi, M., Asaoka, S. and Kitazato, H. (1987). Japan Patent. N. o62, 296, 884.

[28]. Monot, F., Benoit, Y., Ballerini, D. and Vandecasteele, J. P (1990). Appl. Biochem. Biotechnol., 24/25: 375.

[29]. Kazuaki Abe, Sodegaura, Hiromichi Seiki, Mitsuhiro Iwata. (2002). U. S Patent No. 6,402,983.

[30]. Kohashi, H. (1991). Application of fatty acid esters for lubricating oil. Proceedings World Conference Oleochemicals into the 21st Century, 243-250.

[31]. amasa, M., Linko, Y., Helsinki, E. U. (1998). US Patent No. 5,747,434.

[32]. Lamsa, M. (1999). US Patent No. 5,885,946.

[33]. Rizzi, G. P. and or, H. M. (1976). US Patent No. 3,963,699.

[34]. Peters, T. J., Collins, F. J, Elizabeth, N. J. (1962). US Patent No. 3,047,504.

[35]. Matusak, A. H., Stephen, J. M., Scotch, P. N. J. (1964). US Patent3,126,344.

[36]. Hentschel, K. H., Dhein, R., Rudolph, H. (1980). US Patent No., 4,212,816.

[37]. ShootKian, Y., Tian, L. O., Ahmad, S., European Patent Application EP 1533360.

[38]. Akbar, E., Yaakob, Z., Kamarudin, S. K., Ismail, M. and Salimon, J. (2009). EuropeanJournal of Scientific Research., 29, No. 3, 396-403.

Chapter 16

CURRENT STATUS AND IMPACT OF PESTICIDES USE IN AGRICULTURAL CROP IN INDIA

FARHAT ZABI AND CHARUL SOMANI

Department of Science, Smt. SDM PG Girls college, Bhilwara - 311001

ABSTRACT

The purpose of pesticides is to eliminate insects and pests that attack and damage crops. For generations, farmers have employed various insecticides to safeguard their crops. Although pesticides are beneficial to crops, they can have detrimental effects as well. In this review the systematic and comprehensive picture of pesticide exposure to plants and its impact on development and metabolism is presented in this review. Agrochemicals were first introduced many years ago with the intention of increasing agricultural yields and safeguarding crops from pests. Because pests have become accustomed to pesticides and have acquired a tolerance to them, new and increased amounts of chemicals are employed year to protect crops, which can have unintended side effects. Moving towards the end, the paper describe advantages and disadvantages of pesticide and data of pesticides uses in various state and country.

KEYWORDS: Pesticides, Crop, Advantage, Disadvantage, Growth, Residual Effects.

INTRODUCTION

In agriculture, pesticidesnatural or syntheticare used to manage diseases, weeds, and pests that affect different plant species. Pesticides include things like herbicides, insecticides, fungicides, rodenticides, nematicides, and more. Throughout the course of agricultural growth, pesticides emerged as a crucial instrument for crop production enhancement and plant protection. Since insect infestations cause over 45% of the world's food output each year, managing pests effectively with a variety of pesticides is necessary to both reduce pest populations and boost crop yields [1].

Compared to clothing and shelter, food is a more basic human requirement. For the body's development, upkeep, repair, and reproduction, it offers sufficient nutrition. The agriculture industry is the main driver of the economy in India, the second most populous country in the world. Agriculture provides a living for about 64% of the people. India's varied agroclimatic conditions require distinct techniques to agriculture and crop protection, making food security one of the country's top problems. The majority of the increases in agricultural production, given the constraints on growing the area under cultivation, have come from higher productivity obtained from two main inputs: pesticides and fertilizers. In both rich and developing nations, crop losses due to pests and plant diseases are relatively considerable. These are said to be between 10 and 30 percent in the former scenario and 40 and 75 percent in the latter [2].

A pesticide should ideally be harmful to the intended pests but not to undesired species, such as humans. Unfortunately, this is untrue, and as a result, the issue surrounding the proper and improper use of pesticides has emerged. Humans and other living forms have suffered greatly as a result of the widespread use of these chemicals under the motto "if little is good, a lot more will be better. "

This chapter will also discuss the effects of pesticides, uses of pesticides in india, negative effects of pesticides and positive effects of pesticides, residual data etc.

UTILIZATION OF PESTICIDES IN INDIA

Since 293 pesticides are registered in India, it is said that 104 pesticides, which are illegal in two or more countries worldwide and they are still manufactured and used there [3]. Fifty percent of all pesticides used in India for pest control are redirected toward cotton pest control [4].

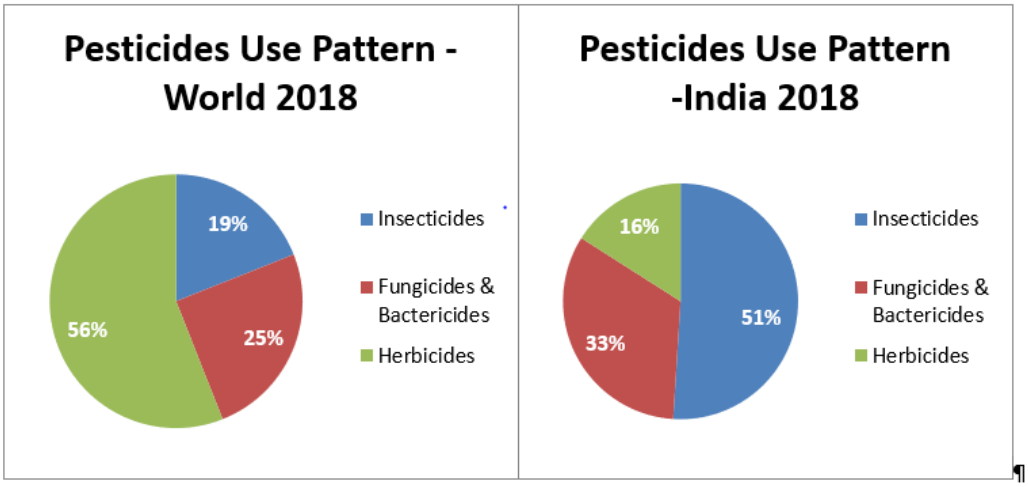


Fig. 2: Pesticide use pattern- Worldwide and India
(Source: http://www. fao. org/faostat/en/#d ata) FAO (2018)

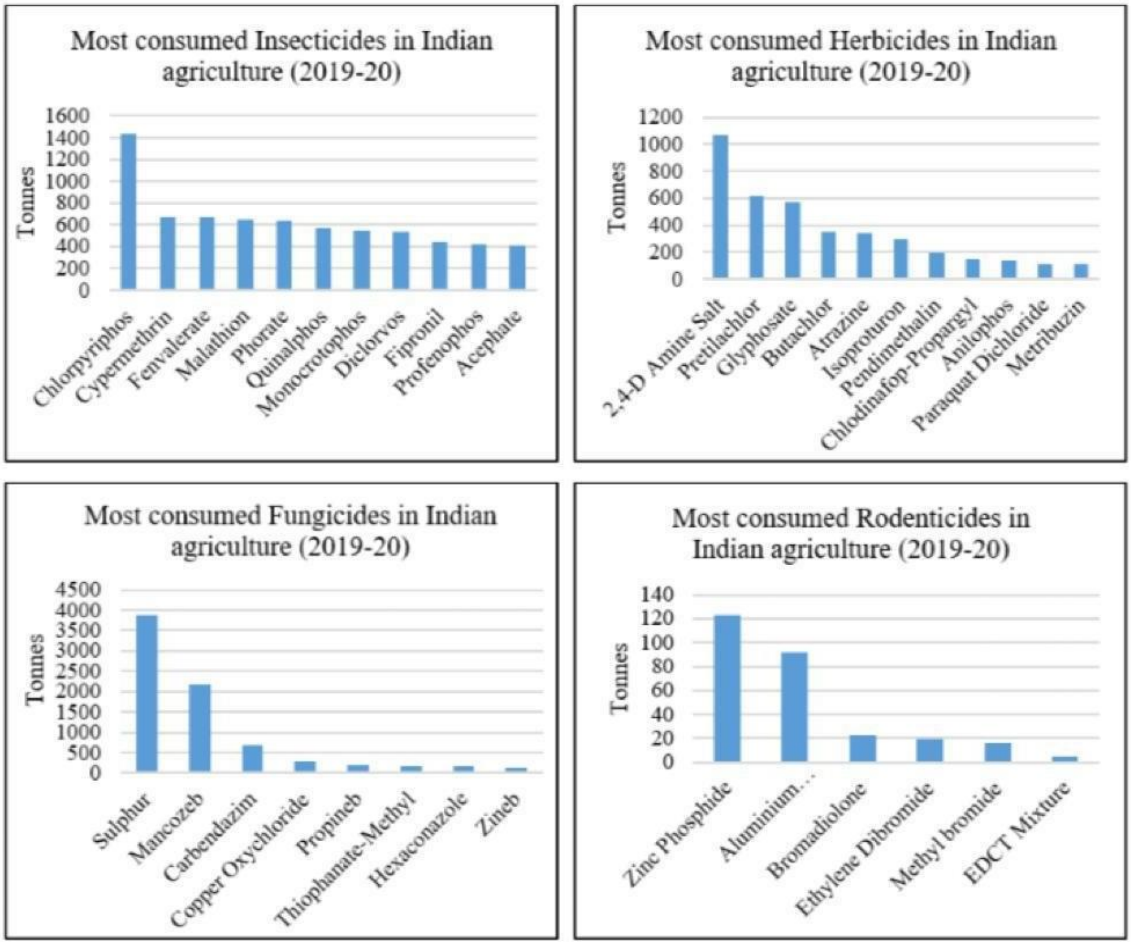


Fig. 3: Most consumed Insecticides, herbicides, fungicides and rodenticides during 2019-20 in India 2019-20 in India (Source: Ministry of Agriculture & Farmers Welfare)

The excessive and reckless use of pesticides has resulted in numerous negative consequences, such as residue in plant parts, insecticide resistance, secondary pest outbreaks, pollution of natural resources, health issues for humans and wildlife, etc. These issues make the transition to environmentally friendly pest management techniques necessary [5].

The overuse and indiscriminate use of pesticides has resulted in numerous negative effects, such as residue in plant parts, resistance to insecticides, secondary pest outbreaks, pollution of natural resources, health issues for humans and wildlife, etc., which makes the transition to eco-friendly pest management techniques necessary [6].

India uses a small amount of pesticide in 2017roughly 0. 31 kg per hectarecompared to 19. 6 kg per hectare in Saint Lucia, 16. 59 kg in Hong Kong, 13. 9 kg in Ecuador, 13. 3 kg in Taiwan, and 13. 07 kg in China. America has cut back on its consumption by 2. 54 kg/hectare [7]. India uses pesticides differently than the rest of the world (Figure 1).

Herbicides, insecticides, and fungicides are all used in India. Most of the total is accounted for by insecticides. While the global pesticide use pattern is herbicides >fungicides+bactericides> insecticides > other pesticides, the current pesticide use pattern in India is insecticides > herbicides >fungicides+bactericides> other-pesticides. India is currently the fourth-largest pesticide producer in the world. Research and Markets estimates that the Indian pesticide market was valued at Rs. 214 billion in 2019. With a compound annual growth rate of 8. 1 percent, the market is projected to reach Rs. 316 billion by 2024 [8]. As shown in Figure 2, chlorpyriphos is the most commonly used pesticide (Figure 2).

PESTICIDES BENEFICIAL EFFECTS

By defending crops against pests and insects. But these are some primary advantages of it.

Enhancing productivity

Pesticides are used in forestry, public health, domestic areas, and, of course, agriculture, which is the backbone of the Indian economy. These uses have yielded enormous benefits. From an estimated 169 million hectares of permanently cropped land, food grain production increased almost fourfold to 198 million tons by the end of 1996–1997 from a meager 50 million tons in 1948–1949. Utilizing high-yield seed varieties, cutting-edge irrigation techniques, and agricultural chemicals has produced this outcome [8]. In most countries, productivity and outputs have also increased significantly. Take the UK's wheat yields and the USA's corn yields, for instance. Numerous factors, such as the use of machinery, improved varieties, and fertilizer, have contributed to increases in productivity.

In order to maximize the amount of produce that can be harvested, pesticides have been essential in the fight against weeds, diseases, and insect pests. [9].

PREVENTING AGRICULTURAL LOSSES AND LOWERING YIELDS

Based on comparisons that included control (weedy) plots, rice in medium-sized fields, even in puddle conditions during the crucial time frame, warranted an economical and effective weed management practice to prevent reduction in rice yield due to weeds that varied from 28 to 48% [10]. Dry land crop yields are decreased by weeds by 37–79%. A 40% reduction in yield is ultimately caused by severe weed infestation, especially in the early stages of crop establishment. Herbicides benefited labour and the economy. [11].

THE FOOD STANDARD

Research from developed nations indicates that diets high in fresh produce are far safer than those with very low levels of pesticide residue in crops. [12]. A diet rich in fruits and vegetables appears to reduce the risk of high blood pressure, heart disease, diabetes, stroke, and other chronic illnesses, such as many

cancers. This evidence is accumulating. [13]. The American diet's health benefits from including apples and blueberries include the fact that their high antioxidant content protects against cancer and heart disease. I. e. Lewis primarily blamed increased pesticide use for better weed control for the increasing of wild blueberry growth and subsequent increases in consumption. [14].

NEGATIVE IMPLICATIONS OF PESTICIDES

What kinds of negative consequences are connected to pesticides?

Physiological Effects of pesticides on crops

Water-soluble pesticides are absorbed and allowed to enter the plant system withthe assistance of transpiration pull. Through transpiration, volatile pesticides enter the atmosphere indirectly through the stomata on leaves. Pesticides are absorbed by plants through their roots, leaves, or roots. The physiochemical characteristics of soil and pesticides, as well as external environmental factors like temperature, humidity, and precipitation, all play a role in the uptake and metabolism of pesticides in the plant system [15]. The way in which pesticides are applied, their quantity, their physiochemical and biochemical characteristics, how they interact with soil, and the stage at which plants are developing are all factors that can influence the uptake of pesticides through the root system and their metabolism in the plant system [16]. Pesticide uptake occurs through two different mechanisms: active absorption through the root system and passive absorption. The former occurs when pesticides are metabolized by the plant system, while the latter occurs when pesticides accumulate in plants and cause bio-magnification in the ecosystem [17]. Additionally, the application of pesticides toxicity to plants results in necrosis, chlorosis, stunting, burns, and leaf twisting [18]. In one of the main factors contributing to the decline in structural vegetation diversity is the overuse of pesticides. [19].

Plants that are sensitive or under stress might be more susceptible to phytotoxicity. Numerous factors, including the use of pesticides, their rate of application, the method of spraying, the climate, the arrangement of the flora, humidity, and the characteristics of the soil, including its moisture content, pH, texture, and microbial activity, all affect toxicity. The application of pesticides has been shown to have a negative impact on crop development and growth [20].

The use of pesticides results in the production of reactive oxygen species, which stresses plants oxidatively [21]. Plant photosynthetic efficiency is eventually decreased as a result of this oxidative stress, which also causes proteins and chlorophyll pigments to degrade [22]. In response to oxidative stress, plants initiate an antioxidative defense mechanism that includes both enzymatic and non-enzymatic antioxidants [23].

In addition to helping with ROS scavenging, antioxidative defense system activation lowers oxidative stress in plants brought on by pesticide toxicity [24].

MORPHOLOGICAL EFFECTS OF PESTICIDES ON CROPS

On crops sprayed with agrochemicals intended to control weeds, visible symptoms are frequently found. Examples of herbicides that harm leaves include acifluorfen, a diphenylether that is used on a variety of crops, including spinach, celery, cotton, soybeans, beans, and peas [25].

On leaves, chlorosis and necrotic patches appear, then the leaves dry out and wither. Additional symptoms in cotton were noted, like reddish-brown patches on the veins of the leaves. When pesticides are sprayed on particular cultures, they may end up on nearby fields and affect the crops that grow there. When the plants are young or in a stage of rapid growth, they are especially vulnerable to stress, which makes this point problematic. A number of studies, for instance, have documented the effects of weed control herbicides sprayed on wheat to one to three-year-old grapevines. Specifically, grapevines exposed

to concentrations ranging from 1/100 to 1/3 of the concentrations sprayed on wheat showed wilted, crinkled, stunted, and distorted leaves with necrotic areas and discolored veins five days after treatment [26 - 29].

Table 1: Effect of Pesticides on Crop Growth Parameters

Agrochemical	Common name	Crop	Affected growth parameter	Reference
Herbicides	Trifluralin	Wheat	Shoot dry weight.	32
	Atrazine Imazethapyr	Pea	Shoot length, fresh and dry weights. Leaf area, shoot and root dry weights.	33 34
	Trichloroacetate	Oat, lettuce, Chinese cabbage	Shoot weight.	35
	Glufosinate	Tomato	Shoot and root fresh weights.	36
	San 9789	Nettle-leaved Goosefoot	Hypocotyl length, leaf number.	37
	Flumioxazin, Chlorsulfuron, Thifensulfuron, Bromoxynil, 2,4-D[a], Glyphosate	Grapevine	Shoot biomass, stem height. Cane weight, leaf area, shoot and internode lengths.	38 27, 29
	Pyrithiobac	Sorghum, corn	Plant height.	30
	Sulfosulfuro, Metribuzin, Bromoxynil-octanoate,	Sunflower	Shoot and root lengths, fresh and dry weights. Shoot dry weight.	31 39
	Ethofumesate	Sugar beet	Root dry weight.	40
Insecticides	Insecticidal soap	Azalea	Shoot growth rate.	41
	Demeton-S-methyl, Dicofol, pirimicarb, Dimethoate	Wild tamarind	Shoot dry weight.	42

As the plants were exposed to the highest concentration of herbicides, the damaged leaves eventually fell, while the stems turned dark red and developed necrotic lesions before finally cracking. New leaves that were growing were restricted to the lower sections of the plants for every applied concentration, several months following exposure. Using 2,4-D on three-year-old plants (62 to 75 percent of injury) in particular caused symptoms to persist four months after treatment, regardless of the herbicide used. A year-old plant was more sensitive than an older plant; 90 days after the herbicide exposure, the injury was 25–32% for chlorsulfuron, thifensulfuron, and bromoxynil, and 100% for 2,4-D. Regarding the latter, symptoms persisted until the end of the growing season. Herbicide damage to grapevine was only partially repaired, as evidenced by the following year's observations of visible symptoms like leaf chlorosis and decreased leaf area. Similarly, pyrithiobac (benzoic acid), which is applied in nearby cotton fields at post-emergence, has an impact on corn and sorghum [30].

Six weeks following the treatments, purple-leaf coloration and onion leafing were seen, which represents 20–30% of the visible damage when the herbicide concentration was 6% of that used on cotton fields. Both crops continued to exhibit symptoms until the end of the growing season. Herbicide residues have the

potential to linger in soils at phytotoxic concentrations and harm subsequently cultivated crop species. According to reports, sunflower plants planted on the same field the following year were impacted by sulfosulfuron (sulfonylurea) applied to a wheat field [31].

DATA OF PESTICIDES RESIDUAL EFFECTS

The European Union has been implementing programs called "Monitoring of Pesticide Residues in Products of Plant Origin in the European Union" since 1996 in order to assess the level of pesticide contamination in food items. Apples, tomatoes, lettuce, strawberries, grapes, and benomyl group and maneb group, or dithiocarbamates, were the subjects of an analysis in 1996 of seven pesticides (acephate, chlopyriphos, chlopyriphos-methyl, methamidophos, iprodione, procymidone, and chlorothalonil) and two pesticide groups. Approximately 9,700 samples on average have been examined for every pesticide or group of pesticides. 5. 2% of the samples for each pesticide or group of pesticides were found to have residues, and 0. 31% of the samples had residues higher than the corresponding MRL for that particular pesticide. Among allthe crops examined, lettuce had the most positive results, with residue levels consistently surpassing maximum residual levels. A maneb group compound in lettuce had the highest value discovered in 1996, corresponding to a mancozeb residue of 118 mg/kg. 13 pesticides were evaluated in five commodities in 1997, including acephate, carbendazin, chlorothalonil, chlopyriphos, DDT, diazinon, endosulfan, methamidophos, iprodione, metalaxyl, methidathion, thiabendazole, and triazophos. (mandarins, pears, bananas, beans, and potatoes). Six thousand samples or so were examined. Most frequently, residues of chlorpyriphos (0. 24%), methamidophos (0. 18%), and iprodione (0. 13%) were found to be above MRLs. About 34% of the commodities under investigation had pesticide residues at or below the MRL, and 1% had residues at levels higher than the MRL. The most common fruits and vegetables with pesticide residues at or below the MRL were mandarins (69%), followed by bananas (51%), pears (28%), beans (21%) and potatoes (9%). Beans (1. 9%) were the most frequently exceeded MRL, with mandarins (1. 8%), pears (1. 3%), bananas and potatoes (0. 5%) following closely behind. Based on the 90th percentile of pesticide residue levels estimated from these commodities, no pesticide or commodity studied exceeds the acceptable daily intake (ADI) [43]. The commodities listed above have the highest levels of residue from the respective pesticides.

CONCLUSION

Pesticides have increased agricultural yield and indirectly benefited society in numerous ways, making them a blessing for both farmers and people worldwide. However, questions concerning the safety of pesticides have been raised due to the risks they pose to the environment and public health. The risks connected to the use of pesticides cannot entirely be eliminated, but they can be avoided in some manner. There are several ways to reduce pesticide exposure and its negative effects, including using well-maintained spraying equipment or switching to alternative cropping practices. The development of safer, more effective, and environmentally friendly pesticide formulations could lessen the negative consequences of using pesticides. Pesticide risks can be reduced if the chemicals are used sparingly and only when absolutely necessary. In a similar vein, the mayhem can be reduced by using a toxic formulation at a low dose or a less toxic formulation. "The right dose differentiates a poison from a remedy," as Paracelsus also famously stated.

REFERENCES

[1]. Tubiello, F. N., Wanner, N., Asprooth, L., Mueller, M., Ignaciuk, A., Khan, A. A., & Rosero Moncayo, J. (2021). Measuring progress towards sustainable agriculture. Food & Agriculture Org. .

[2]. Roy, N. K. (2002). Pesticide residues and their environmental implications. Chemistry of pesticides. CBS, New Delhi, 265-279.

[3]. www.gov.in/sites/default/files/insecticides_pesticides_registered_under_section_93_of_the_insecticides_act_1968_for_use_in_the_country_as_on_30. 06. 2020. pdf
[4]. Mooventhan, P., Murali, R. B., Kumar, J., & Kaushal, P. (2020). NIBSM Publ. Nations, U. (2019). World population prospects Highlights, 2019 revision Highlights, 2019 revision.
[5]. Birthal, P. S., & Sharma, O. P. (2004). Integrated pest management in Indian agriculture.
[6]. Roser, M., & Ritchie, H. (2019). Fertilizer and pesticides. Our world in data.
[7]. Piploda, S., Kantwa, S., Dalal, P. L., Anvesh, K., & Choudhary, S. (2022). Effects of pesticideson environment and human health. Recent Innovative Approaches in Agricultural Science, 10, 164.
[8]. Bureau, I. L. (1993). Indian labour statistics.
[9]. Warren, G. F. (1998). Spectacular increases in crop yields in the United States in the twentieth century. Weed Technology, 12 (4), 752-760.
[10]. Behera, B., & Singh, G. S. (1999). Studies on weed management in monsoon season crop of tomato. Indian Journal of Weed Science, 31 (1and2), 67-70.
[11]. Cooper, J., Dobson, H., & Maritime, C. (2007). Pesticides and humanity: the benefits of using pesticides. Natural Resources Institute, University of Greenwich, UK.
[12]. Krebs-Smith, S. M., Reedy, J., & Bosire, C. (2010). Healthfulness of the US food supply: little improvement despite decades of dietary guidance. American journal of preventive medicine, 38 (5), 472-477.
[13]. Gupta, C. G. Movement of crop protection chemicals in different environmental components.
[14]. Führ, F. (1991). Radiotracers in pesticide studies-- advantages and limitations. Cienc. Cult., 43 (3), 211-216.
[15]. Mwevura, H., Othman, C. O., &Mhehe, G. L. (2000). Study on the levels of organochlorine pesticide residues from selected aquatic bodies of Tanzania. Tanzania: University of Dar es Salaam.
[16]. Sharma, A., Kumar, V., Kumar, R., Shahzad, B., Thukral, A. K., & Bhardwaj, R. (2018). Brassinosteroid-mediated pesticide detoxification in plants: A mini-review. Cogent Food & Agriculture, 4 (1), 1436212.
[17]. Donald, P. F. (2004). Biodiversity impacts of some agricultural commodity production systems. Conservation biology, 18 (1), 17-37.
[18]. Sharma, A., Kumar, V., Singh, R., Thukral, A. K., & Bhardwaj, R. (2016). Effect of seed pre-soaking with 24-epibrassinolide on growth and photosynthetic parameters of Brassica juncea L. in imidacloprid soil. Ecotoxicology and Environmental Safety, 133, 195-201.
[19]. Shahzad, B., Tanveer, M., Che, Z., Rehman, A., Cheema, S. A., Sharma, A., & Zhaorong, D. (2018). Role of 24-epibrassinolide (EBL) in mediating heavy metal and pesticide induced oxidative stress in plants: a review. Ecotoxicology and environmental safety, 147, 935-944.
[20]. Sharma, A., Kumar, V., Yuan, H., Kanwar, M. K., Bhardwaj, R., Thukral, A. K., & Zheng, B. (2018). Jasmonic acid seed treatment stimulates insecticide detoxification in Brassica juncea L. Frontiers in plant science, 9, 1609.
[21]. Xia, X. J., Huang, Y. Y., Wang, L., Huang, L. F., Yu, Y. L., Zhou, Y. H., & Yu, J. Q. (2006). Pesticides-induced depression of photosynthesis was alleviated by 24-epibrassinolide pretreatment in Cucumis sativus L. Pesticide Biochemistry and Physiology, 86 (1), 42-48.
[22]. Xia, X. J., Zhang, Y., Wu, J. X., Wang, J. T., Zhou, Y. H., Shi, K., & Yu, J. Q. (2009). Brassinosteroids promote metabolism of pesticides in cucumber. Journal of Agricultural and Food Chemistry, 57 (18), 8406-8413.

[23]. Sharma, A., Kumar, V., Kanwar, M. K., Thukral, A. K., & Bhardwaj, R. (2017). Ameliorating imidacloprid induced oxidative stress by 24-epibrassinolide in Brassica juncea L. Russian Journal of Plant Physiology, 64, 509-517.

[24]. Komives, T., & Casida, J. E. (1983). Acifluorfen increases the leaf content of phytoalexins and stress metabolites in several crops. Journal of Agricultural and Food Chemistry, 31 (4), 751-755.

[25]. Al-Khatib, K., Parker, R., & Fuerst, E. P. (1993). Wine grape (Vitis vinifera L.) response to simulated herbicide drift. Weed Technology, 7 (1), 97-102.

[26]. Bhatti, M. A., Al-Khatib, K., & Parker, R. (1996). Wine grape (Vitis vinifera) response to repeated exposure of selected sulfonylurea herbicides and 2, 4-D. Weed technology, 10 (4), 951-956.

[27]. Bhatti, M. A., Al-Khatib, K., & Parker, R. (1997). Wine grape (Vitis vinifera) response to fall exposure of simulated drift from selected herbicides. Weed technology, 11 (3), 532-536.

[28]. Bhatti, M. A., Felsot, A. S., Parker, R., & Mink, G. (1998). Leaf photosynthesis, stomatal resistance, and growth of wine grapes (Vitis vinifera L.) after exposure to simulated chlorsulfuron drift. Journal of Environmental Science & Health Part B, 33 (1), 67-81.

[29]. Ghosheh, H. Z., Prostko, E. P., Tingle, C. H., & Chandler, J. M. (2002). Simulated pyrithiobac drift effects on corn (Zea mays) and grain sorghum (Sorghum bicolor). Crop Protection, 21 (7), 529-532.

[30]. Alonso-Prados, J. L., Hernández-Sevillano, E., Llanos, S., Villarroya, M., &García-Baudín, J. M. (2002). Effects of sulfosulfuron soil residues on barley (Hordeum vulgare), sunflower (Helianthus annuus) and common vetch (Vicia sativa). Crop Protection, 21 (10), 1061-1066.

[31]. Clay, S. A., Gaffney, J. F., & Wrage, L. J. (1995). Spring wheat (*Triticum aestivum*) cultivar responses to trifluralin and postemergence herbicides. Weed technology, 9 (2), 352-355.

[32]. Zheleva, D., Tsonev, T., Sergiev, I., & Karanov, E. (1994). Protective effect of exogenous polyamines against atrazine in pea plants. Journal of Plant Growth Regulation, 13, 203-211.

[33]. Royuela, M., Gonzalez, A., Gonzalez, E. M., Arrese-Igor, C., Aparicio-Tejo, P. M., & Gonzalez-Murua, C. (2000). Physiological consequences of continuous, sublethal imazethapyr supply to pea plants. Journal of Plant Physiology, 157 (3), 345-354.

[34]. Radetski, C. M., Cotelle, S., &Férard, J. F. (2000). Classical and biochemical endpoints in the evaluation of phytotoxic effects caused by the herbicide trichloroacetate. Environmental and experimental botany, 44 (3), 221-229.

[35]. You, W., & Barker, A. V. (2002). Herbicidal actions of root-applied glufosinate ammonium on tomato plants. Journal of the American Society for Horticultural Science, 127 (2), 200-204.

[36]. Mitrović, A., Živanović, B., &Ćulafić, L. (2000). The effects of growth regulators on flowering of Chenopodium murale plants in vitro. Biologia plantarum, 43, 451-454.

[37]. Saladin, G., Magné, C., & Clément, C. (2003). Impact of flumioxazin herbicide on growth and carbohydrate physiology in Vitis vinifera L. Plant cell reports, 21 (8), 821-827.

[38]. Follak, S., & Hurle, K. (2003). Effect of airborne bromoxynil–octanoate and metribuzin on non-target plants. Environmental Pollution, 126 (2), 139-146.

[39]. Klingeman, W. E., Buntin, G. D., van Iersel, M. W., & Braman, S. K. (2000). Whole-plant gas exchange, not individual-leaf measurements, accurately assesses azalea response to insecticides. Crop Protection, 19 (6), 407-415.

[40]. European Food Safety Authority. (2011). The 2009 European Union report on pesticide residues in food. EFSA Journal, 9 (11), 2430.

[41]. Dalzell, S. A., & Mullen, B. F. (2004). Application of pesticides suppress foliar proanthocyanidin content in Leucaena species. Animal feed science and technology, 113 (1-4), 191-198.

[42]. Purrington, C. B. (2000). Costs of resistance. Current opinion in plant biology, 3 (4), 305-308.

Chapter 17

A REVIEW ON ANTIOXIDANT PEPTIDES FROM MARINE HYDROLYSATES

S. UMAYAPARVATHI*[1], S. MEENAKSHI[2] AND R. SARAVANAN[3]

[1]Department of Microbiology, New Prince Shri Bhavani Arts and Science College, Medavakkam, Chennai, Tamilnadu, India.
[2]PG & Research Department of Microbiology, Sadakathullah Appa College, ManonmaniamSundarnar University, Tirunelveli, Tamilnadu.
[3]Sri K. G. S. Arts College, Manonmaniam Sundarnar University, Srivaikuntam, Tamilnadu, India.
*Corresponding author E-mail: shanparvathi87@gmail.com

ABSTRACT

Proteins hydrolyzed into different-sized peptides by enzyme hydrolysis or chemical hydrolysis are known as protein hydrolysates. For the purpose of hydrolyzing fish and shellfish proteins, a variety of proteolytic enzymes derived from microbiological, plant, or animal sources are available. Several finfish and shellfish species are used to create protein hydrolysates, which are rich in bioactive peptides. For usage in the prevention and treatment of various diseases, the pharmaceutical and nutraceutical sectors find marine bioactive peptides, particularly antioxidant peptides, to have high potential nutraceutical and medical properties. It is possible to detect most marine species that exhibit biological activity, even though very few bioactive peptides have been found in marine creatures. Therefore, the processing techniques that have been used in recent studies require further improvement to discover more marine bioactive peptides. Some recent studies have reported the in vitro formation of antioxidant peptides from marine sources and their possibilities to be used as alternative antioxidants. In this chapter we will specify the role of antioxidant bioactive peptides, their isolation processes, and their characterization from marine protein hydrolysate.

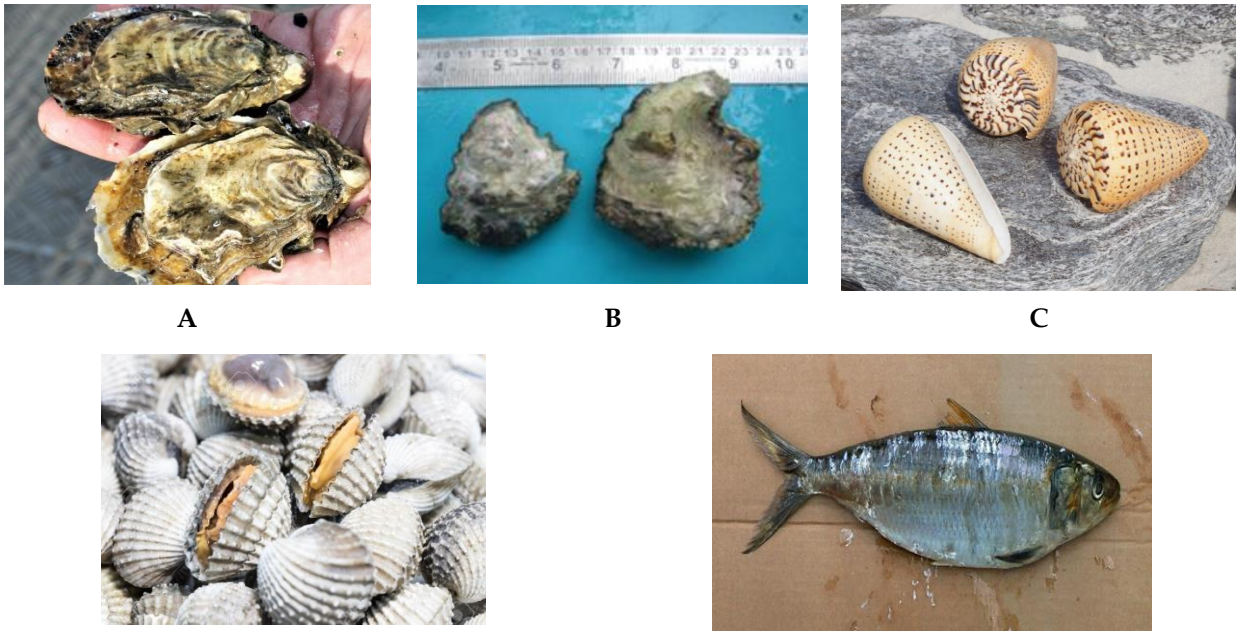
KEYWORDS: Bioactive Peptides, Enzymatic Hydrolysis, Protein Hydrolysates, Anti-Oxidant Peptides

INTRODUCTION

The Marine organisms represent a valuable source of bioactive compounds (Benkendorff, 2010). In the realm of developing bioactive products, the marine environment's biodiversity and the corresponding chemical variety provide an almost limitless supply of novel active ingredients (Jirge and Chaudhari, 2010; Datta *et al.,* 2015). Since marine species live in an environment that is extremely different from the terrestrial one in many ways - one that is competitive, hostile, and demanding - they have produced a totally different kind of compounds. (Aneiros and Garateix, 2004).

The majority of marine life has soft bodies and is fully submerged in its surroundings. Certain organisms never move. To defend themselves from the harshness of their surroundings, they have so evolved biological defense mechanisms, such as the release of mucus containing bioactive substances. These defence systems can be exploited and used in rational drug design (Jha and Xuzi-Rong, 2004). Several molecules isolated from a vast number of marine species have clinical application as supplements and drugs while other molecules are currently in clinical trials (Jirge and Chaudhari, 2010). Numerous of them have unique chemical structures that could result in the creation of completely new medications

and therapeutic agents. Marine molluscs, fish, seaweed, algae, sponges, and other organisms produce secondary metabolites, which are bioactive substances that can be extracted from marine sources. These secondary metabolites include nitrogen heterocyclics, terpenoids, quinones, steroids and isoprenoids (Datta *et al.,* 2015). Bioactive low molecular weight peptides and depsipeptides, as well as lectins, have also been obtained from marine sources (Suarez-Jimenez *et al.,* 2012). Exploitable biological activity that marine organisms have been shown to possess include: antimicrobial activity (Datta *et al.,* 2015; Salehi *et al.,* 2014), anti-cancer and anti proliferation activity (Benkendorff, 2010; Suarez-Jimenez *et al.,* 2012; Chakraborty *et al.,* 2009), free radical scavenging and antioxidant activity (Purwaningsih *et al.,* 2012). These facts introduce marine peptides as a new choice for the obtainment of lead compounds for biomedical research.



A **B** **C**

D **E**

Fig. 1: Marine oyster, *Saccostrea cucullate* (A), oyster, *Crassostrea gigas* (B), Marine gastropod mollusc, *Conus betulinus* (C), Marine Bivalve Mollusc, *Tergillarca granosa* (D), Marine fish sardinella, *Sardinell aaurita* (E)

BIOACTIVE PEPTIDES FROM MARINE HYDROLYSATES

Enzymatic hydrolysis of marine animals has been a common method of producing marine bioactive peptides (Je *et al.,* 2008). The enzymatic hydrolysis of catfish by-products as feed stuff constituents was investigated by Hien *et al.,* in 2021. Furthermore, a number of bioactive peptides have been identified from marine by-products. It has been demonstrated that bioactive peptides originating from marine sources exhibit a wide range of physiological properties, such as antioxidant, antibacterial, and antihypertensive (ACE) inhibitory properties. Nazeer and Srividhya, (2011) isolated and purified bioactive peptide with antioxidant property from the hydrolysates of marine gastropod Conusbetulinus. Three enzymes—trypsin, pepsin, and papain—were applied to the body and viscera of C. betulinus in order to produce peptide hydrolysates. Gel filtration chromatography was used after ion exchange chromatography to purify the active hydrolysates. Metheonine, cystine, histidine, and other active amino acids were present in the purified fraction, according to the HPLC findings. With its increased antioxidant activity, the refined peptide may be able to lower the body's excess free radical load and avert diseases caused by free radicals.

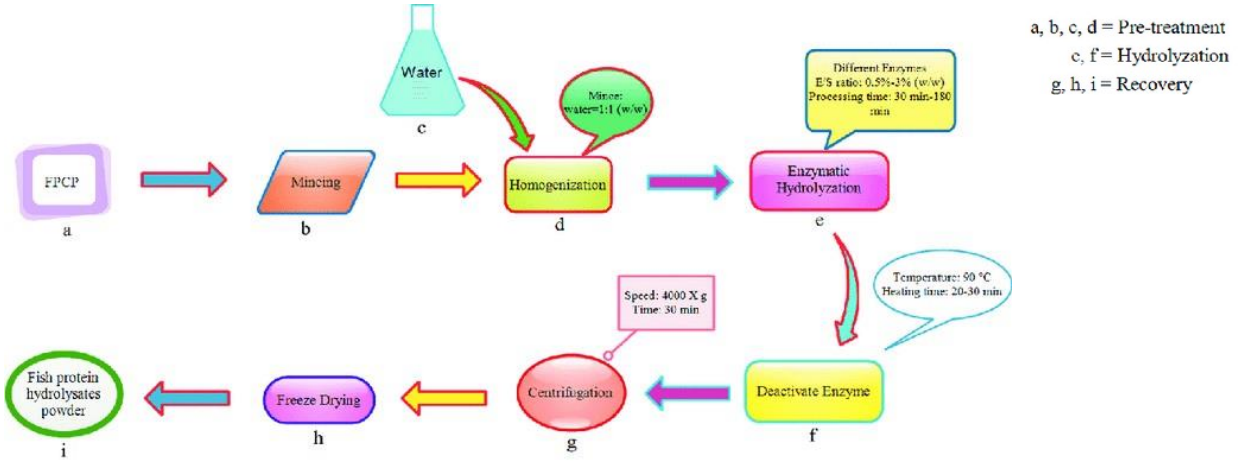


Fig. 2: Flow diagram of the enzymatic hydrolysis method to produce fish protein hydrolysates (Sohail Khan *et al.*, 2020)

In 2012, Sampath Kumar and colleagues isolated and recognized two bioactive peptides possessing antioxidant characteristics from the skin protein hydrolysate of two marine fish species: croaker (Otolithesruber) and horse mackerel (Magalaspiscordyla). The sequences of the peptides from horse mackerel and croaker were determined by electron spray ionization double mass spectrometry (ESI-MS/MS) to be Asn-His-Arg-Tyr-Asp-Arg (856 Da) and Gly-Asn-ArgGly-Phe-Ala-Cys-Arg-His-Ala (1101. 5 Da), respectively. Electron spin resonance (ESR) spectrometry was used to assess the antioxidant activity of these peptides through the use of hydroxyl radical scavenging and 1-diphenyl-2-picryl hydrazyl (DPPH) reactions. The anti-polyunsaturated fatty acid (PUFA) peroxidation activity of both peptides was greater than that of the naturally occurring antioxidant α-tocopherol (Sampath Kumar *et al.*, 2012).

The enzymatic hydrolysates of oysters yielded a new cysteine-rich antimicrobial peptide, CgPep33, that demonstrated efficacy against both Gram-positive and Gram-negative bacteria and fungi. (Liu *et al.*, 2008). CgPep33was purified by using ultrafiltration, ion exchange chromatography on DEAE Sephadex A-25, gel filtration on Sephadex G-25 and high-performance liquid chromatography on a reverse-phase column. All examined bacteria (Escherichia coli, Pseudomonas aeruginosa, Bacillus subtilis, and Staphylococcus aureus) and fungi (Botrytis cinerea and Penicilliumexpansum) showed growth inhibition upon exposure to it.

ANTIOXIDANT PEPTIDES FROM PROTEIN HYDROLYSATES

Bougatef*et al.*, (2010) isolated seven antioxidant peptides from sardinelle (Sardinellaaurita) protein by-products by hydrolyzing the by-products with different proteases. Sardine (Sardinapilchardus) crude enzyme extract produced a hydrolysate with increased DPPH radical-scavenging activity. That hydrolysate was fractionated and purified. Pro-His-Tyr-Leu, Leu-Ala-Arg-Leu, Gly-Gly-Glu, Gly-Ala-His, Gly-Ala-Trp-Ala, and Gly-Ala-Leu-Ala-Ala-His were the amino acid sequences of the purified peptides.

To extract a strong antioxidant peptide from Crassostreagigas oysters, in vitro gastrointestinal digestion was utilized. The peptide, which had the amino acid sequence Leu-Lys-GlnGlu-Leu-Glu-Asp-Leu-Leu-Glu-Lys-Gln-Glu (1. 60 kDa), shown increased efficacy against the peroxidation of polyunsaturated fatty acids (PUFAs) and also scavenged superoxide and hydroxyl radicals, respectively (Qian *et al.*, 2008). A bioactive antioxidant peptide (leu-lys-gln-glu-leu-glu-aspleu- leu-glu-lys-gln-glu) has been isolated from the Oyster, Crassostrea gigas and which exhibits significant inhibitory effect against polyunsaturated fatty acid peroxidation as compared to α-tocopherol and also scavenged hydroxyl radical (IC50 28 μM) and

superoxide radical (IC50 78. 97μM) (Shukla, 2016; Qian *et al.,* 2008). SCAP1, SCAP3, and SCAP7, three antioxidant peptides, were isolated and described by Umayaparvathi *et al., (*2014) using Q-TOF ESI mass spectrometry from oyster Saccostrea cucullate. SCAP1, SCAP3, and SCAP7 were found to contain the amino acid sequence Leu-Ala-Asn-Ala-Lys (515. 29 Da), Pro-Ser-Leu-Val- Gly-Arg-Pro–Pro-Val-Gly-Lys-Leu-Thr-Leu (1,432. 89 Da), and Val-Lys-Val-Leu-Leu-Glu-His-Pro-Val-Leu (1,145. 75 Da).

Furthermore, peptides obtained by hydrolysis with proteolytic enzymes of the viscera and body of the clam (Meretrix casta), resulted in significant DPPH radical scavenging activities and reducing power (Pangestuti and Kim, 2017). Two peptide hydrolysate fractions from the Marine Bivalve Mollusc, Tergillarca granosa, have also been demonstrated to exhibit antioxidant activity (Yang *et al.,* 2019). The peptides with amino acid composition (and thus designated) MDLFTE and WPPD exhibited strong DPPH free radical scavenging (EC50 = 0. 53 and 0. 36 mg/mL, respectively), hydroxyl radical scavenging (EC50 = 0. 47 and 0. 38 mg/mL respectively), superoxide anion radical (EC50 = 0. 75 and 0. 46 mg/mL, respectively) and ABTS cation radical scavenging (EC50 = 0. 96 and 0. 54 mg/mL, respectively) activities, although these antioxidant activities were not sustained at basic pH conditions (pH > 9 for 2. 5 h), high temperatures (>80ºC for 0. 5 h) nor during simulated GI digestion (Yang *et al.,* 2019).

Four of the most prevalent peptide fractions were recently identified by Anh *et al.,* (2023) using LC-MS analysis of hydrolysates from green mussels and oysters. The two fractions found in oysters were Asn-Lys-Gln-Ala (F1) and Val-Val-Val-Asp-Val-Gly-Ile (F2), while the two fractions found in green mussels were Gly-Arg-Thr-Tyr (F3) and Pro-Thr-Gln-Val-Lys-Leu (F4). The IC50 values in DPPH (6. 39 mg/mL for oysters and 10. 4 mg/mL for green mussels) and ABTS (18. 0 mg/mL for oysters and 18. 3 mg/mL for green mussels) were used to assess the antioxidant activity of these peptides. Bioactive peptides have been receiving much interest due to their significantly different amino acid contents (Wang *et al.,* 2017). Certain peptides (SCAP1, SCAP3) that were extracted from oysters (Saccostrea cucullata) have been found to possess antioxidant and anticancer characteristics. (Umayaparvathi *et al.,* 2014; 2015). Qian *et al., (*2020) also identified Antioxidant and anti-inflammatory peptide fraction from oyster soft tissue by enzymatic hydrolysis. In another study Jayaprakash and Perera., (2020) purified and characterized bioactive peptides from cooked New Zealand green-lipped mussel (Perna canaliculus) protein hydrolyzates. More specifically, the ABTS results for Vietnamese green mussel hydrolysate of 81. 61 ± 0. 48% were better than the radical scavenging activity in green-lipped mussel (Perna canaliculus) grown in New Zealand of around 77%.

CONCLUSION

This review demonstrates that marine organisms show major potential as naturalsources of bioactive peptides and amino acids. Inparticular, it highlights that marine-derived hydrolysatescontain significant quantities of structurally diverse proteinsthat could actas substrates for the generation of novelbioactive peptides especially antioxidant peptides. These findings imply the possible use of marine hydrolysate as novel building blocks for the creation of functional foods with antioxidant and anticancer properties.

REFERENCES

[1]. Anand, T. P., Chellaram, C., Kuberan, G., & Archana, H. (2012). Bioactive peptides from marine sources- A Review. Indian J Inno Dev. 1 (S8), 61-64.

[2]. Aneiros, A., &Garateix, A. (2004). Bioactive peptides from marine sources: Pharmacological properties and isolation procedures. Journal of Chromatography B, 803, 41-53.

[3]. Anh, P. T. H., Trang, H. P., Thanh, B. Đ., Trinh, N. T. N., Thang, T. Đ., Phuong, D. L., Tuan, N. N., & Huyen, T. T. (2023). Antioxidant capacity and sequence of peptides derived from oysters and green mussels in Vietnam. International Food Research Journal, 30 (3), 736-749.

[4]. Benkendorff, K. (2010). Molluscan biological and chemical diversity: Secondary metabolites and medicinal resources produced by marine molluscs. Biol. Rev. Camb. Philos. Soc., 85 (4), 757-775.

[5]. Bougatef, A., Nedjar-Arroume, N., Manni, L., Ravallec, R., Barkia, A., Guillochon, D., &Nasri, M. (2010). Purification and identification of novel antioxidant peptides from enzymatic hydrolysates of sardinelle (Sardinellaaurita) by-products proteins. Food Chemistry, 118: 559-65.

[6]. Chakraborty, C., Hsu, C., Wen, Z., & Lin, C. (2009). Anticancer drugs discovery and development from marine organisms. Curr. Top. Med. Chem., 9, 1536-1545.

[7]. Datta, D., Talapatra, S. N., & Swarnakar, S. (2015). Bioactive compounds from marine invertebrates for potential medicines – An overview. Int. Lett. Nat. Sci. Online, 34, 42-61.

[8]. Hien, B. T., Huong, T., Tung, T. T., Diem, L. A., Que, L. X., Hao, D. V. & Thanh, T. V. (2021). Study of enzymatic hydrolysis from catfish by-products as feed stuff ingredients. Vietnam Journal of Agriculture and Rural Development, 4, 80-88.

[9]. Huang, F., Ding, G., Yang, Z., & Yu, F. (2017). Two novel peptides derived from Sinonovaculaconstricta inhibit the proliferation and induce apoptosis of human prostate cancer cells. Mol. Med. Rep., 16 (5), 6697-6707.

[10]. Jayaprakash, R., &Perera, C. O. (2020). Partial purification and characterization of bioactive peptides from cooked New Zealand green-lipped mussel (Perna canaliculus) protein hydrolyzates. Foods, 9 (7), 879.

[11]. Je, J. Y., Qian, Z. J., Lee, S. H., Byun, H. G., & Kim, S. K. (2008). Purification and antioxidant properties of bigeye tuna (Thunnusobesus) dark muscle peptide on free radical-mediated oxidation systems. Journal of Medicinal Food, 11 (4): 629-637.

[12]. Jha, R. K., & Xuzi-Rong. (2004). Biomedical compounds from marine organisms. Mar Drugs, 2, 123-146.

[13]. Jirge, S. S., & Chaudhari, Y. S. (2010). Marine: The ultimate source of bioactives and drug metabolites. IJRAP, 1 (1), 55-62.

[14]. Kanagasabapathy, S., Samuthirapandian, R., & Kumaresan, M. (2011). Preliminary studies for a new antibiotic from the marine mollusc Melo melo (Lightfoot 1786). Asian. Pac. J. Trop. Med. 4, 310-314.

[15]. Kang, H. K., Choi, M. C., Seo, C. H., & Park, Y. (2018). Therapeutic properties and biological Benefits of marine-derived anticancer Peptides. Int J Mol Sci. 19, 919.

[16]. Liu, M., Zhao, X., Zhao, J., Xiao, L., Liu, H., Wang, C., Cheng, L., Wu, N., & Lin, X. (2012). Induction of apoptosis, G0/G1 phase arrest and microtubule disassembly in K562 leukemia cells by Mere15, a novel polypeptide from Meretrix meretrix Linnaeus. Mar Drugs, 10, 2596-2607.

[17]. Liu, Z. Y., Dong, S. Y., Xu, J., Zeng, M. Y., Song, H. X., & Zhao, Y. H. (2008). Production of cysteine-rich antimicrobial peptide by digestion of oyster (Crassostreagigas) with alcalase and bromelin. Food Control,19: 231-235.

[18]. Mitta, G., Vandenbulcke, F., & Roch, P. (2000). Original involvement of antimicrobial peptides in mussel innate immunity. FEBS Letters, 486, 185-190.

[19]. Nazeer, R. A., &Srividhya, T. S. (2011). Antioxidant Peptides from the Protein Hydrolysates of Conusbetulinus. Int. J. Pept. Res. Ther,17: 231-237.

[20]. Oh, Y., Ahn, C. B., Nam, K. H., Kim, Y. K., Yoon, N. Y., & Je, J. Y. (2019). Amino acid composition, antioxidant and cytoprotective effect of blue mussel (Mytilus edulis) hydrolysate through the inhibition of caspase-3 activation in oxidative stress-mediated endothelial cell injury. Mar Drugs, 17 (2), 135.

[21]. Pangestuti, R., & Kim, S. (2017). Bioactive peptide of marine origin for the prevention and treatment of non-communicable diseases. Mar Drugs, 15 (3), 67.

[22]. Pangestuti, R., & Kim, S. (2017). Bioactive peptide of marine origin for the prevention and treatment of non-communicable diseases. Mar Drugs, 15 (3), 67.

[23]. Purwaningsih, S. (2012). Aktivitas antioksidan dan komposisi kimia keong matah merah (Cerithidea obtusa). Indo. J. Mar. Sci. 17 (1), 39-48.

[24]. Qian, B., Zhao, X., Yang, Y., & Tian, C. (2020). Antioxidant and anti-inflammatory peptide fraction from oyster soft tissue by enzymatic hydrolysis. Food Science and Nutrition, 8 (7), 3947-3956.

[25]. Qian, Z. J., Jung, W. K., Byun, H. G., & Kim, S. K. (2008). Protective effect of an antioxidative peptide purified from gastrointestinal digest of oyster Crassostrea gigas against Free Radical Induced DNA Damage. Bioresearch Tech., 99, 3365-3371.

[26]. Salehi, A., Patong, R., & Ahmad, A. (2014). Isolation and characterization of some kind bioactive proteins sponge as antibacterial agent. Int. J. Sci. Tech. Res. (IJSTR), 3 (2), 233-236.

[27]. Sampath Kumar, N. S., Nazeer, R. A. &Jaiganesh, R. (2012). Purification and identification of antioxidant peptides from the skin protein hydrolysate of two marine fishes, horse mackerel (Magalaspiscordyla) and croaker (Otolithesruber). Amino Acids,42: 1641-1649.

[28]. Shukla, S. (2016). Therapeutic importance of peptides from marine sources: A mini review. Indian J Mar Sci. 45 (11), 1422-1431.

[29]. Sohail Khan., Abdur Rehman., Haroon Shah., Rana Muhammad Aadil., Ahmad Ali., Qayyum Shehzad., Waqas Ashraf., Fang Yang., Aiman Karim., Adnan Khaliq., & Wenshui Xia. (2020). Fish Protein and Its Derivatives: The Novel Applications, Bioactivities, and Their Functional Significance in Food Products. Food Reviews International, DOI: 10. 1080/87559129. 2020. 1828452.

[30]. Suarez-Jimenez, G., Burgos-Hernandez, A., & Ezquerra-Brauer, J. (2012). Bioactive peptides and depsipeptides with anticancer potential: Sources from marine animals. Mar Drugs, 10, 963-986.

[31]. Sun, J., Liu, H., Zhou, S., Wang, X., Fan, M., Shen, W., & Liao, Z. (2014). A Novel antimicrobial peptide identified from Mytilus coruscus. Acta Hydrobiologica Sinica, 3, 563-570.

[32]. Umayaparvathi, S., Arumugam, M., Meenakshi, S., & Balasubramanian, T. (2015). Antioxidant Properties of Protein Hydrolysate Obtained from Oyster Saccostrea cucullate (Born, 1778). Journal of Aquatic Food Product Technology, 24, 502-515.

[33]. Umayaparvathi, S., Arumugam, M., Meenakshi, S., Gerald Dra¨ger., Andreas Kirschning.,& Balasubramanian, T. (2014). Purification and Characterization of Antioxidant Peptides from Oyster (Saccostrea cucullata) Hydrolysate and the Anticancer Activity of Hydrolysate on Human Colon Cancer Cell Lines. Int. J. Pept. Res. Ther. 20, 231-243.

[34]. Umayaparvathi, S., Meenakshi, S., Vimalraj, V., Arumugam, M., Sivagami, G., &Balasubramanian, T. (2014). Antioxidant activity and anticancer effect of bioactive peptide from enzymatic hydrolysate of oyster (Saccostrea cucullata). Biomedicine and Preventive Nutrition, 4 (3), 343-353.

[35]. Wang, H., Wei, J., Wu, N., Liu, M., Wang, C., Zhang, Y., Wang, F., Liu, H., & Lin, X. (2013). Mere15, a novel polypeptide from Meretrix meretrix, inhibits adhesion, migration and invasion of human lung cancer A549 cells via downregulating MMPs. Pharm Biol. 51,145-151.

[36]. Wang, X., Yu, H., Xing, R., & Li, P. (2017). Characterization, preparation, and purification of marine bioactive peptides. Bio Med Research International, 2017, 9746720. doi: 10. 1155/2017/9746720

[37]. Yang, X. R., Qiu, Y. T., Zhao, Y. Q., Chi, C. F., & Wang, B. (2019). Purification and characterization of antioxidant peptides derived from protein hydrolysate of the marine bivalve mollusk Tergillarca granosa. Mar Drugs, 17 (5), 251.

Chapter 18

BIOMOLECULE: ECOFRIENDLY BIOPLASTIC

SWATI VILHEKAR*[1], PRERANA P. BHATKAR[2] AND DEEPTI V. GHODEKAR[3]

[1]Institute of Science, Mumbai
[2]Smt Radhabai Sarda Arts, Commerce and Science College, Anjangaon Surji
[3]Institute of Science, Mumbai.
*Corresponding author E-mail: mitubotany@gmail.com

ABSTRACT

What Are Plastics and Where Do They Originate? Plastic was initially defined as "pliable and easily shaped. " It was only lately that it got the term for a class of materials known as polymers. Polymers are comprised of lengthy chains of molecules and have the meaning "of many parts. " Polymers are abundant in nature. Cellulose, the substance that makes up plant cell walls, is a common natural polymer. [20,31]. Almost all synthetic plastics are derived from petroleum and its byproducts. These resources have taken over millions of years to form and are limited in number. Furthermore, plastics manufactured from fossil fuels are typically non-biodegradable. Plastics' growing use has resulted in a rise in plastic garbage, which is frequently disposed as municipal solid waste. As a result, there is an urgent need to produce non-petroleum-based and sustainable feed supplies, which has primarily redirected the focus of many academic and industry researchers towards biobased and biodegradable polymers. Biobased plastics or bioplastics are sustainable, largely biodegradable, and biocompatible, and they reduce our reliance on depleting fossil fuels and are $C0_2$ neutral. However, despite providing a timely and essential need for environmental sustainability, bioplastics have yet to gain a strong position in the plastics world due to less than superior properties of bioplastics compared to their synthetic counterparts. As a result, scientists and engineers worldwide have been investigating ways to enhance the characteristics of bioplastics by blending/compounding them with other polymers and fibres. Green composites, which are made by combining bioplastics and natural fibres, give a sustainable alternative that is completely biodegradable.

KEYWORDS: Bioplastic, Biodegradble Plastic, Material of Bioplastic

INTRODUCTION

NATURE OF PLASTIC

Plastics have progressed from the use of naturally plastic materials (such as gums and shellac) to chemical modification of those materials (such as natural rubber, cellulose, collagen, and milk proteins), and finally to completely synthetic plastics (such as bakelite, epoxy, and PVC). Early plastics were made from organic polymers generated from bio-materials such as egg and blood proteins. Mesoamericans employed natural rubber for balls, bands, and figurines circa 1600 BC. [2]. Bakelite was the world's first entirely synthetic plastic, created in New York in 1907 by Leo Baekeland [1], who popularised the phrase plastics. [9]. Many chemists, including Nobel laureate Hermann Staudinger, have contributed to the materials science of plastics. who has been referred to as "the father of polymer chemistry," and Herman Mark, who has been referred to as "the father of polymer physics. " [9]. What is the difference between polymer and plastic polymer?

DEFINITION OF PLASTIC- Polymers are huge molecules with the same structural unit repeated many times. Plastic is a polymer with a high molecular weight.

NATURE- It might be natural or manufactured. a man-made polymer STRUCTURE – Polymer chains can be either short or long. Polymer chains that are lengthy.

VERSATILITY - The majority of polymers are adaptable. Extremely adaptable Is plastic a kind of polymer? Polymers are all plastics, but not all plastics are polymers. Plastic is a particular sort of polymer. Plastics are man-made and do not exist in nature. [16]. Polymers' repeating units are frequently carbon and hydrogen, but also oxygen, nitrogen, sulphur, chlorine, fluorine, phosphorus, and silicon. [16].

Polymers have very different physical and chemical properties than their monomers. Moreover, according to the number of repeating units in the polymer,

What is Plastic? Plastic is also polymer that has a large molecular mass. The monomers of plastic can be either natural or synthetic. We produce plastic from petrochemicals. Hence, plastic is a synthetic polymer. [16].

Plastics are widely used in a variety of applications, including bottles, bags, boxes, fibres, films, and so on. Plastics can be chemically resistant and thermal and electrical insulators. [26]. The term plasticity here refers to the deformability of the materials used in the production of plastics. Plasticity enables moulding, extrusion, or compression into a wide range of forms, including films, fibres, plates, tubes, bottles, and boxes. Outside the scope of this article, plasticity has a technical term in materials science that refers to the irreversible change in shape of solid substances. Organic polymers are included in the majority of plastics [7].

INTRODUCTION TO BIOPLASTIC

Plastics' extensive usage has become a major cause of worry owing to their harmful influence on the environment, particularly the sources from which plastics are created and their biodegradability. Green composites, which are made by combining bioplastics and natural fibres, give a sustainable alternative that is completely biodegradable. However, studies are being conducted to combine bioplastics with synthetic fillers and/or synthetic plastics with natural fibres. Biocomposites are materials that not only give excellent qualities to fulfil the goal application, but also lessen the carbon footprint on the environment. [12].

The terms 'biobased' and 'biodegradable' are not synonymous. The attribute of biodegradation is tied to a material's chemical structure rather than its resource foundation. In other words, 100% biobased plastics may be non-biodegradable, whereas 100% fossil-based plastics may be biodegradable. [15].

'BIOPLASTIC TYPES'

Bioplastics based on polysaccharides Plastics derived from starch Thermoplastic starch is the most frequently used bioplastic, accounting for over half of the bioplastics market. [33]. Straightforward starch Gelatinizing starch and solution casting can be used to make bioplastic film at home. [24]. Pure starch absorbs humidity and is thus a good substance for the pharmaceutical industry's creation of medication capsules. Pure starch-based bioplastic, on the other hand, is brittle. Plasticizers such as glycerol, glycol, and sorbitol can also be added to allow the starch to be thermo-plastically treated. [21]. By varying the proportions of these additions, the properties of the resultant bioplastic (also known as "thermoplastic starch") may be adjusted to individual applications. Starch may be converted into bioplastic using conventional polymer manufacturing processes. Extrusion, injection moulding, compression moulding, and solution casting are techniques of traditional polymer processing processes that may be utilised to convert starch into bioplastic. [21]. The amylose/amylopectin ratio has a substantial impact on the

characteristics of starch bioplastic. High-amylose starch often has greater mechanical characteristics. [22]. High-amylose, on the other hand Biodegradable Plastics vs. Bioplastics When discussing alternative plastics, two words are frequently misconstrued or used interchangeably when they should not be: bioplastics and biodegradable plastics. [13]. What Exactly Are Bioplastics? We call conventional plastic, plastic that is made from fossil fuels and is non-biodegradable. Most of these plastics take centuries to degrade in the environment, and oil-derived plastics leave harmful residues in the soil or water. However, a material might be classified as a bioplastic if it is biobased and biodegradable or biobased but not biodegradable. [14]. Bioplastics are often manufactured from maize starch, cassava starch, or sugarcane. They are a better alternative to petroleum-based plastic since they disintegrate faster and with fewer pollutants. [14]. However, this might be deceiving because just dumping rubbish of any type in a landfill is not a smart idea. Its disintegration, like that of most organic materials, produces methane gas, a greenhouse gas many times more powerful than carbon dioxide. Bioplastics should instead be transported to a professional composting facility where bacteria may break them down in a controlled manner. [13]. The biomass portion of these plant-based plastics produces methane as it decomposes, and they behave in the water like traditional plastics, disintegrating into microplastics and damaging marine life that confuses them for food. [14].

What Is Biodegradable Plastic, Exactly? Biodegradable plastics, on the other hand, are petroleum-based polymers that have been treated with a degradable component. This phrase is frequently used interchangeably with bioplastics, despite the fact that the two are chemically quite distinct. [13].

Because the process of breaking down the material in a compost pile is strongly dependent on humidity and temperature, the word "biodegradable" can potentially mislead customers. Many polymers with this promise will only biodegrade in industrial settings with high enough temperatures. There are numerous different forms of biodegradable plastics, but the most prevalent are polylactic acid (PLA) and polyhydroxyalkanoates (PHA) derived from starch. PLA has the ability to "look and behave like polyethylene (used in plastic films, packing, and bottles), polystyrene (used in plastic foam and plastic cutlery), or polypropylene (used in packaging, auto parts, and textiles)," whereas PHA is produced by microorganisms that produce plastic from carbon-rich organic material and is used in industrial applications such as injection-molded auto parts. [14].

"Biodegradable" because the process of breaking down starch has less process ability due to its greater gelatinization temperature [23]. Plastics derived from cellulose. Cellulose bioplastics are mostly composed of cellulose esters (such as cellulose acetate and nitrocellulose) and their derivatives, such as celluloid. When cellulose is significantly changed, it can become thermoplastic. One example is cellulose acetate, which is costly and so infrequently used in packaging. Due to their lower hydrophilicity than starch, cellulosic fibres added to starches can increase mechanical characteristics, gas permeability, and water resistance [4]. A team from Shanghai University used a technique known as hot pressing to create a new green plastic based on cellulose [29].

Protein-based plastics Bioplastics can be made from a variety of proteins. For example, wheat gluten, milk, and casein show promising properties as a raw material for various biodegradable polymers [30]. Additionally, soy protein is being considered as another source of bioplastic. Soy proteins have been used in plastic production for over a century, and the body panels of an original Ford automobile were made of soy-based plastic [27]. Because of their water sensitivity and relatively high cost, soy protein-based polymers pose challenges. As a result, combining soy protein with certain commercially available biodegradable polyesters enhances water sensitivity and cost. [36]. Polyesters with aliphatic chains PHB

(poly-3-hydroxybutyrate), PHA (polyhydroxyalkanoates), PHV (polyhydroxyvalerate), polyhydroxyhexanoate PHH, PLA (polylactic acid), and polyamide 11 (PA11) are examples of biobased polyesters. They are all susceptible to hydrolytic breakdown to varying degrees and can be combined with other chemicals. [17]. Polyethylene (Organic) Polyethylene derived from the fermentation of basic agricultural ingredients such as sugar cane and maize, rather than from fossil fuels. [17].

BENEFITS OF BIOPLASTICS

Bioplastics are pushing plastics evolution. Biobased plastic products have two key benefits over traditional plastics: they conserve fossil resources by employing biomass that regenerates (annually) and have the unique possibility for carbon neutrality. Furthermore, biodegradability is a feature of several forms of bioplastics. It provides extra recovery options at the conclusion of a product's life cycle. [15]. Where Are Bioplastics Used Right Now? Bioplastics may appear to be a new age idea, yet they have been around for at least a century. The Ford Model T, for example, was built with maize and soybean oil components. As the difficulties associated with petroleum-based plastics have become more evident, bioplastics are increasingly being utilised to manufacture food containers, supermarket bags, disposable cutlery, packaging, and other items. PLA, in example, has been employed in a variety of applications such as plastic films, bottles, medical equipment, and shrink wrap. It has also been utilised in 3D printing for specialised purposes. Bioplastics have been used in the packaging materials of several major corporations, including Coca-Cola, PepsiCo, Heinz, Ford, Mercedes-Benz, and Toyota. [17].

ENVIRONMENTAL IMPACT OF BIOPLASTIC

Materials such as starch, cellulose, wood, sugar, and biomass are utilised to generate bioplastics in place of fossil fuel resources, making bioplastic manufacturing a more sustainable activity than traditional plastic production [11]. The environmental effect of bioplastics is frequently discussed, as there are several criteria for "greenness" (for example, water usage, energy use, deforestation, biodegradation, and so on) [35,3,25]. As a result, the environmental implications of bioplastics are classified as nonrenewable energy usage, climate change, eutrophication, and acidification [34]. Bioplastic manufacture cuts greenhouse gas emissions and nonrenewable energy use dramatically [11]. Bioplastics would also allow businesses all over the world to improve the environmental sustainability of their goods. [5]. Although bioplastics utilise less nonrenewable energy than traditional plastics and release less greenhouse gases, they can have severe environmental effects such as eutrophication and acidification [34]. Bioplastics have a larger potential for eutrophication than ordinary plastics. Biomass generation during industrial agricultural practises causes nitrate and phosphate to filter into water bodies, resulting in eutrophication, the process by which a body of water becomes too nutrient-rich. [34]. Eutrophication is a global danger to water resources because it creates destructive algal blooms, which create oxygen dead zones and kill aquatic organisms. [28]. Although bioplastics utilise less nonrenewable energy than traditional plastics and release less greenhouse gases, they can have severe environmental effects such as eutrophication and acidification [34]. Bioplastics have a larger potential for eutrophication than ordinary plastics. Biomass generation during industrial agricultural practises causes nitrate and phosphate to filter into water bodies, resulting in eutrophication, the process by which a body of water becomes too nutrient-rich. [34]. Eutrophication is a global danger to water resources because it creates destructive algal blooms, which create oxygen dead zones and kill aquatic organisms. [28]. Certain types of bioplastics as well as conventional plastics containing additives are able to biodegrade. [10]. Bioplastics may biodegrade in a variety of situations, making them more acceptable than traditional plastics. Bioplastics biodegrade in a variety of habitats, including soil, aquatic environments, and compost. Because the structure and content

of a biopolymer or bio-composite influence the biodegradation process, altering the composition and structure may improve biodegradability. Because of their great microbial variety, soil and compost as environmental conditions are more effective in biodegradation composting not only biodegrades bioplastics effectively, but it also considerably decreases greenhouse gas emissions. Bioplastics' biodegradability in compost settings can be improved by adding more soluble sugar and raising the temperature. faster than the infrastructure we need for their safe, circular disposal and multinational Soil environments, on the other hand, include a wide variety of microorganisms, making biodegradation of bioplastics easier. However, bioplastics in soil settings require greater temperatures and a longer biodegradation period. Some bioplastics biodegrade more quickly in bodies of water and marine systems; nonetheless, this poses a risk to marine ecosystems and freshwater. [8]. As a result, it is reasonable to assume that biodegradation of bioplastics in water bodies, which results in the death of aquatic species and polluted water, is one of the negative environmental effects of bioplastics. For the time being, consider bioplastics to be plastic. For the Time Being, Think of Bioplastics as Plastic The reality is that we are producing bioplastics faster than the infrastructure required for their safe, circular disposal, and multinational brands must lead the way on clear, transparent labelling to educate consumers. Until we establish an end-of-life solution for bioplastics, they will end up in landfills or polluting waterways in the same way that conventional plastic does. For the Time Being, Think of Bioplastics as Plastic The reality is that we are producing bioplastics faster than the infrastructure required for their safe, circular disposal, and multinational brands must lead the way on clear, transparent labelling to educate consumers. Until we establish an end-of-life solution for bioplastics, they will end up in landfills or polluting waterways in the same way that conventional plastic does. [19].

CONCLUSION

The bioplastic making by using Agar –agar powder, Gelatin powder and Starch with Glycerol/Glycerine as plasticizer. Different combinations and proportion of ingredients used to form different types of bioplastics. To check their different properties, Physical properties like Tensile strength, Elongation, Thickness, Water absorption capacity of bioplastic were determined using newton meter, Screw gauge, etc. Bioplastic can be characterized by FTIR technique and then bioplastic spectra compared with conventional plastic (HDPE) spectra. Biodegradation test (Natural Degradation) may be conducted with the interval of every 6 days for 21 days to ensured how much percentage of bioplastic degrade in soil in particular time period. Carbon footprint become lesser by use of bioplastic

REFERENCES

[1]. American Chemical Society National Historic Chemical Landmarks. (2015). "Bakelite: The World's First Synthetic Plastic". Retrieved 23 February 2015.

[2]. 2)Andrady AL, Neal MA (July 2009). "Applications and societal benefits of plastics". Philosophical Transactions of the Royal Society of London. Series B, BiologicalSciences. 364 (1526):1977- 84. doi:10. 1098/rstb. 2008. 0304. PMC 2873019. PMID 19528050.

[3]. "Are biodegradable plastics better for the environment?". Axion. 6 February (2018). Retrieved 2018-12-14. v

[4]. Avérous, Luc; Pollet, Eric (2014), "Nanobiocomposites Based on Plasticized Starch", Starch Polymers, Elsevier, pp. 211–239, doi:10. 1016/b978-0-444-53730- 0. 00028-2, ISBN 9780444537300

[5]. Brockhaus, Sebastian, *et al.*, "A Crossroads for Bioplastics: Exploring Product Developers' Challenges to Move beyond Petroleum-Based Plastics. " Journal of Cleaner Production, vol. 127, Elsevier Ltd, 2016, pp. 84–95, doi:10. 1016/j. jclepro. 2016. 04. 003

[6]. Degli-Innocenti, Francesco. "Biodegradation of Plastics and Ecotoxicity Testing: When Should It Be Done. " Frontiers in Microbiology, vol. 5, no. SEP, 2014, pp. 1–3, doi:10. 3389/fmicb. 2014. 00475.

[7]. Ebbing D, Gammon SD (2016). General Chemistry. Cengage Learning. ISBN 978- 1-305-88729-9. 24]. 16, 2018 Posted May. "Polymer vs Plastic: What's the Difference?" Osborne Industries, 16 May 2018. https://www. differencebetween.com/difference-betweenpolymer-and-vs-plastic/

[8]. Emadian, S. Mehdi, *et al.,* (2017). "Biodegradation of Bioplastics in Natural Environments. " Waste Management, vol. 59, Elsevier Ltd, 2017, pp. 526–36, doi:10. 1016/j. wasman. 2016. 10. 006.

[9]. Edgar D, Edgar R (2009). Fantastic Recycled Plastic: 30 Clever Creations to Spark Your Imagination. Sterling Publishing Company, Inc. ISBN 978-1-60059-342-0 – via Google Books.

[10]. Gómez, Eddie F., and Frederick C. Michel. (2013). "Biodegradability of Conventional and Bio-Based Plastics and Natural Fiber Composites during Composting, Anaerobic Digestion and Long-Term Soil Incubation. " Polymer Degradation and Stability, vol. 98, no. 12, 2013, pp. 2583–2591., doi:10. 1016/j. polymdegradstab. 2013. 09. 018.

[11]. Gironi, F., and Vincenzo Piemonte. (2011). "Bioplastics and Petroleum-Based Plastics: Strengths and Weaknesses. " Energy Sources, Part A: Recovery, Utilization and Environmental Effects, vol. 33, no. 21, 2011, pp. 1949–59, doi:10. 1080/15567030903436830.

[12]. Handbook of Bioplastics and Biocomposites Engineering Applications Edited by Srikanth Pilla Wisconsin Institute for Discovery University of Wisconsin-Madison, USA

[13]. https://minipakr.com/blogs/news/biodegradable-vs-bioplastics-what-s-thedifference

[14]. https://earth911.com/business-policy/bioplastics-biodegradable-plasticscompostable-plastics/

[15]. https://www. european-bioplastics. org/bioplastics/

[16]. https://www. rspinc.com/blog/plastic-injection-molding/polymer-vsplastic/#:~:text=The%20terms%20polymer%20and%20plastic,are%20smaller%20than%20plastic%20molecules.

[17]. https://www. urthpact.com/bioplastics-basics/

[18]. https://en. wikipedia. org/wiki/Bioplastic

[19]. https://www. conserve-energy-future.com/causes-effects-and-solutions-toeutrophication. php

[20]. Joseph L. Nicholson and George R. Leighton, (1942). "Plastics Come of Age," Harper's Magazine, August 1942, p. 306.

[21]. Liu, Hongsheng; Xie, Fengwei; Yu, Long; Chen, Ling; Li, Lin (2009-12-01). "Thermal processing of starch-based polymers". Progress in Polymer Science. 34 (12): 1348–1368. doi:10. 1016/j. progpolymsci. 2009. 07. 001. ISSN 0079-6700.

[22]. Li, Ming; Liu, Peng; Zou, Wei; Yu, Long; Xie, Fengwei; Pu, Huayin; Liu, Hongshen; Chen, Ling (2011-09-01). "Extrusion processing and characterization of edible starch films with different amylose contents". Journal of Food Engineering. 106 (1): 95–101. doi:10. 1016/j. jfoodeng. 2011. 04. 021. ISSN 0260-8774.

[23]. Liu, Hongsheng; Yu, Long; Xie, Fengwei; Chen, Ling (2006-08-15). "Gelatinization of cornstarch with different amylose/amylopectin content". Carbohydrate Polymers. 65 (3): 357–363. doi:10. 1016/j. carbpol. 2006. 01. 026. ISSN 0144-8617. S2CID 85239192.

[24]. Make Potato Plastic!. Instructables.com (2007-07-26). Retrieved 2011-08-14.

[25]. Miles, Lindsay (22 March 2018). "Biodegradable Plastic: Is It Really EcoFriendly?". Retrieved 2018-12-14.

[26]. "Plastikos" πλαστι^κ-ός. Henry George Liddell, Robert Scott, A Greek-English Lexicon. Retrieved 2011-07-01. 14]. "Plastic". Online Etymology Dictionary. Retrieved 2021-07-29.

[27]. Ralston, Brian E; Osswald, Tim A. (February 2008). "The History of Tomorrow's Materials: Protein-Based Biopolymers". Plastics Engineering. 64 (2):36– 40. doi:10. 1002/j. 1941-9635. 2008. tb00292. x. ISSN 0091-9578.

[28]. Sinha, E., *et al.,* (2017). "Eutrophication Will Increase during the 21st Century as a Result of Precipitation Changes. " Science, vol. 357, no. July, 2017, pp. 405–08.

[29]. Song, Na; Hou, Xingshuang; Chen, Li; Cui, Siqi; Shi, Liyi; Ding, Peng (2017-05- 16). "A Green Plastic Constructed from Cellulose and Functionalized Graphene with High Thermal Conductivity". ACS Applied Materials & Interfaces. 9 (21): 17914– 17922. doi:10. 1021/acsami. 7b02675. ISSN 1944-8244. PMID 28467836.

[30]. Song, J. H; Murphy, R. J; Narayan, R; Davies, G. B. H. (2009-07- 30)27). "Biodegradable and compostable alternatives to conventional plastics". Philosophical Transactions of the Royal Society B: Biological Sciences. 364 (1526):2127–2139. doi:10. 1098/rstb. 2008. 0289. ISSN 0962- 8436. PMC 2873018. PMID 19528060.

[31]. Susan Freinkel, (2011). Plastics: A Toxic Love Story (New York: Henry Holt, 2011), p. 4.

[32]. Teegarden DM (2004). Polymer Chemistry: Introduction to an Indispensable Science. NSTA Press. ISBN 978-0-87355-221-9 – via Google Books.

[33]. Xie, Fengwei; Yu, Long; Su, Bing; Liu, Peng; Wang, Jun; Liu, Hongshen; Ling (2009-05-01). "Rheological properties of starches with different amylose/amylopectin ratios". Journal of Cereal Science. 49 (3): 371–377. doi:10. 1016/j. jcs. 2009. 01. 002. ISSN 0733-5210Chen,

[34]. Weiss, Martin, *et al.,* (2012). "A Review of the Environmental Impacts of Biobased Materials. " Journal of Industrial Ecology, vol. 16, no. SUPPL. 1, 2012, doi:10. 1111/j. 1530-9290. 2012. 00468. x.

[35]. 35) Yates, Madeleine R., and Claire Y. Barlow. (2013). "Life Cycle Assessments of Biodegradable, Commercial Biopolymers - A Critical Review. " Resources, Conservation and Recycling, vol. 78, Elsevier B. V., 2013, pp. 54–66, doi:10. 1016/j. resconrec. 2013. 06. 010.

[36]. Zhang, Jinwen; Jiang, Long; Zhu, Linyong; Jane, Jay-lin; Mungara, Perminus (May (2006). "Morphology and Properties of Soy Protein and Polylactide Blends". Biomacromolecules. 7 (5):1551–1561. doi:10. 1021/bm050888p. ISSN 1525- 7797. PMID 16677038

Chapter 19

AI ADVANCEMENTS IN DRUG DISCOVERY: A BRIEF OVERVIEW OF RECENT APPLICATIONS

SACHIN S. CHOURASIA

Department of Chemistry, D. B. Science College, Gondia, Maharashtra, India
Corresponding author E-mail: sachinchourasia1409@gmail.com

ABSTRACT

The adoption of artificial intelligence (AI) is on the rise across multiple sectors, with a notable emphasis in the pharmaceutical industry. This review sheds light on the extensive application of AI within the pharmaceutical domain, encompassing areas such as drug discovery, development, and drug repurposing, enhancing pharmaceutical efficiency, and optimizing clinical trials, among others. The review sheds light on the historical aspects of AI in drug development process, its broad and specific applications in various domains of the drug discovery process. The study also introduces few latest AI based model for specific disease mitigation purpose. The analysis questions the projection of AI as panacea for the problems pertaining to the drug discovery and development process. In summary, while AI holds immense promise in drug discovery, it also raises a host of important questions and challenges. Addressing these concerns will be crucial to harness the full potential of AI in revolutionizing pharmaceutical research and improving global healthcare.

KEYWORDS: Artificial Intelligence (AI), Machine Learning (ML), Artificial Neural Network (ANN), QSAR

INTRODUCTION

In recent years, there has been a significant surge in the digitalization of data within the pharmaceutical industry. Nevertheless, this digital transformation presents the formidable challenge of acquiring, analyzing, and effectively utilizing this wealth of information to address intricate clinical issues(Ramesh, 2004). This circumstance underscores the rationale for employing AI, as it possesses the capacity to manage vast datasets through advanced automation(Miles, 2006) as depicted in Figure 1. AI leverages systems and software capable of interpreting and assimilating input data to autonomously make informed decisions aimed at achieving defined objectives.

Fig. 1: Diverse Applications of Artificial Intelligence in the Field of Drug Discovery and Development

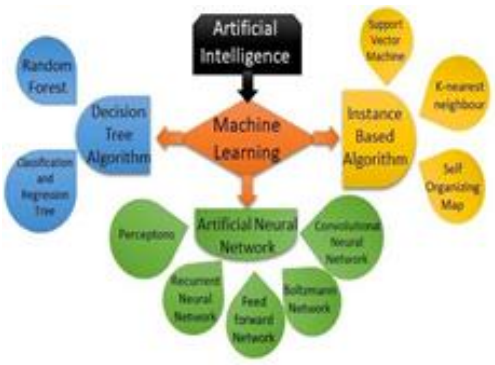


Figure 2: Diverse AI and Machine Learning Fields in the Context of Drug Discovery and Development

DIVERSE SPHERES OF ARTIFICIAL INTELLIGENCE AND PRECISION MEDICINE

AI encompasses a range of methodological domains, including reasoning, knowledge representation, solution search, with one of its core paradigms being machine learning (ML). Machine learning employs algorithms designed to identify patterns within classified datasets.

Within the realm of machine learning, there exists a subfield known as deep learning (DL), which harnesses artificial neural networks (ANNs) (Figure 2). These networks consist of interconnected, complex computational elements akin to 'perceptron,' emulating the electrical impulse transmission observed in the human brain(Beneke, 2019). ANNs encompass a variety of forms, such as multilayer perceptron (MLP) networks, recurrent neural networks (RNNs), and convolutional neural networks (CNNs), which employ supervised or unsupervised training methods(Bielecki, 2019)(Kalyane, 2020). The multilayer perceptron (MLP) network finds applications in tasks like pattern recognition, optimization support, process identification, and control. Typically, MLP networks are trained using one-directional supervised training methods and can serve as versatile pattern classifiers. RNNs are characterized by their closed-loop architecture, enabling them to memorize and retain information, for example the Boltzmann constants and Hopfield networks (Da Silva, 2017)(Medsker, 1999). CNNs are a sequence of dynamic systems featuring localized connections, distinguished by their specific topology. They find utility in tasks related to image and video processing, modeling biological systems, processing intricate brain functions, pattern recognition, and advanced signal processing(Hanggi, 2000). More intricate variations encompass Kohonen networks, RBF networks, LVQ networks, counter-propagation networks, and ADALINE networks(Bielecki, 2019)(Da Silva, 2017). Figure 3 depicts the historical development of AI identifying the disease cancer and subsequent drug discovery.

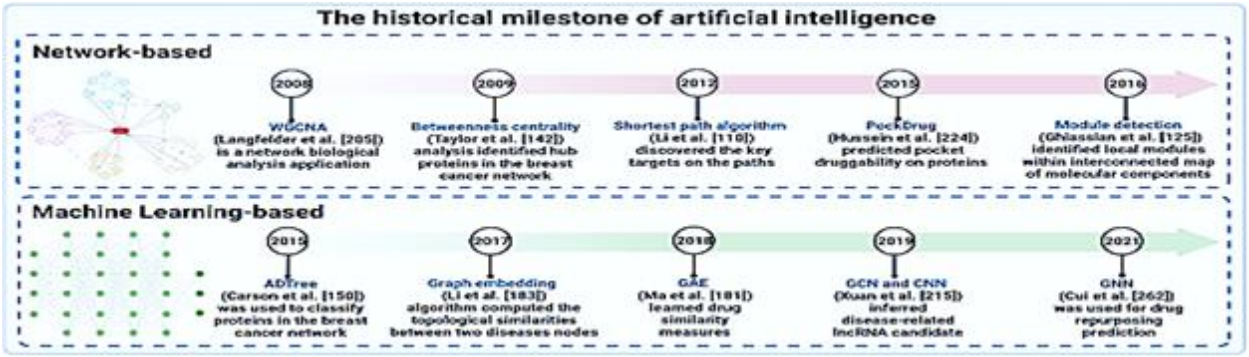


Fig. 3: Historical development AI with respect to cancer identification and drug development (You, 2022)

AI AS A VERSATILE TOOL IN DRUG DISCOVERY

The multimodal AI models(Acosta, 2022) involve amalgamating data from various sources,
including biosensors, genetics, epigenetics, proteomics, microbiome, metabolomics, imaging, textual data, clinical records, social determinants, and environmental factors (Figure 4 & 5). This amalgamated data is then harnessed to create personalized medicine approaches, facilitate real-time pandemic surveillance, conduct digital clinical trials, and deploy virtual health coaching. The work delves into the implementation of methods such as personalized omics for precision health, digital clinical trials, remote monitoring through the 'hospital-at-home' concept, pandemic surveillance, outbreak detection, digital twins, and virtual health assistants.

Fig. 4: Data modalities and opportunities for multimodal biomedical AI(Acosta, 2022)

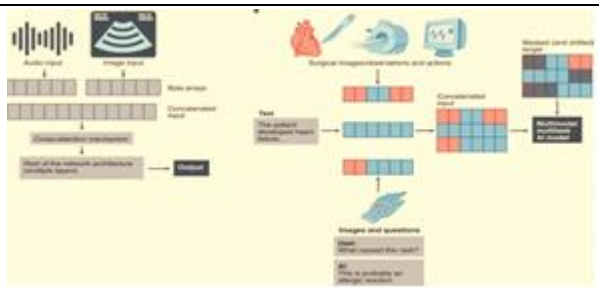


Fig. 5: Simplified illustration of the novel technical concepts in multimodal AI(Acosta, 2022)

Table 1: List of AI-based software for drug discovery, development and analysis(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023)

Reference	Description	Source code
AlphaFold2	Deep learning based model for 3D structure prediction of proteins from amino acid sequences	https://github.com/deepmind/alphafold/
DeepChem	A deep learning library for drug discovery and computational chemistry	https://github.com/deepchem/deepchem
DeepBind	A computational tool to analyze binding between the protein and DNA/RNA	https://github.com/MedChaabane/DeepBind-with-PyTorch
DeepBar	A method for accurate and fast prediction of binding free energy	https://fastmbar.readthedocs.io/en/latest/
Deep-Screening	Web-server based in deep learning for virtual screening of compounds	http://deepscreening.xielab.net/
DeepScreen	High performance drug target interaction	https://github.com/cansyl/DEEPScreen
DeepConv-DTI	A convolutional neural network based model for predicting drug-target interactions	https://github.com/GIST-CSBL/DeepConv-DTI
DeepPurpose	A Deep learning library for drug-target interaction, drug-drug interaction, protein-protein interaction and protein function prediction	https://github.com/kexinhuang12345/DeepPurpose
DeepTox	A deep learning model for toxicity prediction of chemical compounds	http://www.bioinf.jku.at/research/DeepTox/github
AtomNet	A deep convolutional neural network for bioactivity prediction	
PathDSP	A deep learning method for predicting drug sensitivity using cancer cell lines	https://github.com/TangYiChing/PathDSP
Graph level representation	Learning graph representation for drug discovery	https://github.com/ZJULearning/graph_level_drug_discovery
Chemical VAE	An auto-encoder based framework to generate new molecules	https://github.com/aspuru-guzik-group/chemical_vae/
DeepGraphMol	A computational method for molecule generation with desired properties using graph neural networks and reinforcement learning	https://github.com/dbkgroup/prop_gen
TorchDrug	A pytorch based flexible framework for drug discovery models	https://torchdrug.ai/

Table 2: List of software for MD simulation, Modeling, Docking, Visualization and analysis of molecules(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023)

Reference	Description	Pros	Cons	Source code
AMBER	A package for MD simulation	High Performance MD, Comprehensive trajectory analysis tools	License required for parallel CPU or GPU computation	https://ambermd.org/
ACEMD	An accelerated platform for faster and longer biomolecular simulations	Super computer level performance	License required for ful functionality	https://www.acellera.com/
AutoDock Vina	A program for molecular docking and screening	Receptor flexibility, blind docking	Difficult to dock small peptides	https://vina.scripps.edu/
DeePMD	A deep learning package for MD simulation and energy representation	Optimized code, interfaced with Tensorflow	Model compression issues	https://github.com/deepmodeling/deepmd-kit/
RBio3D	R package for the analysis of MD trajectories	Tools for protein-networks, conformations	-	http://thegrantlab.org/bio3d/
Pymol	An interactive platform for visualization of molecules	Homology Modeling, Docking, Virtual Screening	License required for full features	https://pymol.org/2/
Rosetta Commons	A tool for predicting the mutant structure	Protein modeling and folding	Preference for aromatics, Preference for hydrogen bonding	https://www.rosettacommons.org/

The study also confronts the associated issues, including modeling complexities, data-related hurdles, and privacy concerns. Authors(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023) have covered the exploration of databases utilized for target identification(J.Y. Khan, 2020), such as BeFree(À. Bravo, 2015), PKDE4J(M. Song, 2018), as well as various deep learning-based tools(T. Alam, 2021)like

SPiDER(D. Reker, 2014). Similarly virtual screening alogwith optimization tools(Ó. Álvarez-Machancoses, 2019)(Q. Zang, 2017) are of importance. Methodswhich are based on deep learning like DeepConv-DTI(I. Lee, 2019) and DeepAffinity(M. Karimi, 2019)aimed for preclinical trial of drug and prediction of side effect(Woo, 2019)(S. Harrer, 2019) are adressed. In the context of drug approval and post-clinical approaches, the authors recommend the use of Natural Language Processing (NLP)(Garg, 2021) and machine learning (ML)-based systems(N. Khalil Zadeh, 2014). Table 1 refers to the list of AI based softwares for drug discovery, development and analysis(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023). Machine learning algorithms utilizing Graphical Neural Networks (GNN), such as AlphaFold2(J. Jumper, 2021), MolCLR(Y. Wang, 2022), and MoleculeNet(Z. Wu, 2018), are valuable tools for tasks involving classification and regression analysis. Additionally, for the generation of molecules, programs based GNN like MolMP(Y. Li, 2018)can be employed. Quantitative Structure Activity Analysis (QSAR)based models can not only assess the stability but can also predict the specific activity of the potential drug molecules(Rahangdale, 2018). Table 2 gives the list of the softwares for MD simulation, modeling, docking, visualization and molecular analysis(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023).

AI AS SPECIFIC TOOL IN DRUG DISCOVERY

AI and NDD:In a comprehensive review(Uddin, 2019), the utilization of artificial intelligence in the realm of neurodevelopmental disorders (NDD) is explored, covering conditions such as Autism Spectrum Disorder(Xiong, 2015)(Bone, 2015)(Kosmicki, 2015)(Wall, 2012), Epileptic Encephalopathy(Munsell, 2015)(Shoeb, 2009)(Yuan, 2011), Intellectual disability(Quinodoz, 2017)(Smyser, 2016)(Crippa, 2015), Attention deficit hyperactivity disorder(Duda, 2016), and rare genetic disorders(Alipanahi, 2015). Incorporating genomics into the artificial intelligence drug development algorithm will significantly improve the application of precision medicine for NDD (Figure 6). Another emerging domain in machine intelligence is Natural Language Processing (NLP), which has the capacity to automatically convert clinical text into structured clinical data(Sheikhalishahi, 2019).

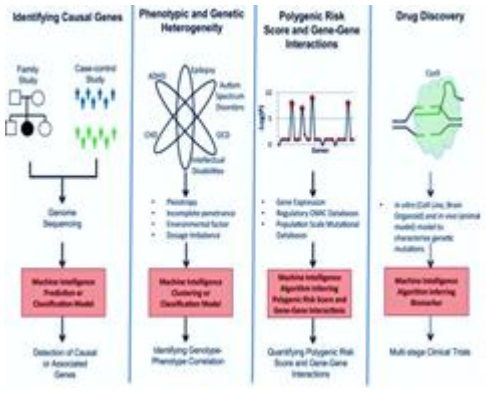


Fig. 6: AI as tool for solving complex problems in NDD(Uddin, 2019)

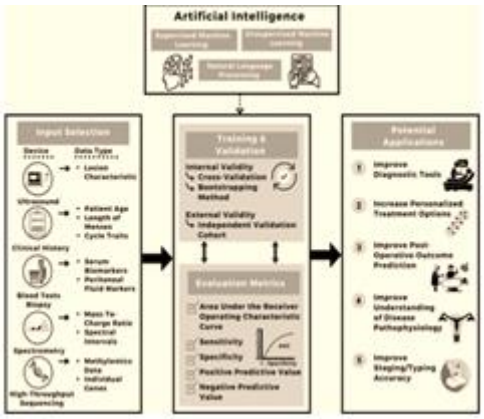


Fig. 7: Potential area of use for AI applications in endometriosis(Sivajohan, 2022)

AI and Endometriosis: In another work(Sivajohan, 2022), AI based 1309 unique records were screened from four databases out of which 36were selected to be worked upon to which techniques like logistic regression followed by decision tree algorithms, random forest, and support vector machines. Roughly 44. 4% (n = 16) of the studies examined the predictive potential of AI approaches in patients with endometriosis, with 47. 2% (n = 17) focusing on diagnostic capabilities, and 8. 33% (n = 3) aimed to enhance the understanding of the disease. These models were constructed using various data types,

including biomarkers, clinical variables, metabolite spectra, genetic factors, imaging data, mixed methodologies, and lesion characteristics. AI models exhibited strong diagnostic and predictive abilities in the context of endometriosis detection, particularly in straightforward classification scenarios (such as distinguishing between cases and controls), which suggests promising prospects for AI in the assessment of endometriosis in the near future (Figure 7).

AI and PD: Presently, there is a lack of effective biomarkers for the diagnosis and monitoring of Parkinson's disease (PD). In response to this, authors have developed an AI model for the detection of PD and the tracking of its progression, utilizing nocturnal breathing signals(Yang, 2022). This model considered substantial dataset encompassing 7,671 individuals, drawing data from various hospitals across the United States and several publicly available datasets. The AI model employs an attention layer that enables it to interpret its predictions in relation to sleep patterns and electroencephalogram data. Moreover, the model can assess PD in the homesetting in a touch less manner, by extracting breathing from radio waves that bounce off a person's body during sleep (Figure 8). The study offers proof that AI can recognize individuals with Parkinson's disease based on their nighttime breathing patterns and can reliably evaluate the severity and progression of the condition. Importantly, results could be validatedusing independent external PD cohort.

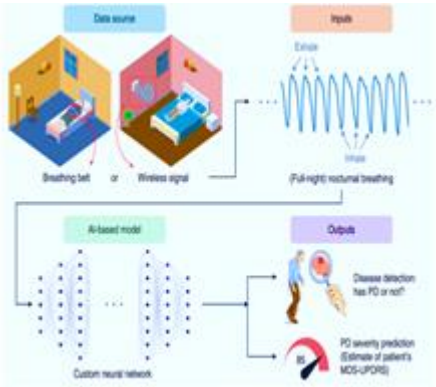


Fig. 8: Artificial intelligence enabled detection and assessment of Parkinson's disease using nocturnal breathing signals(Yang, 2022)

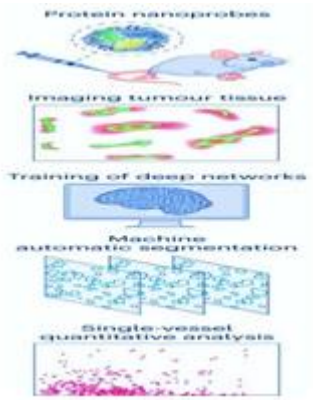


Fig. 9: AI-ML assisted permeability study of nanoparticles in tumour vasculatures(Nuhn, 2023)

AI assisted nanoparticles as antitumor agent: In a research work, authors(Nuhn, 2023)utilize their established ferritin-nanocage system, known for its reliability and precise modifiability, as a carrier model. These carriers are intravenously administered to mice with 32 different subcutaneous tumor types. Subsequently, fluorescent images are collected from tissue sections containing over 67,000 tumor blood vessels. Employing image segmentation-based machine learning technology, the authors establish AI-assisted methods for efficiently analyzing large quantities of microscopic data under high-throughput conditions (Figure 9). This allows for the swift classification of vascular permeability in diverse tumor tissue samples. The doxorubicin-loaded ferritin-nanocages exhibit the ability to directly impede the growth of tumors classified as highly permeable by the machine learning technology. This finding can potentially enhance the delivery of doxorubicin to less permeable tumors, resulting in reduced tumor growth. Nevertheless, further research is necessary to bridge the gap between preclinical investigations and clinical applications.

AI BASED RECENT MODEL FOR DRUG DISCOVERY

DrugnomeAI: Tool to test druggability: In this study, authors employ a stochastic semi-supervised machine learning framework to create DrugnomeAI(Raies, 2022). This tool assesses the likelihood of druggability for each protein-coding gene within the human exome. DrugnomeAI incorporates gene-level characteristics from 15 different sources, resulting in a total of 324 features. Utilizing labeled sets of established drug targets, the tool generates predictions across the entire exome, achieving a median AUC (Area Under the Curve) of 0. 97. Notably, the analysis reveals that features derived from protein-protein interaction networks emerge as the most influential predictors. Furthermore, through the examination of cumulative distribution functions, it became evident that the top 25% of genes ranked by DrugnomeAI account for 95% of genes with clinical support, and 80% of genes with clinical backing are positioned within the top 10% of genes as determined by DrugnomeAI.

DrugRepo: A novel approach to repurposing drugs: This study introduces an innovative scoring algorithm that relies on a combination of chemical and genomic data for the repurposing of drugs across 669 diseases from 22 distinct categories, encompassing conditions like various cancers, musculoskeletal disorders, infections, cardiovascular ailments, and skin diseases. The scoring algorithm is designed using various data types, including chemical structures, drug-target interactions (DTI), pathways, and associations between diseases and genes. DrugRepo(Wang, 2022) serves as a platform for the repurposing or rescue of a wide range of compounds, leveraging both chemical and genomic attributes. Table 3 gives the list of repurposed drugs using DrugRepo. Through the DrugRepo graphical user interface (GUI), users have the ability to select a specific disease, examine approved drugs and their associated targets, as well as candidate compounds. Additionally, users can download the drugs that show potential for repurposing in the context of the chosen disease.

Table 2: Drugs repurposed by DrugRepo at average score≥0. 9(Wang, 2022)

Drug	Repurposed disease name	Actual indications	Average DrugRepo score	Clinical trial phase
Clobetasol	Keratitis	Psoriasis	0.95	NA
Everolimus	Renal cell carcinoma	Subependymal giant cell astrocytoma; Breast adenocarcinoma	0.93	Completed phase 3 (NCT01865747, NCT01668784)
Temsirolimus	Subependymal giant cell astrocytoma	Renal cell carcinoma	0.93	Completed phase 3 (NCT01865747)
Temsirolimus	Breast adenocarcinoma	Renal cell carcinoma	0.92	Completed phase 2 (NCT01111825)
Clobetasol	Chronic myeloproliferative disorder	Allergic rhinitis	0.91	NA
Paliperidone	Developmental disabilities	Schizoaffective Disorder	0.91	Completed phase 3 (NCT00549562)
Alisporivir	Dry eye syndromes	Hepatitis C	0.91	Nil
Terlipressin	Shock	Hepatorenal syndrome	0.91	Completed phase 2 (NCT00481572)
Valproic acid	Bipolar I disorder	Seizures	0.9	Completed phase 1 (NCT01094249)
Ethinyl estradiol	Memory disorders	Turner syndrome	0.9	NA
Ethinyl estradiol	Myocardial infarction	Turner syndrome	0.9	NA

Quris AI : Clinical prediction platform:Through the integration of advanced high-throughput three-dimensional (3D) and multi-organ technologies, real-time monitoring, and the incorporation of genomic diversity in stem cells, work is in the process of developing a Bio-AI Clinical Prediction Platform(Bentwich, I.). This innovative platform aims to provide a dependable means of predicting the clinical safety of drug candidates (Figure 10). It stands out as a groundbreaking system, reducing the reliance on flawed animal testing models and enhancing the accuracy of forecasting which drug candidates will be safe for use in humans. This advancement helps to eliminate the significant costs and time associated with unsuccessful clinical trials. Notably, this platform has demonstrated 85% sensitivity and an impressive 78% specificity when assessing liver toxicity. Additionally, it offers a notably more

cost-effective alternative compared to conventional approaches like organ-on-a-chip methods for achieving the same outcomes.

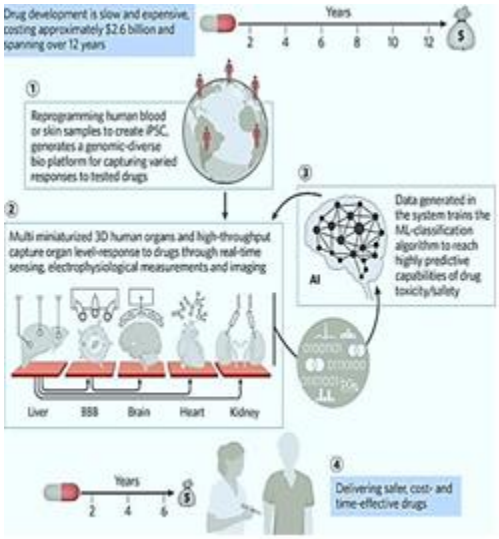


Fig. 10: Outlay of the Quris Bio-AI Clinical Prediction Platform(Bentwich, I.)

ZairaChem: First fully automated AI ML virtual screening cascade: ZairaChem, a tool that leverages AI and MLfor the purpose of quantitative structure-activity/property relationship (QSAR/QSPR) modeling(Chourasia, 2020). ZairaChem(Turon, 2023) operates with full automation, minimal computational demands, and is applicable across a wide range of datasets. Authors have provided details of its complete implementation at the H3D Centre, Africa's leading integrated drug discovery unit, which previously had no existing AI/ML capabilities. Within this context, authors have developed a virtual screening process for the discovery of malaria and tuberculosis drugs, encompassing 15 models designed for various key decision-making assays. The ZairaChem models displayed outstanding performance, achieving AUROC scores well above 0. 75 in most cases. To conclude, authors exemplified how the use of AI and ML in decision-making can lead to a decrease in attrition rates and a swifter advancement of projects during de novo library screening.

Is AI answer to all problems of drug discovery?

AI can help to speed up drug discovery but only if we give it the right data(Mock M. E., 2023):

The characteristics concerning how a drug functions within the body continue to present challenges in terms of predictability, especially when dealing with complex drugs that have multiple targets. The reason for this unpredictability is the shortage of data for accurately modeling these behaviors. Clinical trials, in contrast to many in vitro tests, offer only limited insights. To build efficient machine-learning models, a substantial amount of data related to hundreds or even thousands of proteins is required. To accumulate such data, biopharmaceutical companies must consider sharing information about the physical properties of specific amino acid sequences, the molecules that these proteins interact with, and the mechanisms by which the drugs operate within the body.

AI's potential to accelerate drug discovery need a reality check(Mock M. E., 2023):

In order for AI systems to acquire knowledge and enhance their capabilities, individuals must synthesize and evaluate the molecules proposed by these systems. The outcomes of these tests must subsequently be integrated into the AI systems. Academic computational groups can contribute to some degree by forecasting the properties of molecules, but the estimated values can only offer partial validation for the models. Pharmaceutical companies possess the resources to create and assess the molecules

recommended by their AI systems. Nevertheless, they often keep their findings confidential, partly to prevent their competitors from gaining an advantage.

(Qureshi, AI in Drug Discovery and its Clinical Relevance, 2023):

AI-based approaches in the pharmaceutical sector face numerous challenges(Paul D, 2021), including issues related to understanding the models, ensuring reproducibility, accessing data, labeling data, maintaining privacy, ensuring data quality, and managing computational infrastructure. To address these challenges, there's a requirement for high-quality datasets that are properly labeled for specific biological inquiries and feature suitable representations. It's worth noting that many current data analyses tend to yield very similar results, suggesting that the future of AI in drug discovery may not revolve around developing the perfect analysis method, but instead, it may hinge on posing the right question from the outset (thereby modeling the appropriate endpoint).

CONCLUSION

The current healthcare sector grapples with a multitude of intricate issues, including the escalating expenses of drugs and therapies. It is imperative for society to witness substantial changes in this domain. The integration of AI into pharmaceutical manufacturing holds the promise of creating personalized medications tailored to individual patients, encompassing factors like the ideal dosage and release parameters. The primary concern surrounding the adoption of these technologies relates to potential job displacement and the need for rigorous regulatory measures to ensure the responsible application of AI. It's important to note that these systems are designed to augment human efforts rather than entirely replace them. While there are currently no AI-developed drugs available on the market, and hurdles exist for the seamless incorporation of this technology, it is highly probable that AI will emerge as an indispensable tool in the pharmaceutical industry in the near future.

REFERENCES

[1]. À. Bravo, J. P. -R. (2015). Extraction of relations between genes and diseases from text and large-scale data analysis: implications for translational research. BMC Bioinform, 3 (16), 1-17.

[2]. Acosta, J. F. (2022). Multimodal biomedical AI. Nat Med (28), 1773-1784.

[3]. Alipanahi, B. D. (2015). Predicting the sequence specificities of DNA- and RNA-binding proteins by deep learning. Nat. Biotechnol., 33, 831-838.

[4]. Beneke, F. a. (2019). Artificial intelligence and collusion. IIC Int. Rev. Intellectual Property Competition Law (50), 109–134.

[5]. Bentwich, I. (n. d.). Quris-AI: an artificial intelligence innovator disrupting the drug development process. Retrieved 10 13, 2023, from https://www. nature.com: https://www. nature.com/articles/d43747-023-00026-y

[6]. Bielecki, A. a. (2019). Foundations of artificial neural networks. In Models of Neurons and Preceptrons: Selected Problems and Challanges ((Kacprzyk, Janusz, ed.) ed.). Springer International Publishing.

[7]. Bone, D. e. (2015). Applying machine learning to facilitate autism diagnostics: pitfalls and promises. J. Autism Dev. Disord, 45, 1121-1136.

[8]. Chourasia, S. S. (2020). (2020). Synthesis, QSAR modeling and antimicrobial studies of 1- (4-phenyl) substituted tetrahydro isoquinoline derivatives. Materials Today: Proceedings, 29, 956-963.

[9]. Crippa, A. e. (2015). Use of machine learning to identify children with autism and their motor abnormalities. J. Autism Dev. Disord., 45, 2146-2156.

[10]. D. Reker, T. R. (2014). Identifying the macromolecular targets of de novo-designed chemical entities through self-organizing map consensus. Proc. Natl. Acad. Sci., 111 (11), 4067-4072.

[11]. Da Silva, I. e. (2017). Artificial Neural Networks. Springer.

[12]. Duda, M. M. (2016). Use of machine learning for behavioral distinction of autism and ADHD. Transl. Psychiatry, 6, e732.

[13]. Garg, S. (2021). Drug recommendation system based on sentiment analysis of drug reviews using machine learning. 11th International Conference on Cloud Computing, Data Science & Engineering (Confluence) (pp. 175–181). IEEE.

[14]. Hanggi, M. a. (2000). Cellular Neural Networks: Analysis, Design and Optimization. Springer Science & Business Media.

[15]. I. Lee, J. K. (2019). Deepconv-dti: prediction of drug-target interactions via deep learning with convolution on protein sequences, PLoS.comput. Biol., 15 (6).

[16]. J. Jumper, R. E. (2021). Highly accurate protein. Natrue, 596 (7873), 583-589.

[17]. J. Y. Khan, M. K. -A. (2020). Toward preparing a knowledge base to explore potential drugs and biomedical entities related to Covid-19 automated computational approach. JMIR Med. Inform, 8 (11).

[18]. Kalyane, D. e. (2020). Artificial intelligence in the pharmaceutical sector: current scene and future prospect (The Future of Pharmaceutical Product Development and Research (Tekade, Rakesh K., ed.) ed.). Elsevier.

[19]. Kosmicki, J. A. (2015). Searching for a minimal set of behaviors for autism detection through feature selection-based machine learning. Transl. Psychiatry, 5, e514.

[20]. M. Karimi, D. W. (2019). Deepaffinity: interpretable deep learning of compound–protein affinity through unified recurrent and convolutional neural networks. Bioinformatics, 35 (18), 3329–3338.

[21]. M. Song, M. K. (2018). Application of public knowledge discovery tool (pkde4j) to represent biomedical scientific knowledge,. Front. Res Metr. Anal, 3 (7).

[22]. Medsker, L. a. (1999). Recurrent Neural Networks: Design and Applications. CRC Press.

[23]. Miles, J. a. (2006). The potential application of artificial intelligence in transport. IEE Proc. -Intell. Transport Syst. (153), 183–198.

[24]. Mock, M. E. (2023). AI can help to speed up drug discovery—but only if we give it the right data. Nature, 621 (7979), 467-470.

[25]. Mock, M. E. (2023). AI's potential to accelerate drug discovery need a reality check. Nature, 622, 217.

[26]. Munsell, B. C. (2015). Evaluation of machine learning algorithms for treatment outcome prediction in patients with epilepsy based on structural connectome data. Neuroimage, 118, 219-230.

[27]. N. Khalil Zadeh, M. S. (2014). Intelligent sales prediction for pharmaceutical distribution companies: a data mining based approach. Math. Probl. Eng. 2014.

[28]. Nuhn, L. (2023). Artificial intelligence assists nanoparticles to enter solid tumours. Nat. Nanotechnol., 18, 550-551.

[29]. Ó. Álvarez-Machancoses, J. F. -M. (2019). Using artificial intelligence methods to speed up drug discovery. Expert Opin. Drug Discov., 14 (8), 769–777.

[30]. Paul D, S. G. (2021). Artificial intelligence in drug discovery and development. Drug Discov Today, Jan;26 (1), 80-93.

[31]. Q. Zang, K. M. (2017). In silico prediction of physicochemical properties of environmental chemicals using molecular fingerprints and machine learning. J. Chem. Inf. Model, 51 (1), 36-49.

[32]. Quinodoz, M. e. (2017). DOMINO: using machine learning to predict genes associated with dominant disorders. Am. J. Hum. Genet., 101, 623-629.

[33]. Qureshi, R. I. (2023). AI in Drug Discovery and its Clinical Relevance. Heliyon.

[34]. Qureshi, R. I. (2023). AI in Drug Discovery and its Clinical Relevance. Heliyon, 9 (e17575).
[35]. Rahangdale, P. K. (2018). Quantitative structure activity relationship and biological activity studies of 4-methyl-2- (4-substituted phenyl) quinoline derivatives. Asian J Chem, 30 (3), 479-482.
[36]. Raies, A. T. (2022). DrugnomeAI is an ensemble machine-learning framework for predicting druggability of candidate drug targets.commun. Biol., 5, 1291.
[37]. Ramesh, A. e. (2004). Artificial intelligence in medicine. Ann. R. Coll. Surg. Engl (86), 334–338.
[38]. S. Harrer, P. S. (2019). Artificial intelligence for clinical trial design. Trends Pharmacol. Sci., 40 (8), 577–591.
[39]. Sheikhalishahi, S. e. (2019). Natural language processing of clinical notes on chronic diseases: systematic review. JMIR Med. Inf., 7, e12239.
[40]. Shoeb, A. H. (2009). Application of Machine Learning to Epileptic Seizure Onset Detection and Treatment. Harvard-MIT Division of Health Sciences and Technology.
[41]. Sivajohan, B. E. (2022). Clinical use of artificial intelligence in endometriosis: a scoping review. npj Digit. Med., 5, 109.
[42]. Smyser, C. D. (2016). Prediction of brain maturity in infants using machine-learning algorithms. Neuroimage, 136, 1-9.
[43]. T. Alam, S. S. (2021). Deep learning in biomedical text mining: contributions and challenges. Multiple Perspectives on Artificial Intelligence in Springer, 169-184.
[44]. Turon, G. H. (2023). First fully-automated AI/ML virtual screening cascade implemented at a drug discovery centre in Africa. Nat Commun, 14, 5736.
[45]. Uddin, M. W. -S. (2019). Artificial intelligence for precision medicine in neurodevelopmental disorders. npj Digit. Med., 2 (112).
[46]. Wall, D. P. (2012). Use of artificial intelligence to shorten the behavioral diagnosis of autism. PLoS ONE, 7, e43855.
[47]. Wang, Y. A. (2022). DrugRepo: a novel approach to repurposing drugs based on chemical and genomic features. Sci Rep., 12, 21116.
[48]. Woo, M. (2019). An ai boost for clinical trials. Nature, 573 (7775), S100.
[49]. Xiong, H. Y. (2015). RNA splicing. The human splicing code reveals new insights into the genetic determinants of disease. Science, 347 (1254806).
[50]. Y. Li, L. Z. (2018). Multi-objective de novo drug design with conditional graph generative model. J. Cheminform, 10 (1), 1-24.
[51]. Y. Wang, J. W. (2022). Molecular contrastive learning of representations via graph neural networks. Nat. Mach. Intell., 1-9.
[52]. Yang, Y. Y. (2022). Artificial intelligence-enabled detection and assessment of Parkinson's disease using nocturnal breathing signals. Nat Med, 28, 2207–2215.
[53]. You, Y. e. (2022). Artificial intellignece in cancer target identification and drug discovery. Sig. Trasduct. Target Ther., 7 (156).
[54]. Yuan, Q. Z. (2011). Epileptic EEG classification based on extreme learning machine and nonlinear features. Epilepsy Res., 96, 29-38.
[55]. Z. Wu, B. R. (2018). Moleculenet: a benchmark for molecular machine learning. Chem. Sci., 9 (2).

Chapter 20

IMIDAZOLIUM-CARBOXYLATE COORDINATION POLYMERS: AN OVERVIEW

CHATLA NAGA BABU

Department of Chemistry, Adikavi Nannaya University Campus, Tadepalligudem, 534101
Corresponding author E-mail: nagababu.chatla@gmail.com

ABSTRACT

Construction of functionalized coordination polymers (FCPs) have been the subject of interest in last few decades due to their fascinating architectures and versatile applications in catalysis, gas storage, separation, luminescence, electrical conductivity, magnetism, and nonlinear optics. The suitable organic spacers, metal precursors and synthetic methodologies are the essential criteria to design the FCPs with different physical properties. Therefore, the choice of organic spacer is extremely important to fine-tune the structural and desired functional properties of FCPs through coordination mode or non-covalent interaction mode

KEYWORDS: Angstrom, Dimethyl Sulfoxide, Fourier Transform-Infrared, Isoreticular Metal-Organic Framework, N-Heterocyclic Carbine, Porous Coordination Polymer, Powder X-Ray Diffraction Technique, Thermogravimetric Analysis.

INTRODUCTION

Porous solids are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but throughout the bulk of the material. Not surprisingly, traditional applications of porous materials thus involve ion exchange, adsorption (for separation) and catalysis, and many of these benefit from the high order [1]. The pores of solids are classified according to size: pore sizes in the range of 2 nm and below are called micropores, those in the range of 2 nm to 50 nm are denoted mesopores, and those above 50 nm are macropores. The distribution of sizes, shapes and volumes of the void spaces in porous materials directly relates to their ability to perform the desired function in a particular application. The need to create uniformity within the pore size, shape and volume has steadily increased over recent years because it can lead to superior applications properties. Classically porous materials are inorganic materials, carbon-based materials and inorganic-organic polymers (Figure 1). A large number of inorganic porous materials have been developed e. g. Zeolites.

Zeolites are traditional inorganic microporous crystalline materials, which are built from an infinitely extending three dimensional network of $[SiO_4]$. $^{4-}$ and $[AlO_4]$. $^{5-}$ tetrahedral units linked to each other by the sharing oxygen atoms [2,3]. The general formula for a zeolite is $M_{x/n}$ [$(AlO_2)_x$ $(SiO_2)_y$]. mH_2O, where M is an alkali or alkaline earth cation, n is the valence of the cation, m is the number of water molecules per unit cell, x and y are the total number of tetrahedral per unit cell [4]. The first zeolite, stilbite, was discovered by Cronstedt in 1756, who found that the mineral lost water rapidly on heating and seemed to boil. The name “zeolite” comes from the Greek words “Zeo” (boil) and “Lithos” (stone), literally meaning “the rock that boils”. The crystallization water of zeolite is in the form of water molecules existing in the framework structure of zeolite. So, this is particularly called "zeolitic water. " Even when dehydrated by heating or the like, the structure of zeolite is not destroyed. The space areas, where crystallization water

used to be, remain as they are in the form of a cavity. This looks like the structure of a piece of sponge. Zeolite, according to its characteristics, strongly absorbs gas and moisture into those cavities. Zeolites naturally form when fresh groundwater or sea water reacts with volcanic ash and take anywhere from 50 to 50,000 years to complete their formation. Natural zeolites were first used by the Romans to filter their drinking water. Synthetic zeolites were first observed in 1862 [5]. Synthetic zeolites can produce much faster and in phase-pure state and in more uniform fashion. More than 150 zeolite types have been synthesized and 40 naturally occurring zeolites are known [6]. Zeolites are traditionally used in water filtration, refrigeration, construction, and aquariums. Zeolites came to prominence industrially, when Mobil patented the synthetic ZSM-5 catalyst in 1977 for the conversion of methanol to petroleum [7].

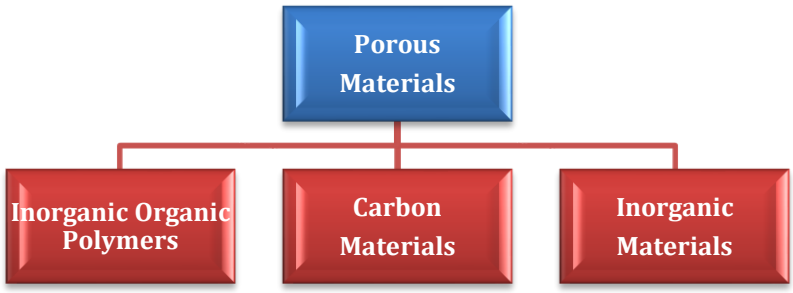


Fig. 1: Classification of porous materials.

Aluminophosphates ($AlPO_4$-n, n represents a particular structure type) are constructed alternation of corner sharing AlO_4 and PO_4 tetrahedrons units, and which build up a 3D neutral framework with channels and/or pores of molecular dimensions. The new family of microporous crystalline aluminophosphates was reported in 1982 [8]. The general formula is represented as $[Al^{III}P^{V}O_4]$. $yR.\ nH_2O$, where R denotes organic template and many AlPOs have crystal structures, which are not perceived in zeolites. Further AlPOs developed through substitution via incipient wetness impregnation, ion exchange or isomorphous substitution. Thus examples are silocoaluminophosphates, metalloaluminophosphate, metalaluminophosphates and metallophosphates [9-11].

Aluminophosphates ($AlPO_4$-n, n represents a particular structure type) are constructed alternation of corner sharing AlO_4 and PO_4 tetrahedrons units, and which build up a 3D neutral framework with channels and/or pores of molecular dimensions. The new family of microporous crystalline aluminophosphates was reported in 1982 [8]. The general formula is represented as $[Al^{III}P^{V}O_4]$. $yR.\ nH_2O$, where R denotes organic template and many AlPOs have crystal structures, which are not perceived in zeolites. Further AlPOs developed through substitution via incipient wetness impregnation, ion exchange or isomorphous substitution. Thus examples are silocoaluminophosphates, metalloaluminophosphate, metalaluminophosphates and metallophosphates [9-11].

Pyrolysis of carbon-rich materials leads to the formation of perhaps the most well-known carbon porous compound known as activated carbon [12]. Due to their high surface areas and porous nature, activated carbons have been used as adsorbents throughout time by a wide array of industries ranging from medical to military [13]. While activated carbon has the benefit of possessing high surface areas and adsorption capacities, their graphene structures suffer from a lack of order. This inconsistency prevents activated carbons from being used as materials for application in catalysis. In fact, the distribution of the pores in activated carbons may range as widely as 20 Å to several thousand Å [14]. However, despite their lack of order, activated carbons have been a useful material for applications in gas adsorption and separation, solvent removal and recovery, and water purification for many years.

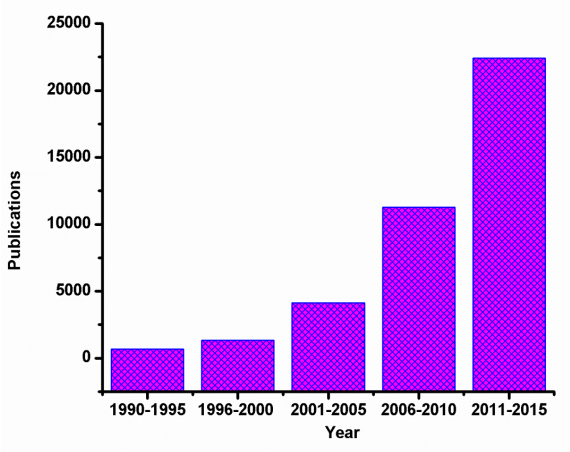


Fig. 2: The number of publications containing keywords "coordination polymers" or "metal organic frameworks" in graph with respect to five years period from 1990, survey by SciFinder

Porous coordination polymers (PCPs) are an emerging class of hybrid porous materials fashioned by a self-assembled network in between inorganic unit and multidentate organic spacers. Now a day, porous coordination polymers have been alternative to the former two classes of porous materials, based on its structure regularity, high porosity, high surface area and highly designable frameworks. The progress on "coordination polymer" from 1990 to 2015 is shown in Fig. 2. The phrase, "coordination polymers" appeared in the beginning of 1960s, and area was first reviewed in 1964 [15]. Prior to the late 1980s, a variety of polymeric metal-organic coordination compounds were exposed, such as Holfmann type complexes and Prussian blue compounds. These examples motivated scientists to aiming to discovery a new class of materials. Since the early 1990s, research on the structures of porous coordination polymers has increased greatly, and examples with functional micropores soon started to appear. Robson etal. reported a porous coordination polymer capable of an anion exchange in 1990 [16]. The first catalytic properties of the 2D $[Cd^{II}$ $(4,4'\text{-bpy})_2$ $(NO_3)_2]$. coordination polymer was studied with reaction of benzaldehyde and cynotrimethylsilane by Fujita etal. in 1994 [17]. The adsorption of guest molecules was studied separately by the group Yaghi [18]. and Moore [19]. in 1995. The metal-organic framework (MOF) word was promoted by Yaghi*et al.,* in 1995 [20]. In 1997, Kitagawa etal. reported the gas adsorption phenomena at ambient temperature [21]. In 1999, the motivated report is delivered by Yaghietal., which is the isolation of MOF-5 [22]. and also, the concept of isoreticular MOFs was reported in 2002 [23].

PCPs can be made via different methods: solvothermal, hydrothermal, direct mixing, sonochemical, vapour diffusion, microwave heating, etc. The solvothermal method is normally used and involves heating a mixture of organic spacers and metal precursor in a solvent system. The solvents include, for example, dimethylformamide (DMF), diethylformamide (DEF), dimethyl sulfoxide (DMSO), water, ethanol, methanol, dioxane, and mixtures thereof. Among these solvents, DMF dissolve the reactants but also deprotonate the carboxylic acids. In addition, variables in the reaction conditions including reagent concentration, time, temperature, P^H and fractional volume filling of the vessel are important parameters as well [24].

PCPs/MOFs are commercially produced by BASF and Sigma-Aldrich. Preferably, PCPs/MOFs are constructed by using two components, namely metal/metal nodes/SBU and organic spacers [25]. The porous coordination polymer pore size/shape and overall porous activity can be tuned by logically designing the suitable organic spacers [26]. In general, the organic spacers may be N-functionalised (pyridyl, imidazole, triazoles) [27,28]., O-functionalised (carboxylates) [29]., S-functionalised (sulfonate)

[30]., P-functionalised (phosphates) [31]., etc and mixed thereof [32]. In general, the bidentate or multidentate organic spacers are well utilized [33].

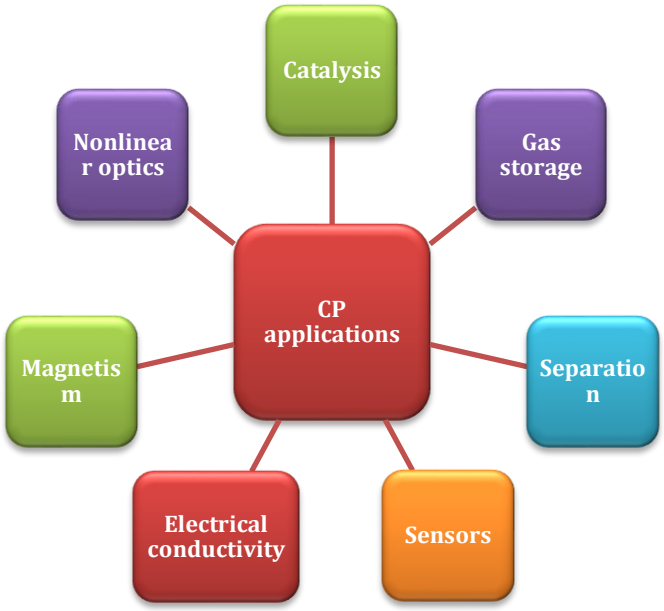


Fig. 3: Applications of porous coordination polymers [34-40]

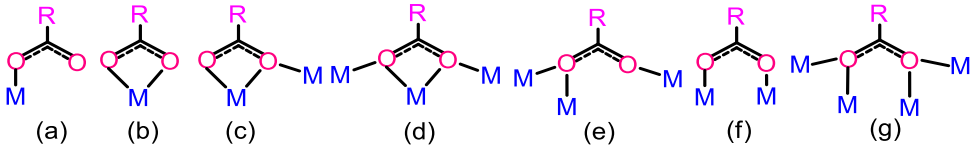


Fig. 4: Probable metal-binding modes of carboxylate spacers [41]. : (a) μ_1-η^0:η^1; (b) μ_1-η^1:η^1; (c) μ_2-η^1:η^2; (d) μ_3-η^2:η^2; (e) μ_3-η^1:η^2; (f) μ_2-η^1:η^1; (g) μ_4-η^2:η^2

Among all, the multidentate carboxylate organic spacers are excellent ligands for the synthesis of coordination polymers affording structures with a diverse range of topologies and conformation with the carboxylate group able to a metal center as a mono-, bi-, or multidentate ligand. The possible metal-binding motifs of carboxylate linkers are shown in Fig 4. The suitable organic spacers, metal precursors and synthetic methodologies are the essential criteria to design the FCPs with different physical properties. In addition, the non-covalent interactions such as hydrogen bonding, π···π, M···π, C–H···π and anion···π interactions play a key role in FCPs to increase the dimensionality, supramolecular topology and porosity. Therefore, the choice of organic spacer is extremely important to fine-tune the structural and desired functional properties of FCPs through coordination or non-covalent interaction modes. Within these organic spacers, the imidazolium carboxylic acids are of special interest as they have [C–H]. $^{\delta+}$ functional group (potential functional group for anion reorganization and post modification to generate N-heterocyclic carbene tethered catalytically active metal centers) along with excellent functional group tolerance at N-positions.

Imidazolium salts are having different structural versatility like water solubility, chirality, functionalization, chelation, chirality, immobilization, ionic liquids, water solubility and catalysis [42]. Moreover other interesting structural features are the presence of acidic proton and counter anions (Fig. 5). The acidic proton is NCHN. Preferably, this proton forms the efficient hydrogen bonding network with counter anions, solvent molecules and other guest molecules. Notably, the counter ions play a key role in anion exchange (F^-, PF_6^-, BF_4^-, $H_2PO_4^-$, HPO_4^{2-}, HSO_4^-) and not only these type of anions and also biologically important anions like DNA, RNA, ADP, ATP, GTP, etc [43].

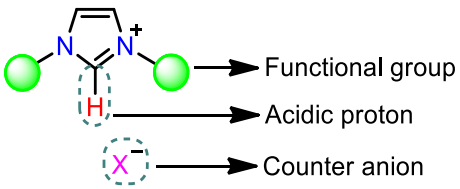


Fig. 5: Functional centers in imidazolium salt

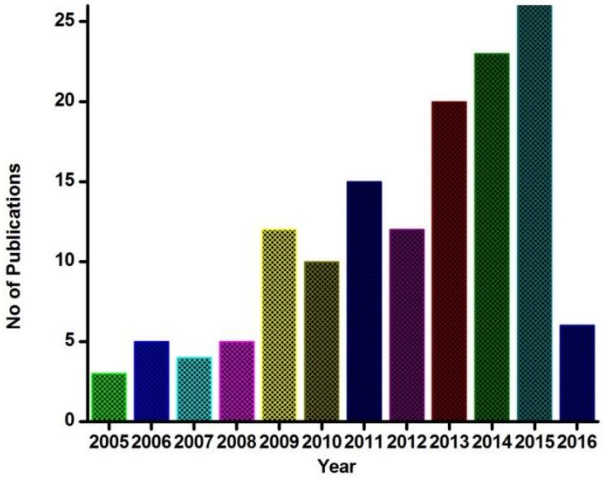


Fig. 6: Number of publications related to imidazolium carboxylate based coordination polymers

Imidazolium salts can be synthesized easily and the starting materials are readily available [44]. Besides the NNC-H group in imidazolium salts can be a potential functional group for pre/post modified M-NHC synthesis. Since the discovery of stable N-heterocyclic carbenes (NHCs), these complexes have found widespread use in catalysis, in which they serve both as nucleophilic catalysts and as ligands in metal-mediated reactions [45]. Thus imidazolium carboxylate coordination polymer chemistry is considerably different from the conventional neutral carboxylate coordination polymers. The publications of imidazolium carboxylate based coordination polymers with respect to the year are shown in Fig. 6.

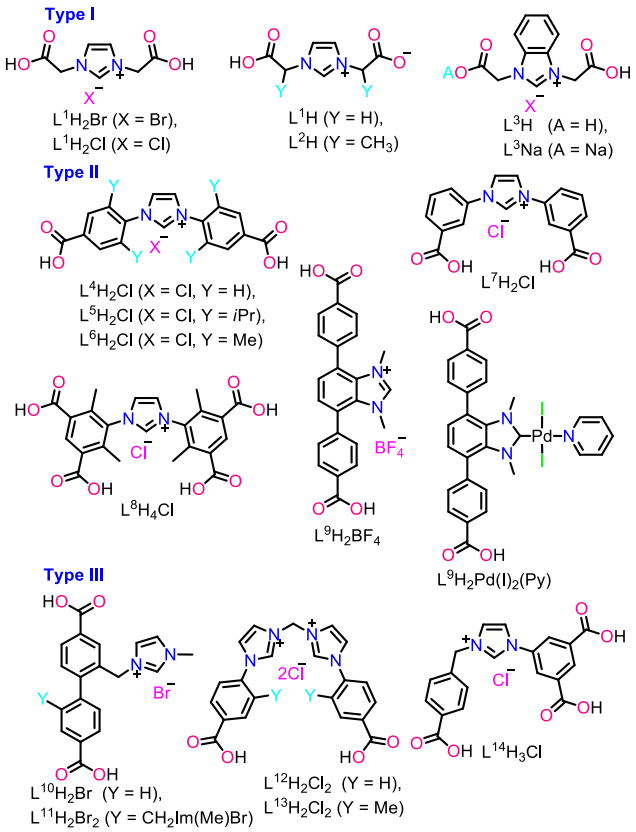


Fig. 7: The known imidazolium carboxylic acid spacers

The known imidazolium carboxylates can be classified as three types (Fig 7).

Type I, Imidazolium with flexible carboxylate arms;

Type II, Imidazolium with rigid carboxylate arms;

Type III, Imidazolium with flexible CH_2 and rigid carboxylate arms.

CONCLUSION

Metal–organic frameworks (MOFs) are coordination networks formed by self-assembly of metal ions or clusters and organic linkers. The functionalities and versatilities of MOF materials are enhanced by designing the frameworks with linkers, which have extra active functional groups that can be modified presynthetically, in situ, or postsynthetically. The carbenic carbon in N-heterocyclic carbenes enhances the potential of MOFs synthesized from azolium-containing linkers. In this chapter, we provide a survey and discussion of N-heterocyclic carbene precursor-containing MOFs and their various applications. Novel catalytic materials are highly demanded to perform a variety of catalytic organic reactions. MOFs combine the benefits of heterogeneous catalysis like easy post reaction separation, catalyst reusability, high stability and homogeneous catalysis such as high efficiency, selectivity, controllability and mild reaction conditions. The possible organization of active centers like metallic nodes, organic linkers, and their chemical synthetic functionalization on the nanoscale shows potential to build up MOFs particularly modified for catalytic challenges. Highlighting the key features of MOFs as catalysts based on the active sites in the framework.

REFERENCES

[1]. S. Kitagawa, R. Kitaura, and S. -I. Noro. Angew. Chem. Int. Ed. 43, (2004) 2334.

[2]. D. W. Breck. Zeolite Molecular Sieves: Structure, Chemistry and Use. John Wiley & Sons, p. 4.

[3]. G. D. Stucky, and J. E. MacDougall. Science 247, (1990) 669.

[4]. V. H. Bekkum, E. M. Flanigen, P. A. Jacobs, and J. C. Jansen. Introduction to zeolite science and practice. 2nd. Revised Edn., Elsevier, Amsterdam, 1991.

[5]. H. de Sainte Claire Deville. C. R. Hebd. Séance Acad. Sci. 52, (1862) 324.

[6]. "Zeolites: Industry Trends and Worldwide Markets in 2010" (Review of report, www. newsletters.com/map/prod/722220. html), Technical insights, Inc.

[7]. F. G. Dwyer, F. V. Hanson, and A. B. Schwartz. US patent 4,035,430, "Conversion of methanol to gasoline product", mobil oil corporation, New York, NY (dated 12 July, 1977).

[8]. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen. J. Am. Chem. Soc. 102, (1982) 1146.

[9]. B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan, and E. M. Flanigen. J. Am. Chem. Soc. 106, (1984) 6092.

[10]. E. M. Flanigen, B. M. Lok, R. L. Patton, and S. T. Wilson. Pure and Applied Chemistry 58, (1986) 1351.

[11]. M. Hartmann, and L. Kevan. Chem. Rev. 99, (1999) 635.

[12]. S. M. Manocha. Sadhana 28, (2003) 335.

[13]. H. Marsh. Activated Carbon. Elseviser, Amsterdam, 2006.

[14]. D. W. Breck. Zeolite Molecular Sieves: Chemistry, and Use. John Wiley & Sons, New York, 1974.

[15]. "Coordination Polymers": J. C. Bailar, Jr., Prep. Inorg. React. (1964) 1.

[16]. B. F. Hoskins, and R. Robson. J. Am. Chem. Soc. 112, (1990) 1546.

[17]. M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura. J. Am. Chem. Soc. 116, (1994) 1151.

[18]. O. M. Yaghi, G. Li, and H. Li. Nature 378, (1995) 703.

[19]. D. Venkataraman, G. B. Gardner, S. lee, and J. S. Moore. J. Am. Chem. Soc. 117, (1995) 11600.

(a) O. M. Yaghi, and H. Li. J. Am. Chem. Soc. 117, (1995) 10401; (b) O. M. Yaghi, and G. Li. Angew. Chem. 34, (1995) 207.

[20]. M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, and S. Kitagawa. Angew. Chem. 117, (1997) 1844.

[21]. H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi. Nature 402, (1999) 276.

(a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keefe, and O. M. Yaghi. Science 295, (2002) 469; (b) O. M. Yaghi, M. Eddaoudi, H. Li, J. Kim, and N. Rosi. Patent, WO 2002/088148, 2002; (c) H. K. Chae, D. Y. Siberio-Pe´rez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, and O. M. Yaghi. Nature 427, (2004) 523.

[22]. N. Stock, and S. Biswas. Chem. Rev. 112, (2012) 933.

(a) D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe M, and O. M. Yaghi. Chem. Soc. Rev. 38, (2009) 1257; (b) J. J. Perry IV, J. A. Perman, and M. J. Zaworotko. Chem. Soc. Rev. 38, (2009) 1400.

[23]. F. A. A. Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiro, and J. Rocha. Chem. Soc. Rev. 41, (2012) 1088.

[24]. S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinnoshita, and S. Kitagawa. J. Am. Chem. Soc. 129, (2007) 2607.

(a) J. Yang, T. Hu, and T. C. W. Mak. Cryst. Growth Des. 14, (2014) 2990; (b) J. Guo, D. Sun, L. Zhang, Q. Yang, X. Zhao, and D. Sun. Cryst. Growth Des. 12, (2012) 5649; c) H. -J. Lee, P. -Y. Cheng, C. -Y. Chen, J. -S. Shen, D. Nandi, and H. M. lee. CrystEngComm 13, (2011) 4814.

[25]. W. Xuan, C. Zhu, Y. Liu, and Y. Cui. Chem. Soc. Rev. 41, (2012) 1677.

[26]. S. Horike, S. Bureekaew, and S. Kitagawa. Chem.commun. (2008) 471.

A. K. Gupta, A. K. Srivastava, L. K. Mahawar, and R. Boomishankar. Cryst. Growth Des. 14, (2014) 1701.

[27]. R. Singh, and P. K. Bharadwaj. Cryst. Growth Des. 13, (2013) 3722; (b) M. Li, Q. Ling, Z. Yang, B. -L. Li, and H. -Y. Li. CrystEngComm 15, (2013) 3630; (c) Z. Su, J. Xu, J. Fan, D. -J. Liu, Q. Chu, M. -S. Chen, S. -S. Chen, G. -X. Liu, X. -F. Wang, and W. -Y. Sun. Cryst. Growth Des. 9, (2009) 2801; (d) D. Sun, Z. -H. Yan, V. A. Blatov, L. Wang, and D. -F. Sun. Cryst. Growth Des. 13, (2013) 1277.

[28]. S. Kitagawa, R. Kitaura, and S. -I. Noro. Angew. Chem. Int. Ed. 52, (2013) 270.

[29]. Selected examples for catalysis: (a) J. -Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, and J. T. Hupp. Chem. Soc. Rev. 38, (2009) 1450; (b) L. Q. Ma, C. Abney, and W. B. Lin. Chem. Soc. Rev. 38, (2009) 1248; (c) K. S. Jeong, Y. B. Go, S. M. Shin, S. J. Lee, J. Kim, O. M. Yaghi, and N. Jeong. Chem. Sci. 2, (2011) 877; (d) A. Corma, H. Garcia, F. X. Llabres, and I. Xamena. Chem. Rev. 110, (2010) 4606; (e) M. Yoon, R. Srirambalji, and K. Kim. Chem. Rev. 112, (2012) 1196.

Chapter 21

FLEXIBLE CADMIUM COORDINATION POLYMERS: AN OVERVIEW

CHATLA NAGA BABU

Department of Chemistry, Adikavi Nannaya University Campus, Tadepalligudem, 534101
Corresponding author E-mail: nagababu.chatla@gmail.com

ABSTRACT

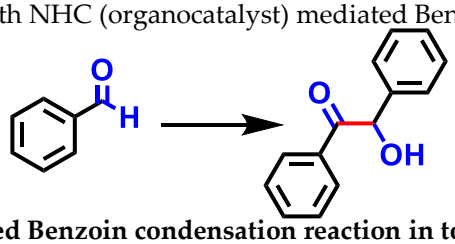
The functional coordination polymers (CPs) with transitionmetal cores have stimulated great interests for not only the diverse structures but also their potential technological applications in fields such as drug delivery [1]., gas storage [2]., luminescence [3]., catalysis [4]., separations [5,6]. The CPs with versatile topologies derived by multifunctional organic building blocks often exhibit structural diversities and tunable functionalities, especially those bearing multidentate bridging ligands because of their tunable coordination fashions under different experimental conditions [7]. However, the structural uncertainty of CPs is an inherent characteristic of a self-assembled system [8]., which can be mainly attributed to the steric factors and crystallization conditions. Thus, a detailed study of supramolecular isomerism is essential to understand the self-assembled system of CPs. It is well-known that the plenty of cadmium coordination polymers exhibiting fascinating structures and various properties, such as luminescence, have been synthesized [9].

KEYWORDS: Angstrom, Dimethyl Sulfoxide, Fourier Transform-Infrared, Isoreticular Metal-Organic Framework, N-Heterocyclic Carbine, Porous Coordination Polymer, Powder X-Ray Diffraction Technique, Thermogravimetric Analysis

INTRODUCTION

Although d–d transitions are not expected for Cd (II) due to a d^{10} closed shell electronic configuration, ligand-to-ligand charge transfer (LLCT) and ligandto-metal charge transfer (LMCT) have been reported [10]. To achieve this goal, one effective way is the selection of suitable organic ligands as antenna chromophores, which can improve the emission efficiency of cadmium cations. The functional coordination polymers (CPs) with transitionmetal cores have stimulated great interests for not only the diverse structures but also their potential technological applications in fields such as drug delivery [1]., gas storage [2]., luminescence [3]., catalysis [4]., separations [5,6]. The CPs with versatile topologies derived by multifunctional organic building blocks often exhibit structural diversities and tunable functionalities, especially those bearing multidentate bridging ligands because of their tunable coordination fashions under different experimental conditions [7]. However, the structural uncertainty of CPs is an inherent characteristic of a self-assembled system [8]., which can be mainly attributed to the steric factors and crystallization conditions. Thus, a detailed study of supramolecular isomerism is essential to understand the self-assembled system of CPs. It is well-known that the plenty of cadmium coordination polymers exhibiting fascinating structures and various properties, such as luminescence, have been synthesized [9]. Although d–d transitions are not expected for Cd (II) due to a d^{10} closed shell electronic configuration, ligand-to-ligand charge transfer (LLCT) and ligandto-metal charge transfer (LMCT) have been reported [10]. To achieve this goal, one effective way is the selection of suitable

organic ligands as antenna chromophores, which can improve the emission efficiency of cadmium cations. As of now, a lot of aromatic oxygen/nitrogen donor ligands have been demonstrated to be chromophoric antenna ligands, which are good sensitizers to stimulate cadmium ion luminescence. Among the various luminescent multidentate ligands, flexible multidentate ligands with imidazole groups have the ability to form various types of topological architectures with photoluminescent properties [11]. The flexible multidentate ligands with imidazole groups can be derived using aryl spacers or alkyl spacers. The study for coordination polymers containing the aryl or alkyl substituted bis (imidazole) and tris (imidazole) have already been widely reported with fascinating architectures and interesting properties, whereas only a few coordination polymers based on the anthracene substituted bis (imidazole) have been observed [12–16]. Over the past decade, various thiazolium, imidazolium and triazolium salts have been developed as organocatalysts for the Benzoin condensation reaction under mild conditions with high selectivity. As a result, a large number of Benzoin condensation processes have been well established using different types of NHCs [30]. In this chapter, we attempted to use fivemol% cadmium coordination polymers 1-2 as NHC-like catalysts for Benzoin condensation reactions in toluene (Scheme 3). The catalytic reactions were analysed with benzaldehyde under ambient temperature in the presence of four mol% base to activate imidazole moieties. The reactions were carried out for 12 h to obtain the Benzoin product with very good yield (63-95%, table 2, entries 1-6). As reported in entries 8-10 (Table 2), the Benzoin condensation reaction was carried out using five mol% of insitucadmium nitrate and ligands (L# andL^) in the presence of four mol% potassium tertbutoxide. Similarly, the reactions were studied using only ligands (L# andL^) as organocatalysts. However, the yield of entries 8-10 is not appreciable compared to catalysts 1-2 (Table 2, entries 1-6). Thus, the insitu generated carbene centres in coordination polymers 1-2 are responsible for the catalytic activities. Noteworthy that the catalytic efficiency of 1-2 is comparable with NHC (organocatalyst) mediated Benzoin condensation reaction.



Scheme 1: Catalyst mediated Benzoin condensation reaction in toluene at room temperature

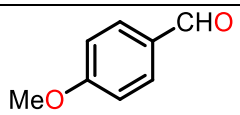
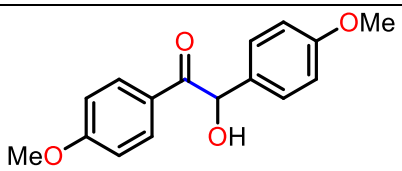
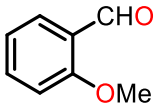
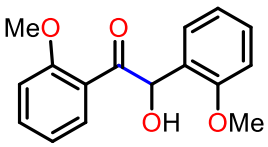
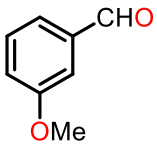
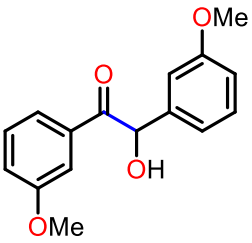
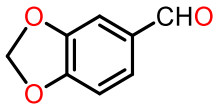
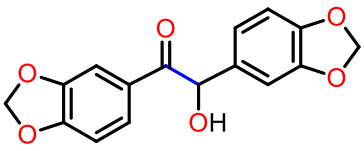
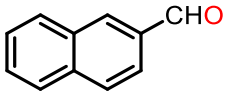
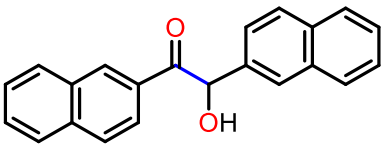
Table 1: The comparison of catalytic efficiency of 1 and 2

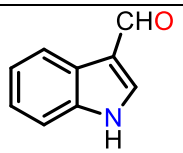
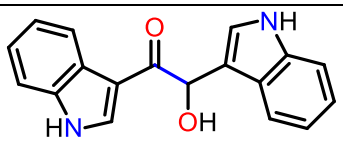
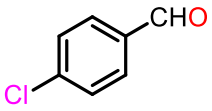
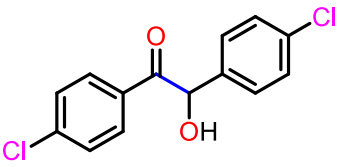
Entry	Cat. (5 mol%)	Solvent	Base	Yield (%)[a]	Time
1	1	Toluene	KOtBu	89	12h
2	1	THF	KOtBu	75	12h
3	1	Toluene	Cs_2CO_3	63	12h
4	1	Toluene	K_2CO_3	67	12h
5	1	Fluoro Benzene	KOtBu	80	12h
6	2	Toluene	KOtBu	95	12h
7	-	Toluene	KOtBu	15	1d
8	L#	Toluene	KOtBu	40	1d
9	Cd $(NO_3)_2$. $4H_2O$	Toluene	KOtBu	12	1d
10	L^	Toluene	KOtBu	38	1d

[a]Determined by ^1H NMR spectroscopy.

Furthermore the functional group tolerance of 2 was evaluated for a range of substituted aromatic aldehydes (Table 3). Catalyst 2 is highly active for 4-chlorobenzaldehyde (Table 3, entry 7), while 2-naphthaldehyde (Table 3, entry 5), 3-methoxybenzaldehyde (Table 3, entry 3) and 4-methoxybenzaldehyde (Table 3, entry 1) gave considerable yield. Notably, Indole-3-aldehyde (Table 3, entry 6) depicted the poor yield.

Table 2: Evaluation of catalyst 2 scope

E	Substrate	Product	Yield (%)[a]
1			72
2			69
3			83
4			68
5			82

6			40
7			85

[a]Isolated yields by column chromatography, E; Entry.

REACTION CONDITION OF BENZOIN CONDENSATION REACTIONS

Oven dried Schlenk was charged with catalysts (5 mol%), benzaldehyde then dried under vacuum for 5 min. Solvent (5 mL) was added under nitrogen condition to the reaction mixture, evacuated for few seconds, refilled with nitrogen then KOt-Bu (4 mol%) was added to the reaction mixture under nitrogen condition at room temperature. The reaction progress was monitored by TLC. The reaction mixture was diluted with water (10 mL) and DCM (10 mL). The organic phase was separated, washed with brine solution (7 mL), dried over anhydrous sodium sulphate then the reaction mass was concentrated under reduced pressure to get crude compound. The crude compound was absorbed on silica gel (100-200 mesh) for purification then petroleum ether and 10% ethyl acetate/petroleum ether (200 mL) were poured on column to separate the final product.

CONCLUSION

The unique structural feature of imidazole ring with desirable electron-rich characteristic is beneficial for imidazole derivatives to readily bind with a variety of metals and associates through diverse weak interactions, thereby exhibiting broad structural diversity. Besides, the imidazolium salts enable many emerging applications including catalysis, nanocomposites and reaction solvents, and CO_2 absorbents. In particular, the imidazolium carboxylic acids are of special interest as they have [C–H]. $^{\delta+}$ functional group (potential functional group for post modification to generate N-heterocyclic carbene) along with excellent functional group tolerance at N-positions. Particularly, numerous imidazole and their derivatives have been extensively used in the coordination chemistry to generate various types of applications with high potency, which have shown the enormous development value.

REFERENCES

[1]. P. Hocarjada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris, C. Serre, Chem. Rev., (2012) 1232.

[2]. J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, Chem. Soc. Rev. 41, (2012) 2308; (b) L. J. Murray, M. Dincaˇ, J. R. Long, Chem. Soc. Rev. 38, (2009) 1294; (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, Chem. Rev. 112, (2012) 724; (d) J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao, Y. Q. Lan, Chem. Sci. 3, (2012) 211

[3]. Y. J. Cui, Y. F. Yue, G. D. Qian, B. L. Chen, Chem. Rev. 112, (2012) 1126; (b) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, Chem. Soc. Rev. 38, (2009)1330.

[4]. Z. Wang, G. Chen, K. Ding, Chem. Rev. 109, (2009) 322; (b) A. Corma, H. García, F. X. L. i Xamena, Chem. Rev. 110, (2010) 4606; (c) M. Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 112, (2012) 1196; (d) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, Chem. Soc. Rev. 38, (2009) 1450.

[5]. J. R. Li, J. Sculley, H. C. Zhou, Chem. Rev. 112, (2012) 869.

[6]. M. Kurmoo, Chem. Soc. Rev. 38, (2009) 1353; (b) M. Du, C. P. Li, C. S. Liu, S. M. Fang, Coord. Chem. Rev. 257, (2013) 1282; (c) O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr, J. T. Hupp, Nat. Chem. 2, (2010) 944; (d)D. W. Bruce, D. O'Hare, R. I. Walton (Eds.), Molecular Materials, Wiley-VCH, Weinheim, 2010.

[7]. W. Zhang, R. G. Xiong, Chem. Rev. 112, (2012) 1163; (b) P. Horcajada, C. Serre, D. Grosso, C. Boissiere, S. Perruchas, C. Sanchez, G. Ferey, Adv. Mater. 21, (2009) 1931; (c) H. C. Zhou, J. R. Long, O. M. Yaghi, Chem. Rev. 112, (2012) 673.

[8]. M. D. Plessis, L. J. Barbour, Dalton Trans. 41, (2012) 3895.

[9]. C. -D. Wu, P. Ayyappan, O. R. Evans, W. Lin, Cryst. Growth Des. 7, (2007) 1690; (b) H. Deng, Y. -C. Qiu, Y. -H. Li, Z. -H. Liu, R. -H. Zeng, M. Zeller, S. R. Batten, Chem.commun. 19, (2008) 2239; (c) J. -Y. Zhang, Q. Yue, Q. -X. Jia, A. -L. Cheng, E. -Q. Gao, CrystEngComm 10, (2008) 1443; (d) B. Joarder, A. K. Chaudhari, S. K. Ghosh, Inorg. Chem. 51, (2012) 4644; (e) J. Qin, N. Qin, C. -H. Geng, J. -P. Ma, Q. -K. Liu, D. Wu, C. -W. Zhao, Y. -B. Dong, CrystEngComm 14, (2012) 8499; (f) S. Hou, Q. -K. Liu, J. -P. Ma, Y. -B. Dong, Inorg. Chem. 52, (2013) 3225; (g) Y. -Q. Sun, S. Deng, Q. Liu, S. -Z. Ge, Y. -P. Chen, Dalton Trans. 42, (2013) 10503; (h) D. -S. Chen, L. -B. Sun, Z. -Q. Liang, K. -Z. Shao, S. Z. -M. Wang, H. -Z. Xing, Cryst. Growth Des. 13, (2013) 4092; (i) Z. Cui, J. Qi, X. Xu, L. Liu, Y. Wang, J. Solid State Chem. 205, (2013) 142; (j) J. Sun, D. Zhang, L. Wang, R. Zhang, J. Wang, Y. Zeng, J. Zhan, J. Xu, Y. Fan, J. Solid State Chem. 206, (2013) 286.

[10]. S. L. Zheng, X. M. Chen, Aust. J. Chem. 57, (2004) 703; (b) S. N. Wang, Coord. Chem. Rev. 215, (2001) 79; (c) R. C. Evans, P. Douglas, C. J. Winscom, Coord. Chem. Rev. 250, (2006) 2093.

[11]. H. Deng, Y. -C. Qiu, Y. -H. Li, Z. -H. Liu, R. -H. Zeng, M. Zeller, S. R. Batten, Chem.commun., (2008) 2239.

[12]. H. Motegi, L. Hu, C. Slebodnick, B. E. Hanson, Micro. Meso. Mater. 129, (2010) 360.

[13]. L. -Y. Yao, L. Qin, T. -Z. Xie, Y. -Z. Li, S. -Y. Yu, Inorg. Chem. 50, (2011) 6055.

[14]. J. -L. Du, X. -L. Zhu, P. Li, ActaCryst. Sect. C: Cryst. Struct.commun. 68, (2012) m281.

[15]. W. -Q. Kan, J. Yang, Y. -Y. Liu, J. -F. Ma, Polyhedron 30, (2011) 2106.

[16]. P. Suresh, A. Samanta, A. Sathyanarayana, G. Prabusankar, J. Mol. Struct. 1024, (2012) 170.

[17]. G. M. Sheldrick, ActaCrystallogr. Sect. A 46, (1990) 467.

[18]. G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, UniversitätGöttingen, Göttingen, 1997.

[19]. P. van der Sluis, A. L. Spek, ActaCryst. A 46, (1990) 19

[20]. J. Sanchiz, P. Esparza, S. Dominguez, A. Mederos, D. Saysell, A. Sánchez, R. Ruano, J. M. Arrieta, J. Chem. Soc. Dalton Trans. (2001) 1559; (b) L. Pan, X. Huang, J. Li, J. Solid State Chem. 152, (2000) 236; (c) N. Niklas, F. Hampel, G. Liehr, A. Zahl, R. Alsfasser, Chem. Eur. J. 23, (2001) 5135; (d) M. A. Romero, M. N. Moreno, J. Ruiz, M. P. Sánchez, F. Nieto, Inorg. Chem. 25, (1986) 1498; (e) P. Arranz-Mascarós, R. López-Garzón, M. D. Gutiérrez-Valero, M. L. GodinoSalido, J. M. Moreno, Inorg. Chim. Acta 304, (2000) 137; (f) G. Mendoza-Diaz, G. Rigotti, O. E. Piro, E. E.

Sileo, Polyhedron 24, (2005) 777; (g) J. M. Grevy, F. Tellez, S. Bernés, H. Nöth, R. Contreras, N. Barba-Behrens, Inorg. Chim. Acta 339, (2002) 532; (h) E. R. Acuña-Cueva, R. Faure, A. Illán-Cabeza, S. B. Jiménez-Pulido, M. N. Moreno-Carretero, M. Quirós-Olozábal, Inorg. Chim. Acta 342, (2003) 209; (i) F. Hueso-Ureña, S. B. Jiménez-Pulido, M. N. Moreno-Carretero, M. QuirósOlozábal, J. M. Salas-Peregrín, Inorg. Chim. Acta 277, (1998) 103.

[21]. E. Katsoulakou, V. Bekiari, C. P. Raptopoulou, A. Terzis, E. Manessi-Zoupa, A. Powell, S. P. Perlepes, Inorg. Chem.commun. 14, (2011) 1057.

[22]. B. Barszcz, A. Jabłon´ ska-Wawrzycka, K. Stadnicka, S. Hodorowicz, Inorg. Chem.commun. 8, (2005) 951.

[23]. B. Barszcz, S. Hodorowicz, K. Stadnicka, A. Jabłon´ ska-Wawrzycka, Polyhedron 24, (2005) 627.

[24]. B. Barszcz, S. Hodorowicz, A. Jabłon´ ska-Wawrzycka, K. Stadnicka, J. Coord. Chem. 58, (2005) 203.

[25]. J. Y. Zhang, A. L. Cheng, Q. Yue, W. W. Sun, E. Q. Gao, Chem.commun., (2008) 847.

[26]. B. Barszcz, A. Jabłon´ ska-Wawrzycka, K. Stadnicka, J. Jezierska, Polyhedron 27, (2008) 3500.

FRONTIERS IN CHEMICAL, BIOLOGICAL AND PHARMACEUTICAL SCIENCES VOLUME III

(ISBN: 978-93-95847-85-8)

About Editors

Mr. Mukul Machhindra Barwant working as an Assistant professor, Department of Botany, Sanjivani Arts Commerce and Science College Kopargaon. He has more than 5 years of teaching and industrial experience. He has published 29 research articles in the Notational and International journal as well as the conference presented. He has published 10 book chapters in Immortal publication, 10 Edited books with ISBN. His Publication reputed journal like Springer, Elsevier, CRC Press, Taylor and Francis and UGC care list Journal. He is also work as Reviewer of journal and publisher more than 30 and also Editorial Board member 10 Journal .he also Have Membership of Society of Learning Technology (SOLETE) Prasadampadu Vijayawada, Andhra Pradesh, India 2021 life time He have received award like BEST PRESENTER AWARD-2021,BEST PRESENTER AWARD-2021, AIB-VSC-BEST YOUNG SPEAKER AWARD, YOUNG RESEARCHER AWARD 2021, SARDAR VALLABHBHAI PATEL: THE IRON MAN OF INDIA:2021 ACADEMIC AWARD FOR THE BEST YOUNG SCHOLAR, BEST RESEARCHER AWARD INSO 2022, LIFE TIME ACHIEVEMENT AWARD he have published 03 patent in Government of India, Abstract Presented in 08 Conference. Participation of 32 Conference, 45 Workshop, 121 Webinar, 20 Seminar guest lecture and 09 certificate Course.

Dr. Bassa Satyannarayana Working as an Assistant Professor in Department of Chemistry, Gout M.G.M P. G. College, Itarsi, Madhya Pradesh for more than three years. He has vast experience in Teaching, Research and administrative work more than five years. He also acts as a Nodal officer of SWAYAM courses. He acts as an Incharge of College Website. He acts as a Head of the Department of Chemistry. He did his PhD in chemistry under the guidance of Dr S Paul Douglas in the department of engineering chemistry, AUCE (A), Andhra University, Visakhapatnam on 2017. My research area is Nano Catalysis and Organic synthesis. He qualified 2 times CSIR-UGC-JRF, 5 times GATE-2014-2019 with 163 rank, APSET, BARC (OCES/DGFS), BPCL (Chemist), IOCL (Asst.Quality control Officer), and UPSC (Senior Scientific officer) exams. He qualified Assistant professors (College Cadre) exams of different PSC like MPPSC, UKPSC, GPSC and HPSC etc. he has bagged the BEST ACADEMACIAN AWARD – ELSEVIER SSRN-2020 for his outstanding enthusiasm and workability. He awarded by Nagar Palika, Itarsi for his contribution in teaching field. He has 5 Indian Patents and 2 Australian Patents to his credit so far. He has 15 research publications, 12 books, 8 books as Editor and 2 book chapters both internationally and nationally to his credit. 1 book translated to 5 different foreign languages like Italian, Portuguese, Spanish, and Russian etc. He has presented few papers, attended many workshops and organized webinars/seminar/workshops of both International and National conferences, seminars etc.

Bhumi Publishing

ISBN 978-93-95847-85-8
9 789395 847858