



Back to Basics:
A Multidisciplinary Approach
to Organic Living and
Waste Management

*Jogamaya
Devi College
Interdisciplinary
Volume 3*



Back to Basics: A Multidisciplinary Approach to Organic Living and Waste Management

Jogamaya Devi College Interdisciplinary Volume 3

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FROM PRINCIPAL'S DESK

Hello Readers!

It's time to present yet another E-Book published by Jogamaya Devi College. As per tradition, the college Research Committee who are in charge of publishing such E-Books, chose the multidisciplinary topic "Back to Basics: A Multidisciplinary Approach to Organic Living and Waste Management" as theme of the present volume. This is going to be the second such volume to be published in 2022.

My heartfelt thanks go to the committee members especially the enthusiastic editors for their effort towards fostering creativity and knowledge transfer.

With thanks and best wishes,

Principal

FROM THE RESEARCH COMMITTEE, JOGAMAYA DEVI COLLEGE

The Research Committee, Jogamaya Devi College hereby presents the peer-reviewed interdisciplinary volume entitled “*Back to Basics: A Multidisciplinary Approach to Organic Living and Waste Management*”; which is the sixth electronic multidisciplinary book published by the committee so far, and the second one in this calendar year. Designated as the Jogamaya Devi College Interdisciplinary Volume 3, 2022, it features eight articles from a wide spectrum of disciplines, submitted by the teachers and researchers of different colleges, universities and research institutions. Each article has been critically reviewed by at least one specialist from the related field, and in a few cases, by more than one reviewer from different disciplines.

The Research Committee has been publishing one or two interdisciplinary volumes each year since 2018, with original works and review articles pertaining to different environmental and socio-economic issues. In the end of 2021, when the normal academic activities were gradually resuming after a long spell of “new normal”, the Research Committee was looking for a theme for its next publication. Since all of us were still recovering from all-pervasive impacts of the COVID-19 catastrophe at that time, an obvious choice as our next theme was the pandemic-induced environmental, social and economic issues. It was endorsed by almost all concerned and we were about to finalize it. However, Dr. Nandini Bhattacharjee, Associate Professor of Chemistry of our college, came up with a new idea – she suggested the present theme, explaining the necessity to highlight the modern trends of organic living and application of age-old traditional procedures for addressing contemporary problems. At first, we were somewhat apprehensive regarding the feasibility of such a publication, because this topic was not familiar to the teachers and researchers who were our prospective authors, and sufficient number of articles may not be received. But our members and other teachers encouraged us to give it a try, and finally we decided to publish two interdisciplinary volumes this year – one on the impacts of the COVID-19 pandemic, and the other on the present theme. The first one has already been published in June, 2022, and can be accessed from ‘College Publications’ page of the website of our college. And now, thanks to the untiring efforts of Dr. Kaushik Kiran Ghosh, Dr. Payel Mandal and Dr. Shila Neogi, who were the editors of this volume, we are publishing the second one also.

Throughout the entire work, we have been aptly guided and assisted by a number of prominent academicians and researchers from various institutions. Prof. Dr. Amitava Das, Professor, Department of Chemical Sciences, IISER Kolkata and Prof. Dr. Kousik Pramanick, Professor, Department of Life science, Presidency University have enlightened us with their valuable comments and suggestions. Both of them had extended their generous helps to our earlier publications as well. This volume is also enriched with the pertinent

advices of Dr. A. P. Das, Retired Professor, North Bengal University; Dr. Ajoy Kumar Bhaumik, Department of Applied Geology, IIT(ISM), Dhanbad; Dr. Chaitali Bhattachariya, Department of Chemistry, Netaji Nagar College for women; Dr. Dola Chakraborty, Department of Geology, Durgapur Govt. College; Prof. Dr. Gautam Aditya, Department of Zoology, Calcutta University; Prof. Dr. Goutam Ghosal, Department of English, Visva-Bharati, Shantiniketan; and Dr. Mala Neogy, Department of Botany, A.P.J. Abdul Kalam Government College.

Two such publications in one year would not have been possible without the unstinting cooperations of our respected Principal, Dr. Srabani Sarkar, who is the ex-officio publisher of this edited volume.

Finally, we thank all our esteemed colleagues for their encouragements and help, and hope for their continued support in all our future endeavours.

Sushree Chakraborty
and
Bhaskar Ghosh,
Joint Convenors,
Research Committee,
Jogamaya Devi College

FROM THE EDITORS' DESK

In the modern era, the immediate necessity is to pay much more attention to save the nature from the adverse effects of the ever-increasing population, urbanization and industrialization to a holistic approach. Organic living refers to a lifestyle that is good for human health and also for the environment. Waste management, on the other hand, requires a comprehensive effort for recycling of the toxic waste materials, or their safe disposal in order to prevent their harmful effects on the individuals and also on the environment. Jogamaya Devi College Interdisciplinary volume 3, 2022 focuses on the dual aspects of mitigation of this problem – the organic living that facilitates reduced use of industrially synthesized materials in all walks of life, and the management of the industrial wastes to save our environment from their detrimental effects.

Environment of water safety and security is a major concern nowadays. The application of oxide nanoparticles photocatalytic technology in waste water treatment and environmental safety has been presented in the article of Dr. Amit Dalui. Emphasis is put on the application of nano TiO_2 and ZnO photocatalytic technology in waste water treatment and recent achievements in scientific research are established in his article.

Environmental contamination is one of the major global problems in the present times faced by urbanized and developing countries. Phytoremediation, or the use of plants for environmental remediation, is an eco-friendly, cost-effective, scientific alternative to the traditional methods of environmental clean-up. *In vitro* plant cell and organ cultures are convenient laboratory tools for phytoremediation research. We are enriched with a brief idea about the potentiality of plant *in vitro* cultures for phytoremediation of heavy metals from Dr. Anrini Majumder's article.

The recent pandemic situation led to an unprecedented rise in the production and use (as well as overuse) of alkali-based and alcohol-based disinfectants. But all of them have certain detrimental effects on the human health and also on the environment. The contribution of Dr. Bhaskar Ghosh explains the correlation between the internal structures, chemical compositions and properties of clay minerals that make them suitable as cleaners and disinfectants, and discusses the present situation and future prospects of the clay-based sanitisers.

The paper of Dr. Kuntal Narayan Chaudhuri and Dr. Shreyashi Chaudhuri briefly reviews the agricultural heritage of the Apatanis, tribes of Northeast India, as a model 'green' farming system that promotes 'organic living' and examines the vital role played by Apatani women with innovative strategies based on indigenous knowledge in this endeavour in an attempt to understand their 'silent' contribution in advancing solution to critical issues on the global agenda of ensuring food and nutritional security to all while protecting the environment.

Dr. Molia's paper is on organic waste recycling, in which organic wastes and their recycling methods have been discussed. It also covers the significance of organic waste recycling and its barriers and challenges.

Dr. Ranu Naskar gives a view about urban solid waste pollution in India. Her discussion also includes waste management strategies having three main components viz. source reduction, recycling and disposal. Its management steps include collection, storage and recovery of recyclable materials, transportation, treatment, and disposal.

Dr. Smita Ray draws the readers' attention towards environmental deterioration, need of sustainable development and effectiveness of green audit. Water conservation, biodiversity preservation, afforestation, use of bio fertilizers, waste management etc. comes under the purview of green audit. Abiding to these guidelines also overcomes the health hazards. She highlights the objectives, protocols, scopes and authorities concerned with green audit. Activities involved in pre-audit, on-site audit and post-audit stages are outlined in her article.

Dr. Soma Mandal depicts the interrelationship between indigenous women and nature, a key concept that has been explored in ecofeminism. Her article investigates how Rukmani depend on natural means for survival and also attempts to correlate the concept of environmental survivalism.

From a large number of articles submitted for publication in this volume, we could select only the above eight after the initial scanning by the editors and thorough reviews by eminent academicians from different disciplines.

We express our heartfelt appreciation to all the authors and reviewers without whom it would not be possible to publish this volume. We are very much grateful to Dr. Chaitali Bhattachariya and Dr. Dola Chakraborty for reviewing one of the articles of this volume. We feel deeply indebted to Dr. Bhaskar Ghosh and Dr. Sushree Chakraborty, joint convenors of Research Committee, Jogamaya Devi College for their continuous support and valuable suggestion to improve the presentation of this volume. We express our sincere thanks and gratitude to our honourable Principal, Dr. Srabani Sarkar, for the support and encouragement we have received in different stages of the work and we are also grateful to the teachers of our college for their inspiration. We conclude this with a hope that this humble effort will satisfy its intended readers, the teachers, researchers and students, and this will definitely encourage us to create a better volume in future.

Kaushik Kiran Ghosh
Payel Mandal
Shila Neogi
(Members of the Editorial Board)

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Developments of Oxide Based Nano-photocatalyst in Waste Water Treatment Technology: A Brief Overview

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Abstract: Clean potable water is critical for all living organisms. Various organic and inorganic contaminants have been detected in various water bodies that contribute to the source of potable water. Such contaminants are typically toxic and hazardous to the living organism. Thus, removal or degradation of these contaminants from industrial waste prior to the discharge into the environment is essential. Nanotechnology showed great potential in developing new processes for water purification and decontamination. Particularly, heterogeneous photocatalysis involving nanocrystals (NCs) appears to be one of the most promising technologies. Nanoscale metal oxides have been widely investigated for photocatalytic water purification due to their distinct size, physical and chemical properties such as large surface area, high charge transport and stability. Very few review articles are reported that specifically address metal oxide NCs and their application in the treatment of wastewater. In this review article, we have discussed the application of different photocatalytic processes for the treatment of waste water using oxide-based NCs with an aim to address the crucial issue of a sustainable environment. Emphasis is put on the application of nano TiO_2 and ZnO photocatalytic technology in wastewater treatment and recent achievements in scientific research are discussed in this article. We have discussed the designing of advanced photoreactor technology for industrial-scale waste water treatment. Finally, conclusive remarks regarding current studies and unsolved challenges of nano particles based photocatalytic technology are put forth for future perspective.

Keywords: Semiconductor, photocatalysis, wastewater, oxide-NCs, nanotechnology

1. Introduction

In modern civilization, water contamination has increased globally due to rapid industrialization and the massive population explosion (Lijuan et al. 2012, Ren et al. 2021). In 2020, a report of the United Nations on World Water Development also cautioned that change in the water cycle will also pose serious risks to food security, energy production, human wellbeing, economic development, and the option for an all-inclusive sustainable development (World-Water-Development-Report 2020). Various technological measures have been adopted so far in addressing the issue of wastewater treatment and decontamination of waterbodies (Zularisam et al. 2006, Yagub et al. 2014, Azimi et al. 2017). However, these processes are generally energy expensive and has complex mechanisms involved for transforming pollutants into by-products while treating wastewater. In this context, nanotechnology which is an interdisciplinary field covering a wide range of streams including the frontier of chemistry, physics, materials, medicine and biology provides an efficient solution for photocatalytic degradation of pollutants (Ratner & Ratner 2003, Yang 2003). NCs possess a high surface to volume ratio, large area and small sizes, and have a strong adsorption reactivity and capacity pollutants (Ratner & Ratner 2003, Yang 2003). Various types of NCs, including carbon

nanotubes, zerovalent metal NCs, semiconductor NCs, metal oxide NCs, nanocomposites and heterostructures have been reported worldwide for the disintegration of bacteria, emerging pollutants, organic pollutants, and inorganic anions (Pruden & Ollis 1983, Horikoshi & Serpone 2020). Semiconductor NCs based photocatalysts operating in ambient conditions is a cost effective and green technology which can degrade organic pollutants present in wastewater into CO₂ and other small molecules, and reduce or oxidise inorganic pollutants into harmless substances (Pruden & Ollis 1983, Horikoshi & Serpone 2020, Li et al. 2019). Metal oxide semiconductor NCs which are low cost, highly abundant and nontoxic are promising for heterogeneous photocatalysis of both organic and inorganic pollutants (Naseem & Durrani 2021). The metal oxide NCs possess a wide bandgap which permits both oxidation of water and reduction of protons which is the main helpful factor to enhance the photocatalytic activity (Naseem & Durrani 2021). Also, metal oxide NCs display excellent light absorption properties, outstanding charge transport characteristics, which are suitable in the photocatalytic system for the treatment of wastewater (Naseem & Durrani 2021). Among various semiconductor NCs, oxide semiconductor NCs like ZnO, TiO₂ are the most investigated photocatalysts because of their electronic band structure, photostability, chemical inertness and commercial availability (Schneider et al. 2014). However, the metal oxide photocatalysis is restricted due to the poor quantum efficiency and the fact that it could only absorb the UV light of the solar spectrum. The developing directions of photocatalysis need catalysts with higher catalytic performance, which includes doping, heterojunction formation, alloying, composite formation and so on (Naseem & Durrani 2021).

In this review article, we overview the development and advances of oxide NCs in photocatalytic removal or degradation of several common categories of water pollutants. In this article, we have reviewed the current research progress on oxide-based nano photocatalysts, designing, and structural modifications. We have also discussed the insight of photocatalytic mechanism, intermediates formation and designing of photocatalytic reactors. Through this article, we hope to provide forward-looking ideas and prospects for the future development of more advanced photocatalysts useful for water waste treatment.

2. Discussion

2.1. Nanocrystals

Nanoscience and nanotechnology related to the materials that have dimensions in nanometers or one-billionth (10⁻⁹) of a meter, at minimum, one external dimension is in the range of 1-100 nm are called NCs. NCs show superior chemical, biological, mechanical, electrical, magnetic and optical properties which are often significantly different from their corresponding bulk counterparts (Schneider et al. 2014). All these properties depend on the size, shape, composition, defects and interface which can be tailored by proper design and synthesis process (Rao et al. 2004). Semiconductor NCs have different energy bands called valence and conduction bands. The energy gap between the top of the valence band and the bottom of the conduction band is called the bandgap. The electronic states in crystals are different from the isolated atom. (Figure 1a) Semiconductor materials can be elemental or compound type. They

are mainly composed of periodic groups of IV (e.g. Si and Ge), II-VI (e.g. ZnO, CdS and CdSe), III-V (e.g. InP and InAs), IV-VI (e.g. PbS, PbSe, SnS, SiO₂) combination (Rao et al. 2004, Zhao et al. 2004, Wu & Zelenay 2013, Rowland et al. 2014). Elemental semiconductors like Si and Ge have four valence shell electrons. In II-VI, III-V and IV-VI compound semiconductors there are eight valence shell electrons shared by two pairs of nearest atoms. The elements belonging to the II, III and IV groups are more electropositive whereas V and VI group elements are more electronegative. So, because of the electronegativity difference between the constituent elements, the covalent character is predominant in III-V and IV-VI semiconductors whereas II-VI semiconductors have more ionic character (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003).

2.2. Quantum confinement effect

When the length scales of material are below the de-Broglie wavelength of an electron, the electron gets confined in a spatial dimension resulting in new unique properties which are different from the bulk (Figure 1a). Semiconductor NCs show unique optoelectronic properties due to the restricted motion of electrons i.e., quantum confinement effect (Ioannou & Griffin 2010). Upon absorption of a photon, an electron gets excited from the valence band of the semiconductor to the conduction band leaving a positively charged hole in the valence band (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003). Due to the coulomb attraction between the electron and the hole, they form a loosely bonded pair known as an exciton. The separation distance between the electron and hole pair in an exciton is termed as exciton Bohr radius (Ratner & Ratner 2003, Yang 2003).

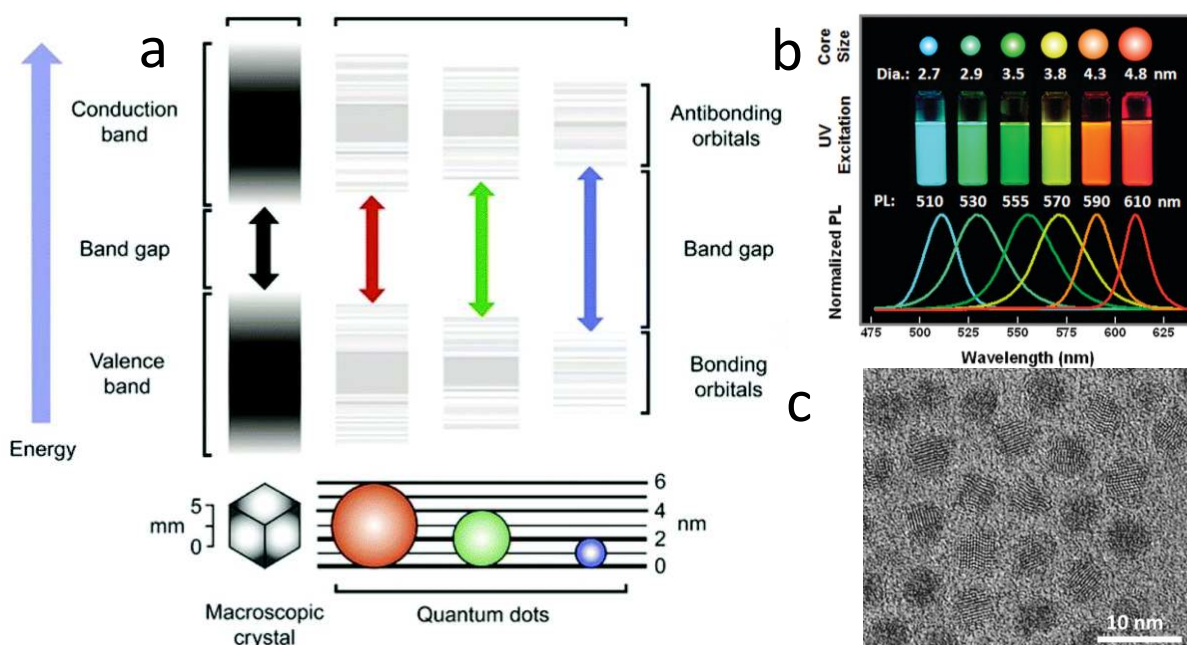


Figure 1. (a) Comparison of the energy band of bulk and nano semiconductor materials due to effect of quantum confinement. Electronic states in a bulk semiconductor and quantum dots (QDs) made of the same material with different diameters (Ioannou & Griffin 2010). Reproduced with permission from Informa UK Limited, copyright 2010. (b) Schematic, photograph, and photoluminescence (PL) spectra illustrating progressive color changes of CdSe/ZnS with increasing nanocrystal size. The larger band-gap energy of smaller QDs of the same material leads

to lower PL wavelengths (large QDs are red and small QDs are blue) (Algar et al. 2011). Reproduced with permission from American Chemical Society, copyright 2011. (c) Transmission electron micrograph of CdSe/ZnS QDs (Talapin et al. 2001). Reproduced with permission from American Chemical Society, copyright 2001.

Dielectric constant of the semiconductor materials reduces the strength of Coulomb attraction (Ratner & Ratner 2003, Yang 2003). Thus, smaller exciton binding energy implies a larger spatial separation of electron and hole and eventually has a larger excitonic Bohr radius (Ratner & Ratner 2003, Rao, et al. 2004). Semiconductor NCs in nanometer length scale where charge carriers are confined in all three spatial dimensions are called Quantum dots which display unique optoelectronic properties and immense applications in the field of science and technology (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003). Figure 1b shows the fluorescence colour of the highly luminescence CdSe/ZnS quantum dots upon excitation of UV light (Algar et al. 2011). This photoluminescence colour originated from the recombination of the exciton. The transmission electron microscopic image of the quantum dots is shown in figure 1c (Talapin et al. 2001).

2.3. Tuning the properties of the NCs

The most fascinating property of semiconductor NCs is the modulation of electronic structure as a function of size. As the size of the semiconductor crystals decreases from the bulk size to nanometer regime, the electronic structure is altered from the continuous electronic bands to discrete or quantized electronic levels and therefore the size of the NCs defines the optoelectronic properties of the NCs. (Figure 1) In semiconductor NCs both linear and non-linear properties arise as a result of transitions between electron and hole quantum size levels. Other ways of tuning of NCs properties includes changing shape, composition, formation of heterojunction, doping etc. which will be beyond our scope to discuss in this short overview (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003).

3. Photocatalytic application

Catalysis refers to a process that influences the rate of a chemical reaction using a substance (catalyst) that remains unconsumed at the end of the reaction. A catalyst participates during a reaction and only alters the activation barrier for the transition state and thus, influences the rate of the reaction. A positive catalyst accelerates the chemical transformation, while a negative catalyst retard the process. A catalyst does not change the overall value of the equilibrium constant and the overall free energy for the reaction when compared with the analogous uncatalyzed reaction (Cotton et al.1994). Depending upon the phase of the catalyst compared to the reactant, the catalysts can be classified as homogeneous or heterogeneous catalyst. In homogeneous catalysis, the reactant and the catalysts are in the same phase whereas in the heterogeneous catalysis, catalysts are in a different phase with respect to the reactants (Pagni 2001). A nanomaterial-based catalyst is an example of heterogeneous catalysis. Here, catalysts can be easily separated from the reaction mixture by means of physical or chemical methods. NCs with smaller size have high surface area with available surface- active sites with high interfacial charge carrier transfer rates leading to higher catalytic activities compared to

their bulk counterpart. Photocatalysis, where photons are used for catalytically activating chemical reactions on the surface of photosensitized catalysts, remains one of the leading hubs of research for harvesting solar light (Teoh et al. 2012). Efficient separation of exciton leads to greater photocatalytic efficiency. Metal semiconductor heterostructure or semiconductor-semiconductor heterostructure and composite of semiconductor material have shown efficient charge separation ability and hence better photocatalytic efficiency (Yang 2003, Lijuan et al. 2012, Ren et al. 2021). However, in this short review, we have little scope to cover the photocatalytic activity of all these systems. We will discuss mostly the photocatalysis reaction of oxide-based NCs specially ZnO and TiO₂.

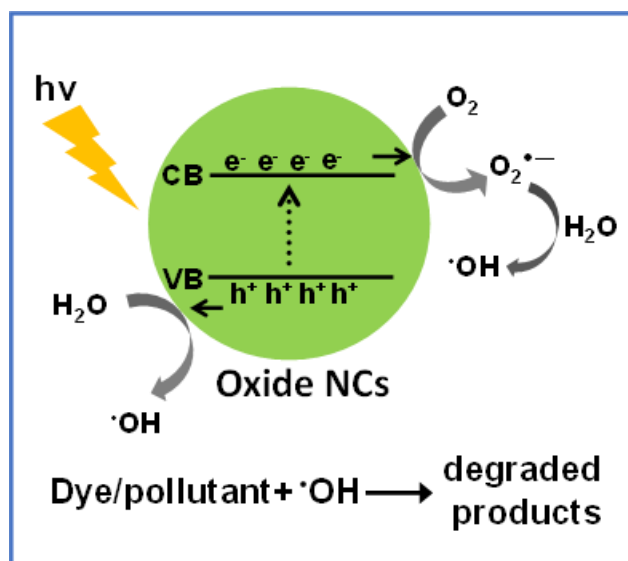
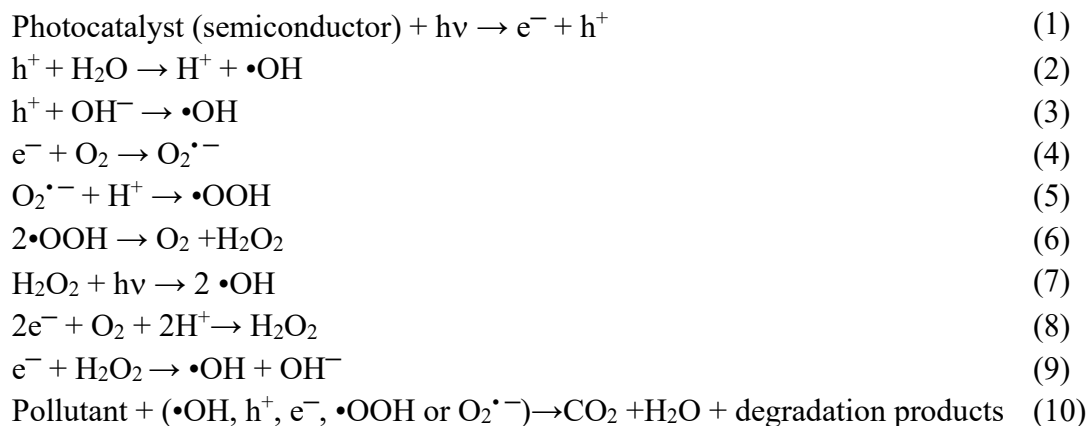


Figure 2. Schematic illustration of the photocatalytic degradation of pollutant by oxide NCs with details reactions pathways.

3.1. Photocatalytic reaction mechanism

Semiconductor materials possess an energy bandgap (E_g) which is an important parameter for photocatalysis reaction. Bandgap of the semiconductor NCs is tuneable by changing the size, shape and composition. On excitation of light, electron (e^-) from the valence band (VB) of the semiconductor excite into the conduction band (CB), leaving holes (h^+) in the valence band (Figure 2). For bulk materials, these photogenerated electron-hole pairs (i.e., exciton) are difficult to separate from each other and undergo recombination easily (Ratner & Ratner 2003, Yang 2003). However, for materials at nanoscale dimension, it becomes easy for the separation of electron holes. Photogenerated electrons and holes undergo various surface reactions to generate active oxidative radicals which are responsible for the photodegradation of pollutants (Ratner & Ratner 2003, Yang 2003, Lijuan et al. 2012, Ren et al. 2021) (Figure 2). Photogenerated electrons are widely considered as reductants for directly reducing some heavy metal ion pollutants. Also, photogenerated electrons can react with dissolved oxygen in water to produce superoxide radicals ($O_2^{\cdot-}$) which undergo further reactions to produce $\cdot OH$ radicals. On the other side, photogenerated holes react with water or hydroxyl ion (OH^-) to produce hydroxyl ion ($\cdot OH$) and can also participate directly in the oxidative decomposition of the

pollutants (Lijuan et al. 2012, Ren et al. 2021) (Figure 2). For heterogeneous photocatalysis using NCs, pollutants first adsorb on the surface of the NCs. Then upon photoexcitation electron-hole pairs are generated in NCs which also benefit charge mobility and enhance its redox ability. Then the charge carrier undergoes a series of chemical reactions with the active species generated by the NCs and pollutants to obtain degradation products (Lijuan et al. 2012, Ren et al. 2021). All the redox reactions discussed above are listed below (equation 1-10).



3.2. Photocatalytic degradation of pollutants in waste water

3.2.1. Removal/degradation of organic pollutants (Dyes, phenol, pharmaceuticals)

There are different types of organic pollutants found in wastewater. These pollutants can be classified as hydrocarbon, dyes, phenolic compounds, surfactants, organohalides, organonitro compounds etc (Lijuan et al. 2012, Ren et al. 2021). These organic pollutants are chemically stable, toxic and carcinogenic (Wang et al. 2014). Carey et al reported the catalytic degradation of polychlorinated biphenyls by TiO_2 under UV light which laid the foundation stone for the research of photocatalysis (John et al. 1976). Semiconductor NCs based photocatalysts have been widely investigated for degrading a wide range of organic pollutants in which the photocatalyst degrades organic pollutants into readily biodegradable compounds or less toxic molecules which are further mineralized into CO_2 and H_2O .

Thousands of dyes are available in the market which are used in industrial processes for the synthesis of wide range of products ((Lijuan et al. 2012, Wang et al. 2014, Ren et al. 2021). Among which methylene blue (MB), Methyl orange (MO), Rhodamine B (RhB), Methyl red (MR) are most common and all are water soluble, not readily biodegradable and harmful for the ecosystem. During oxide NCs based photocatalysis, photogenerated holes (h^+) and H_2O react to form highly oxidising hydroxyl radicals whereas photogenerated electrons react with oxygen to form superoxide ions which further react with H_2O to generate hydroxyl radicals (details in the photocatalysis reaction mechanism). These radicals with potent oxidising power react with dye pollutants to degrade into CO_2 and H_2O or less harmful small chemical compounds (Lijuan et al. 2012, Ren et al. 2021). Zhao et al. reported ZnO microstructures of different morphologies like twining-hexagonal prism, twining-hexagonal disk, sphere and flower-like respectively (Zhao et al. 2013).

Table1: Photocatalytic degradation of organic pollutants

Type of waste water	Classified/characteristic	Pollutants/chemicals	Catalysts	References
Dye waste water	Dye: Water-soluble, not readily biodegradable, harmful to the ecosystem	Methylene Blue	NiO, ZnO, ZnTiO ₃ , TiO ₂	Jayakumar et al. 2017, Petrovicová et al. 2021
		Methyl orange	ZnO, TiO ₂	Raliya et al. 2017
		Rhodamine 6G, Rhodamine B	TiO ₂ , ZnO, AgZnO	Abdullah et al. 2011, Doina et al. 2012, Majumder et al. 2020
		Anthraquinone dye	TiO ₂	Routoula et al. 2020
		Azo dye	ZnO	Chen et al. 2017
Phenolic wastewater	Highly soluble in water, acutely toxic, biologically recalcitrant	Phenols Phenols BPA	Cu-NiO CuO-TiO ₂ TiO ₂ -x @ZIF-67	Ethiraj et al. 2020, Çınar et al. 2020, Tang et al. 2020
Pharmaceutical wastewater	Anti-biotics: Water-soluble, not readily biodegradable, harmful to the ecosystem Anti-inflammatories High polarity, hydrophilicity, the absorption coefficient	Sulfamethazine	ZnO	Yi et al. 2018
		Amoxicillin	TiO ₂	Emad et al. 2010, Varma et al. 2020, Balarak et al. 2021
		diamyl phthalate, butyl benzylphthalate, methyl p-hydroxybenzoate ibuprofen	ZnO TiO ₂	Emad et al. 2010, Vela et al. 2018, Khalaf et al. 2020
		Cloxacillin	TiO ₂	Emad et al. 2010, Ana et al. 2010
		Oxolinic acid, Diclofenac	TiO ₂	Emad et al. 2010, Ana et al. 2010
		Cephalexin, and Oxytetracycline	ZnO, TiO ₂ , Fe ₃ O ₄	Blady et al. 2011

	Lipid regulators	Metformin Amoxicillin metformin	TiO ₂ -ZrO ₂ TiO ₂	Chinnaiyan at al. 2018, Carbuloni et al. 2020
Pesticide wastewater	Toxicity, biological resistance	Kappa furan, carbofuran pesticides, melathion	TiO ₂ , ZnO	Emad et al. 2010, Blady et al. 2011, Khan et al. 2020
		Dieldrin, Deltamethrin	TiO ₂	EL-Saeid et al. 2021
		Armour mix phosphorous	TiO ₂	Wang et al. 2010
		Organophosphorous pesticides	TiO ₂	Doong & Chang. 1997
Explosive waste water	Contains highly toxic nitroaromatic compounds, hazardous to environment, animal and human	TNT	TiO ₂ , WO ₃ /Fe ₃ O ₄	Lee et al. 2002, Reza at al. 2021
		RDX	TiO ₂	Lee et al. 2002
		HMX	TiO ₂	
Chlorine hydroxybenzene waste water	Compared to phenol, chlorophenolic compounds are more toxic and have more bioaccumulative potential, very low biodegradability.	Chlorinated phenol	TiO ₂ , ZnO	Dionysios at al. 2000, Elkady et al. 2017
Nitrobenzene waste water	Toxic to microorganism and environment	Nitrobenzene	TiO ₂ , Ag-Cu ₂ O	Wang et al. 2010, Chen et al. 2021

They showed that flowerlike ZnO exhibited higher photocatalytic activity due to its morphology, surface defects, bandgap and surface area. In 2020, Saifuddin et al reported the photocatalytic degradation of organic pollutants by MFe_2O_4 ($M = Co, Ni, Cu, Zn$) catalyst (Gupta et al. 2020). These photocatalysts are highly suitable for the remediation of dye-contaminated wastewater. They have demonstrated that dye degradation mechanism in the UV/ H_2O_2 /ferrite system was primarily driven by the formation of $\bullet OH$ radicals and holes, which was confirmed by scavenger studies and fluorescence spectroscopy (Figure 3). Table 1 demonstrates photodegradation of organic pollutants by metal oxide NCs such as ZnO, TiO_2 , doped metal oxide and composite system.

Petroleum hydrocarbon pollutants are persistent important pollutants containing alkanes, olefins and polycyclic aromatic hydrocarbons (Douglas et al. 2012). It is well known that marine environments are the ultimate and largest sink of petrochemical pollutants and has become a critical issue to effectively treat hydrocarbon pollutants in the aquatic environment (Varjani 2017). In this line, NCs based photocatalysts are promising candidates for the photodegradation of petrochemical hydrocarbons. Younesi et al reported that TiO_2 NCs in zeolite matrix works as efficient photocatalysts for the removal of organic pollutants from petrochemical refinery wastewater (Ghasemi et al. 2016). Two-dimensional g- C_3N_4 nanosheet reported having good efficiency for photocatalytic removal of petroleum hydrocarbon in water (Yang et al. 2020).

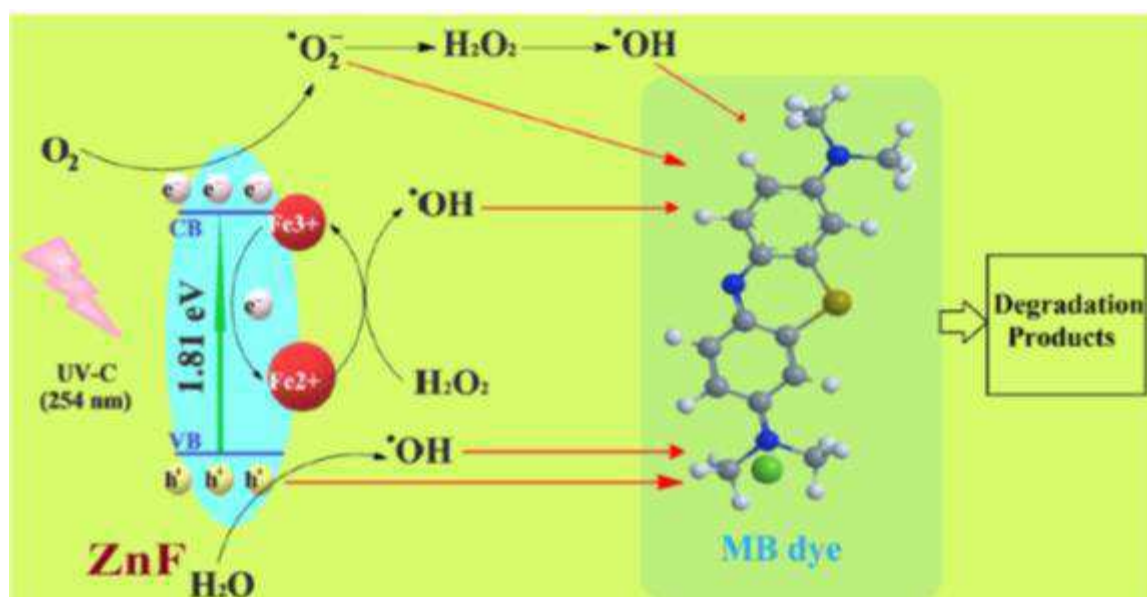


Figure 3. Schematic illustration of the photocatalytic degradation process of MB dye onto Zn ferrite photocatalyst (Gupta et al. 2020). Reproduced with permission from Springer Nature Limited, copyright 2020.

Phenolic compounds are reported to be highly soluble in water, carcinogenic, acutely toxic and biologically recalcitrant. Phenol in wastewater is introduced via a large number of industrial processes such as petroleum production, refineries, manufacturing of paints, pharmaceuticals and pesticides (Maszenan et al. 2011). It is reported that photocatalytic degradation of 4-nitrocatechol produces benzoquinone, hydroquinone and some organic acids (Ahmed et al. 2010). The synergistic effect of hydroxyl radical and superoxide radical leads to the

degradation of phenol. Also, p-n heterostructure of CuO-TiO₂ with band alignment and efficient charge separation ability exhibit good efficiency towards photocatalytic degradation of methylene blue as well as 4-nitrophenol under visible light irradiation (Çinar et al. 2020). Fe₃O₄ NCs with magnetic properties also exhibit high efficiency for photocatalytic removal of phenolic compounds as adsorption sites of the phenolic compounds are provided by the defect state of the Fe₃O₄ NCs (Bui et al. 2020). TiO₂ NCs demonstrate high activity for photocatalytic degradation of biphenyl compounds (Tang et al. 2020).

In modern day, anti-inflammatory drugs have been widely used for many physiological treatments. TiO₂ nanoparticle was reported to be a very effective catalyst for photodegradation and mineralization of dichlofenac in aqueous solution (Achilleos et al. 2010, Günel et al. 2019). TiO₂ nanocatalyst can also be effective for the removal and destruction of ibuprofen which is used to relieve pain and rheumatism (Khalaf et al. 2020, Akel et al. 2020).

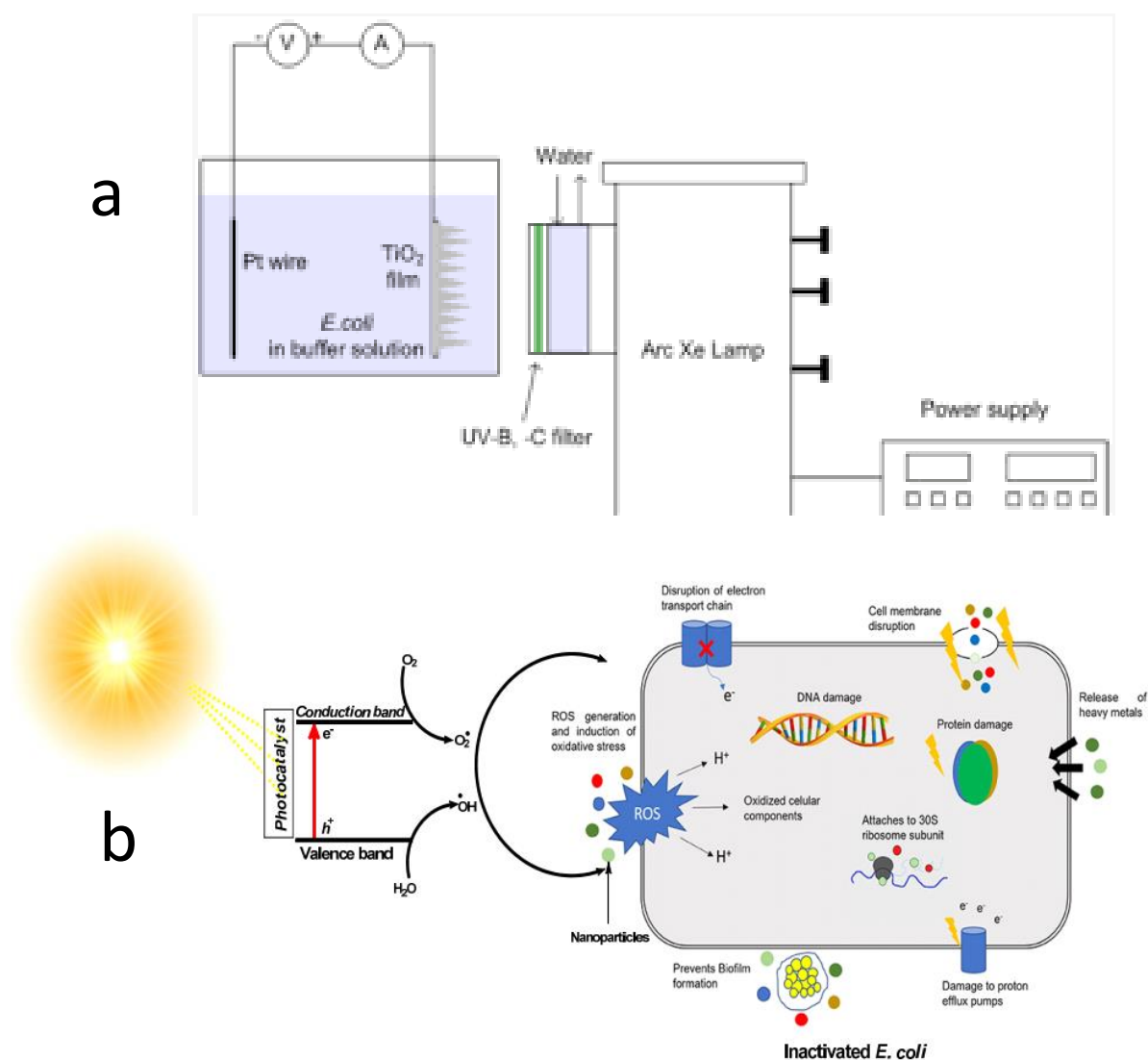


Figure 4. (a) Photoelectrochemical and photocatalytic *E. coli* inactivation set-up (Park et al. 2013). Reproduced with permission from MDPI, copyright 2013. (b) Mechanism of photocatalytic inactivation of *E. coli* (Ajiboye et al. 2021). Reproduced with permission from MDPI, copyright 2021.

Metformin drug is commonly used for hyperglycemia and type-2 diabetes. This drug can enter into the environment through various sources and create pollution to marine and other water resources. Carbuloni et al. reported that TiO_2 and $\text{TiO}_2\text{-ZrO}_2$ photocatalyst exhibit high efficiency for photocatalytic removal of metformin in sewage and water (Carbuloni et al. 2020). TiO_2 nano photocatalysts were also effective for degradation of amoxicillin and metformin (Prashanth et al. 2021).

3.2.2. Removal of Pesticides

Pesticides are one of the major sources of water pollution. All pesticides are carcinogenic and have toxic effects on living organisms, ecosystems and human health even in trace amounts. Semiconductor NCs based photocatalysis technology has been widely investigated for the photodegradation of pesticides. Oxide NCs such as TiO_2 , ZnO are reported to be very effective for the photodegradation of pesticides (Taghizade et al. 2020). Ce-doped TiO_2 nanoparticle was reported for photocatalytic degradation of triazophos and profenofos pesticides (Liu et al. 2019).

3.2.3. Inactivation and degradation of microorganisms

Verities of microorganisms present in the wastewater cause fatal diseases to living organisms and human health. Microorganisms like enterovirus cause different gastrointestinal diseases, adenoviruses cause respiratory diseases, salmonella causes colitis, dysentery and meningitis. TiO_2 photocatalysts could kill bacteria in water through the generation of reactive oxygen species (ROS) (Wu et al. 2010). Since then, ROS mediate water treatment technology through the destruction of toxic microorganisms has become the focus of research. The ROS on microorganisms acts in the following ways: ROS destroys the coenzyme A on the cell membrane, reduces or inhibit cellular respiratory or ROS from entering the cell further to oxidize nucleic acid, proteins and eventually cause cell death (Wu et al. 2010). Apart from the laboratory standard photocatalytic reaction, instruments are also available for the photocatalytic treatment of waste water and the production of safe drinking water. In a recent review article, Onwudiwe et al. demonstrated the photocatalytic inactivation method of E. Coli from water. Different photocatalysts for effective inactivation of E. coli and the mechanism involved are discussed in detail (Ajiboye et al. 2021). A portable and easy to use photocatalytic reactor design has also been reported based on the TiO_2 nanotube as photocatalysts (Park et al. 2013, Ajiboye et al. 2021). Using this reactor can inactivate 5-log of E. coli within 10 seconds. A rechargeable battery is used as source of energy for the LED fitted into the reactor light source and TiO_2 nanotube is used as photocathode. The design of this novel photoreactor is shown in Figure 4.

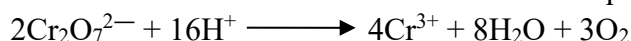
Table 2: Photocatalytic degradation/removal of inorganic pollutants from wastewater

Type of waste water	Classified/characteristic	Pollutants/chemicals	Catalysts	Mechanism	References
As containing waste water	As: carcinogenic and highly toxic	As(III)	Fe-BF/H ₂ O ₂ ZnO TiO ₂ /C	Photooxidation Photooxidation Photooxidation	Yao et al. 2012, Rivera-Reyna et al. 2013, Wei et al. 2022,
Heavy metal ion containing waste water	Cr: Carcinogens, harm human skin and internal organs; Hg: High toxicity, tendency to bioaccumulate Pb: Toxicologica, fatal	Mn(II)	TiO ₂	Photooxidation	Li et al. 2003
		Ti(I)	TiO ₂	Photooxidation	
		Hg(II)	TiO ₂ α -Fe ₂ O ₃ / g-C ₃ N ₄	Photoreduction Photoreduction	Khalil et al. 2002, Kadi et al. 2020
		Cr(VI)	ZrO ₂ , TiO ₂ -ZrO ₂ , Mn ₃ O ₄ @ ZnO/Mn ₃ O ₄	Photoreduction Photoreduction Photoreduction	Botta et al. 1999, Li et al. 2017, Yan et al. 2020
		Pb(II)	TiO ₂ Fe ₃ O ₄ @ C@TiO ₂	Photoreduction Photoreduction	Murrini et al. 2008, Bi et al. 2019
CN ⁻ containing waste water	interfere with cellular respiration, inhibition of cytochrome oxidase	CN ⁻	TiO ₂	Photooxidation	Hidaka et al. 1992
NO ₂ ⁻ containing waste water	Toxic to human and animals, causes blue baby syndrome	NO ₂ ⁻	Fe ³⁺ /TiO ₂ /SiO ₂	Photooxidation	Jin et al. 2001

3.2.4. Removal of heavy metals and toxic anions

Accumulation of heavy metals with high concentration leads to the toxicity in living system. Different types of heavy metals with large quantity are produced due to development of metallurgy, mining, nuclear and chemical manufacturing. Heavy metals can modify the gene of living organism by binding with nucleic acids, protein and metabolites leading to destruction of living cell and fatal health problems. As heavy metals are not biodegradable, it actually gets enriched in the living organism through food chain and drinking water (Wang et al. 2020). Hence, it is very much essentials to remove these heavy metals in waste water before release into the ecosystem. Photocatalysis is an alternate way to remove such heavy metal ions from water where photocatalysts reduces toxic high valent heavy metal ion into lower-valent ions or zero-valent metals ions.

Higher valent chromium (Cr) is ions are carcinogenic, which directly harm human skin and internal organs (Wang et al. 2020). Chromium ions are introduced into the ecosystem either as oxyanions (e.g., CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^-) or cations (Cr^{3+}). Higher valent chromium Cr(VI) present in the oxyanions form reduces into Cr^{3+} in acidic or neutral aqueous solution.



Different nano photocatalysts have been widely investigated for the reduction and removal of Cr(VI) into lower valent Cr(III) (Table 2). In 2017, Liu et al reported the synthesis of $\text{BiVO}_4\text{-Fe}_3\text{O}_4$ heterostructure photocatalytic system using a solvothermal method and adopted it as a photoreduction catalyst to the removal of Cr(VI) in water under visible light irradiation (Chen et al. 2021). BiVO_4 system itself showed a potential method for the economic-friendly removal of high valence metals with easier separation in the water (Figure 5).

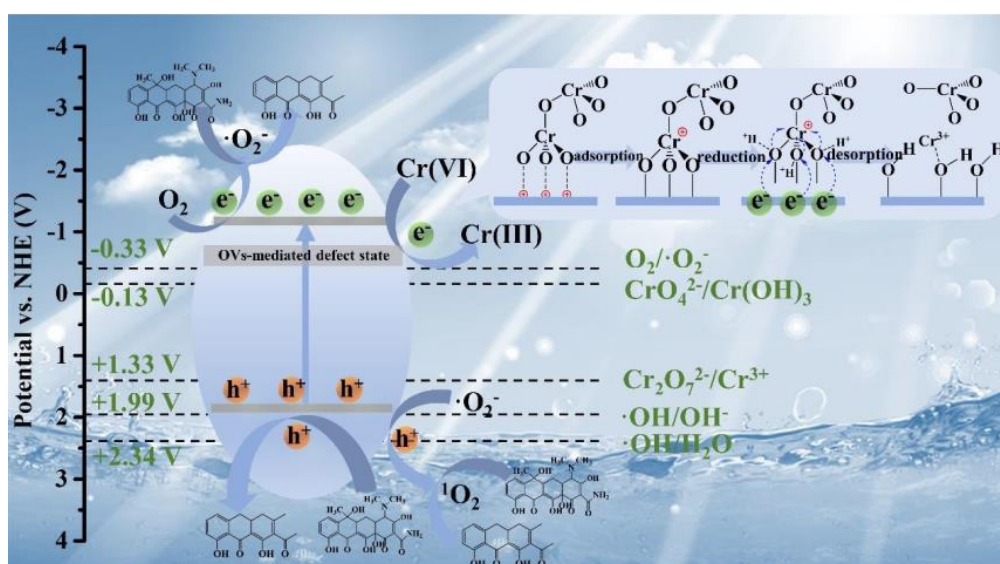
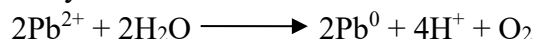


Figure 5. Proposed oxygen vacancy induced charge transfer mechanism on BiVO_4 semiconductor and photo-reduction of Cr(VI) in waste water under visible light irradiation (Chen et al. 2021). Reproduced with permission from American Chemical Society, copyright 2021.

Lead imparts several toxicological effects on human health and even leads to fatal health problems. Lead pollution in the ecosystem come from municipal sewage, mines and chemical production. The Photocatalysis method was reported to be an effective method for the removal of Pb(II) from aqueous solutions (Murrini et al. 2008, Peter et al. 2017, Hosseini & Mohebbi 2020). The possible photocatalysis reactions are as follows:



Magnetic $\text{Fe}_3\text{O}_4@\text{C}@\text{TiO}_2$ oxide heterostructure system showed potential for capturing and removing of Pb(II) (Peter et al. 2017, Bi et al. 2019). $\text{TiO}_2/\text{Al}/\text{Fe}$ NCs magnetic composite system reported to be very effective for removal of a variety of heavy metals ions including Cr(III), Cu(II) and Pb(II) (Peter et al. 2017, Wang et al. 2020).

Mercury (Hg) can damage human health through inhalation of mercury vapour or organic mercury ingestion through aquatic organisms such as Minamata Disease (Hadi et al. 2015). Most of the mercury contamination comes from industrial wastewater mainly from industrial discharge such as a chlor-alkali, plastics, batteries, electronics, and used medical devices. Hg(II) ion can be deposited into mercury metal by the following equations:



Many photocatalysts have been widely investigated for the photoreduction of mercury ions till date. $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanocomposite system showed a high photocatalytic reduction of mercury compared to pure Fe_2O_3 NCs and $\text{g-C}_3\text{N}_4$ nanosheet (Kadi et al. 2020). In addition to the above-mentioned ions, others heavy metal ions such as Arsenic (As), Uranium (U), and cadmium (Cd) are also difficult to biodegrade, quickly accumulate in living organisms and are highly toxic even at very low concentrations (Table 2). $\text{Fe}_2\text{O}_3/\text{C}$ nanocomposite system showed a higher capacity for the photooxidation of As(III) to As(V) which is easy to remove by adsorption (Liu et al. 2019). Chowdhury et al. demonstrated that Y-sensitized TiO_2 photocatalysts can be very effective for the removal of Cd(II) ions (Chowdhury et al. 2017). The pH of the solution is an important factor for photocatalytic reaction efficiency. Metal oxide NCs like TiO_2 , Fe_2O_3 is proven to be very effective for the removal or degradation of these toxic anions from the wastewater (Table 2).

3.2.5 Design of photocatalytic Reactors

The rational designing of photocatalytic reactors plays an extremely important role for the photocatalytic treatment of wastewater in an industrial scale (Sacco et al. 2020). At present, most photocatalytic reactions are limited to the experimental stage and difficult to put into practice in the industry. So, the development of a new and efficient photocatalytic reactor is a crucial factor to accelerate the application of photocatalysis in practical industrial-scale applications. In 2021, in a minireview article, Enesca et al described the parameter for designing of a photocatalytic reactor and its operating parameters (Enesca 2021). In this article, two main aspects have been considered such as photoreactor geometries (cylindrical and rectangular), and analyses the correspondence between the photoreactor concept characteristic

(working regime, volume and flow rate), irradiation scenarios (light spectra, irradiation period and intensity) and the photocatalytic process parameters (photocatalyst and doses, pollutant type and concentration, removal efficiency) (Figure 6). Cylinder photoreactor consist of TiO_2/WO_3 heterostructure exhibit high efficiency for the photocatalytic removal of different organic pollutants (phenols, pharmaceutical active compounds, dyes etc.) (Enesca 2021). On the other side, a rectangular reactor allows a higher versatility of the irradiation source orientation and photocatalyst can be immobilized on the reactor wall. Rectangular photoreactor allows maximum production of oxidative species required for degradation of organic pollutants (Figure 6) (Enesca 2021). It is worth mentioning that for designing an efficient photoreactor several parameters such as pH, temperature, oxygen concentration, the concentration of ion scavenger need to monitor critically. However, the development prospect of photocatalytic water treatment is promising and efficient reactor with an optimized model are worth exploring.

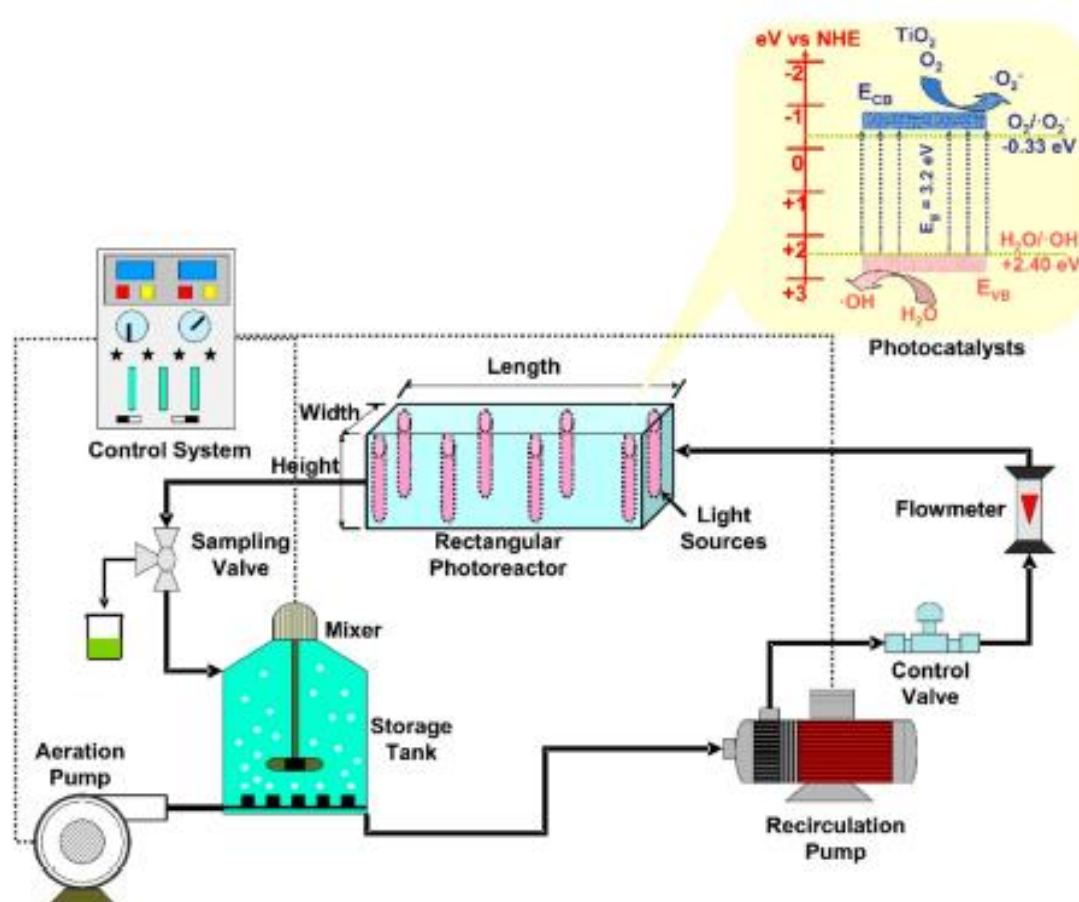


Figure 6. Schematic presentation of a rectangular photoreactor components using TiO_2 photocatalysts (Enesca 2021). Reproduced with permission from MDPI, copy right 2021.

4. Summary and future perspective

In summary, this review article summarized the progress and perspective of NCs based photocatalysis technique for the application of wastewater treatment. Firstly, the prospect of NCs for the photocatalytic reaction was discussed. Then mechanism of the photocatalytic reaction process was introduced. After that, recent advances in photocatalytic removal of

several common categories of water pollutants were explained in detail using examples of some oxide NCs. Also, strategies to improve photocatalytic performance such as composite and heterostructure formation were discussed. To realize photocatalytic treatment of pollutants in wastewater, many aspects of the photocatalysis must be considered. For better understanding of the photocatalysis mechanism requires theoretical and computational study for investigation of surface transformation and chemical changes at molecular level during the photocatalytic degradation. Also, experimental finding and theoretical calculations should be combined to provide better reaction mechanism at the interface. Utilization of advance characterization techniques like mass spectroscopy, NMR are found to be useful for exploring these reaction intermediates and better understanding reaction pathways and degradation mechanism of various water pollutants. From analysing of all the factors, it may point out that although there is promising advancement in synthesis and efficiency of the photocatalyst, most of the photocatalytic experiments reported are performed in laboratory conditions whereas photochemical treatment of industrial waste water or natural wastewater involves large degree of complexity. Hence, further development of photocatalytic system is essential including designing of efficient photoreactor with optimization of photocatalyst concentration and recycling.

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Plant *in vitro* cultures for phytoremediation of heavy metals

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Abstract: *Environmental contamination/pollution is one of the major global problems in the present times faced by urbanized and developing countries. It is caused by natural processes like geological erosion or anthropogenic activities like industrialization as well as agricultural practices. Contaminants or pollutants can be in the form of chemicals released by these processes or in the form of energy such as heat, light, radioactive waves etc. Polluted environment can lead to contamination of groundwater reservoirs, imbalances in the food chain and therefore poses a major threat to the very existence of living beings! Among the different contaminants present are the heavy metals, which are chemical elements with relatively high atomic weights and atomic numbers. Common examples of concern which are hazardous to plants, animals and human beings include cadmium (Cd), mercury (Hg), lead (Pb), arsenic (As). Some others like copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn) can be classed as essential for the normal biochemical and physiological processes when present within limits. Mostly these metals originate from various activities such as industrial and agricultural processes. Heavy metals cannot be degraded by any physical or biological processes; therefore, these metals remain in the environment and can enter the human body through the food chain via crops, causing a plethora of diseases. Thus, appropriate remediation measures are to be taken to prevent these heavy metals from contaminating the environment. Although several physical and chemical methods have been applied for eliminating contaminants from the environment, these are costly and have other drawbacks. Phytoremediation or the use of plants for environmental remediation, is an eco-friendly, cost-effective, scientific alternative to the traditional methods of environmental clean-up. The method is based on the natural ability of plants to uptake chemicals from the air, water and soil and to metabolize a number of these chemicals in their tissues. In vitro plant cell and organ cultures are convenient laboratory tools for phytoremediation research. Plant tissue culture is a technique used for the aseptic culture of plant cells, tissues, organs and their component parts (explants) under defined physical and chemical conditions. Unlike field grown plants, these cultures can be maintained indefinitely under aseptic conditions, free from geographic and seasonal barriers. Also, being grown in sterile conditions, these cultures are free from microbial contamination and can therefore be used easily to discriminate between the responses of plant cells grown in presence or absence of microorganisms which are normally present in the rhizosphere or plant tissues. The present review gives a brief idea about heavy metals, phytoremediation and the potentiality of plant in vitro cultures for the phytoremediation of such metals.*

Keywords: Contaminant, environment, phytoremediation, pollutant

1. Introduction

Environmental pollution is a serious global issue affecting the wellbeing of all living beings. Pollutants, either organic or inorganic, are released into the environment as a result of natural geological processes (erosion, saline seeps) or from extensive anthropogenic activities (agricultural practices, urbanization, industrialization etc.) as a result of the rise in global population (Cherniwchan 2012, Wu et al. 2016a). Among the pollutants are radionuclides,

agrochemicals, heavy metals and metalloids, organic compounds, oil spills etc. (Hu et al. 2010, Sunitha et al. 2012, Prakash et al. 2013, Ron & Rosenberg 2014, Su et al. 2014, He et al. 2015, Malik et al. 2017). These pollutants are either non-biodegradable or degrade very slowly, resulting in their accumulation in the ecosystems, which can ultimately be deleterious for the survival of the entire living world. Thus, a lot of effort has been given for developing remediation strategies for environmental clean-up. Although various traditional techniques like incineration, irradiation, soil washing, pump and treat, surfactant flushing, activated carbon adsorption or extraction have been used for remediation of environmental pollution (Bedmohata et al. 2015, Gautam & Gotmare 2016, Nidoni 2017), in most cases their applications are limited by high costs, requirement of huge labour, safety hazards and threats to the environment (Doran 2009, Ali et al. 2013). Therefore, research was focussed on the development of other efficient and reliable biological techniques to clean-up the environment and phytoremediation appeared to be an attractive alternative. Plant tissue culture has emerged as an efficient tool for phytoremediation research. The present review gives a brief idea about heavy metals, the process of phytoremediation and the application of plant tissue culture techniques used for the phytoremediation of such metals, which are hazardous.

2. Heavy metals and their adverse effects on the living world

Heavy metals (HMs) are a group of chemical elements which are metallic in nature, have relatively high atomic weights and atomic numbers (Yan et al. 2020). HMs may be formed naturally because of paedogenic weathering, erosion, volcanic activities (Kordrostami et al. 2019) or through anthropogenic activities like industrialization and urbanization. Addition of fertilizers and pesticides in agriculture, sewage sludge consumption, metal mining and smelting, electroplating, medical applications, burning of fossil fuels etc. are some of the factors contributing to the contamination of the environment by heavy metals (Muradoglu et al. 2015, Iqbal et al. 2016, Hamzah et al. 2016, Chen et al. 2016, Shi et al. 2018). Depending on their biological role, HMs are classified as essential [required for normal physiological and biochemical processes within the plant body, namely, copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn)] and non-essential [lead (Pb), arsenic (As), cadmium (Cd), mercury (Hg), with no defined function in the plant body] (Cempel & Nikel 2006, Fasani et al. 2018). Both of these groups of HMs at higher concentrations are toxic to the living beings, affecting cell membranes, DNA structure, enzyme properties, cell function or may be even carcinogenic (Wu et al. 2016b, Mishra et al. 2019, Shakya & Agarwal 2020). These HMs cannot be degraded by any biological, chemical or physical process and persist in the environment for long periods of time, posing a threat (Wuana & Okieimen 2011, Suman et al. 2018). The common HMs/metalloids found in contaminated areas include Cd, cobalt (Co), Hg, Pb, As, Zn, Cu, Ni, and chromium (Cr) (Dubey et al. 2018). These metals enter and bioaccumulate in the animal and human body through the food chain via the crops, finally affecting human health (Rehman et al. 2017, Rainbow 2018). Ingestion of food crops contaminated with HMs can cause a plethora of serious complications in the human body such as the reduced intelligence and learning ability, mental retardation, fatigue, anaemia,

depression, cardiovascular problems and damage to nervous system due to Pb exposure (Kazemipour et al. 2008; Singh & Kalamdhad 2011, Grover & Jhanda 2017; Santa Maria et al. 2019), Itai-itai disease due to chronic Cd exposure (Pan et al. 2010); kidney dysfunction and anaemia due to Zn (Duruibe et al. 2007); corrosion of mucosa, hepatic system failure, damage of kidney and central nervous system due to Cu (Singh & Kalamdhad 2011, Karim 2018) etc. Some other maladies include skin irritation and nervous system complications due to Ni (Argun et al. 2007); abortion, nervous breakdown and skin rashes due to Hg (Duruibe et al. 2007); cancer due to Cr and cancer and immune system dysfunction due to As (Duruibe et al. 2007). Apart from these, HMs also cause other diseases such as neurological disorders (Parkinson's disease, Alzheimer's disease, schizophrenia), nutrient deficiency, hormonal imbalance, obesity, respiratory and skin disorders, brain damage, various types of allergies and asthma, endocrine disorders, chronic viral infections, enzyme dysfunction, metabolic changes, infertility, nausea and vomiting, headache and dizziness, irritability, gene degradation, premature aging, memory loss, anorexia, joint inflammation, hair loss, osteoporosis, insomnia and even death (Mishra et al. 2019; Pirsheh et al. 2016; Wasana et al. 2017).

HMs can also have adverse effects on plants. Although not directly involved, forms of these elements absorbed by plants can affect their growth and development (Rostami & Azhdarpoor 2019). These metals can inactivate proteins and enzymes and disrupt metabolism of sugar (Kordrostami et al. 2019). Plant cells are stressed and injured by the production of oxygen-free radicals (Liang & Yang 2019) mainly in the chloroplasts and mitochondria. Oxidative stress cause oxidative damage to lipids, proteins, nucleic acids (Kordrostami & Mafakheri 2021). Important physiological processes in plants like photosynthesis, respiration and growth are affected (Mishra et al. 2006). Pb, a common HM contaminant, has been found to inhibit seed germination, root elongation, development of seedling, plant growth, transpiration, chlorophyll production (Kumar et al. 2017). Another HM, Hg, has been reported to inhibit plant growth, affect nutrient uptake (Patra & Sharma 2000) and the photosynthetic system (Patra et al. 2004).

So, the presence of HMs in the environment beyond standardized limits is not desirable. Vegetation is affected causing extinction of species, human health is seriously affected as well as soil fertility is affected, causing soil erosion. So, it is extremely important to prevent HMs from entering our environment and to remediate sites already contaminated with these pollutants.

Generally, soils contaminated with HMs can be remediated by non-biological methods such as excavation, extraction or stabilization of polluting ions or other physical and chemical methods. But as mentioned earlier, these methods are not only expensive and limited by other factors, but might also destroy the physical and chemical properties of soil (El Rasafi et al. 2017). So alternative biological remediation methods using plants have been used for

removal of HMs from contaminated areas because of cheapness and simplicity of the methods (Osman 2018) and phytoremediation using plants is one such method.

3. Phytoremediation

Phytoremediation is a solar energy driven technique where plants' natural ability to uptake chemicals and convert them into nontoxic, readily harvestable forms in their tissues is being utilized to clean up pollutants from contaminated water, air or soil (Doty 2008, Doran 2009). It is an inexpensive and eco-friendly process as plants are used to contain, sequester and detoxify pollutants from contaminated areas (Ashraf et al. 2019). Plants are autotrophs, capable of absorbing a variety of allelochemicals and xenobiotic compounds through their roots. Once inside the plant body, the harmful compounds can be volatilized, metabolized or mineralized, generating simpler compounds. In fact, 'xenome' or a biosystem has been defined which can detect, transport and detoxify xenobiotic compounds in the plant cell (Edward et al. 2005). A wide variety of plants, both monocots and dicots, can uptake, sequester and metabolize pollutants from polluted areas of land and water (Ashraf et al. 2019). Ideally, there are certain criteria to be fulfilled by a plant species to be chosen for phytoremediation – it should be high biomass producing, should be tolerant to the toxic effects of the pollutants, should be easy to cultivate and hardy in nature, should have high absorption capability and should be non-attractive to herbivores (Adesodun et al. 2010, Sakakibara et al. 2011, Shabani & Sayadi 2012). Removal of contaminants from polluted sites (phytodecontamination) and their stabilization, thus preventing their movement and harmful effects, are the key aspects of this technique (Sadowsky 1999).

Plants utilize diverse mechanisms (*viz.* phytoextraction, phytodegradation, phytostabilization, phytovolatilization, rhizodegradation, phytofiltration) to degrade, remove or immobilize the contaminants. Phytoextraction refers to the process of absorption of contaminants by plant roots and their subsequent translocation to aerial parts or in other words, plants are used to extract contaminants from the soil (Doty 2008, Jacob et al. 2018). This method is considered to be the most applicable phytoremediation strategy for the recovery of HMs and metalloids from contaminated soils (Ali et al. 2013, Sarwar et al. 2017). Plants used for phytoextraction should be highly tolerant to the toxic effects of HMs, should be able to extract and accumulate high concentrations of HMs in their aboveground parts, should be fast growing with abundant shoots and highly developed root systems (Seth 2012, Ali et al. 2013). Mention may be made of two categories of plants which are especially suited for phytoextraction of HMs from contaminated sites. Plant species with the capability to accumulate very high amounts of HMs in their aerial parts without any phytotoxicity are known as hyperaccumulators (Rascio & Navari-Izzo 2011; van der Ent et al. 2013). Under identical conditions, hyperaccumulators can accumulate metals at 100-fold higher levels than that of non-hyperaccumulating species (Rascio & Navari-Izzo 2011). At present, more than 450 plant species from about 45 angiosperm families have been classified as hyperaccumulators (Suman et al. 2018). Examples include *Thlaspi caerulescens*, the Zn

hyperaccumulator, *Sedum alfredii* hyperaccumulating Zn, Pb, Cd, *Pteris vittata* hyperaccumulating As, Cr, Cu, *P. cretica*, *P. biaurita* hyperaccumulating Pb, different species of *Alyssum* accumulating Ni to a large extent, *Medicago sativa*, *Brassica juncea*, *B. nigra*, the Pb hyperaccumulators etc. (Assunção et al. 2001, Srivastava et al. 2006, Bani et al. 2010, Kalve et al. 2011, Koptsik 2014). The second category of plants suitable for phytoextraction include the high biomass producing crops, such as *Helianthus annuus*, *Cannabis sativa*, *Nicotiana tabacum* and *Zea mays* (Herzig et al. 2014). Grasses such as *Trifolium alexandrinum*, with a short life cycle, high growth rate, high rate of biomass production, high stress tolerance are also suitable for phytoextraction of HMs such as Cu, Pb, Cd and Zn (Malik et al. 2010, Ali et al. 2012).

Organic pollutants (*viz.* chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, herbicides, pesticides etc.) are phytodegraded either by plant endogenous enzymes or enzymes which are secreted (Suresh & Ravishankar 2004, Doty 2008). Plants suitable for this process are *Blumea malcolmii*, *Phragmites australis*, *Pontedaria crassipes* etc. (Kagalkar et al. 2011, He et al. 2017, Gong et al. 2019).

In phytostabilization or phytosequestration, plants stabilize the polluted soil to check its movement to the surroundings, instead of eradicating the pollutant from such site (Sadowsky 1999). This strategy uses metal-tolerant plant species to immobilize or inactivate contaminants such as HMs or organic contaminants under the ground and decrease their bioavailability. Thus, the contaminants fail to migrate into the ecosystem (Marques et al. 2009, Kafle et al. 2022). Plants with a fast growth rate capable of producing large biomass and dense rooting system are especially suited for this strategy as roots play a crucial role in immobilizing pollutants, stabilizing the structure of the soil and preventing soil erosion (Yan et al. 2020). Plant species specifically used for phytostabilization include *Eupatorium cannabinum*, *Solanum nigrum*, species of *Salix* etc. (Gonzalez et al. 2019, Yang et al. 2019, Li et al. 2019).

In yet another mechanism, known as phytovolatilization, harmful compounds after being taken up by the roots are converted into less toxic volatile forms and released into the atmosphere by the process of transpiration through the stomata of the leaves (Mahar et al. 2016). Organic pollutants and HMs like Se, Hg and As can be removed through this process (Mahar et al. 2016). Examples of plant volatilisers include *B. juncea*, *Juncus effuses*, *Phragmites australis* etc. (Banuelos et al. 1997, Wiessner et al. 2013, San Miguel et al. 2013). However, through this technique, pollutants will continue to contaminate the ambient air as pollutants are only transferred to the atmosphere from the soil in the volatile form.

In cases where the contaminants cannot be degraded by plants only, association with rhizosphere colonizing bacteria has been proposed to augment the process of phytoremediation *explanta* (outside the plant body) (Ontañón et al. 2014). This process is called rhizodegradation. The contaminant degrading microbes get nutrients and energy from

the plant root exudates. The method is mostly applicable for removing organic contaminants. Plants known to utilize rhizodegradation include *Cynodon dactylon*, *Rubus fruticosus*, species of *Cucurbita* etc. (Alagić et al. 2016, Ely & Smets 2017, Nguemté et al. 2018).

Phytofiltration is the eradication of pollutants from aquatic environment by terrestrial and aquatic plants like, *B. juncea*, *Setaria italica*, *Pistia stratiotes*, *Salvinia auriculata*, *S. minima*, *Azolla filiculoides*, *Carex pendula*, *Platanus mexicana*, *Solanum diversifolium*, *Asclepius curassavica*, etc. (Arthur et al. 2005, review by Kristanti et al. 2021). Such plants have high tolerance towards HMs and fast growth rates. Rhizofiltration (use of roots), caulofiltration (use of shoots) or blastofiltration (use of seedlings) are some of the strategies used for the removal of contaminants from polluted surface water, ground water or waste waters (Mesjasz-Przybyłowicz et al. 2004, Kristanti et al. 2021). Contaminants like HMs are either absorbed by or adsorbed onto the root surface during rhizofiltration to clean up contaminated ground or surface water resources (Kafle et al. 2022). The pH of the rhizosphere is changed by the root exudates, causing precipitation of HMs on the plant roots, thus further inhibiting the movement of these contaminants to the ground water (Javed et al. 2019).

Yet another technique is phytodesalination, where salt-tolerant plant species are used to extract excess amounts of salts from the soil; an excessive amount of salt in the soil affects normal plant physiology, inducing salt stress in plants (Kafle et al. 2022). Halophytic plants are mostly used for this purpose.

Further details about these processes have been discussed previously (Majumder & Jha 2012). One or more of these mechanisms may be used by plants to eradicate pollutants from polluted site, depending upon the chemical nature of contaminant present, contaminated environment or the plant species used (Kafle et al. 2022). For instance, heavy metals get accumulated in plant tissues after uptake, whereas organic pollutants are mostly degraded (Mahar et al. 2016, Saleem et al. 2020). Contaminated ground water can be remediated through methods like phytodegradation, phytovolatilization, rhizofiltration, rhizodegradation and phytodegradation whereas surface and wastewater contaminations can be treated by rhizofiltration, phytodegradation or rhizodegradation. Contaminations in soil, sediments or sludges are remediated through phytoextraction, phytodegradations, phytostabilization, rhizodegradation or phytovolatilization (Kafle et al. 2022). To enhance the efficacy of phytoremediation, various aids like biochar, ethylene diamine tetraacetic acid (EDTA), endophytic bacteria or arbuscular mycorrhiza are added, which either reduce the toxicity or increase the availability of pollutants or promote the growth of plants, thereby assisting in the phytoremediation process (Kafle et al. 2022).

Being a less expensive, passive, solar driven and eco-friendly process, the method is advantageous over other conventional non biological strategies used for environmental clean-up and is gaining popularity and wide acceptance by society and regulatory agencies. Soil fertility is also improved because of the release of various organic matters to the soil (Wuana

& Okieimen 2011; Jacob et al. 2018). The rhizosphere also harbours microbes which beneficially degrade and detoxify toxic substances (Doty 2008). However, as the method is based on plants for decontamination, it is time consuming, taking several growing seasons to clean up a contaminated site. The method may also be dependent on species, season and on the plant age, with young plant roots displaying greater absorption capacity compared to older plants (Tangahu et al. 2011, Song et al. 2019). Also, contaminants present beyond the reach of plant roots cannot be eradicated using this method (Doran 2009). Another limiting factor is the inhibition of plant growth by high concentration of contaminants (Tangahu et al. 2011). Also, there are chances of contamination through the food chain as animals may feed on plants which have accumulated toxic compounds. Other advantages and limitations of phytoremediation have been discussed elaborately previously (Majumder & Jha 2012).

4. How do plants defend themselves from HMs?

Plants have the capability to accumulate and excrete HMs (Kordrostami et al. 2019). According to Edelstein & Ben-Hur (2018) there are basically three groups of plants depending on how they grow in soils contaminated by HMs - (a) plant species preventing the entry of HMs in their aerial parts; (b) species where metals are accumulated in the aerial parts and returned back to the soil; and (c) species concentrating HMs in their aerial parts at concentrations much higher than that in the soil. Due to the presence of well-organized metal transfer systems, plants can absorb metals from the soil and transfer and store them in their aerial parts, as indicated by the higher levels of metals found in the shoots as compared to the roots (Kordrostami & Mafakheri 2021).

A series of complicated processes such as mobilization of HMs, uptake by roots, xylem loading, transport from root to shoot, cellular compartmentation and sequestration etc. are involved in the accumulation of HMs in plant tissues (Yan et al. 2020). Mostly present in the insoluble form in the soil, which plants cannot absorb, HMs are made bioavailable to the plants through the release of root exudates by plants which alter the pH of the rhizosphere, thus increasing metal solubility (Dalvi & Bhalerao 2013). This metal enters the root cells, where the ions can form complexes with chelators like organic acids. These complexes are then immobilized either in the extracellular or intracellular spaces (Ali et al. 2013). The metal ions subsequently translocate to the shoots and are finally distributed in the leaves where these are sequestered either in cell walls or vacuoles (Tong et al. 2004). Different types of complexing agents and metal ion transporters are involved in the uptake and translocation of HMs in plants (Yan et al. 2020).

To implement phytoremediation successfully, detoxification of HMs is essential (Thakur et al. 2016). Plants adopt two defence strategies, i.e., avoidance and tolerance, to cope up with the toxicity of HMs accumulated in the plant body (Hall 2002). Avoidance, considered the first line of defence, is a strategy through which plants can control the uptake of HMs and can restrict the movement within the plant body (Dalvi & Bhalerao 2013). The second strategy is

tolerance, considered the second line of defence. It is carried out through various mechanisms such as inactivation, chelation and compartmentalization of heavy metal ions (Dalvi & Bhalerao 2013). Also, the anti-oxidative defence system of plants plays an important role in response to heavy metal stress (Yan et al. 2020).

5. A brief idea about plant *in vitro* culture:

Plant *in vitro* culture or plant tissue culture (PTC) is a technique of aseptic culture of cells, tissues, organs and their component parts under defined physical and chemical conditions *in vitro* (Street 1977). Theoretically, a plant body can be cut into small parts known as 'explants' and under appropriate conditions, each of these explants can develop into a whole new plant. The two main aspects of the concept, first developed by Austrian botanist Professor Gottlieb Haberlandt, are *in vitro* proliferation of a single plant cell and development of a new plant from the proliferated tissue. In fact, each cell of the plant body has the capability to give rise to a new plant (cellular totipotency).

In vitro culture of plant parts requires some basic prerequisites, of which, an aseptic or sterile environment for the cultivation process is of primary importance, as the technique of PTC aims at fast production of pathogen-free plants. Being nutrient rich, PTC media support the growth of bacteria and fungi which outgrow the cultured plant tissue, ultimately destroying the culture. Also, the toxic wastes produced by these microorganisms inhibit the growth and development of plant cells and tissues. Sterilisation of explants, glasswares, plasticwares, instruments, nutrient media, transfer areas and culture rooms are therefore important in PTC practices and is carried out using various methods suitable for the purpose. The second prerequisite is a culture medium containing the nutritional components (macro- and microsalts, vitamins, carbon source, organic nitrogen) indispensable for the growth, development and maintenance of the cultured cells, tissues or organs. Different types of PTC media are in use. Various kinds of plant growth regulators (PGRs) are often added to the culture media to obtain the desirable results. Physical factors like photoperiod, temperature, relative humidity are also tightly controlled for the proper growth, development and maintenance of the cultured tissue. The success of any PTC protocol depends on the proper coordination of all these factors and on the type of explant selected, age, physiological condition of the donor plant etc.

As defined, PTC refers to the *in vitro* culture of either whole plants or any plant part (viz. organs, seeds, embryos, anthers, single cells which may be dedifferentiated, protoplasts etc.). Accordingly, there can be various types of cultures such as seed culture, embryo and endosperm culture, meristem culture (culture of shoot apical meristems), anther and pollen culture, protoplast culture (culture of cells without cell walls), culture of differentiated organs like roots, shoots, buds etc. Another interesting form of PTC is the culture of clumps of disorganized, undifferentiated cell masses called 'callus', formed when mature plant cells revert to a meristematic state by dedifferentiation. Callus cells can be totipotent, capable of

regenerating complete plants or can differentiate organs like roots, shoots or embryos by redifferentiation. Theoretically, any kind of living plant tissue can be transformed to callus masses depending upon the origin and physiological state of the explant, the genotype of the donor plant, the environmental condition in which the donor plant is cultivated and a balance between two PGRs – auxin and cytokinin. Apart from other applications, callus cultures are important sources of a wide variety of economically important phytochemicals (review by Halder et al. 2021). Single cell populations, small groups of cells and larger aggregates of cells are often grown in a liquid medium under agitation and aeration. Such cell suspension cultures are most commonly initiated from friable callus masses and also from cells isolated from plant materials through mechanical or enzymatic methods.

Yet another very interesting form of culture is that of the ‘hairy roots’. In higher plants, the hairy root syndrome is characterized distinctly by the development of adventitious roots with profuse root hairs at or next to the site of infection by a soil borne bacterium known as *Agrobacterium rhizogenes* (Sevon & Oksman-Caldentey 2002). Following infection of wound sites in plants by *A. rhizogenes*, certain genes (the transferred DNA or T-DNA genes) are transferred from the bacterium to the plant, which get stably integrated in the plant genome and are expressed, resulting in the development of the hairy root phenotype. These roots are highly branched, plagiotropic, capable of rapid growth on phytohormone free culture medium, remain genetically and biochemically stable over extended periods (Sevon & Oksman-Caldentey 2002). Often referred to as ‘phytochemical factories’, these roots can biosynthesize higher or analogous amounts of compounds which are naturally produced by the roots of the mother plant (Lorence et al. 2004). Presently, hairy roots are being used for producing economically important plant secondary metabolites, for expressing genes for the production of foreign proteins to be used for therapeutic purpose (antibodies, vaccines, cytokines), enzymes, molecular farming, elucidation of biosynthetic pathways, phytoremediation research as well as for the biotransformation of exogenous substrates (Häkkinen 2014, Gharari et al. 2020, Perotti et al. 2020).

6. The role of plant *in vitro* cultures in phytoremediation studies

The technique of plant tissue culture has emerged as a useful tool for phytoremediation research. In contrast to field grown plants, which have a limited lifespan, plant *in vitro* cultures can be propagated indefinitely, free from seasonal and geographic barriers and are easily available on demand (Doran 2009). Thus, the time required for any experimental investigation is considerably reduced. *In vitro* culture has been used as model plant systems to study plant cell responses to toxic compounds, the metabolic processes involved in their degradation and the end products formed (Majumder and Jha 2012). As tissue cultured plants are grown under aseptic conditions in the laboratory, free of any pathogens, responses of plant cells can be easily distinguished from the responses of microorganisms residing within the plant body or in the rhizosphere (Van Aken & Schnoor 2002). Also, since callus and plant cells in suspension lack various barriers (viz. leaf wax, bark, cuticle, epidermis etc.) which

otherwise regulate the penetration of compounds in whole plants, *in vitro* culture can result in greater and uniform uptake of compounds than whole plants (Lucero et al. 1999). Plant tissue culture has emerged as an excellent approach for studying the responses of plants to contaminants without the interference of other factors. Studies can be carried out under controlled conditions which are not possible for field grown plants (Doran 2009). Large quantities of contaminants can be fed to *in vitro* cultures otherwise unavailable from the soil, allowing the recovery of amounts of metabolites suitable for analytical studies for further research (Laurent et al. 2007). Isolation of the products of reaction and purification of such products are easier in cultured cells compared to whole plants due to the presence of less amounts of starch, chlorophyll and other pigments in cultured plant cells (Schmidt 2001). Also, plant tissue culture represents a vital technology for the incorporation of foreign genes into plants for the development of transgenic plants with improved phytoremediation capabilities. Being organized structures, hairy roots are analogous in structure and property to the organs in whole plants, thus offering clear ideas about the biological behaviour of roots in nature (Doran 2009). Other advantages and disadvantages of plant *in vitro* cultures in phytoremediation research have been discussed in details in the previous review (Majumder and Jha 2012). Few examples of plant *in vitro* cultures employed successfully for the accumulation of heavy metals are tabulated below (Table 1).

7. Conclusion

HMs are environmental pollutants having serious impacts on the wellbeing of living organisms including human beings. Phytoremediation is a cost-effective, environment-friendly approach which utilizes plants to remediate environmental contaminants through diverse mechanisms such as phytoextraction, phytostabilization, rhizofiltration, phytovolatilization, phytodesalination, phytofiltration etc. The present review highlights how plant *in vitro* cultures play a crucial role in phytoremediation research, particularly for the accumulation of heavy metal contaminants. These *in vitro* cultures act as supplementary model systems, providing a better understanding of the consequences of contaminants inside the plant body; the information obtained thereof can be used for field plant trials.

Table 1: Heavy metal accumulating *in vitro* cultures of some selected plant species

Plant species	Family	Type of culture used	HM accumulated	Reference
<i>Solanum nigrum</i> L.	Solanaceae	Hairy roots	Zn Cd	Subroto et al. 2007 Ye et al. 2020
<i>Ailanthus altissima</i> (Mill.) Swingle	Simaroubaceae	<i>In vitro</i> grown shoots	Cu, Zn, Mn	Gatti 2008
<i>Alyssum murale</i> M. Bieb.	Brassicaceae	Hairy roots	Ni	Vinterhalter et al. 2008
<i>Armoracia rusticana</i> G. Gaertn.	Brassicaceae	Hairy roots	U (uranium)	Soudek et al. 2011
<i>Brassica juncea</i> (L.) Czern.	Brassicaceae	Hairy roots	Zn, Ni	Ismail & Theodor 2012
<i>Prosopis laevigata</i> (Humb. & Bonpl. Ex Willd.) M.C. Johnst.	Fabaceae	Cell suspension	Pb	Maldonado-Magaña et al. 2013
<i>Nicotiana tabacum</i> L.	Solanaceae	Hairy roots	As	Talano et al. 2014
<i>Alyssum bertolonii</i> Desv.	Brassicaceae	Hairy roots	Ni	Ibañez et al. 2016
<i>Hyptis capitata</i> Jacq.	Lamiaceae	Hairy roots	Cu	Malik et al. 2016
<i>Bacopa monnieri</i> (L.) Wettst.	Plantaginaceae	<i>In vitro</i> cultures	Cr, Cd	Jauhari et al. 2017
<i>Limncharis flava</i> (L.) Buchenau.	Alismataceae	Callus	Pb, Mn, Cd, Fe	Wardani et al. 2017
<i>Dittrichia viscosa</i> (L.) Greuter	Asteraceae	Micropropagated plantlets	As	Guarino et al. 2018
<i>Lemna minuta</i> Raf.	Araceae	Hairy roots	Cr	Paisio et al. 2018
<i>Brassica oleracea</i> L.	Brassicaceae	Callus	Pb	Sadeghi et al. 2019
<i>Lantana camara</i> L.	Verbenaceae	Callus	Cr, Pb, Cd	Tahtamouni et al. 2020
<i>Brassica napus</i> L.	Brassicaceae	Hairy roots	Cr	Perotti et al. 2020
<i>Verbascum phrygium</i> Bornm.	Scrophulariaceae	<i>In vitro</i> germinated seedlings	Zn	Akin 2021
<i>Armeria maritima</i> Girard ex Boiss.	Plumbaginaceae	<i>In vitro</i> multiplied shoots	Cd, Mn, Pb, Zn	Purmale et al. 2022

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Clay-based cleaners and disinfectants: A back to basic approach for cleanliness and sanitisation

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Abstract: *With the widespread dispersal of pathogens, toxins and all sorts of harmful chemicals throughout the globe, the demand for suitable cleaners, hand sanitisers and surface disinfectants are increasing day by day. Most of the conventional sanitisers are alkali-based, like the soap cakes, liquid soaps, and detergents; or alcohol-based liquids, gels, or sprays. The recent pandemic situation led to an unprecedented rise in the production and use (as well as overuse) of such disinfectants. But all of them have certain detrimental effects on human health and also on the environment.*

Since reducing the use of disinfectants is not possible in the present scenario, the only solution is to find out a better alternative that can effectively clean a surface without causing any harm. The natural clays, owing to their unique physical and chemical properties, can remove from a surface a wide variety of viruses, bacteria, grease and dirt. In some cases, clay minerals assist in the bactericidal actions of cations like Fe^{2+} , Cu^{+} etc. In contrast to the alcohols and alkalis, the clays don't have any significant detrimental effect on human health – instead of damaging the skin, the clay-based disinfectants may contribute to skin nourishment. Furthermore, clays are readily available everywhere, and their purification processes are also simple and less expensive. This makes them suitable for large-scale production of low-cost skin sanitisers and surface disinfectants, thus helping the developing economies to meet the challenges of the ever-increasing demands for these products.

This contribution explains the correlation between the internal structures, chemical compositions and properties of clay minerals that make them suitable as cleaners and disinfectants, and discusses the present situation and future prospects of the clay-based sanitisers.

Keywords: clays, clay minerals, hand sanitisers, disinfectants, cation exchange capacity, adsorption

1. Introduction

Clays occur in almost all the inhabitable places on Earth, and primarily form by weathering of rocks. Their easy availability and a number of unique properties facilitate their application as one of the earliest materials to be used by the human civilisation: even the most primitive cultures utilised it for different purposes. The applications of clays have always been many and varied, ranging from pottery, masonry, production of tools and equipment, medicines for topical and oral uses etc. Among all these, the application of clays as cleaners and disinfectants are of utmost importance – very few natural substances can match the clays in this field. It is one of earliest cleaning agents to be used by man, and was possibly the most widely used one until the large-scale industrial production of alkali-based soaps in 19th – 20th Centuries. The use of alcohol-based sanitisers started much later and was initially restricted

among the medical professionals. It is only during the recent global pandemics of 21st Century that the use of alcohol-based sprays and hand-rubs greatly increased, though their relatively higher prices make them less popular than the alkali-based cleaners among the masses.

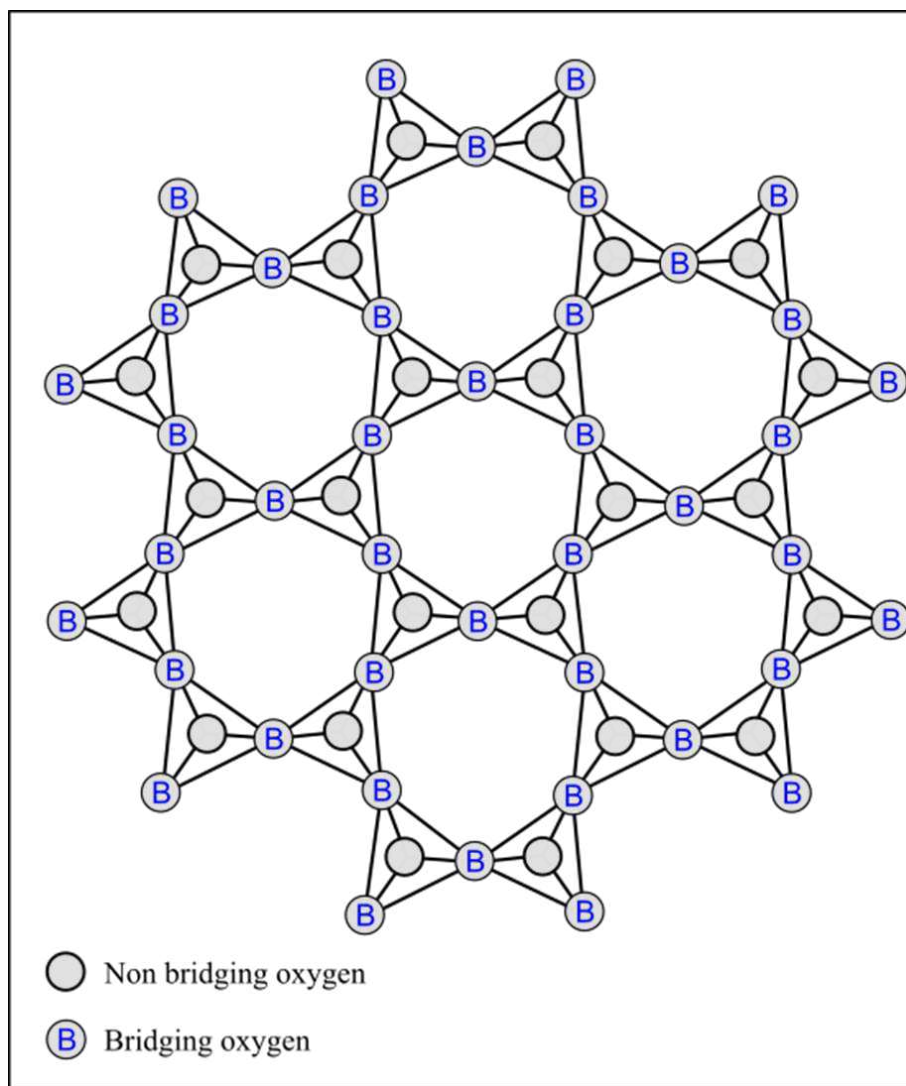
However, the conventional sanitisers, both the alkali-based and the alcohol-based ones, have certain detrimental effects on human health and also on the environment (see Chapter 6, Section 6.2 of Ghosh & Chakraborty 2022 for a comprehensive explanation). Moreover, some sections of the masses may not afford these sanitisers in sufficient quantities, especially in the developing countries. This contribution suggests a ‘back-to-basic approach’ for sanitisation that involves manufacture of more effective but less expensive disinfectants from clays. Meeting the requirements of an interdisciplinary volume, a brief description of clays, clay minerals and clay derivatives are given in Section 1, which may help the readers of different disciplines to understand the subsequent sections. Sections 3 and 4 explain the mechanisms of the protective actions of clay minerals against viruses and bacteria respectively. Production of different types of clay-based disinfectants have been described in Section 5. The advantages of the clay-based sanitisers over the other commonly used sanitisers, and their future prospects are discussed in Section 6. Finally, the article has been concluded with some recommendations for the future.

2. A brief overview of clays, clay minerals and their properties

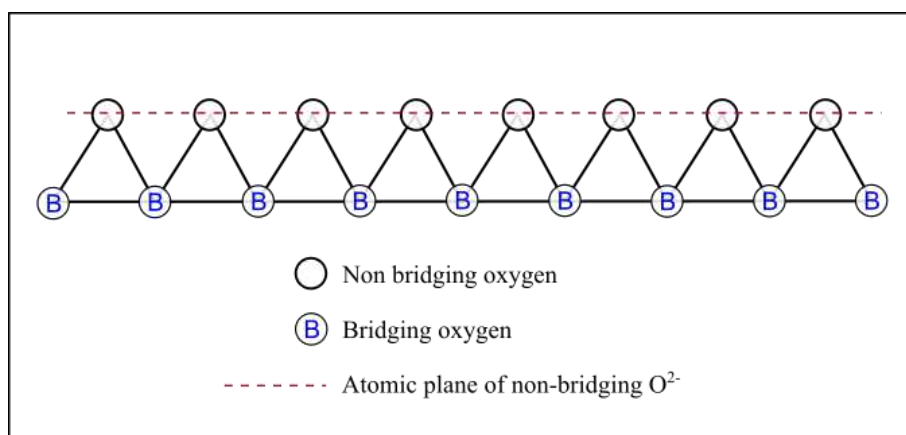
2.1. What the clays actually are

The term **clay** refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim & Martin 1995, 1996). Kaolin, china clay, bentonite, bleaching earth, ball clay, fire clay, refractory clay etc. are the common types of clay that satisfy the above definition.

The essential constituents of clays are the clay minerals, associated minerals, and some non-mineral matters or associated phases. The **clay minerals** are a number of mineral species belonging to the phyllosilicate subclass of silicate class, which impart plasticity to clays, and harden upon drying or firing (Guggenheim & Martin 1996). The clay minerals are therefore responsible for the distinctive physical properties of the clays. It is important to note that all the phyllosilicate minerals present in clay are not clay minerals. The **associated minerals** are the minerals generally present in a natural clay that are not plastic when wet and do not harden by drying or firing. They include some phyllosilicates (like talc, muscovite, chlorite etc.), other silicates (such as quartz and feldspars), and minerals of other classes (like corundum, gibbsite, boehmite, diaspore, magnetite, hematite, etc.). The **associated phases** are the amorphous constituent of clay, like allophone, imogolite, particles of peat, humus etc. A detailed discussion on clays and their constituents is given in Ghosh (2013).



[A]



[B]

Figure 1: A. Schematic diagram showing the arrangement of SiO₄ tetrahedra in clay minerals, in **apical view (plan view)** where the observer faces the non-bridging apical oxygen of each tetrahedron. It may be noted that there are three bridging oxygens in each tetrahedron, thus forming a layered

structure. All the minerals of phyllosilicate subclass have the same internal arrangement of tetrahedra. Not to scale.

B. Schematic diagram showing the arrangement of SiO_4 tetrahedra in clay minerals, in side view (elevation). All the minerals of phyllosilicate subclass have the same arrangement. It may be noted that all the non-bridging oxygens are facing the same direction. Not to scale.

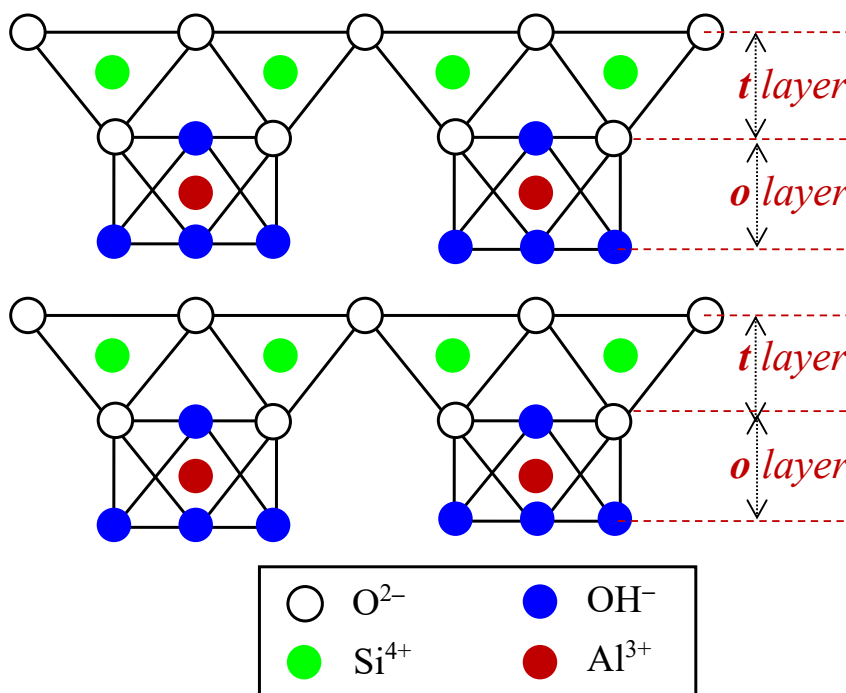
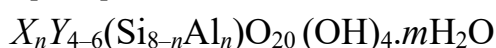


Figure 2: Schematic side view of clay minerals with $t - o$ structures, showing the internal arrangement of anions and cations in the tetrahedral and octahedral layers in side view. Minerals of kaolinite group have this structure. Not to scale.

2.2. The composition and structure of clay minerals

The clay minerals, like all other minerals, are essentially natural, inorganic solids. Each of them has a definite composition and a fixed, distinctive internal structure. They belong to the phyllosilicate subclass in the silicate class, and are categorized into six groups based on their compositions and structures: kaolinite, illite, smectite, vermiculite, palygorskite-sepiolite, and mixed layer clays. All of them consist of the anionic group $[\text{SiO}_4]^{4-}$ where one Si^{4+} is surrounded by four O^{2-} , to form a $[\text{SiO}_4]^{4-}$ tetrahedron. The general chemical composition of all the clay mineral groups can be expressed with the following structural formula. One formula unit comprises eight $[\text{SiO}_4]^{4-}$ tetrahedra.



$X = \text{K}, \text{Na}$ or Ca at 12-fold coordination sites.

$Y = \text{Al}, \text{Mg}$, or Fe at octahedral coordination sites.

n = number of Si^{4+} substituted by Al^{3+} in each formula unit of eight tetrahedral coordination sites. $n = 0$ in the clay mineral species with no substitution of Si^{4+} by Al^{3+} at the tetrahedral site.

m = number of H₂O molecules in each formula unit of eight tetrahedral coordination sites. In some clay mineral species, there is no H₂O molecule; i.e., $m = 0$.

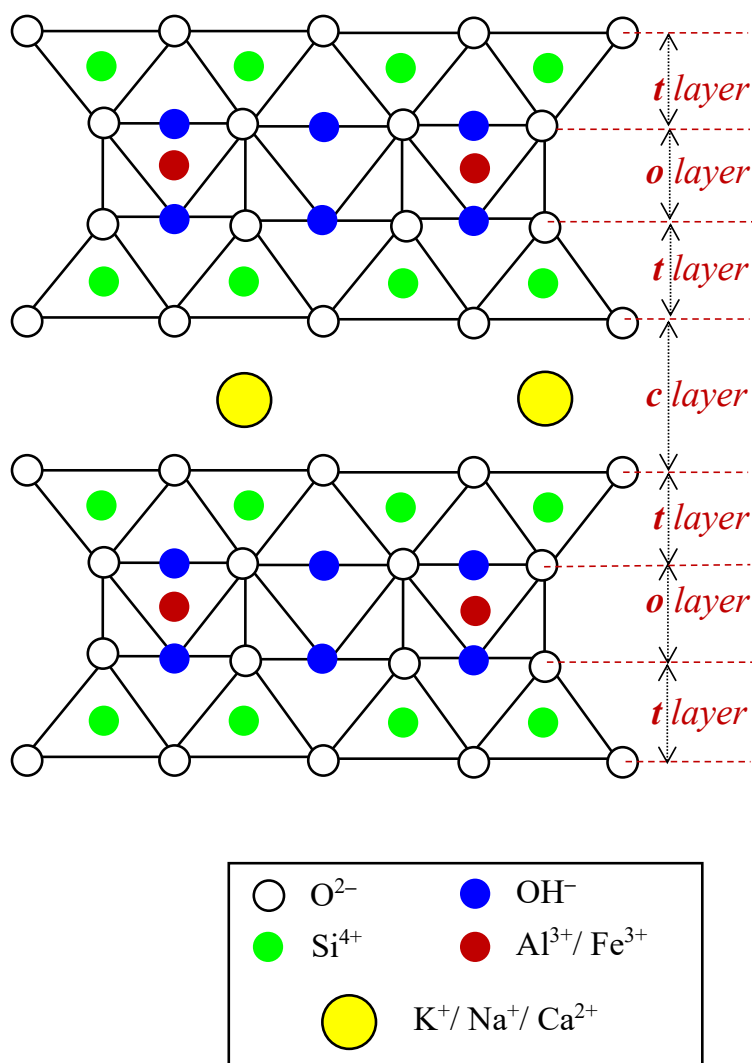


Figure 3: Schematic side view of clay minerals with **dioctahedral** $t-o-t-c$ structures in side view, showing the array of anions and cations in the tetrahedral and octahedral layers. $2/3^{\text{rd}}$ of the octahedral sites in each $t-o$ layers are filled up with trivalent cations, and the remaining $1/3^{\text{rd}}$ are vacant. Not to scale.

It may be noted that if $n = 0$, then $X = 0$, i.e., no cation at 12-fold coordination sites. Talc has this composition: $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$. The mica group minerals, on the other hand, have substitution in their tetrahedral sites and consequent inclusion of monovalent cations (e.g., muscovite and biotite) or divalent cations (e.g., margarite). Both compositional types are found among the clay minerals.

All the minerals of phyllosilicate subclass, including those belonging to the six clay mineral groups, have a **layered structure**; i.e., each tetrahedron is connected to three other tetrahedra by sharing three apical O²⁻, thus forming a continuous layer of $[\text{SiO}_4]^{4-}$ tetrahedra or t -layer (Figures 1A, 1B). Each tetrahedron in the t -layer thus comprises three **bridging O²⁻**, which

connect it to three other adjacent tetrahedra; and one **non-bridging** O^{2-} , which is not shared with another tetrahedron. All the non-bridging O^{2-} are on the same side of the t -layer of a phyllosilicate mineral, thus forming a continuous atomic plane of non-bridging O^{2-} in the t -layer (Figure 1B).

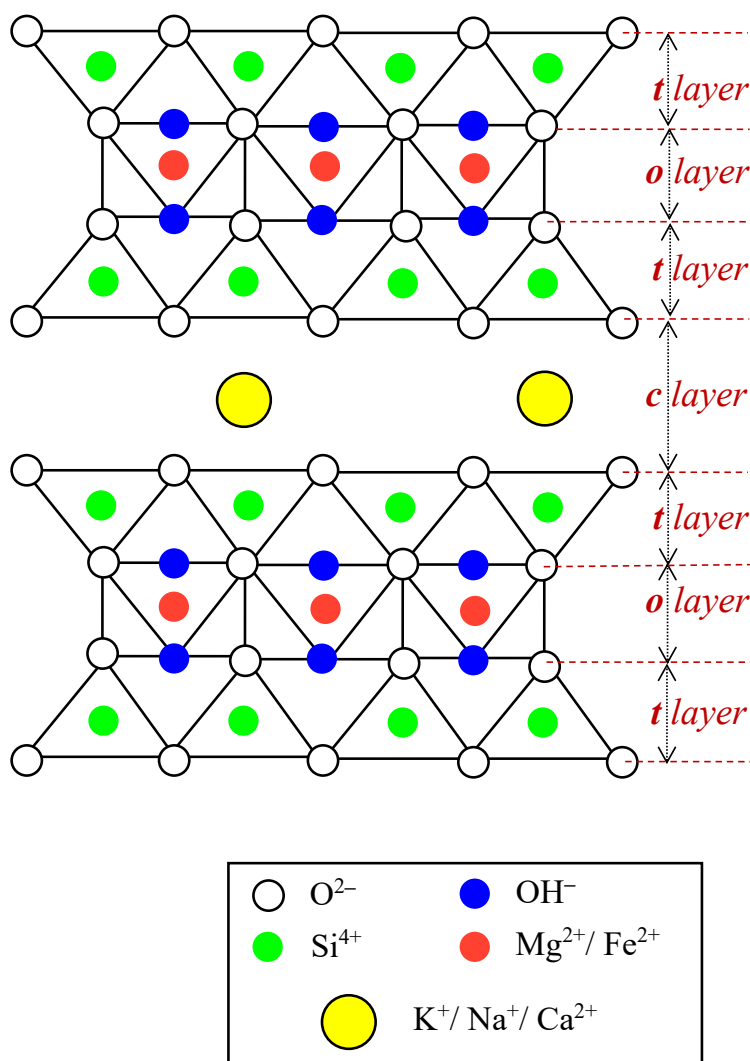


Figure 4: Schematic side view of clay minerals with **trioctahedral** $t - o - t - c$ structures, showing the array of anions and cations in the tetrahedral and octahedral layers in side view. All of the octahedral sites in each $t - o$ layer are filled up with divalent cations, and site is vacant. Not to scale.

The non-bridging O^{2-} and the hydroxyl groups in a t -layer are coordinated with bivalent or trivalent cations (commonly Mg^{2+} , Fe^{2+} , Al^{3+} etc.) in octahedral coordination sites. Those octahedra form a continuous layer of octahedra or o -layer parallel to the t -layer.

The minerals of kaolinite group have one t -layer connected to one parallel o -layer, forming a structural unit comprising $t - o$ layers (Figure 2) that are bonded together by weak van der Waals force.

In the minerals of illite, smectite, and vermiculite groups, there are two parallel *t*-layers with one *o*-layer in between them. In most of these minerals, a number of tetrahedral Si^{4+} are substituted by Al^{3+} , resulting in a charge imbalance. The excess negative charge is balanced by inclusion of monovalent or bivalent cations in between two *t* – *o* – *t* layers, thus forming a *t* – *o* – *t* – *c* structure where *c* represents the **interlayer cations**. If the octahedral cations are trivalent like Al^{3+} , then two-third of the octahedral sites in the *o*-layers are filled up and one-third are vacant. Such clay minerals are called **di-octahedral** (Figure 3). In contrast, the **tri-octahedral** minerals (Figure 4) have their octahedral sites occupied by divalent cations like Mg^{2+} or Fe^{2+} , thus all the octahedral sites are filled up.

In the clay minerals of palygorskite-sepiolite group, the cation-centred octahedra are linked together in linear array to form long chains. These octahedral chains, with much vacant spaces in between them, are connected to the *t*-layers.

2.3. Properties of clay minerals that are important in their anti-pathogenic actions

In most cases, the clay minerals disinfect a surface by removal of viruses and bacteria from that surface through adsorption (see Section 3 and 4.1). Adsorption is a process in which a gas, liquid, or solid (an adsorbate) is held on the surface of a solid adsorbent (after Skoog et al. 2014). The unique internal structures and chemical compositions of the clay minerals enable them to adsorb a wide range of metal ions, organic molecules, and microbes. The capacity of a clay mineral to adsorb a certain substance depends largely on the following factors (Ghosh & Chakraborty 2022, Chapter 1, Sections 1.5, 1.6, 1.7 and the references therein).

- (i) **Specific surface area:** The total surface area of a solid per unit mass is its specific surface area (SI unit: m^2 / kg), which depends largely on its shape. A thin, flat particle (having length \approx breadth \gg thickness) has much greater specific surface area than an equidimensional particle (having length \approx breadth \approx thickness) of the same material.

The clay minerals have a layered internal structure, with very weak bond between two successive *t* – *o* – *t* layers. As a result, they can break very easily along the interlayer spaces (i.e., in between two *t* – *o* – *t* layers), forming very thin grains known as **clay flakes** with very high specific surface area. This provides greater surface area for adsorption per unit mass, thus enhancing their adsorption capacity.

- (ii) **Cation exchange capacity (CEC):** In the clay minerals of illite, smectite and vermiculite groups, some of the tetrahedral Si^{4+} are substituted by Al^{3+} . Some octahedral cations may also be substituted by other cations of lower charge. These substitutions produce a net negative charge on their *t*–*o*–*t* layers, which is balanced by the interlayer cations like K^+ , Ca^{2+} , Na^+ , and Mg^{2+} . But these cations are easily are

replaced by the heavy metals, like Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} etc., when the clay flakes are in contact with a liquid containing these cations. This phenomenon is known as **cation exchange** between the clay minerals and the surrounding liquid, and the **cation exchange capacity** (CEC) of a clay mineral is the number of moles of positive charge it can absorb per unit mass (after Raymond & Brady 2016). Its SI unit is Milli equivalents per 100 grams (meq/100 g).

- (iii) **Surface roughness of clay particles and size of the adsorbates:** A smooth adsorbent surface provides nearly equal area for the adsorption of small and large adsorbate particles. But on an uneven adsorbent surface, the smaller particles will have greater area for adsorption. The viruses and the smaller bacteria are therefore readily adsorbed by clay flakes.

The larger bacteria may not be removed by adsorption, but some of them are destroyed by the clay-induced bactericidal processes (see Section 4.2).

3. Protective actions of clays against viruses: Virus adsorption and removal

The clay minerals cannot destroy the viruses – they can only remove the viruses from a surface through adsorption and flocculation (Carlson et al. 1968).

In the mineral world, the clay minerals have the distinctive ability of adsorbing a wide range of microorganisms, metals, and organic molecules, which largely facilitate their application as cleaners and disinfectants. The process of adsorption involves the adhesion of particles to the surface of a solid. As the size of the viruses are very small, they are readily adsorbed by clay flakes in an aqueous medium.

But many viruses do not lose their abilities of infection and causing harm to human health even when they are adsorbed on the clay surfaces. It is therefore essential to remove the adsorbed viruses from the system. The clay particles suspended in an aqueous system, in presence of electrolytes, have the tendency to form **coagulates** or **flocs**. The floc, being heavier than water, settles at the bottom of that aqueous system, and can thus be removed easily by decantation or filtration.

The protective action of clays against the viruses therefore depends largely on processes of adsorption and flocculation (coagulation), which are briefly explained in this section.

3.1 The mechanism and controlling factors of virus adsorption on clay surface

The virus adsorption on clay is favoured by the cation concentration in the system. Other factors remaining same, the virus removal from a system increases with the total concentration of cations. But different types of cations are not equally effective. In a given experimental condition (Carlson et al. 1968), the virus removal capacities of kaolinite,

montmorillonite and illite were found to be greatest in presence of Na^+ (99%), less with Al^{3+} (98%), and still less with Ca^{2+} (89% to 96%). It has been inferred that the viruses are attached to the clay surfaces by formation of a **clay-cation-virus bridge**. Just as a bridge connects two separate landmasses, the cations connect the viruses the surfaces of a clay particle.

The major controlling factors of the virus adsorption mechanism of clay minerals are described below.

- (i) **Cation Exchange Capacity:** The CEC of the clay mineral is an important controlling factor – those having higher CEC were reported to show greater capacity of virus removal from a solution. The ability of montmorillonite to adsorb greater quantity of virus than kaolinite in an experiment was attributed to the higher CEC of montmorillonite (Lipson & Stotzky 1983).
- (ii) **Nature of interlayer cations:** The natural clay minerals are generally heteroionic, i.e., they contain different types of cations in their interlayer spaces. **Homoionic** clays, having only one type of interlayer cation, are prepared to compare the virus adsorption capacities of different cations, e.g., homoionic Na^+ kaolinite. Comparing different types of homoionic kaolinites having Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Al^{3+} , the following sequence was established in order of decreasing adsorption of virus (Lipson & Stotzky 1983, Sykes & Williams 1978):
$$\text{Na}^+ > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+.$$
- (iii) **Van der Waals bond and hydrogen bond:** Some workers suggested that the attraction causing the aggregation of clay and virus was the combined effects of weaker interactions (van der Waals bonding and H- bonding) than the strong electrostatic forces (Greenland et al. 1965, Stotzky 1980, Lipson & Stotzky 1983, Block et al. 2016).
- (iv) **Other possible factors:** Electrophoretic mobility of the clay particles, and the zeta potential of the clay minerals in a solution are the other factors that may affect virus adsorption on clays (Carlson et al. 1968). Certain organic molecules like proteins, if present in the system, impeded the virus adsorption. These proteins possibly occupied some adsorption sites on the clay surfaces, thus reducing the number of adsorption sites available for the viruses.

The adsorbed viruses are strongly attached to the surface of clay, and are not easily separated. Transmission electron microscopy studies revealed that the bonds that link the viruses to the clay cause some shape distortion of the viruses – they become flattened with increased surface area at their contacts with clay (Block et al. 2016). This increased contact surface may further strengthen the bonding between them.

Though the shapes of the adsorbed viruses may change, their internal structures generally remain intact. The viruses are therefore still infectious after adsorption, and must be removed from a surface for disinfecting it. This can be done by the following two ways.

- (i) A semisolid mixture of clay and water, like a clay pack or clay poultice, may be rubbed on a surface or left on it for some time to adsorb the viruses from it. Then the mixture is

to be washed with clean water, to remove the clay along with the viruses. This process was prevalent in many parts of the world for hand sanitisation, disinfecting utensils, kitchenware etc. before the large-scale industrial production of soaps, and is still practised in some rural areas of our country.

- (ii) An aquatic system may be cleared of viruses by adding clay particles in sufficient quantity. These particles remain suspended in water for certain time, then form flocs, and settle slowly at the bottom. The viruses entrapped on the surfaces of the clay particles in that floc can be removed from the system by decantation or filtration.

The viruses are so small that they cannot be separated from a liquid medium with the finest bacteria filter. They can remain suspended in a liquid for such a long time that it is not practicable to separate them by decantation as well. But those adsorbed on the surfaces of clay particles in a floc can be separated easily by both methods. The process of flocculation has been described in the next subsection.

3.2 Removal of the viruses through flocculation

Flocculation (agglomeration or coagulation) is the process by which particles suspended in a liquid adhere to one another, to form a large cluster of particles. In many cases, the clay particles have a **net negative charge** on their surface. Cations, if present in the solution, are electrostatically attracted by the clay particles. These cations may create a positively charged layer on the clay surface, and hold together two or more clay particles like a bridge. In the presence of these cations, the clay particles thus connect together to produce the flocs (after Chibowski 2011).

The cations with higher valences have greater flocculation powers, e.g., Al^{3+} , Ca^{2+} , and Na^{+} have successively less flocculation powers. Also, increase of cation concentration in a system brings about faster flocculation.

Some laboratory investigations indicate that virus adsorption on the clay particles takes place first, and the flocculation of the particles occurs later. There is no significant amount of virus entrapment during or after the flocculation (Schaub and Sagik 1975, Lipson and Stotzky 1983).

4. The protective actions of clays against bacterial infections

The clays can remove several types of bacteria from a system by adsorption. They also assist in the bactericidal actions of some metals, which destroy some bacteria species in a series of chemical reactions. These two protective actions of clays are described briefly here.

4.1. Removal of bacteria from a surface by adsorption

Some types of bacteria, especially the relatively smaller forms, can adhere to the surfaces of clay particles by **electrostatic attraction** to form biofilms (Calvaruso et al. 2006, Freebairn et al. 2013). The edges of the ultrathin clay particles are generally positively charged, while the surfaces of some bacteria are negatively-charged. Such bacteria are linked to the positively-charged edges of the clay minerals by electrostatic attraction. In case of kaolinite, bacteria are largely attached along the positively charged edges of the octahedral sheets and tetrahedral sheets. In addition to the edges, the basal surfaces of a few clay minerals contain a feeble positive charge, which may also contribute in the adsorption of some bacteria to a lesser extent (Wu et al. 2011, Kang et al. 2013, Tuson & Weibel 2013, Cygan & Tazaki 2014, Wu et al. 2014, Huang et al. 2015).

Another possible mechanism may be the formation of a **clay-cation-bacteria bridge**, connecting the negatively charged bacteria cells to the clay surfaces by the interlayer cations like Na^+ , Ca^{2+} , etc. (Perdrial et al. 2009, Warr et al. 2009), similar to the clay-cation-virus bridge (see Section 3).

Some workers have suggested a few other factors that possibly contribute to the adsorption of bacteria on clay surfaces, such as the **hydrophobic attraction** (van Oss 2008, Poorni & Natarajan 2013), the **Lewis acid-base interaction** (Sharma & Hanumantha 2003, Bayoudh et al. 2009), and the **combined effects of van der Waals forces and electrical double layer forces** (Kim et al. 2010). The definitions and brief explanations of these factors are given in Section 2.2.2 of Ghosh & Chakraborty (2022).

The adsorption of bacteria on clay surfaces is largely controlled by the ionic concentrations and pH of the system; and the surface properties of bacteria like their protein covers, extracellular polymeric surface covers, hydrophobicity, and charge characteristics (Hong et al. 2012).

The electrostatic attraction between bacteria surfaces and clay particles decreases in mildly to strongly alkaline condition, and is highly favoured in acidic condition (Hong & Brown 2006, Castro & Tufenkji 2007, Jia et al. 2011, Cai et al. 2013, Hong et al. 2014, Zhang et al. 2015). At low level of ionic concentration ($<0.01 \text{ mole L}^{-1}$ of MgCl_2), the adsorption of certain bacteria forms on kaolinite and montmorillonite is found to increase when ionic strength increases. But bacterial attachment on clay surfaces decreased significantly when the salt concentration is higher than 0.01 mole L^{-1} (Hong et al. 2014).

Although the true mechanisms for adsorption of bacteria by clay minerals are yet to be fully understood, it is quite evident that if a surface is cleaned with a mixture of clay and water, some types of bacteria will adhere to the clay flakes and will be removed from that surface.

4.2. Bactericidal processes activated by clay minerals

Clays cannot destroy bacteria by themselves. But some types of clays, known as the **bactericidal clays**, enable the metal ions like Fe^{2+} to penetrate into certain bacteria and destroy them, through a series of chemical and biochemical reactions. It has been suggested that Cu^+ and Al^{3+} present in the bactericidal clays may also contribute in the destruction of bacteria. While copper has multiple toxic effects on bacteria cells, aluminium possibly killed them by impeding the inflow of cell nutrients and the outflow of wastes (Warnes et al. 2011, Williams et al. 2011).

Table 1. Some common bacteria species that can be destroyed by the bactericidal actions of clays, as reported by Haydel et al. (2008), Cunningham et al. (2010), Williams et al. (2011).

Bacteria Species	Diseases Caused
<i>Escherichia coli</i>	Enteric diseases
<i>Mycobacterium marinum</i>	Causes a tuberculosis-like illness in fish. Can infect humans when injured skin is exposed to a contaminated aqueous environment (Akram & Aboobakar 2022).
<i>Mycobacterium smegmatis</i>	A non-pathogenic bacteria used in scientific researches, though in some rare cases it is suspected of causing tuberculosis (Reyrat & Kahn 2001).
<i>Pseudomonas aeruginosa</i>	It is a multidrug-resistant bacteria that can cause pneumonia, septic shock, infections in urinary tract and gastro-intestinal tract etc. (UK Standards for Microbiology Investigations 2022, Diggle & Whiteley 2020).
<i>Salmonella enterica</i>	Salmonellosis, which is a food-borne disease causing diarrhea, fever, abdominal cramps, and vomiting.
<i>Serovar typhimurium</i>	It causes gastroenteritis in humans.
<i>Staphylococcus aureus</i>	Causes pulmonary infections (e.g., pneumonia and empyema), gastroenteritis, meningitis, toxic shock syndrome, urinary tract infections, skin and soft tissue infections such as carbuncles, cellulitis etc. (Tong et al. 2015). Multi-drug resistant strains developed from it (Taylor & Unakal 2022).
<i>Staphylococcus epidermidis</i>	Generally infects through healthcare-associated infections, entering the bloodstream during device insertions in patients. It accounts $\sim 1/5^{\text{th}}$ of bloodstream infections in ICU patients, and prosthetic valve endocarditis infections (Otto 2009).

The bactericidal actions of Fe^{2+} can destroy *Escherichia coli*, which is a major cause of enteric diseases in humans, along with a few other common bacteria listed in Table 1.

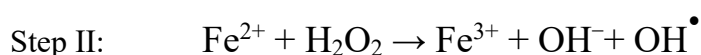
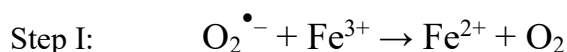
A comprehensive description of the bactericidal actions of Fe^{2+} is given in Ghosh & Chakraborty (2022), Section 2.2.1, p. 37 – 42. A brief outline is given here.

- (i) The bacteria cells contain enzymes that catalyse oxidation-reduction reactions. These redox enzymes may produce H_2O_2 and superoxide ion ($\text{O}_2^{\bullet -}$) inside the cells (Messner & Imlay 1999, 2002).

- (ii) The penetrated Fe^{2+} reacts readily with H_2O_2 , to produce Fe^{3+} , hydroxide (OH^-) and hydroxyl (OH^\bullet) radical, as described in the **Fenton reaction** (Fenton 1894).



- (iii) Inside the bacteria cells, Fe^{3+} can also synthesize OH^\bullet by reacting with the intracellular superoxide, as described in the **Haber – Weiss reaction** (Haber & Weiss 1934).



- (iv) The OH^\bullet thus produced can damage the bacterial DNA by reacting with the sugar and the base moieties, leading to sugar fragmentation, strand scission, and base adducts (Imlay and Linn 1986, Hagensee and Moses 1989, Park and Imlay 2003). This causes the destruction of the bacteria.



The exact role of clay in this process, however, is yet to be fully understood. They presumably assist in the bactericidal actions of Fe^{2+} in the following two ways.

- The iron-rich clays act as the sources of Fe^{2+} .
- Fe^{2+} is soluble in water and can penetrate into the bacteria cells only at a certain pH and oxidation state. The clay minerals, when present as suspension in water, act as a buffer to maintain the required pH and oxidation state.

These two roles of clay minerals are discussed in the next two subsections.

4.2.1 Clay as a source of Fe^{2+}

The bactericidal clays are more iron-rich than the other clays (Williams et al. 2008, 2011, Cunningham et al. 2010). Iron is present in the constituent clay minerals, associated minerals and associated phases of these clays, in fully reduced state (Fe^{2+}) or partially reduced state (mixture of Fe^{2+} and Fe^{3+}). Some of common iron-bearing constituents of bactericidal clays are listed in Table 2, which may release Fe^{2+} in a clay-water mixture and initiate the bactericidal process.

4.2.2 Clay minerals acting as buffers in the bactericidal reactions of metals

In a chemical system, a **buffer solution** resists changes in pH when it is diluted or when acids or bases are added to it (Skoog et al. 2014). A buffer also tends to resist the change of other chemical properties related to pH, like its oxidation–reduction potential (Eh), concentration of certain ions etc. When all these chemical factors are within a certain range, a system is favourable for some chemical, biochemical and geochemical reactions.

The bactericidal process of Fe^{2+} in a water-clay mixture involves the successive formation of a number of short-lived compounds in a series of chemical reactions. The pH and oxidation state of the reaction system are the two most important factors to make these reactions possible. Clay minerals present in the system act as the buffers to maintain the pH and Eh favourable for dissolution of Fe^{2+} and Cu^+ , and maintain the stability of these cations in the solution. Furthermore, the anaerobic condition created by the clay minerals is favourable for penetration of Fe^{2+} and other metals into the bacteria cells (Williams et al. 2011).

Table 2. Some common Fe^{2+} -rich constituents of clays, including clay minerals, associated minerals, and associated phases. (After Velde 1995, Chapter 2 and Bergaya et al. 2006, Chapter 1).

Mineral Species	Chemical Composition
Montmorillonite	$(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe})_4[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4.n\text{H}_2\text{O}$
Diocahedral vermiculite	$(\text{Ca}, \text{Na})_{0.6-0.9}(\text{Mg}, \text{Fe})_6[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4.m\text{H}_2\text{O}$
Illite[1]	$(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Fe}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2.\text{H}_2\text{O}$
Chamosite [2]	$(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$
Biotite	$\text{K}(\text{Mg}, \text{Fe})_3(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$
Hornblende	$\text{Ca}_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$
Hematite	Fe_2O_3
Maghemite	Fe_2O_3
Goethite	FeOOH
Lepidocrocite	FeOOH
Pyrite	FeS_2

Mineral compositions:

[1] <http://webmineral.com/data/Illite.shtml>. (See Internet Resources No. 5).

[2] <http://webmineral.com/data/Chamosite.shtml>. (See Internet Resources No. 6).

5. Application of clays and their derivatives as sanitisers and surface disinfectants

Natural clays of various types have been used as hand sanitisers and cleaners long before the discovery of the microbes. The systematic study of the internal structures of minerals (including phyllosilicates) started in the early part of 20th Century, and the relation of the structure and composition of the clay minerals with their antimicrobial actions were studied much later than that. But since the onset of human civilisation, the common people learnt from their experiences that the natural clays have the unique property of cleaning surfaces from toxins, dirt and greases. The ancient medicine men and the medieval chemists also observed that the clays can heal infections and resist some diseases. In almost all the ancient cultures, clay is one of the ingredients of traditional medicines. In the present age, however, the scientific knowledge acquired about the clay minerals and their actions on the pathogens have facilitated the formulation of more effective disinfectants from the clays and their derivatives. This section gives a brief overview of the application of clays and clay-based formulations as hand washes (used with water), dry hand sanitisers and disinfectant hand gels (used without water), and surface disinfectants that can substitute detergents.

5.1 Natural and purified clays as hand wash

There is a common belief that soaps are better disinfectants than clays or other natural substances. But several surveys carried out on adults and children showed that post-defecation scrubbing of hands with soil, ash, and soap were equally effective in reducing the levels of faecal coliforms. Hoque & Briend (1991) carried out an empirical study in the slums of Dhaka, Bangladesh with a group of twenty volunteers, aged 18 to 35 years, for five consecutive days. The volunteers were divided into five groups. The members of three groups used soap, mud and ash for post-defaecation washing, the fourth group used plain water, and the fifth group, designated as the 'control group', did not wash their hands. An orange-yellow coloured mud of pH = 6.5, collected in those slums, was used in the study. It was sterilized by heating for 3 hours at 110 °C before handwashing, for removing any pre-existing pathogens. The fingertips of each volunteer were sampled for faecal coliform bacteria after each defecation. The result of this study showed that 60% (12 out of 20) of the samples collected from control group were contaminated, while soap, mud and ash reduced bacterial contamination to 20%. It proved that mud was equally effective as soap in reducing the coliform counts. For this reason, the workers suggested not to promote any expensive or less available washing agents whose superiority to traditionally used mud have not been established.

A number of subsequent surveys showed similar results. In Bangladesh, 32.1% of urban population and 55.5% of rural population were found to use soil or mud for post-defecation handwashing, but no significant difference was reported between them and the soap-users in terms of coliform infection (Hoque et al. 1995a, 1995b, 2003, Baker et al. 2014).

Bangladesh Demographic and Health Survey (2007) also suggested that clean and dried soil should be promoted for handwashing, because it can effectively resist many infectious and parasitic diseases. Citing the result of this survey, Bloomfield and Nath (2009) stated that a large population of Bangladesh belonging to the low-income group cannot afford soaps; and if washing hands with mud (and other traditional substances) is actively discouraged, that may deprive these people from any hand hygiene.

It is important to note here that in most of the above studies, natural soil or mud was used for washing hands. A standard sample of soil contains only 45% clays (clay minerals + other minerals + non-mineral substances), and the remaining 55% are organic matters, water and gases (see Ghosh 2013 and references therein for details). Clays in purified form are expected to be much more effective as hand sanitisers. Some commercial houses have claimed to produce bath soaps with kaolinite clay that can purify the skin and nourish it as well (Internet Resources No. 1).

Bentonite is a natural clay composed predominantly by montmorillonite. Das & Tadikonda (2020) suggested a technique for hand sanitisation using bentonite paste (a thick mixture of bentonite and water) to prevent the transmission of viruses and bacteria through dermal

contacts. When applied topically on hand or any other part of the body, the ultrathin montmorillonite flakes of this paste are expected to bind strongly to the pathogens, and remove them from the skin surface when the paste is washed with water.

5.2 Clay-based dry sanitisers and hand gels to prevent infection without causing skin desiccation

All types of hand washes are needed to be rinsed and wiped off after rubbing them on skin, therefore always require a sufficient supply of water, which restrict their use in certain situations. That also makes the process of hand sanitisation more time consuming, hence inconvenient for medical professionals who need frequent hand washes. The ‘dry’ sanitisers are preferred in such cases, which are applied on the hand and can be rubbed lightly until dry, without needing to be washed off the hand with water. Most of such dry sanitisers are alcohol-based, though some commercial houses claim manufacturing some clay-based formulations. One such product prepared by mixing natural green clay and eucalyptus oil has been claimed to eliminate 99.9% of common germs on rubbing gently on hand. It becomes dry and can be dusted off the hand without rinsing and washing (Internet Resources No. 2). Some mixtures prepared by infusion of essential oil and clay have been claimed to clear the skin and also hair (Internet Resources No. 3).

Disclaimer: The efficacy of the commercial products cited in this section, or their side effects (if any), have not been tested or verified in the present work.

Frequent use of hand washes and hand sanitisers makes the skin dry, which may lead to skin irritation and some types of skin diseases. The gel-based sanitisers keep the skin moisturised and protect it from drying. A clay-based sanitiser gel was suggested by Hoang et al. (2021), composed of zinc amino-clay and the extract of a desert plant *Opuntia humifusa*. The ZnAC present in this formulation can effectively sanitise the skin, while *O. humifusa* extract is found to prevent skin desiccation caused by frequent washing. Moon et al. (2020) described the other beneficial effects of *O. humifusa* extract on human skin.

Hoang et al. (2021) claimed that the sanitiser prepared by them is much more preferable than the conventional ones due to their highly effective disinfectant power, very little or no toxic effect, and prevention of skin dryness and irritation even after frequent uses.

5.3 Clay-based surface disinfectants and detergents

Da Silva-Valenzuela et al. (2014) studied the applicability of different types of clays for the production of detergents, and inferred that purified bentonite was the most appropriate material for this purpose. Purification was recommended for the removal of associated minerals and associated phases from the detergent, which may contain Fe^{2+} and other transition elements and may put undesirable stains on the objects. Furthermore, the impurities like quartz grains may scratch and tear the clothes during washing. According to these

workers, the swelling capacity, pH, high CEC, and rheological properties (i.e., viscosity, elasticity, stress-strain relation, response to force etc.) of montmorillonite present in the purified bentonite make it suitable for the production of liquid detergents.

Application of bentonite-water mixture has also been suggested for washing and sterilising the medical gears and other surfaces infected with viruses (Das & Tadikonda 2020). Bentonite slurry may be sprayed on those surfaces, and then washed with water. This sanitisation process is expected to prevent the infection of the SARS-CoV-2 and other highly infectious pathogens through different sources of surface-to-hand transmissions.

It may be added that the clay minerals of smectite and vermiculite group are very much effective antimicrobial agents, but their use in the clay-based detergents are restricted owing to the presence of Fe^{2+} and other transition elements as octahedral cations. The transition elements have a strong property of imparting colours, which may stain or decolourise the clothes. Better suited for this purpose are kaolinite, illite, and other white clay minerals, which do not contain the transition elements as essential constituents. Some commercial laundry soaps prepared with kaolinite have been claimed to be effective for cleaning clothes without any change of colour (Internet Resources No. 1). A list of clay-based detergent liquids and powders are given in the Internet Resources No. 4.

Disclaimer: The commercial products cited in this section have not been tested in the present work to verify or confirm their efficacy as disinfectants or their side effects, if any.

6. Discussions: Future prospects of clay-based sanitisers and surface disinfectants

6.1. Harmful effects and drawbacks of the conventional sanitisers

The following four categories of common sanitisers that are widely used now-a-days are referred to here as conventional sanitisers.

- (i) Alkali-based bath soaps and liquid hand washes
- (ii) Alcohol-based hand rubs
- (iii) Alcohol-based surface sprays
- (iv) Alkali-based detergent powders and liquids

All the above have some detrimental effects on human health and environment, which are briefly explained below.

The alkali-based soaps and liquid hand washes have a high pH, ranging from 9.01 to 10 (Tarun et al. 2014), and their frequent use may increase the skin pH, damage of the protective acid mantle of the skin, dehydrate the skin, and cause irritability. Damage of the acid mantle can worsen the conditions of patients already suffering in skin diseases like acne, eczema, dermatitis, and rosacea (Pahr 2018). In addition, increase of skin pH causes long term skin

infections like acne vulgaris, owing to the rapid growth of the bacteria *Propionibacterium* (Baranda et al. 2002, Korting et al. 1987, Prakash et al. 2017).

The alcohol content in the alcohol-based hand rubs is 70% by weight, while that in the surface sprays vary from 30% – 60% (Alhmidi et al. 2017, Jiang et al. 2021). During their application, some amount of alcohol evaporates quickly and mixes in the surrounding air, which is inhaled by the users and all the people in the immediate vicinity (Bessonneau & Thomas 2012). The surface sprays possibly release more alcohol vapour in the air than the hand rubs, but the latter is bound to cause some alcohol intake through dermal absorption (Institut National de Recherche et de Sécurité 2007). Recent investigations revealed that frequent use of ethanol-based disinfectant sprays may significantly change the indoor air quality through release of volatile organic compounds and nano-sized particles, thus causing serious human health risk (Jiang et al. 2021). All these unintentional alcohol intakes, if continues for a long time, may lead to a number of serious health issues, including irritation of eye, nose, and throat; damage of the mucus membrane; nerve disorders, nausea, dizziness, and in extreme cases, abnormal decrease of body temperature and blood pressure (Tonini et al. 2009, Bessonneau et al. 2010, MacLean et al. 2017).

Although the detergents increase the skin pH to a lesser extent than the alkali-based soaps, their frequent uses may cause dermatitis and increase of the skin permeability, leading to adsorption of toxic materials through the skin (Gfatter et al. 1997, Nielsen et al. 2000). The surfactants and bleaching agents used in the detergent can cause skin and eye irritations and if ingested, may damage the endocrine system. Some chemicals present in common types of detergents, like nonylphenol ethoxylates, are reported to be carcinogens.

Phosphate-containing detergents, transported to water bodies from the washing areas, may cause eutrophication that leads to continual oxygen depletion, thus affecting the natural ecological balance in those water bodies (Effendi et al. 2017, Cohen and Keiser 2017). Surfactants like Sodium Lauryl Sulphate present in the detergents, when mixed with the water in ponds and lakes, are detrimental to the fishes as well as the people consuming them (Borah 2022). Other harmful effects of the detergents include reducing the growth of the bacterial population in sea water (Effendi et al. 2017), and damaging the gills and the protective mucus covering of the fishes (Lenntech 2022).

A few other disadvantages of the conventional sanitisers are given below.

- (i) **High expense and less availability:** Good quality alkali-based soaps and liquid hand washes, which cause less harm to the skin, are generally expensive. The alcohol-based hand rubs are even costlier, which make them inaccessible to a large section of the society. If the people of low-income group are prohibited from using the traditional cleaning agents, and compelled to use the conventional ones, many of them will be deprived from any sort of hand hygiene (see Section 5.1 for details).

Furthermore, large scale production of high-quality conventional disinfectants require long, complex industrial procedures, and it is difficult to increase their production abruptly within a short time due to economic and technological constraints. Therefore, during the last pandemic situation, these products were not available in sufficient quantities even to those who could afford them.

- (ii) **Problems of large-scale production:** Large factories of soaps and detergents may pollute soil and water, thus causing serious threat to the surrounding environment. The water bodies near the waste-disposal sites of many such plants have exceptionally high pH of water.

The raw materials necessary for the large-scale production of the alkali-based and alcohol-based cleaners may not be available everywhere. Some countries may therefore require to import the raw materials to set up the industries, or purchase the finished products, which will reduce the accessibility of these essential commodities to the inhabitants of those countries, especially in the latter case.

- (iii) **Other factors:** Using bar soaps and liquid handwashes need a supply of sufficient quantity of water and access to basin etc., which make them difficult to use in many situations, e.g. for the travellers on the move.

The alcohol-based sanitisers, in contrast, do not require water. But although they can effectively disinfect the hands, they cannot clean them from dirt and grease. This restricts their uses as handwashes under many situations, e.g., after fixing a car, having a traditional Indian meal, or working in a garden with mud, dirt and manures.

The next section explains how the limitations of the conventional sanitisers can be overcome with clays and clay-based formulations.

6.2. Advantages of clay-based sanitisers

A major concern for the pharmacists is the ability of the pathogen to evolve into drug-resistant strains. Most anti-microbial drugs use some chemical processes to destroy the pathogens, which may be useless against the newly evolved forms. The anti-microbial actions of clays, in contrast, largely depend on adsorption which is a physical phenomenon, with the exception of assisting in the bactericidal actions of metals (explained in Section 4.2). The clays are therefore effective against newly introduced mutant varieties as well.

From the economic point of view, the clays are readily available almost everywhere, and are less expensive than the raw materials of the commonly used sanitisers. For hand washing purposes, the natural clays do not need any complex purification processes; as established from the studies carried out in Bangladesh (described in Section 5.1). The abundance and

ubiquity of clays facilitate large scale production of clay handwashes anytime and anywhere, and no hefty investment is needed for establishing such production plants.

The therapeutic and economic advantages described above undoubtedly brighten the prospect of clays as the sanitising agent of future. It has, however, a few other edges over its competitors, as stated below.

- (i) Owing to their unique internal structures, the clay minerals can bind easily to a wide variety of organic and inorganic substances in their interlayer spaces, which enable the preparation of better-quality hand sanitisers and disinfectants (e.g., those described in Sections 5.2 and 5.3).
- (ii) Instead of causing any harm to the skin, the clay minerals can actually nourish the skin. The pH of clay-water mixture is similar to that of the skin (Pan-on et al. 2018). Thus, the clay facial masks do not disturb the normal skin pH. Topically applied clay masks have drying effects on the skin. This adsorbs the excessive sebum, oil, bacteria, and metabolic toxins from the skin pores that cause lesioned skin, acne and other skin issues. (Ducrotte et al. 2005, Herrera et al. 2000, Meier et al. 2012). The clay packs can also increase the blood flow and supply of oxygen in the skin, thus making the skin healthy (Poensin et al. 2003). Other health benefits of clay masks include skin cell contraction to reduce wrinkles, exfoliation of dead skin cells, and retaining skin moisture (Carretero et al. 2006, Pan-on et al. 2018).
- (iii) Being one of the basic components of the environment, clay is not generally harmful to the environment. When mixed with the soil, they enrich the soil. They can also purify the water in natural water bodies by adsorption of microbes, heavy metals, and harmful organic molecules. The clay purification plants or the factories of clay-based sanitisers are therefore not a serious threat to the environment, excepting a few situations described in the next section.

6.3. On the flip side

When the clays are used for handwashing in the traditional ways, a small amount of it is taken from nature, purified, and the desired cleaning agents were prepared. The quantity of the raw materials and products involved in this process is so small that it does not cause any significant health hazards or environmental pollution, even in local scale.

But the large clay-based industries necessitate extraction of huge amounts of clays from the mines. Clay flakes, being exceedingly fine, are easily airborne, thus increasing both PM_{2.5} and PM₁₀ in significant quantities in the air. The clay particles are mainly released in the air during the excavation and blasting operations, and through wind erosion of the exposed clay beds after mining operations. The clay particles in the overburden dumps may also contribute to the air pollution. The large clay mines are therefore potential sources of air pollution in varying degrees.

The large factories of all the clay-based products may dump a large amount of clay in their waste disposal sites. If not properly managed, these sites can also release particulate matters in the air.

Prolonged exposures to the particulate matters may create respiratory troubles like shortness of breath, cough, pneumoconiosis etc. in humans and animals. In a few cases, the asbestos associated with some clay minerals were reported to cause lung cancer. Particularly prone to these diseases are the workers of clay-based industries and the inhabitants in the immediate vicinity of the factories (Wagner et al. 1987, Gibbs 1990, Wagner 1990, Gibbs et al. 1992, Gibbs & Pooley 1994, Wagner et al. 1998).

It may be added here that unlike many other air pollutants, the airborne clay flakes are not toxic or poisonous; and can create health issues only in very high concentrations and by prolonged exposure (Wagner et al. 1998), which may be avoided by adopting the proper remedial measures.

7. Conclusion

This contribution, within its limited scope, has attempted to provide an overview of the anti-microbial actions of clay minerals, their present uses as disinfectants – both per se and combined with other substances, their advantages over the other disinfectants, and the few drawbacks of their large-scale utilisation. With this discussion in the backdrop, the following recommendations may be put forward.

- (i) Clay minerals, owing to their unique internal structures and consequent properties, should be used in the production of hand sanitisers, surface disinfectants, and detergents.
- (ii) There should be further investigations to understand the interrelation between the internal structures, compositions, properties, and the antimicrobial actions of the clay minerals, for their better utilisation in this field.
- (iii) Further researches are recommended to formulate clay-based disinfectants by combining clay minerals with different types of antibacterial and antiviral substances, which will be more effective than pure clays.

For preparation of better-quality hand-gels, clay minerals may be infused with natural moisturisers like plant extracts. Finding the correct materials, their correct proportions, and the appropriate procedures for preparation also require extensive studies, like the one performed by Hoang et al. (2021) described in Section 5.3.

- (i) The residues of all the cleaners and disinfectants, after their applications, finally go to the nature in some form or other. Some antimicrobial metals, such as copper, zinc etc., may bring about soil and water contamination. It may be anticipated that if these metals are used in clay-based disinfectants, their residues may cause some environmental issues. Some plant-based ingredients, like the extracts of *Aloe vera*, rosemary, grape seed, olive

leaves, green tea and sage have antibacterial actions, and have been reported to destroy various gram positive and gram negative bacteria (Klančnik et al. 2010, Fani & Kohanteb 2012). These plant extracts may be combined with the clay minerals to produce more effective clay-based disinfectants, which are expected to be environment-friendly as well.

- (ii) Some antibacterial plant matters also have moisturising and anti-inflammatory properties, like *Aloe vera* leaves. The hand rubs prepared by combining their extracts with the clay minerals are expected to protect the skin from infections and also nourish it. Further investigations are required in this field.
- (iii) Site selection for a new industrial plant is based on a number of factors, and the easy availability of raw materials is one of the most important among them; for example, an iron and steel plant cannot be established in a desert area rich in iron ores, if there is no proximal source of water and coal. The easy availability and ubiquity of clays facilitate the establishment of factories of clay-based handwashes anywhere required. The simple, inexpensive procedures for purification of natural clays enables setting up small, low investment purification plants. Smaller establishments will use less quantity of raw materials, and will release less amount of particulate matters in the air.

De-centralised industrial production of clay-based sanitisers is therefore highly recommended, in small manufacturing units spread all over a country, instead of large factories concentrated at certain places.

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The Art of ‘Organic’ Living: Lessons from Apatani Women in Ziro Valley of Arunachal Pradesh in Northeast India

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Abstract: *The Apatani of Ziro valley, Arunachal Pradesh, stand out as an indigenous community of settled agriculturists in the ecocultural landscapes of the Eastern Himalaya. Their biocultural heritage is an ingenious hill farming system of fish cultivation in paddy fields, integrated animal husbandry and with social forestry. This progressive hill farming system produces two staples in one agricultural plot to accomplish balanced diet at the source itself. This is economically viable and ecologically sound. This advanced ‘organic’ farming system sustainably uses, manages and conserves local resources to balance agriculture and the biodiversity underlying the functioning of the food production system. Their ‘green’ and ‘clean’ agricultural practices promote harmonious coexistence of people and their environment. Like other tribes of Northeast India, the Apatani people are poised at the crossroads of tradition and modernity. Both men and women are involved in the traditional rice-fish farming. However, like other patriarchal milieus, these women are excluded from the decision-making process. The world’s tribal and rural women often engage in multiple livelihood strategies, and along with their domestic chores silently perform monotonous agricultural work which necessitates insight into local plant resources, and the Apatani women are no exception to this. This is an endeavour to relook at the Apatani agricultural heritage as a model green farming system that promotes organic living, and focuses on the ‘silent’ role played by these women with their knowledge-based innovations in an attempt to understand their contributions in advancing solutions to the critical global issue of ensuring food and nutritional security while protecting the environment.*

Keywords:

Agricultural heritage, Apatani, ecological sustainability, traditional knowledge, women

1. Introduction

The term ‘sustainability’ implies a compromise between the human aspiration for a better quality of life on the one hand, and the limits of nature on the other hand (Kuhlman & Farrington 2010). During the course of its long history from the Neolithic revolution to the scientific and industrial revolution and beyond, agriculture emerged among nomadic hunting-gatherings and evolved throughout with the innovation of shifting cultivation and sedentary farming, to culminate into intensive agriculture. The human concern for preserving natural resources for posterity is a perennial one. In the hunting-gathering stage, the worry was about annihilation of game. In the agrarian phase the anxiety was of losing soil fertility. In the industrial age the apprehension is of environmental holocaust. Early cultures, nearly 12,000 years ago, domesticated plants and animals to ensure a reliable food production system that

buttressed the growth of the early cities and civilization. The Colombian exchange, about 500 years ago, triggered the globalization of plants and animals. The industrialization of agricultural production in the last 300 years allowed the skyrocketing of human population. However, intensification of food production and poverty elevation are linked (Mozumdar 2012). The turbulent first half of the last century triggered a technological response in the form of the so-called ‘green’ revolution in its second half. Food grain yields doubled in only 40 years for the first time in history (Khush 2001). However, this also drastically altered traditional farming practices at a global scale within a span of only a few decades (Shiva 1991). Soon, the ambivalence so typical of technology manifested itself with undesirable ecological, and even social consequences (Pingali 2012). The bumper harvests from high-input monocultures that relied on high-cost, energy-inefficient and more-polluting external resources such as modern crop varieties, intensive irrigation, farm mechanization and agrochemicals were deleterious to the health of humans and the environment (Evenson & Gollen 2003). Today, the global food production system faces the dual challenge of meeting the food and nutritional security for an ever-growing world population on one hand, and maintaining the productive health of the ever-shrinking global agroecosystems on the other hand. In this century, the effort was to reverse this trend and grow food through biodiverse farming with minimum use of irrigation, farm machinery, mineral fertilizers, and synthetic chemicals. These sustainable agricultural practices adopted alternatives as low-input polycultures with low-cost, energy-efficient and less-polluting local resources to provide greater resilience in the face of economic, environmental and social challenges (Jackson et al. 2007). The need for replacing high-risk ‘dirty’ technologies with low-risk ‘clean’ technologies has led to the adoption and diffusion of ‘green’ agricultural practices as the emerging trend in global agriculture (Rogers 1983). The ‘green’ technology is an umbrella term for environment-friendly practical solutions from production to usage of a product, that promotes economic development as well as ensures the long-term health of people and the environment. ‘Organic’ farming has been defined in multiple ways, and in essence refers to a self-reliant agricultural production system that relies more on management of the wider ecosystem itself, rather than outside support. Traditional societies, unlike modern ones, relate to nature in terms of custodianship (Verschuuren et al. 2010). Their resource management practices have been well-documented worldwide among diverse cultures and environments (Berkes 1999; Berkes et al. 2000). Traditional agricultural systems have co-evolved with local natural and cultural systems, exhibiting social and ecological rationale manifested in their traditional knowledge-based sustainable resources utilization practices. These, as an intermediate between hunting-gathering traditions providing local subsistence, and modern farming technologies supporting global mass-production, have achieved the critical balance between exploitation and conservation of natural resources (Jeeva et al. 2006). Reviving them would be the true ‘green’ revolution that would restore this harmony of agroecosystems with ecological principles that underlie all food production systems. This art of ‘organic’ living among the world’s traditional communities are model food production systems that, in the context of inter-generational equity, espouses care for the environment not only because of its intrinsic value, but also in to preserve the assets for future generations. Gender roles in

traditional and modern agriculture is a recurrent theme of study as these shed light on the role of women in agrarian and even industrial societies. Women, the most important workforce engaged in exhausting tasks, form the backbone of global agriculture. Dictated by social norms to manage daily domestic chores as daughters, wives and mothers, they also pursue multiple livelihood strategies as farmers, gardeners, herbalists, plant gatherers, plant breeders, seed custodians to manage local plant resources as food and medicine to ensure the wellbeing of their family. However, in rural settings, their hard work and key role as producer of food, earner in household economy, and custodian of intangible cultural heritage, remain largely unacknowledged by society at large. Furthermore, despite their key services, customary laws limit their participation in decision-making processes at home, and in the field, plantations and marketplaces, thus increasing the level of inequality vis-à-vis their partners. However, empowered women farmers are in the best position to lead their communities in the conservation, even revival, of the traditional sustainable 'green' practices of their 'organic' farming heritage.

2. Apatani People of Ziro Valley

Northeast India with its incredible blend of diverse ethnicities, is home to small and diverse ethnic groups with distinctive historical, geographical, cultural and social attributes (Ali & Das 2003). The Apatani people are native to the secluded Ziro valley (22°34'N, 88°24'E) in Lower Subansiri district of Arunachal Pradesh in North-east India. This miniscule (1,058 km²) hilly terrain (1,524 – 2,738 m) is hidden in the sub-tropical ranges of Eastern Himalaya – a part of the Himalaya Biodiversity Hotspot. Although they belong to the Tani tribal group of central Arunachal Pradesh, the Apatani language, beliefs and customs are distinct from all the others. They belong to the Mongoloid stock (Goswami & Das 1990) and speak a Tibeto-Burmese dialect of the Tani language group (Post & Kanno 2013). They (traditionally) adhere to the shamanistic Tani religion called Donyi-Polo (Blackburn 2010). Their 60,000 population is largely concentrated in seven traditional villages (*lemba*), and their satellite hamlets, as well as increasingly in the towns of Hapoli and Old Ziro located at the two ends of the Ziro valley (Kani 2012). They are endogamous, and socially organized into 78 exogamous clans (*Halu*) and sub-clans (*Tulu*) among them (Blackburn 2010). The tribal council (*buliang*) comprising of clan elders dispenses their traditional self-governance (Elwin 1988). The Apatani people are the custodians of a rich intangible cultural heritage which profoundly reflects their close relationship with their physical environment (Chaudhuri & Chaudhuri 2016). Like the myriad other tribes of India's Northeast, this indigenous micro-culture is now poised at the crossroads of tradition and modernity.

3. Agricultural Heritage of the Apatani People

The traditional agriculture of the indigenous communities in Northeast India ranges from shifting to sedentary agriculture (Majumder et al. 2011). This region, with climatic and ethnic diversity, harbours genetic resource in Asian rice (*Oryza sativa*) as local staple. Unlike the

slash-and-burn (*jhum*) cultivation of their neighbours (Karthik et al. 2009), the Apatani people are settled agriculturists whose cultural landscape confirms to the paradigm of harmony between nature and humans. Their agroecosystems are extensive terraced rice fields (33 km²) surrounded by forested mountains (288 km²), drained by Kale and its tributaries (Rai 2005). Based on their traditional agroecology moulded by their environment, the Apatani people have adopted a plethora of 'green' practices to sustain their rich but fragile agroecosystems along with its biodiversity, to support their traditional way of life. This 'organic' lifestyle is in tune with the now popular idea: reduce, reuse and recycle. The centrepiece of their agricultural heritage is the sedentary farming perfected over centuries in the form of paddy-cum-fish cultivation, linked with animal husbandry and social forestry, to form a 'circular' economy. This exemplifies a highly diverse, well-integrated and noticeably advanced indigenous farming system. Among the disparate methods of fish farming practiced in ubiquitous rice agroecosystems of Northeast India, the Apatani people are the best exponents of mountain valley rice-fish farming (Das 2002). Their *jebi-aji* agriculture, an integrated farming system, concurrently farms rice and fish in the same plot. On the terraced slopes (Figure 1a), native cultivars of japonica rice (*O. sativa* var. *japonica*) or *pyapin* (Dollo et al. 2009) are grown with the exotic common carp (*Cyprinus carpio*) or *aji-ngiyi*, in the plots (*aji*), and finger millet (*Eleusine coracana*) or *sarse* on earthen bunds (*agher*) separating them. Other exotic and native fish-species are also stocked (Nimachow et al. 2010). Farming the primary crop (rice) along with a secondary crop (fish), and even a tertiary crop (millet), is not only an economically viable (Rahman et al. 2012), but also an ecologically sound (Noorhosseini-Niyaki & Bagherzadeh-Lakani 2013) practice. Along with these cereals, a host of other native food crops and wild edibles adds up to an amazing agrobiodiversity (Sundriyal & Dollo 2013). These terraced paddy fields are also the natural habitats of indigenous hill-stream fishes (Nimachow et al. 2010). Their animal husbandry consisting of rearing livestock, including *mithun* (*Bos frontalis*), a semi-domesticated regional bovine of cultural significance (Rai 2005). Their social forestry is centred on bamboo plantations and pine groves (Rechlin & Varuni 2006).

4. Apatani Women as 'Organic' Farmers

The Apatani women traditionally have distinctive nose plugs and face tattoos, a tradition of 'uglification' to save themselves from abduction in the past (Bharadwaj & Boruah 2020). In Apatani society, monogamy is a rule (Kani 2012). The social order is patriarchal, patrilocal and patrilineal, and inheritance rule is primogeniture (Hazarika 2011). The tribal council elders are all men (Elwin 1988). Therefore, women in general, are marginalized and silenced across their social, legal and administrative spheres. Ursula (1953) first reported the role of Apatani women in agriculture and crafts. Haimendorf (1962) documented their hard work in doing monotonous farm jobs alongside daily domestic chores. These women follow a traditional agricultural calendar for maintaining optimum agricultural productivity (Dutta 2015). Each farming activity is linked with festivals in their natural and social settings. The male tribal council administers the integration of land units and utilization of limited

resources of the Ziro valley (Rai 2005). Traditionally, women work alongside men in the fields, gardens and plantations (Kani 1993). However, with distinct gender roles, women till, sow, transplant and harvest the crops, as well as maintain and repair bunds, trails, fences and drains, (Figures 1b-d). All daily and seasonal agricultural activities involve communal labour of traditional farmer groups called *patangajing* (Dollo et al. 2009). Although administered by the male tribal council, women are key members of all these groups. They lead the farm work in the rice terraces, except those operating in the forested periphery. Overlooked in most studies on this agricultural heritage is the pivotal role of the Apatani women. These women farmers, intimately interacting with their environment as part of their daily work, not only hold traditional ecological knowledge (Yamang & Singh 2021), but also transmit them across generations. The oral tradition of the Apatani people is the *miji-migung* (Blackburn 2010). The *miji* represents complex ritually chanted verses of male shaman priests (*Nyibu*) during agrarian festivals to communicate with the ‘spirit’ world of ancestors for wise council in determining the agricultural almanac. Possibly, their shamanic state of trance involves access and retrieval of cultural memory from the subconscious mind for the practical purposes of social coordination in pre-scientific cultures (Joralemon 2001). However, these further exclude women from decision making in agricultural activities. In contrast, the *migung* consists of myths, legends and tales about the origin of crops, livestock and human social order, spoken in ordinary conversational prose as part of daily activities, usually narrated by grandmothers, mothers and older siblings to the youngsters to assume the didactic function of cultural transmission of traditional knowledge, including those related to agriculture, in this pre-modern society with no traditional writing system in the past (Bouchery 2016). In their myths, Ayo Diilyang Diibu the first wife of Abotani, the forebear of humankind, is the ideal women and an epitome of hard work bringing bountiful harvests. It is a belief that women who follow her footsteps would never face starvation (Dinsu 2018). One story about Abotani’s devious second wife Tiinii Rungya reveals her indolence. Pretending to work hard in the rice paddy she demands bamboo tools for weeding, but keeps them idle. Soon, the rice field turn into a grassy wasteland. There was no grain left even for planting the next crop. Therefore, in their unique agricultural heritage, men may decide when to work, but it is the women as informal educators who infuse how to work. These women as ‘organic’ farmers play a vital role in agricultural operations as a bulk of the workforce, often as leaders, and this is well-integrated with their practical knowhow of local plant and other resources. All round the year, on a rotational basis, women farmers as workers or leaders are singlehandedly involved in ingenious approaches to the management of agronomic resources such as land, water, nutrient and forests, as well as innovative solutions to agronomic problems such as weed and pest infestations, using their ‘clean’ and ‘green’ solutions. The following sections highlight the ‘green’ technology of these women as ‘organic’ farmers, with the details of their traditional knowledge-based management practices in these agroecosystems to sustain their indigenous food production system along with the substructure of the local biodiversity.



Figure 1: Rhizipisciculture of Apatanis women in Ziro valley, Arunachal Pradesh. **(a)** View of the agroecosystems in May. **(b)** Rice transplantation in May. **(c)** Rice harvesting in October. **(d)** Rice threshing in October.

4.1. Land Management Practices

The Ziro valley is a mosaic of settlements (*ude*) among human-modified and natural habitats. The key to the successful agriculture by Apatani women is their diversified land-usage pattern (Dollo et al. 2009) that links rice terraces (*aji-ager*) with houses (*ude*), gardens (*ballu* and *yollu*), pastures (*polang*), pig pens (*alyigiiri*), granaries (*nesu*), burial grounds (*nendunenchang*), plantations (*bije* and *sansung*), forests (*moorey* and *myodi*) and sacred groves (*ranthii* and *sarosani*). Integrated rice-fish farming allows optimal use of limited land resources (Frei & Becker 2005). Paddy fields, as agriculturally-managed lentic wetlands, can be used for fish culture under wet conditions, although these are not primarily designed for fish farming (Halwart & Gupta 2004). The agroecosystem of Apatani women perfectly blends wet rice farming with aquaculture with four physical modifications that favour pisciculture: raised bund height to retains more water, fish pits provide refuge in dry conditions, drainage system controls water level, and fish screens prevent their escape. The terraces are levelled and small (250 to 3,000 m²) plots are separated by high (0.2 to 0.5 m) earthen bunds fortified with bamboo, cane or timber chips from their plantations. The ideal levelling of plots and presence of bunds reduce soil erosion. The finger millet on the bunds

fortifies them, functions as soil binder, and prevents soil erosion. Weeds such as *Houttuynia cordata* or *siya-haman*, are not weeded out on the bunds and performs the same function. The contiguous natural woodlands and human-made plantations also check soil erosion (Rechlin & Varuni 2006). The bunds are repaired at the beginning of the farming season (late January), marked by the Murung festival as a fertility rite. The *aji-lenda* farmers group often led by a woman entitled *lenda-kagenee*, constructs and repairs bunds. In plots near forests, crops are protected from wildlife damage with fencing (*narung*) made with bamboo, cane and timber from their plantations. This is done after the farming season (late November). Women of the *sulu-sikhii* farmer group build and mend fencings. In February, rice and millet seedlings are raised in nurseries (*miding*) in the most fertile plots. *Huta*, a wooded trowel is used. The *tanser-patang* farmer group led by a woman *patang-ahtoh* prepares seed beds and sows seeds stored by women as expert seed collectors from their previous harvest. In March, paddy fields are levelled and prepared, denoted by the Myoko festival celebrating kinship. Each paddy field has a small (25 – 35 cm deep) trench as fish pit (*siikho*). The *konchi-patang* farmer group led by a woman *patang-ahtoh* prepares the fields. *Sampeyee*, a wooden shovel is used. In April, rice transplantations begin and fingerlings raised in spawn ponds (*ngyi super*) are first released into the pits. The *halying-patang* farmer group led by a woman *patang-ahtoh* transplants rice in the plots (Figure 1b). Holes are made for planting rice in the plots with *kdu*, a wooden stick with metal tip, and millet on the bunds with *dum*, another wooden stick with sharp tip. During monsoons, the fish moves into waterlogged fields and feeds on the naturally available food and nutrients of this wetland ecosystem. No additional feeding is done. The water is drained out during fish harvest after two-three months. *Takhung*, a funnel-like bamboo trap ensnares the fishing at water outlets. The remaining fish retreats into the pits where they are caught with *tajer*, a conical bamboo net. Sometimes fish is also captured in paddy field itself with *barju*, a basket-like bamboo net, or *ngiyi-pakhe*, a tray-like bamboo trap. The harvested fish is transported live to the market in *ajii-piiwa*, a finely-woven, conical basket made of bamboo or cane. The Apatani women successfully manage their diverse farmlands with early and late ripening rice landraces (Dollo et al. 2009). Early-maturing low-yielding ones e.g., *Ahreh Emmo* are grown in remote plots facing greater risk of wildlife intrusion, inferior fertility and poor irrigation. These are harvested in July. Late-maturing better-yielding ones e.g., *Hatii Emmo* are planted in nearby plots with favourable conditions. These are harvested in October. Terraces with early-maturing rice produce only one fish harvest, while late-maturing ones allow up to three. The rice fields are classified and managed based on water retention capacity of the soil. The *jebi* has clayey soil and high water-retention capacity compared to *ditor* with sandy soil. In the soft field, less fish is stocked than the hard ones to reduce risk of damage to the paddy. Crops such as millets and maize are also cultivated in drier uphill plots (*yaapyo*). In July, the principal agricultural festival of *Dree* is celebrated with rituals for plentiful harvest. The *enthee-patang* farmer group often led by a woman *patang-ahtoh* harvests the crop (Figure 1c), followed by *in situ* threshing (Figure 1d) and transfer to granaries. *Taggi*, a small metal sickle, is used to harvest rice, millet and maize. *Yapyo*, a large tray, is used for winnowing the grains. This rhizipisciculture is a model food production system for developing societies with the

simultaneous production of low-cost plant carbohydrate and animal protein in an agricultural plot to accomplish a balanced staple at the source itself. Therefore, with these ingenious ‘green’ practices, the Apatani women efficiently manage their limited land-resources of their agroecosystems.

4.2. Water Management Practices

In the Ziro valley, like indigenous farming systems of other tribal communities of northeast India, wet rice cultivation is essentially rain-fed. Integrating rice and fish culture allows optimal use of the water resources as well (Frei & Becker 2005). The rhizipisciculture of the Apatani women involves careful management of the seasonally-available rainwater. Paddy fields are classified as *jebi*, *aane* and *ditor* depending on the increasing need for irrigation (Rai 2005). Kiiley and its tributaries provide limited water supply for irrigation. The rice terraces receive enough water through a complex system of rainwater harvesting and its efficient management. Each rain-fed stream (*kley*) in the adjoining forests is channelized into a series of irrigation canals running along the edges of the valley. Each terrace level receives enough water supply through a network of carefully designed primary channels (*siikho*), secondary channels (*pakho*) and tertiary channels (*hehte*). In each rice field, continuous inflow of water from an earthen feeder channel (*siigang*) takes place through wooden or bamboo pipes (*hubur*). The continuous outflow of excess water from higher to lower terraces involves a ditch (*muhgo*) with a similar pipe. All water inlets and outlets are blocked with bamboo screens to prevent fish escape. Blocking or reopening a connecting pipe with mud and grass allows draining and flooding of plots at a desirable depth. During transplantation, 1-2 cm water level is maintained. This is later gradually raised to about 15 cm. This ensures inundation of rice fields, especially for late ripening rice varieties. Paddy fields are drained during weeding cycles and harvesting. Bamboo fences and plantations along the embankments of canals and streams hold the soil together. Pegs and pebbles are placed in the earthen channels of canals as energy dissipaters. Soil binding reeds such as *Phragmites karka* or *pepu* is grown on these beds. These traditional measures control soil erosion. During the long fallow season centred on December, the *jebi* plots are kept dry but the *ditor* plots are kept inundated. The canals and trenches are also repaired along with the bunds before the farming season (late January). The women in the *bogo* farmers group are engaged in constructing and repairing the irrigation works. In August, the peak season for rice cultivation, the women perform the *Yapung* ritual for adequate rainfall. Therefore, these innovative ‘green’ practices of the Apatani women ensure efficient management of the limited water resources available in their agroecosystems.

4.3. Nutrient Management Practices

The agroecosystems of the Ziro valley, like any other wet rice farming system in the world, suffer from nutrient washout. However, the Apatani women farmers maintain soil fertility by ‘organic’ means only, and that essentially includes recycling of natural nutrient and waste.

Integrated rice-fish farming improves soil fertility through nutrient recycling (Frei & Becker 2005). The fish plays a key role. They feed on soil detritus, planktons, periphytons, benthos and other aquatic biota of paddy-fields. These habitats in Arunachal Pradesh are conducive for plankton growth (Saikia & Das 2008). Fish excreta added to the soil is an organic fertilizer. The feeding activities of the common carp, a benthic feeder, loosens the soil to increasing dissolved oxygen that accelerates microbial activity at the water-soil interface and improves mineral availability for the crop (Giap et al. 2005). In comparison to rice monocultures, integrated rice-fish farming exhibits higher mineral content of the soil and faster plant biomass accumulation (Duanfu et al. 1995). The paddy fields also receive natural nutrient washout from the surrounding hills. Houses and granaries built on higher elevations supply decayed and decomposed waste drained out to the fields below. *Azolla*, an aquatic fern capable of nitrogen fixation, grow in water-logged paddy fields as biofertilizer. The Himalayan alder (*Alnus nepalensis*) or *rwme*, a non-leguminous tree capable of nitrogen fixation, is planted as agroforestry to enrich the soil (Rai 2005). Panicle harvesting is practiced. Threshing is done in the field. Local rice cultivars are tall with high straw yield. These agricultural wastes are left to decay in the fallow fields. During land preparation, decomposed straw (*liisii*) is added to enrich the soil. Undecomposed materials are incinerated on dry terraces and the ash (*muyuo*) fertilizes the soil. The Apatani women also integrate rice-fish farming with animal husbandry (Rai 2005) and social forestry (Rechlin & Varuni 2006). All local organic wastes are recycled to replenish the humus in the farm soil. The women dump household waste as well as rice chaff (*piinang*), firewood ash (*mubu*), pig excreta (*alyi-ekha*), poultry droppings (*paropai*), cow dung (*sii-ekha*), weeds (*tamih*) and leaf litter (*ankho*) into the rice fields near the villages during fallow season for replenishing the soil fertility. After harvest, cattle graze on the terraces and their dung gets naturally recycled. This fallow season itself also help to regain the depleted soil nutrients. Plant biomass is recycled into compost by traditional method of dumping and covering with a thin layer of soil for decomposition. Measures taken to control soil erosion help conserve soil fertility. The choice of the rice cultivars depends on nutrient status of the soil. In March, the *Myokung* ritual is performed for soil fertility. Thus, these novel 'green' approaches of the Apatani women, include recycling household and farm wastes, help them successfully manage, by organic means, the soil fertility of the agroecosystems.

4.4. Weed Management Practices

The agroecosystems of the Ziro valley, like any other paddy farming system, face the problem of weed infestation. Weed management below the threshold level in agroecosystems is important for sustaining productivity (Singh et al. 1996). Nutrient-rich paddy fields are easily infested with algae and herbaceous weeds that compete with the crop for light, water and nutrients. Commonly weeds in the upland paddy fields of northeast India are *Echinochloa crus-galli* subsp. *crus-galli* and *Cyperus iria* (Chanu et al. 2010). The Apatani women employ only 'organic' means for weed management. The *konchi-patang* farmer group led by a woman *patang-ahtoh* is engaged in weeding (*ahru-hodo*) the paddy fields.

Kele, a long-handled bamboo hoe with sharp metal tip is used for weeding during tillering (May-June) and flowering (September). The short metal-tip *pale* is used in gardens. Surplus free-floating aquatic weeds such as *Azolla* are fished out. Manual weeding loosening the soil to causes water turbidity detrimental to fish growth. These women farmers avoid this problem by draining their paddy fields during weeding and the fish retreats into the refuge pits. Paddy fields biodiversity helps in the biological control of weeds (Hajek 2004). Finger millet growing on the bunds suppresses weeds. Fish farming is now an important element of integrated weed and pest management in rice monocultures (Berg 2002). Water-depth in paddy fields stocked with fish inhibits the growth of paddy field weeds in general (Manna et al. 1969). Microphytophagous (algivorous) and macrophytophagous (herbivorous) fish control algae and weeds in the paddy fields (Piepho & Alkamper 1991). The common carp is an opportunistic omnivore in the paddy fields. While foraging on benthic organisms, it incidentally feeds on epiphytic algae (Saikia & Das 2008) and roots, buds, leaves and stems of weeds (Piepho & Alkamper 1991). As bottom feeders they also indirectly reduce weeds by uprooting plants, making the water turbid for photosynthesis (Moody 1992) and devouring seeds (Chapman & Fernando 1994). Hence, these inimitable ‘green’ practices of the Apatani women allow efficacious management, by organic means, of weed infestation in their agroecosystems.

4.5. Pest Management Practices

The agroecosystems of the Ziro valley, like the other rice farming systems in the world, also face the problems of pests and pathogens. The Apatani women farmers again cope with this by ‘organic’ means only. The fish again plays a key role. The common carp feeds on numerous potential rice pests like zooplanktons, zoobenthos and small aquatic fauna such as molluscs and insects (Saikia & Das 2008). The efficacy of fish as a biocontrol agent of pests depends on their position in this habitat. In flooded paddy fields, if the fish pit as not more than 10% of the area, the common carp frequents the rice plants rather than their refuge (Halwart et al. 1996). This carp is the best-known biocontrol agent of the golden apple snail (*Pomacea canaliculata*), a polyphagous herbivore that attacks rice plants across Asia (Teo 2006). The diet of this benthophagic fish in paddy fields significantly comprises of molluscs (Ardiwinata 1957). It predares on juvenile snails which are small enough to fit into the opening between their pharyngeal teeth, crushes the shell, ejects shell fragments, and consumes the flesh (Halwart et al. 2014). This carp is also useful against insect pests of rice such as plant hoppers, stem borers and leaf folders (Yuan 1992). The fish predares on the neonate larvae which, after hatching, often suspend themselves from the rice leaves. Indirectly, the fish also feeds upon aquatic weeds in paddy fields which act as hosts for rice pests. Halwart (1994) concludes that the presence of fish in flooded paddy fields reinforces the natural, well-balanced pest-predator interactions in the natural ecosystem. Rice ear-head bug (*Leptocoris oratorius*) is a common rice pest in northeast India (Chanu et al. 2010). This is ingeniously managed by the Apatani women by fixing short wooden or bamboo sticks in the paddy fields with impaled frogs, crabs or salted fish captured from the rice paddy

itself, to distract the adult bugs away from the crop (Singh & Bag 2002). Furthermore, the common carp is known to reduce anopheline (*Anopheles* spp.) and culicine (*Culex* spp.) larval populations (Halwart & Gupta 2004). Fish, in general, can also indirectly reduce incidence of fungal diseases by aerating the soil and accelerating the decomposition of organic remains. The common carp strips diseased leaves near the base of the rice plants that are sources of fungal inocula. This also improves air and light availability making the microclimate unfavourable for fungal growth (Guang-Ang 1995). In April, the *Tamu* ritual, and in July, rituals of the *Dree* festival, are done to protect crops from pests. Therefore, again with the help of these pioneering ‘green’ practices, the Apatani women commendably manage, by organic means, pest influx in their agroecosystems.

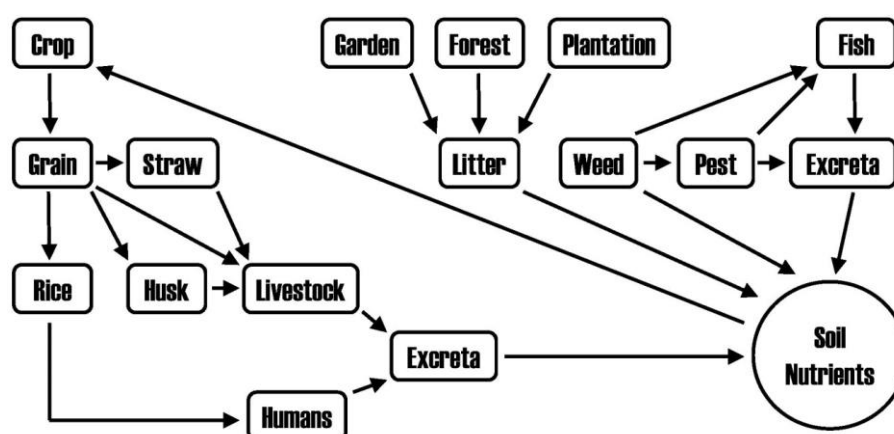


Figure 2: Resource recycling system in the organic farming model of the Apatani women in Ziro valley, Arunachal Pradesh.

5. Conclusion

The intangible cultural heritage of the less technologically-advanced communities, are shaped by their natural environment. Their reverence for nature, entrenched in their way of life, permeates into every facet of their language, culture and wisdom. In traditional agriculture, the environmental stewardship of autochthonous societies is reflected in their beliefs and practices, knowledge and skills, aiming at the conservation of bioresources and biodiversity in natural and modified ecosystems as the foundation of their food production systems. These subaltern cultures emphasize upon harmony, rather than subjugation, in defining their relation with nature. Today, biodiversity of agroecosystems is receiving global attention due to the role in its functioning. This agrobiodiversity is becoming increasingly endangered by changing farming practices with the shift to monocultures, modern cultivars, intensive irrigation, farm mechanization, toxic agrochemicals, and destruction of natural refuges. There is growing global awareness about adopting the ‘green’ practices of ‘organic’ farming that puts greater reliance on ecological goods and services for sustainable food production, and less damage to the environment, biodiversity and human health. The Apatani women farmers of northeast India, with traditional knowledge-based management practices based on biodiversity, as well as lore and beliefs that underlie them, are a good example of a traditional

agricultural society practicing environment-friendly strategies to ensure food, health and livelihood security for the community. This enviable ‘art’ of organic living of these marginalized and silenced women engaged in rice-fish farming is a model system for promoting the idea of ‘green’ biodiversity-based agricultural practices elsewhere. These women shun ‘dirty’ external modern inputs to espouse ‘clean’ local traditional inputs from their limited natural resources through the sustainable use, management and conservation of their agricultural resources, and effective management of problems in agriculture. Agricultural inputs are minimal, with no profligacy. These are inexpensive, safe and easily-available. No monoculture is practiced. Polyculture is the rule. No modern cultivars are used. Local landraces are nurtured. No farm machinery is used. All agricultural operations are manually performed with indigenous tools and implements. Even draught animals are not employed. Human labour is a major input. No agrochemicals such as inorganic fertilizers, synthetic algicides, fungicides, herbicides, insecticides or molluscicides are used. Compost, biofertilizers and green manure are used to manage soil fertility in their fallow agriculture. Biological control is employed to manage incidence of weeds and pests. Nothing goes to waste. Everything gets recycled (Figure 2). These women with multiple livelihoods as farmers, homemakers, gardeners, planters, foresters, fully explore all the three key features of ‘green’ technology, viz. reduce, reuse and recycle, in their ‘organic’ farming. From the Apatani women, the ‘daughters of the soil’ in a neglected corner of the biodiversity-rich Eastern Himalaya, the key lessons draw from their economically viable, ecologically bearable, socially equitable food production system are about insightful and engaging ways and means of living in harmony with nature and sparingly, but diligently, using her assets to promote economic development without compromising on environmental protection and public health.

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Organic Waste Recycling

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Abstract: *Organic wastes contain materials which originated from living organisms. There are many types of organic wastes and they can be found in municipal solid waste, industrial solid waste, agricultural waste, and wastewaters. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments. Present paper on Organic waste recycling in which discussed on Organic wastes, Organic waste recycling, Methods of organic waste recycling, Process (General Steps / Mechanism) of organic waste recycling, Significance of organic waste recycling and Barriers and Challenges of organic waste recycling.*

Key Words: Waste recycling

1. Introduction

Organic wastes contain materials originated from living organisms. There are many types of organic wastes, and they can be found in municipal solid waste, industrial solid waste, agricultural wastes, and wastewaters. Organic wastes are often disposed of with other wastes in landfills or incinerators, but since they are biodegradable, some organic wastes are suitable for composting and land application. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. Because of recent shortages in landfill capacity, the number of municipal composting sites for yard wastes is increasing across the country, as is the number of citizens who compost yard wastes in their backyards. Some of the organic materials in municipal solid waste are separated before disposal for purposes other than composting. The organic fraction of industrial waste covers a wide spectrum including most of the components of municipal organic waste, as well as countless other materials. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments.

2. Organic wastes

Solid organic waste is primarily understood as organic-biodegradable waste, and it contains about 80-85% moisture content. The most common sources of organic wastes include agriculture, household activities, and industrial products. Green waste like food wastes, food-soiled paper, non-hazardous wood waste, landscape waste, and pruning wastes are some of

the examples of biodegradable or organic wastes. Recently, however, the concept of organic waste management and recycling has been introduced and implemented.

Organic wastes have been an important source of pollution in the environment. Some of the common types of organic wastes usually found in nature include the following:

2.1 Cattle wastes. Cattle manure and fodder constitute organic wastes in the form of cattle wastes. Besides, poultry wastes and piggery wastes also add the number of organic wastes of animal origin. Cattle waste is also an important soil fertilizer that provides a high concentration of micro and macronutrients for crop growth and soil fertility. Cattle wastes are animal wastes that are of animal origin and act as good resources of organic matter.

2.2 Food wastes. Fruit and vegetable canning industries, frozen vegetable industries, and fruit drying industries, along with residential areas and hotels or restaurants, are the major producers of food waste. Some of the examples of food waste include peelings, cores, leaves, fruits, twigs, outer skins, and sludge. Food wastes account for about 30% of total organic waste in nature via natural and artificial means.

2.3 Municipal solid wastes. Municipal solid wastes include the more common wastes that are generated in our daily life in the form of product packaging, grass clippings, furniture, clothing, bottles, food scraps, appliances, paint, newspapers, and batteries. These wastes are generated from residential areas, schools, hospitals, and businesses.

3. Organic waste recycling

Organic waste recycling is the process of organic waste management where organic wastes are recycled or converted into useful matter by different recycling methods.

Biological treatments are among the most convenient and effective alternatives for treating organic waste. The excess moisture content increases the volume of waste while lowering their incinerator temperatures, causing an overall load of waste disposal. The need for organic waste recycling has increased over the years as waste management has become an emerging issue in most metropolitan cities. The primary objective of organic waste recycling is to maintain a sustainable cycle where the biodegradable fraction of organic waste is converted into useful organic manure or fertilizer through various recycling techniques.

4. Methods of organic waste recycling

There are different methods of organic waste recycling, each of which can be used for a particular group of waste to produce some form of useful organic matter. Some of the common methods are described below:

4.1 Anaerobic digestion. Due to the negative impacts of land filling and incineration, anaerobic digestion has been proposed due to the cost-effective technology for renewable energy production and treatment of high moisture and energy-rich material. The biogas

produced by anaerobic digestion includes gases like methane, carbon dioxide, and a trace amount of hydrogen and hydrogen sulphide.

4.2 Animal feed. Feeding organic waste to animals is a simple and easy method of waste recycling. However, the direct feeding of organic waste to animals might result in some health issues in such animals. One of the most common and efficient ways of recycling organic waste is by giving agricultural and food waste to cattle and other animals as food. This also helps the farmers as they do not have to buy extra animal feed and eventually, helps the economy.

4.3 Composting. Compost bins are most suitable for use in houses to compost simple kitchen waste and garden cuttings. Composting is an aerobic process that takes place under correct conditions of moisture and biological heat production. Even though all organic matter can be composted, some materials like woodchips and paper take much longer to compost than food and agricultural wastes. Large scale composting is conducted in large reactors with an automated supply of oxygen and moisture to generate large tons of compost for industrial applications. There are different composting systems ranging from simple, low-cost bin composting to highly technical high-cost reactor systems.

4.4 Immobilized enzyme reaction. Enzymes like esterase's can be used to esterify oils to form biodiesel. Immobilization of enzymes also supports the reuse of biocatalysts for multiple processes which then reduces the cost of chemical and enzymatic processes. The use of enzymes over chemical catalysts in the treatment of wastewater and other similar waste products reduces the formation of by-products and significant energy inputs. The use of immobilized enzymes during organic waste recycling allows the degradation activity even under non-ideal environments as not exactly right for a particular purpose, situation, or person no ideal circumstances. All of these processes allow for a more economical and efficient way of waste management.

4.5 Rapid thermophilic digestion. A rapid thermophilic digester works six to ten times faster than a normal biodigester. Enzymes like esterase's can be used to esterifies oils to form biodiesel. Immobilization of enzymes also supports the reuse of biocatalysts for multiple processes which then reduces the cost of chemical and enzymatic processes. Rapid thermophilic digestion is the process of rapid fermentation of organic wastes by activating fermenting microorganisms at high temperatures. The process of thermophilic digestion is an exothermic process that maintains a thermophilic condition at 55-65°C. The use of enzymes over chemical catalysts in the treatment of wastewater and other similar waste products reduces the formation of by-products and significant energy inputs. The use of immobilized enzymes during organic waste recycling allows the degradation activity even under non-ideal environments. All of these processes allow for a more economical and efficient way of waste management.

4.6 Rendering. Rendering is the process of conversion of waste animal tissues into stable and usable forms like feed protein. Rendering, however, has some disadvantages like it cannot

completely degrade waste products like blood. Some cases of non-animal products can also be rendered down to form pulps.

5. Process (General Steps/Mechanism) of organic waste recycling

The overall process of organic waste recycling begins with the collection of waste materials which are then passed through various steps to obtain a usable form of organic matter. The general steps/ mechanism of organic waste recycling can be explained as below:

5.1 Collection. The first step in the organic waste management of recycling is the collection of waste materials which can either be on a small scale in a kitchen or on a large scale in industries. A sufficient amount of waste matter needs to be collected in appropriate bags so that they can be moved to the site of recycling. In the case of composting, the organic waste is collected in a pit, whereas that in a digester is collected in the digester.

5.2 Decontamination. An important step in organic waste recycling is the decontamination of waste in order to avoid its harmful effects. This step is particularly important while dealing with organic waste from industries. Besides, any non-biodegradable substance like glass, plastic, and bricks, if present, should be removed during this step.

5.3 Preparation. Before the organic waste is added to a recycling system, it should be prepared. Some methods might even require a period of stabilization prior to recycling, in which case, the time should be designated. The method of preparation employed depends on the type of recycling method chosen. For, e.g., composting requires shredding and stacking of organic waste, whereas an immobilized enzyme system requires immobilized enzymes.

5.4 Recycling process. Depending on the nature of the organic waste and desired end products, an appropriate method of recycling should be adopted. Human wastes like sewage and faecal wastes should be recycled via anaerobic digestion whereas sewages can be treated with thermophilic digesters.

5.5 Screening and grading. The obtained residues or compost are then screened into different sizes to be used for different purposes. Depending on the application of the end products, grading and screening are essential.

6. Significance of organic waste recycling

Organic waste recycling has multiple advantages that help prevent the problems that arise with the accumulation of waste products in nature. Some of the common advantages or significances of organic waste recycling are:

Some compost prepared with appropriate substrate work as bio control agents to prevent and control plant diseases. The separation of organic and inorganic wastes also improves the efficiency of non-organic recycling. The generation of bio fertilizers by recycling process improves the quality of soil, which then increases soil fertility and plant growth. Landfills

tend to increase the emission of greenhouse gases, and the recycling of such wastes into less harmful wastes decreases such emissions. Recycling of organic wastes also reduces the concentration of waste remaining for less efficient processes like landfill and incineration. Organic matter recycling increases the organic content of the soil, which improves soil fertility and provides essential nutrients to plant, increasing crop yield.

7. Barriers and Challenges of organic waste recycling

Even though organic waste recycling is a novice and important method of waste recycling, there are some challenges that limit the use of recycling methods. Some of the most prominent barriers or challenges of organic waste recycling are: Microbial degradation of organic waste might result in the formation of airborne microorganisms or bioaerosols, which may pose potential risks like respiratory disorders on the plant workers and adjacent residents. Recycling process like composting generates odours which might cause air pollution or discomfort. Air pollution is a mixture of solid particles and gases in the air. Car emissions, chemicals from factories, dust, pollen and mold spores may be suspended as particles. Water pollution is the contamination of water sources by substances which make the water unusable for drinking, cooking, cleaning, swimming, and other activities. Pollutants include chemicals, trash, bacteria, and parasites. Some selected groups of persistent organic pollutants like chlorinated dioxins, polycyclic aromatic hydrocarbons, and organochlorine pesticides are accumulated in solids during the treatment process.

8. Conclusion

Present paper on Organic waste recycling in which discussed on Organic wastes, Organic waste recycling, Methods of organic waste recycling, Process of organic waste recycling, Significance of organic waste recycling and Barriers and Challenges of organic waste recycling. Organic wastes contain materials which originated from living organisms. There are many types of organic wastes and they can be found in municipal solid waste, industrial solid waste, agricultural waste, and wastewaters. Organic wastes are often disposed of with other wastes in landfills or incinerators, but since they are bio degradable, some organic wastes are suitable for composting and land application. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. Because of recent shortages in landfill capacity, the number of municipal composting sites for yard wastes is increasing across the country, as is the number of citizens who compost yard wastes in their backyards. Some of the organic materials in municipal solid waste are separated before disposal for purposes other than composting. The organic fraction of industrial waste covers a wide spectrum including most of the components of municipal organic waste, as well as countless other materials. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments.

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Urban Solid Waste Pollution in India: Its Impact and Management

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Abstract: In recent decades high population density in major cities and metropolis of India has resulted into large quantities of solid waste generation. The ever-increasing materialistic demands of city bound people has increased municipal solid waste disposal manifold. Improper management of both domestic biodegradable as well as non-biodegradable wastes in urban cities and metropolises causes environmental pollution of that area disrupting the environmental hygiene. Since personal protective equipments are the primary line of defense against COVID-19, the pandemic and post-pandemic periods have increased the use of plastics and disposable items manifold imparting serious threat to environment and diversity. Its improper management causes environmental pollution and decline of environmental health. Moreover, ground water pollution due to industrial effluents and municipal waste is becoming an ever-increasing concern in many cities of India. Some major causes include runoff from poorly treated waste water, leakage from underground storage and old landfills, and industrial waste dumps near aquifers. Hence, the present study attempts to analyze the effects of variable solid wastes generated in India using data from print and electronic media.

Since solid waste management is an important factor for maintaining environmental health and hygiene, municipal waste management in India needs more attention in present scenario. Its management requires more effectiveness by increasing manpower, spreading awareness, timely collection of bins, and reducing financial issues. Dumping of solid waste in many cities and towns due to lack of proper space has become an emerging problem in India. The expansion of municipal solid wastes and biomedical wastes are further endangering the habitats and organisms. An urban solid waste management strategy includes integrated management system having three main components viz. source reduction, recycling and disposal.

Keywords: Municipal solid wastes, plastics, face mask, ground water, Solid waste management, COVID-19.

1. Introduction

The urbanization, industrialization, significant rise in population growth, and high population density is contributing to the generation of large quantities of solid waste in the country. Due to lack of proper space solid waste are being dumped in open area in many cities and towns. The roads and tourist places are being found littered with vivid plastic bottles and bags in most cities and metropolises. In India, high population growth and economic development are contributing many serious environmental issues. The most important environmental influence is the urban solid waste pollution associated with landfill leachate causing contamination of groundwater and surface water. Poorly managed landfill causes leachate migration to groundwater resource. Since disposal of municipal solid waste through open dumping has been the most common waste disposal method in

India, it is posing environmental and human health risk. One of the major threats to ground water quality deterioration is the disposal of municipal solid waste in non-engineered landfill (Kamboj & Choudhary 2013, Rathod et al. 2013, Maiti et al. 2015). This may lead to contamination of drinking water supplies through contaminated aquifers or surface supplies (Singh & Mittal 2011, Mishra et al. 2018). The population living in the vicinity of dumping sites are prone to severe health problems such as respiratory illness, eye irritation, and stomach problems (Singh et al. 2021). One of the most common problems associated with ill designed landfills and poorly managed solid waste is attraction of large number of vectors causing vector borne diseases like Dengue fever (Vidyavathy 2018). The non-hazardous solid waste routinely collected from a city, town and village, and being transported to a disposal site is the municipal solid waste (MSW). Municipal solid waste includes all trash or garbage from home and commercial places, such as food, paper, glass, metals, plastics, leather, sanitary and other wastes. The improper management of municipal solid waste disposal and the by-products like leachate and gaseous products arising from it is posing hazardous effect to human beings and other organisms as well. Hence, for maintenance of environmental health and hygiene, urban solid waste management needs attention in India. According to 2016 estimate of World Bank, India produces 277.1 million tonnes of municipal solid waste every year, which is expected to touch 387.8 million tonnes in 2030, and 543.3 million tonnes by 2050 (TOI 2020). The ever-increasing population and fast urbanization have made solid waste management a challenge in India. As per current government estimates, there is about 65 million tonnes of waste generation annually in India, and over 62 million tonnes of it are Municipal Solid Waste (MSW). Only about 75-80 percent of the total municipal waste is collected, and out of this only 22-28 percent is deposited at dump yards (Pavithra 2021).

The collection and disposal of solid wastes is under the control of Municipal Corporation. Composition of municipal solid waste varies in different seasons both qualitatively and quantitatively depending on several parameters like locations, climatic conditions, and habits of the people in the vicinity (Agarwal et al. 2013). The seasonal changes in composition influence the quality of recyclable and residual wastes. This in turn affects the quality of emissions from landfills, and the quality of incineration residues as well. The solid wastes in the form of domestic biodegradable as well as non-biodegradable wastes include both combustible and non-combustible types. Combustible wastes include paper, wood, plastics, textiles, rubbers, and garden wastes, while non-combustible include metals, glass, stones, ceramics etc. The composition of urban solid waste varies greatly depending upon its source, locality and activities, which include domestic wastes, commercial wastes, institutional wastes, construction wastes, burning ashes, animal waste, industrial solid waste, biomedical waste, agricultural solid waste, and sewer cleaning sludge. Biomedical waste includes anatomical waste, pathological waste, infectious waste, hazardous waste, and other waste generated from hospitals, clinics, nursing homes, health care units, medical labs, and research laboratories that require specific handling. They include plastic disposable syringes, needles, blades, blood bottles, catheters, expired drugs, empty medicine bottles, surgical masks, liquid wastes etc. In developing countries like India, the biomedical waste generated during pandemic period has added to the already existing solid

waste management issues. According to the Central Pollution Control Board (CPCB), India generated nearly 146 tonnes of biomedical waste every day related to COVID-19 treatments. Further, India produced 45,308 tonnes of COVID-19 biomedical waste between June 2020 and May, 2021, which was an addition to the 615 tonnes of biomedical waste a day being produced before COVID-19 (HT 2021).

During COVID-19 pandemic period human health and the healthcare materials were given more emphasis as compared to environment. Since plastics are flexible, lightweight and easily available, it became the most preferred raw material by several industrial sectors including the healthcare sector. The healthcare materials included in PPE kit are medical gloves, face shield, head cover, hand sanitizers, face masks, whole body aprons, and shoe covers. The type of plastic used in manufacture of various PPEs is polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC) (Klemes et al. 2020). The face mask production in highly accelerated rate, and its daily uses are resulting into increased sources of COVID-19 associated waste generation. The increase in COVID-19 associated waste and its improper management practices is increasing the potential risk of food chain contamination. Finally, the lack of awareness of environmental pollution, people negligence, and improper management of municipal wastes are the prime causes of solid waste pollution issues (Kothari et al. 2021).

2. Ground Water Pollution Through Municipal Solid Waste Landfill: Impact of Leachate

Municipal solid wastes are generated from household, offices, and commercial units containing paper glass, plastics, metals, and organic matter. Ground water pollution due to municipal solid waste leachate is of great concern in many cities and metropolises like Delhi and Kolkata (Kamboj & Choudhary 2013, Maiti et al. 2015, Singh & Mittal 2011). Though, the disposal is done commonly through a sanitary landfill, the problem is arising with the older landfills where the pollutants are percolating down to the groundwater aquifers. After the waste being deposited at the landfill, percolation of leachate takes place to the porous ground surface, where contamination of associated aquifers occurs making it unfit for domestic water supply and other uses.

Some of the major causes of groundwater pollution in urban areas due to MSW are, industrial waste dumps above and near aquifers, leakage from underground storage containing hazardous substances, seeping out from the bottom of old landfills, and poorly designed and maintained septic tanks. Since in many cities there is no segregation of waste at the source point, and no separate landfills for different type of wastes, a common landfill site receives all kinds of wastes such as debris, chemical materials, biomedical wastes, PPEs, liquid wastes, agricultural wastes, oil products etc. In majority of cases pre-treatment is not being practiced for all MSWs or hazardous waste before dumping. Moreover, the landfills remain uncovered at the sites. The characteristics of leachate from an active landfill vary due to age, type of wastes dumped, and the climatic conditions.

Very often the leachate is drained directly into the surface water, thereby reaching the groundwater aquifer. Various studies have reported contamination of groundwater resources by MSW landfill particularly from uncontrolled and unmanaged landfills (Mor et al. 2006, Jhamnani & Singh 2009, Kamboj & Choudhary 2013, Mishra et al. 2016). Several investigations have been carried out on impact of landfill leachate on surface and groundwater quality in metropolitan cities like Delhi and Kolkata from time to time. A case study of Okhla landfill, Delhi revealed the presence of potentially high pollution levels in both old and fresh leachate (Singh & Mittal 2011). The leachate samples collected from different time periods of the year showed variability in its characteristics in terms of age and dumping locations. Data depicts significant rise in physiochemical parameters, showing high concentrations of Total Dissolved Solids (TDS), high values of Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), and ammonia in both fresh and old leachates, which were significantly higher than municipal sewage, indicating potential threat to adjacent water resources and groundwater quality. Heavy metals like Pb, Cd, Mn, Cr, Fe, and Ni were found to be several times higher in all leachate samples than drinking water standards as prescribed by the US EPA. This indicates the disposal of refuse solid wastes like fluorescent light bulbs, waste batteries, food cans, materials made of iron, metal alloys, electronic objects, construction debris etc. Similar studies were carried out at various locations in Gazipur area, New Delhi on landfill leachate and its impact on ground water quality (Kamboj & Choudhary 2013, Alam et al. 2020). The grab samples of leachate and ground water samples were collected and analysed as per standard procedure. Higher value concentrations of various physiochemical parameters were recorded depicting unsuitability for household purposes. Moreover, the leachate proved to be highly toxic for the fishes which may be due to the synergistic effect of the combination of complex pollutants.

Based on another case study carried out in a closed landfill site of Dhapa, Kolkata, West Bengal, the characterization of leachate and its impact on surface and ground water quality was found to be exceedingly high in accordance to related studies (Maiti et al. 2015). According to study, leachate was highly contaminated with organic matters having high values of TDS (8994.16 ± 6239 mg/l), COD (4191.66 ± 2282 mg/l), Cl^- (4356.65 ± 1304 mg/l), and two heavy metals viz. Pb (0.56 ± 0.33 mg/l) and Hg (0.42 ± 0.44 mg/l) exceeding their respective standards as specified in “Municipal Solid Wastes (Management and Handling) Rules, 2000” for disposal of treated leachates (MPCB (MEF-GOI) 2000). In surface water samples, TDS and concentrations of Hg and Pb were above their respective permissible limits. In case of ground water samples, Total Hardness (TH), TDS value, and Cl^- concentrations were above the permissible limits recommended by Bureau of Indian Standards (BIS 2012).

3. Plastic Pollution and Environmental Challenges

One of the major components of ‘Municipal Solid Waste’ is plastic, especially single-use products chocking land and ocean. In recent years, plastic wastes have become a universal

pollutant all over the world due to its demand, rise in production, and improper solid waste management. Much of the plastic produced each year is being discarded after single-use, some of which are dumped in landfills and some find their way to aquatic ecosystems. According to a report of 'The Economic Times' released on April 05, 2022, India is generating about 3.5 million tonnes of plastic waste annually, and the per capita plastic waste generation has almost doubled over the last five years (ET 2022).

Plastics, in the form of macroplastics and microplastics are causing toxic effect to human and other organisms both in land and water bodies (Cole et al. 2011, De-la-Torre 2020). They either remain as large plastic debris, called macroplastics or breakdown into minute pieces less than 5 mm in size in the form of microplastics. Microplastics are widely distributed in soil, air, and freshwater ecosystems in the form of primary and secondary microplastics. Primary microplastics are microscopical that are manufactured, whereas secondary microplastics are created from the degradation of larger plastic products like water bottles, soda bottles, fishing nets, plastic bags etc. The major sources of microplastics are sewage treatment plants, cosmetic industry, textile industry, manufacturing industries, packaging and shipping industry. The large macroplastic debris is often ingested by birds, reptiles, and mammals causing premature death (Wilcox et al. 2018). Recent data depicts that both macroplastics, and microplastics whose size is less than 5 mm, are found to be ingested by variety of animal species like fishes, sea birds, sea turtles, marine mammals, and even smallest plankton (Garcés-Ordóñez et al. 2020, Zheng et al. 2021). Hence, through sustainable solid waste management, the consumption of single use plastic products could be reduced and avoided, along with increased rate of recycling at the same time. In this context, the Ministry of Environment and Central Pollution Control Board has recently launched several green initiatives for plastic waste management (PWM), and to beat plastic pollution.

4. Impact of Covid-19 Associated Waste (CAW) on Human and Environment

In recent years the challenging impacts of COVID-19 pandemic on human and environment is the generation of huge quantities of healthcare waste. The production and consumption of PPEs has been increased drastically with increased use of plastics and disposable items resulting into increased sources of CAW generation (Ranjan et al. 2020). Off PPEs, single use face masks like surgical masks and N95 masks are imparting an environmental risk due to their improper management. Since face masks are the primary line of defence to protect from COVID-19 as per guidelines of W.H.O., its production and utility has increased enormously all over the world. Based on a report of 'Centre for Science and Environment', June 2021, there was a significant increase in COVID -19 related biomedical waste generation during second wave in India. In April 2021, India generated 139 tonnes of biomedical waste, which escalated to 203 tonnes per day indicating an increase of 46 percent (CSE 2021). According to Central Pollution Control Board (CPCB), India generated 47200 tons of COVID-19 associated waste between

August, 2020 and June, 2021, which includes face masks, gloves and other medical items (Krishnan 2022). Also, the government of India has made obligatory in wearing face masks in public places. Face masks are made up of non-woven materials incorporating polypropylene (PE) and polyethylene (PE) plastic, which can take as long as 450 years to decompose according to experts. After being discarded, the PPEs are thrown away as municipal solid waste, of which some makes its way into fresh and marine water bodies. The presence of enough face masks on the seashore indicates the lack of awareness and mismanagement practices, leading to harmful effects to the aquatic life. A survey was carried out in six beaches of Tamil Nadu along the coast of India for the presence of PPE, particularly face masks and gloves (Gunasekaran et al. 2022). Result depicts the presence of face mask (98.39 %) as the most abundant type of PPE.

The disposable masks, gloves, and other medical wastes in significant amounts are making their way to garbage piles across cities, posing challenge to its collection and disposal. Microplastics formed by the degradation of plastic products used in PPE's pose disastrous impacts on human and environment. The use of face masks unprofessionally is creating severe problem in the environment both as a solid waste open dump, and as microplastic pollution in the marine as well as freshwater ecosystems. Since face masks are easily ingested by fishes and aquatic microorganisms, the microplastics get easily incorporated into the food chain affecting the humans (Aragaw 2020). Under environmental conditions these face masks break down into smaller sizes less than 5 mm particles, and contribute to microplastic pollution. Experiments were carried out artificially to estimate the release of microfibrils by a surgical mask dumped in marine environment. Results depicted that a single surgical mask might release upto 173000 fibres a day. (Saliu & Lasagni 2021).

5. Sustainable Solid Waste Management and Practices

As because of fast urbanization and rapid population growth, developing countries like India is less able to tackle projected waste disaster issues and its management. Solid waste management is being offered by local government which includes complete process of collection, transportation, treatment, analysis, and disposal of waste. But municipal authorities often dispose the solid waste to an open dump yard in the vicinity of city. Since in India, the infrastructure and technology for waste management are not much advanced, the open dumping practices should be replaced by engineered landfills in order to prevent soil contamination. However, solid waste management practices can minimize the amount of solid wastes with further reduction in its amount in landfills. Avoidance and reduction in the amount of waste generation can be achieved by maximizing efficiency, and reducing consumption. Moreover, the residual waste could be converted into a useful resource. For recycling the material is collected from consumers, remanufactured, and once again sold to consumers, thus conserving the resources, and reducing the volume of refuse to be disposed. Due to scarcity of proper land filling areas across cities, various methods are adopted to reduce the volume of wastes. Incineration could be done to reduce the volume of wastes to 20% to 30% of the original volume. Again, by the process of Pyrolysis, which

is combustion in the absence of oxygen, volume of wastes could be reduced, and the residues are economically important. Further, biomedical solid wastes are discarded after proper treatment, which includes incineration, deep burial, autoclaving, chemical disinfections, shredding, and disposal in municipal landfills.

Sustainable solid waste management consists of a sequence of steps comprising waste minimization and resource reduction, reuse, recycle, and safe disposal (Thomas and Leon 2020). Its management steps include collection, storage and recovery of recyclable materials, transportation, treatment, and disposal. Some of the important sustainable waste management practices to make our lifestyle sustainable, and more environment friendly are-

- (i) Managing degradable and non-degradable wastes.
- (ii) Replacing single-use products with reusable ones.
- (iii) Household waste recycling.
- (iv) Recycling biodegradable wastes and e-wastes.
- (v) Reducing plastic products in daily use.
- (vi) Going for paperless practices.

6. Conclusion

The developing countries like India are already facing the challenges of solid waste management, due to high population density, lack of awareness in rural areas, accelerated urbanization as well as recently overcome severe pandemic situation. The insufficient and improper waste management practices are posing potential risk to humans and other organisms of terrestrial and aquatic life with severe risk of food chain contamination. The COVID-19 pandemic has changed the types and amount of waste being generated in the last two years. The recycling part of waste management sector still needs innovation, especially after post pandemic period to overcome the surge in biomedical waste. There is great need of sustainable utilization of COVID-19 associated products and sustainable management of COVID-19 associated wastes. For maintaining health and hygiene, municipal solid waste management needs more attention in India. Finally adopting sustainable solid waste management system, which focuses on avoidance, reduction, reuse, recycling, treatment and disposal, resources could be utilized efficiently.

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Green Audit and Sustainable Development

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Abstract: *Worldwide anthropogenic factors have contributed to environmental and ecological degradation and catastrophes in an alarming rate since the inception of civilization. Over the last few centuries, increase in population, urbanization and industrialization in an unplanned manner has worsened the situation. Today we are more concerned about the quality of environment we are handing over to our future generations. Thus, means of organic living has percolated into all human activities although a lot is yet to be done. Much of the organic practices have stemmed from the policy-oriented research on sustainable development involving its three pillars – social, economic and environmental approaches. Although several policies related to sustainable development have been drafted, there is a need for periodic assessment, measuring and accounting of ecological components to govern the implementation of policies. Green audit undertaken by organizations primarily ensures that human activities are in sync with environmental policies. ‘Green’ symbolises eco-friendly or not being harmful to the environment. Acronymically it stands for “Global Readiness in Ensuring Ecological Neutrality” (GREEN). According to ISO 14000, green audit is a systematic and documented verification evaluating environmental impact of human activities. “Green Auditing”, an umbrella term, also called as ‘Environmental Auditing’. This chapter highlights the objectives, protocols, scopes and authorities concerned with green audit. Activities involved in pre-audit, on-site audit and post-audit stages are outlined. The points analysed in the green audit gives a guideline to daily organic practices to be adopted in daily lives. Water conservation, biodiversity preservation, planting trees, use of bio fertilizers, waste management, going plastic free, switching to alternative energy comes under the preview of green audit. Abiding to these guidelines also overcomes the effects of hazardous environment on human health. Historical man-made disasters have triggered the need for cautionary and preparedness measures to be followed by organizations. Every level of the society holds responsibility towards environmental conservation. Calculating the total carbon footprints at individual and organizational level must be made into a mandatory practice in order to protect the environment and sustain human health. Methodical advancement keeping in mind the all-round benefits of present and future stakeholders come within the interest of green audit. The green audit was first put into use in USA in the early 1970s. Even after five decades, several shortfalls are noticeable. Lack of awareness and enforcement, cumbersome data retrieval, absence of Standard Accounting policy and intangible outcomes restricts the proper execution and its implied benefits. Focused and dedicated implementation shall definitely benefit both the planet and its inhabitants in the long run. Often it has been realized that traditional and indigenous practices when amalgamated into urban lifestyle paves way for sustainable use of natural resources. The aim of this chapter is to draw the readers’ attention towards environmental deterioration, need for sustainable development and effectiveness of green audit. In this respect, a confluence of traditional knowhow and technological advancement is prophesied.*

Keywords: Sustainable development, Green audit, Organic living

1. Introduction

The environment directly affects the survival of diverse biological organisms on this planet. Human beings have made use of scientific innovations to better the quality of life. This has however gone overboard to an extent that irreversible damage has been done to the environment. As the world copes with environmental hazards, environmental sustainability and implementation of eco-friendly approaches have become important issues. A vast majority of the global population have come within the prerogative of increasing population, civilization, industrialization and urbanization (Patil et al. 2019). This in turn has led to a lifestyle far removed from the organic way of living by our ancestors which was less deleterious to the environment. At this junction the only possible solution is bringing about a balance in the use of development-oriented technology while preserving the environmental quality. Environmental scientists and policy makers introduced ‘sustainability’ into the mainstream in the 1980s (Purvis et al. 2019). In order to save the planet, a thorough assessment is needed to make ‘sustainability’ from concept to reality. Measuring individual and organizational carbon footprint, Environmental Impact Assay, meeting Sustainable Development Goals and Green Auditing are such monitoring mechanisms. Here the relevance of Green Auditing in Sustainable Development is discussed. Practices like tree plantations, organic manuring, efficient waste management, use of renewable energy and reduction in consumption of non-renewable energy have been identified as some of the green measures to reduce environmental pollution. Thus, blending traditional way of living and technological advancement can save the earth we inhabit.

2. Why the concern?

Natural calamities and climate changes have threatened human survival and socio-economic stability several times in the past. Irrational human activities have been, and still continue to be the primary reason behind such threats. Unless mankind adopts efficient natural resource management strategies, the existence of our future generations will be endangered (Klarin 2018). Development must cater to our current needs without compromising on what we hand over to the coming generations.

3.1. Concept of sustainable development:

Sustainable development stands upon the Triple bottom line concept:

- i. Environmental sustainability - maintaining the environment while supporting human life and activities
- ii. Social sustainability – maintaining human rights and dignity
- iii. Economic sustainability – maintaining financial resources for supporting life and living standards

Hence equal emphasis is laid on development and sustainability although the two terms appear to be contradictory to each other (Sharpley 2000). Sustainability literally means “a

capacity to maintain some entity, outcome, or process over time” (Jenkins 2009) and performing activities without exhausting the resources on which that capacity depends. Development on the other hand implies advancement in infrastructure, political power and economic policy (Klarin 2018). According to UNDP 2015, the most valid development indicator Human Development Index (HDI) takes into account different categories of socio-cultural, economic, ecological and political growth. Thus, long term benefit can only be attained by blending sustainability and development as far as practicable. The holistic nature of Sustainable Development was highlighted by the Brundtland report as inclusive of protection of ecology, heritage and biodiversity (WCED 1987). A number of organizations and institutions participated in the implementation of the concept of sustainable development. The foundation of United Nations (UN) in 1945 with headquarters in New York (UN 2015) marked the first step. In 1968 the Activities of United Nations Organizations and Programmes Relevant to the Human Environment was framed which laid the groundwork for the establishment of the world’s leading environmental authority, United Nations Environment Programme (UNEP). In 2022, UNEP completes 50 years of its service to mankind in terms of improving life quality while preserving nature for the future. The time frame for evolution of sustainable development is intricately woven with the progress of civilization itself as outlined in Figure 1, 2. Till today, the world tries to abide to the 17 Sustainable Development Goals as formulated by the UN.

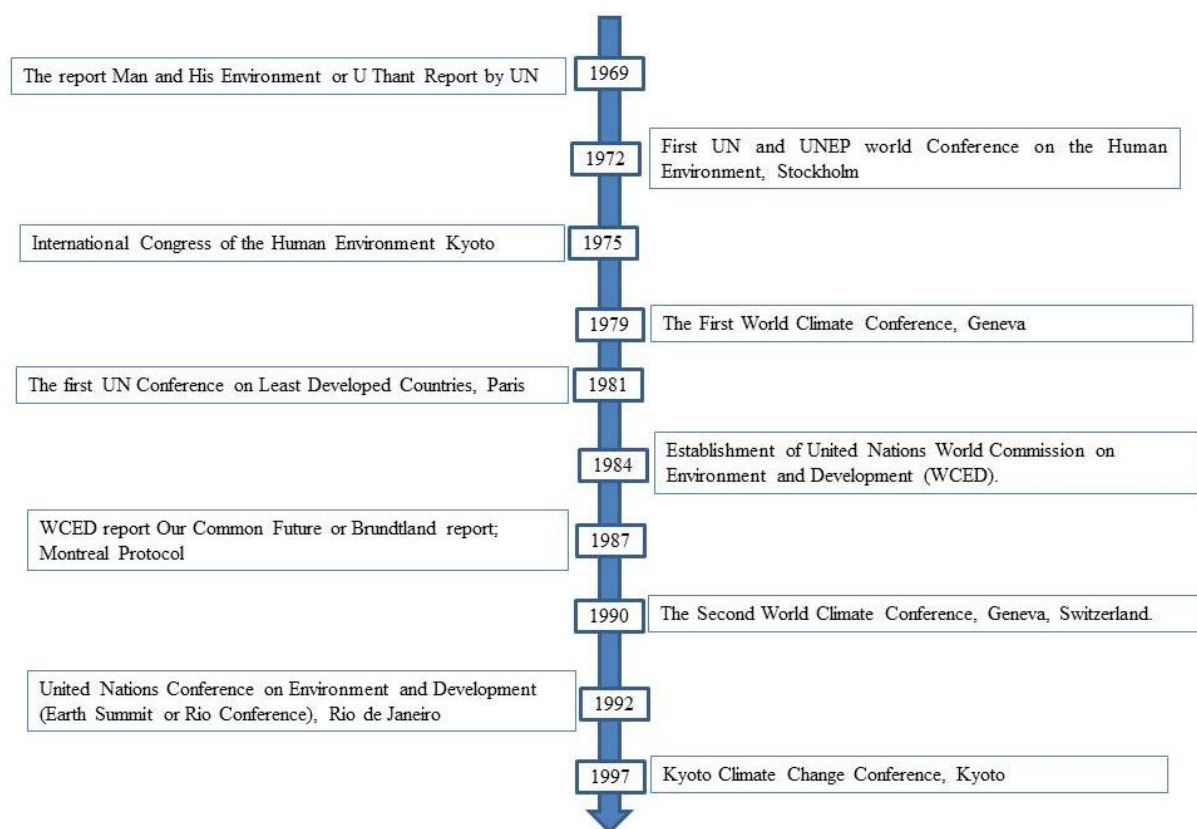


Figure 1: Time frame for progress in Sustainable Evolution during the 20th century

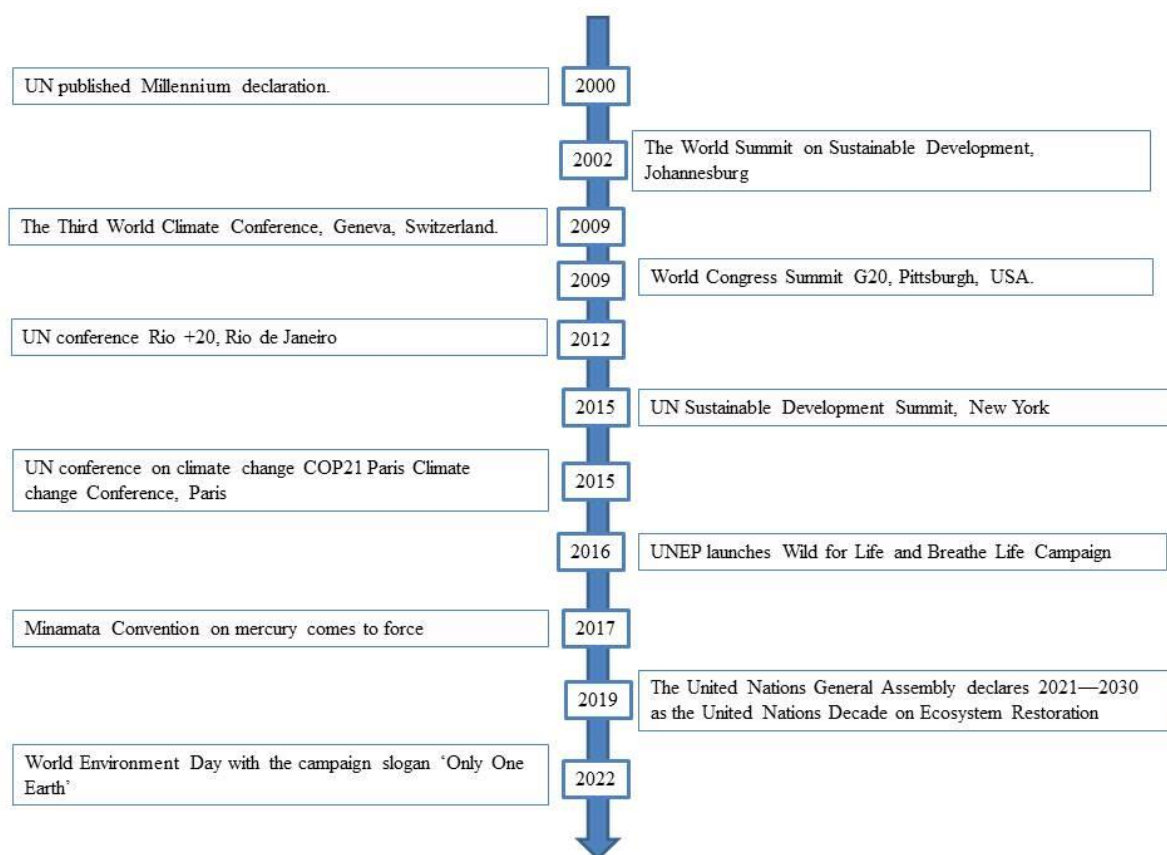


Figure 2: Time frame for progress in Sustainable Evolution during the 21th century

3.2. Challenges towards Sustainable Development:

Environmental opportunities and constraints largely influence holistic development. Impact of degradation of nature is manifested through poverty, hunger and shelter destruction. Such detrimental effects on basic human needs have sabotaging effects on quality of human beings, their intellectual and creative potentialities. Thus, future oriented development goes hand in hand with preservation of ecology. Human development must be considered in relation to global carrying capacity, as exhaustion of natural resources is an absolute natural restraint (Holden et al. 2014). Non-renewable resources are more vulnerable as no amount of effort can replenish these. Sustainable development indicators (SDIs) are aimed at measuring, monitoring and assessing the sustainable development. Although there has been involvement of several government agencies, national and international NGOs, social scientists, environmentalists and workers; universal applicability of the indices is under realized. Another hindrance is the inaccessibility of data for the calculation of indicators (EEA 1999, 2003, 2005, European Commission 2001ab, 2005, 2007, 2009, 2012; Eurostat 2012, 2013, 2014, 2015, OECD 2000, 2001, UNCSD 1996, 2001, UNDESA 2007). The Brundtland report pointed out that the concept of sustainable development is somewhat restricted to western techno-centric development as opposed to human development in relation to environmental sustainability as proposed by the International Union for Conservation of Nature (Sharpley

2000). Poverty eradication without harming the environment is also neglected (Lele 1991). Enhanced need of crop productivity prompted the need for chemical fertilizers and pesticides which has uncontrollably affected the environment leading to lowering of productivity and availability of fertile land. The Earth Summit +5 (New York 1997), and the World Summit on Sustainable Development or Rio +10 in 2002 revised certain agenda of the 1992 Rio Conference. In spite of certain positive outcomes, the problem of global implementation remained. The Rio +10 conference held in Johannesburg noted greater natural degradation and widening of the gap between developed and underdeveloped countries (UN 2002). Subsequent conferences have analysed the progress and problems in the past period of assessment. In 2012 the 20th anniversary of the World Summit in Rio, was observed in Rio entitled ‘*From Rio to Rio +20*’ which adopted the resolution *The future we want* (UN 2012, UNEP 2012). In 2022, Sweden hosted World Environment Day with the campaign slogan ‘*Only One Earth*’. Accordingly, the focus in the coming days is ‘*Living Sustainably in Harmony with Nature*’.

4. Green Audit – a step towards living sustainably:

“Green Auditing” or ‘Environmental Auditing’ is an umbrella term used for assessing ecological impact of human activities. Green or sustainable accounting was first brought into common use by economist Professor Peter Wood in the 1980s. ‘Green’ epitomizes eco-friendly or not being environmentally harmful. Acronymically it stands for “Global Readiness in Ensuring Ecological Neutrality” (GREEN). According to ISO 14000, green audit is a systematic and documented verification evaluating environmental impact of human activities. Its scope spans a systematic, documented, periodic and objective review of practices in accordance to environmental requirements. It aims to inculcate environmentally safe practices such as effective waste management, use of alternative energy sources, tree plantation, and ensuring carbon neutrality. Evaluating our own activities constitutes a basic step towards organic living.

4.1. Perspectives of Green auditing:

1. Preliminary survey on existing green practices with relation to waste management, conservation of biotic and abiotic resources and effective utilization strategies
2. Identifying areas where implementation of green measures is needed
3. Developing green policy framework
4. To inculcate environmental awareness among people
5. Measuring and reporting the environmental impact of undertaken activities at a site
6. Analysis and troubleshooting of problems pointed out by Audit Report

4.2. Methodology of Green auditing:

Green auditing can be primarily classified into three types depending on the nature of assessee:

1. Environmental compliance audits review the company's or site's legal compliance status
2. Environmental management audits provide guidance to comply to environmental performance standards
3. Functional environmental audits measure the impact of a particular activity

The phases of auditing are categorized as pre-audit, audit and post-audit steps. The components of each phase are outlined in Figure 3.



Figure 3: Protocol followed during Green Auditing

5. How Green audit sustains development?

Green audit monitors environmental protection while considering cost-cutting strategies such as waste minimization and management. This approach befits the three pillars of sustainable development namely environmental, social and economic sustainability. It empowers organizations to frame a better environmental performance. As academic institutes nurture the future generations, it is now imperative for them to submit green audit report as a part of the corporate social responsibility of the institutions. Scientific innovations have eased life at the cost of harming the environment we live in. This in turn has taken a toll on human health and quality lifestyle. Thus awareness, conscious living and periodic self-assessment are much needed. The audit presents guidelines, methods and implementation strategies for environmental protection. It must be undertaken by any industry, organization, institute and housing complex. It thus ensures safety of stakeholders and while aiming to minimize disasters.

6. Conclusions

The world has witnessed several manmade disasters which has jeopardized the very existence of life in the affected areas. The Bhopal Gas Tragedy (Bhopal 1984), the Chernobyl Catastrophe (Ukraine 1986), the Exxon-Valdez Oil Spill (Alaska 1989), Jilin Chemical Plant Explosion (China 2005) and the Deepwater Horizon Oil Spill (Mexico 2010) are some of the frightening ones. Green auditing conceptualized in the early 1970s aims at inspecting organizational activities having the potentiality of environmental degradation beyond permissible limit. Abiding by the auditing regulations enables reduction in environmental contamination which in the long run has adverse effect on human health and wellbeing. Organizations need to take responsibilities for periodic assessment through competent authorities for sustaining quality living for the present and the future generations. Ensuring the implementation of relevant rules and regulations, improving procedures and material capability, analysing potential duties, and determining cost reduction strategies (Shelke 2022) are looked into. These in turn help to meet the wider goal of sustainable development adopted by the UN. Interestingly, the solution to the problem of environmental degradation can be largely overcome by adopting traditional way of life while enjoying the benefits of technological advancements. Awareness on our part today shall ensure the world to be a liveable place for the coming generations.

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Rukmani in her Garden: A View of an Organic Living in Nectar in a Sieve

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Abstract: *Literary representation of 'organic living' often trespasses into the boundaries of sciences. However, it is also possible to relocate and reinvestigate some literary texts in order to unveil the close relationship between these two realms. Kamala Markandaya's text 'Nectar in a Sieve' remains pertinent to the context of depicting interrelationship between woman and her organic farm which has provided her sustenance. The text uniquely posits a response to the forces of urbanization which threatens this relationship. This paper endeavours to contextualize Markandaya's text from the perspective of a negotiation between two lives- one lived in sync with nature and another which is away from it. Woman in her garden also incites readers to reinvestigate the interrelationship between indigenous women and nature-a key concept that has been explored in ecofeminism. The paper will also explore how the protagonist's retreat to the life of her choice at the end of the novel emphasizes her intrinsic relationship with the land.*

Keywords: Ecofeminism, urbanization, organic farm

In an age of increasing technological development that often undercuts the narrative of sustainability, it is imperative to look back to the kind of life that is lived in sync with nature. In literature one is reminded of the idyllic life evoked in the pastoral in which nature is very much a part of our living realm. However, it can also be observed that in the capitalized society nature is often seen as a commodity and designed for pleasure. Michael Bunce posits that country retreat often alters the meaning of the rural landscape as it provides 'pleasure rather than economic sustenance. It becomes a private landscape controlled by the power' (qtd in Gaard, 56). Living in sync with nature remains therefore, problematical because it interrogates dual aspects of preserving nature-one is preserving nature for its own sake and the other is restoring it as a space for capital gain. Our relationship with nature which is often described as 'the other' in cultural discourse remains, therefore, a contentious issue which requires critical investigation. Eminent ecofeminist Vandana Shiva in her book 'Staying Alive' has described Prakriti as an embodiment and manifestation of the 'feminine principle' which nurtures creativity, and ensures inter-relationship of all beings. Coining the term 'maldevelopment' she posits that the process of development 'is the violation of the integrity of organic, interconnected and interdependent systems, that sets in motion a process of exploitation, inequality, injustice and violence' (Shiva, 5). Women's biological alignment with nature has been, however, under critical investigation because it draws the flaw of essentialism. It is also observed that women share a close relationship with nature based on

their lived experiences which have been either systematically omitted or devalued in cultural discourses. Bina Agarwal has observed that third world women, as a heterogeneous entity, share multiple relationships with nature and this relationship should be based on the material reality of their lived experiences over any ideological construct. Poor women need to collect fodder, food, water from their surroundings in order to provide sustenance for their families. Ironically their narratives remain primarily absent in the development discourse. This paper intends to focus on Kamala Markandaya's fiction 'Nectar in a Sieve' which registers this absence and analyses the relationship of Rukmani, the central character in the novel, with her land.

Kamala Markandaya (1924-2004) occupies a unique position among Indian novelists. A.K Bhatnagar observes that her novels represent reality 'in a natural way' and her characters 'follow their minds and face life as a natural man should do'. It is this quality which makes her works intrinsically different from other novelists such as R.K. Narayan, Bhabani Bhattacharya, Mulk Raj Anand and Raja Rao (Bhatnagar, 3). *Nectar in a Sieve* (1954) was Markandaya's first novel for which she was internationally acclaimed. Her other novels - *A Handful of Rice* (1966), *The Coffers Dams* (1969), *Two Virgins* (1973), *The Nowhere Man* (1972) and *Bombay Tiger* (1982) - poignantly portray themes of east-west encounter, displacement and intricacies of human relationships. Writing about the 'ambivalent relationship' between women and the environment, particularly depicted in the writings of postcolonial women authors, Gurpreet Kaur observes that writers like Kamala Markandaya, Anita Desai, Gita Mehta, Arundhati Roy have retained the social issues a key part of their writing (Kaur, 388). Markandaya's text *Nectar in a Sieve* as an early response to these issues underpins the conflict of rural life and industrialization. This novel which came out in 1954, has been widely discussed from various perspectives. On one hand it deals with themes of hunger and degradation, on the other hand it also shows how one's connection with the land and belief in traditional values negotiate with forces of modernity which causes urbanization and industrialization.

The novel pivots around the character of Rukmani, a village girl who gets married to Nathan at the age of twelve. Her father as the headman of the village has lost his affluence because of the new centralization of power, hence she gets married to an ordinary peasant unlike her sisters who are married off to wealthy husbands. The small, thatched mud house with its doorway decorated with a garland of mango leaves symbolizing happiness and good fortune is her new home. The blue sky and tender trees greet her and the gentle brook soothes her soul. Rukmani treasures this memory till the rest of her life. Rukmani shared an intimate relationship with the river- as a bride of only a week she followed it to find a suitable place for washing. She walked for nearly an hour to find a wide stretch of water and a beach. With her saree tucked up above her knees, she stood in water, washing clothes using a little of washing powder. She feels immensely contented as she lives amidst nature with a loving husband taking care of her – in her words 'While the sun shines on you and the fields are green and beautiful to the eye, and your husband sees beauty in you which no one has seen

before, and you have a good store of grain laid away for hard times, a roof over you and a sweet stirring in your body, what more a woman ask for?' (9). The text locates Rukmani in her surrounding and shows how she strives to maintain a symbiotic relationship with her land. When she builds her home in a new place she finds the land as a means of sustenance. It yields whatever she needs – 'The soil here was rich, never having yielded before, and loose so that it did not require much digging. The seeds sprouted quickly, sending up delicate green shoots that I kept carefully watered, going several times to the well nearby for the purpose' (10). The garden that she tends yields lustrous vegetables – pumpkin, brinjals which she sells in the market and earns for the family. Her gardening skill drew admiration from her husband who now adored her as a 'clever woman'. Rukmani was much pleased though she 'tried not to show her pride'. Gradually from a simple village girl she becomes confident and ambitious – 'I planted beans and sweet potatoes, brinjals and chillies, and they grew well under my hand, so that we ate even better than we had done before' (11). Rukmani's garden not only provides sustenance for her family but also fills her with a sense of wonder.

'Now that I did not work in the fields I spent most of my time tending my small garden: the beans, the brinjals, the chillies and the pumpkin vine which had been the first to grow under my hand. And their growth to me was constant wonder' (14).

Planting and getting crops evokes a kind of pastoral life which is primordial in its essence. Her relationship with the land, garden in particular, has been investigated from ecofeminist perspectives by the critics. Dana C Mount has observed that 'Rukmani experiences her own physical, emotional, sexual and psychological development through her work in the garden and the growth of vegetables,' (Mount,3). She also posits that her relationship with her land is mediated through labour and this relationship is also vulnerable as Rukmani has to fight against vagaries of nature to survive. She is aware of the uncertainty of nature- "that sometimes we eat and sometimes we starve ..." (132) and yet it is the source of sustenance for her. She gradually becomes a mother of several children and lives a very simple life with little demand for any extravagant need. Thus, in Rukmani's narrative Markandaya records how lives of rural women are embedded in nature. In their simple way of living Rukmani and Nathan celebrate the birth of their son with utmost pleasure and happiness. But Rukmani's relationship with her land places her in a very curious interdependent survival mode which is not only peaceful and fulfilling but also susceptible to nature's whims. Thus, Markandaya writes that 'Nature is like a wild animal that you have trained to work for you. So long as you are vigilant and walk wearily with your thought and care, so long as will it give you its aid; but look away for an instant, be heedless or forgetful, and it has you by the throat.' (42) The kind of challenges that this way of life encounters is also threatening. Nathan and his family starve due to drought and storm for a long period of time. Yet nature also regenerates and provides prosperity. After the hardship the family is able to survive – crops are grown, a new hope of survival assures them all.

The text records how the process of urbanization leaves its deep impact not only on the environment of the concerned village but also on the socio-economic orientation of the villagers whose lives are intrinsically dependent on the place where they live, particularly the poor peasants. Rukmani's own sons, Arjun and Thambi, are not willing to join their father on the farm on the ground that they do not own the land. There are people like Kunthi, Kali, Janaki and others who are ready to reconcile with their changing fate but Rukmani 'stood in pain, envying such easy reconciliation and clutching in my own two hands the memory of the past, and accounting it a treasure' (32). She fails to accept the gradual encroachment of the new regime even when her husband. Nathan advises her to '.. Bend like grass that you do not break'. She is deeply affected when children cannot play in the playground, market prices become too high and there are crowds with full of clamours. She felt how they are going to be ousted from the land of their own- 'In our maidan, in our village he stood, telling us to go.' Cement, sheets of tin and corrugated iron, coils of rope and hemp were placed in the village and invaded the country with clatter and din. Rukmani, ridiculed as a village girl mourns for the absence of birds who '... have forgotten to sing, or else their calls are lost to us' (31). The tranquillity of the village life is forever lost and young girl like Ira cannot move freely but has to get married too early. The encroachment of the tannery is a threat to their existence as it tries to engulf the land. The basic simple life of the farmers changes as they are now choosing the lives of a tannery labourer. Finally, the owner of their land sells the land to the tannery and Rukmani and her husband are bound to leave the country. They move to the city where they are forced to work as labourer in a stone factory.

While the first section of the novel reflects a symbiotic life lived in harmony with nature, the second part records Rukmani's struggle in an alien land which threatens to register her survival strategies. Dispossessed of their land Rukmani and her husband fall prey to hunger and degradation in the city. Rukmani works as a letter writer and a reader but later she starts working in the quarry. The description of the quarry which mutilates the body of nature by blasts using gunpowder reminds one of the tanneries that transformed the rural environment. Though the quarry was on a hillside, it was not the calm and pleasant hill with which Rukmani was familiar. It was 'an enormous irregular crater strewn with boulders and lined with jagged rocks, its side pitted with holes of varying size' and the sharp, vertical falling of the land shows the violation wrought on the body of the hill (176). Nathan accustomed to work on the field succumbs to the extreme stress and hazardous existence. Rukmani after losing her husband decides to go back to the village with a newly found orphan Puli who has provided help in the city.

In the village she is united with her daughter and son with whom she renews her life. Her decision to cling to what Dana C. Mount describes as the 'land-based community ethic' is an assertion of her inextricable relationship with her land. Rukmani's choice to be back to the organic farm where she experienced self sufficiency and happiness also reflects how one's symbiotic relationship with nature ultimately wins over technological development which fails to include poor village woman like Rukmani in its narrative. In her choice to go back to

the village which remains vulnerable to industrial progress, Rukmani defies the forces by embracing the values of love and care. It is true that this retreat does not guarantee her peace but the touch of her land rejuvenated her spirit – ‘I looked about me at the land and it was life to my starving spirit’ and this nearness to her land made her forget the suffering she had. Her son’s assertion not to get worried because ‘We shall manage’ may not sound convincing, yet it is an assertion of their bond based on love and affection, an assurance of their spirit to fight against all odds when they are near to their land.

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Developments of Oxide Based Nano-photocatalyst in Waste Water Treatment Technology: A Brief Overview

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Abstract: Clean potable water is critical for all living organisms. Various organic and inorganic contaminants have been detected in various water bodies that contribute to the source of potable water. Such contaminants are typically toxic and hazardous to the living organism. Thus, removal or degradation of these contaminants from industrial waste prior to the discharge into the environment is essential. Nanotechnology showed great potential in developing new processes for water purification and decontamination. Particularly, heterogeneous photocatalysis involving nanocrystals (NCs) appears to be one of the most promising technologies. Nanoscale metal oxides have been widely investigated for photocatalytic water purification due to their distinct size, physical and chemical properties such as large surface area, high charge transport and stability. Very few review articles are reported that specifically address metal oxide NCs and their application in the treatment of wastewater. In this review article, we have discussed the application of different photocatalytic processes for the treatment of waste water using oxide-based NCs with an aim to address the crucial issue of a sustainable environment. Emphasis is put on the application of nano TiO_2 and ZnO photocatalytic technology in wastewater treatment and recent achievements in scientific research are discussed in this article. We have discussed the designing of advanced photoreactor technology for industrial-scale waste water treatment. Finally, conclusive remarks regarding current studies and unsolved challenges of nano particles based photocatalytic technology are put forth for future perspective.

Keywords: Semiconductor, photocatalysis, wastewater, oxide-NCs, nanotechnology

1. Introduction

In modern civilization, water contamination has increased globally due to rapid industrialization and the massive population explosion (Lijuan et al. 2012, Ren et al. 2021). In 2020, a report of the United Nations on World Water Development also cautioned that change in the water cycle will also pose serious risks to food security, energy production, human wellbeing, economic development, and the option for an all-inclusive sustainable development (World-Water-Development-Report 2020). Various technological measures have been adopted so far in addressing the issue of wastewater treatment and decontamination of waterbodies (Zularisam et al. 2006, Yagub et al. 2014, Azimi et al. 2017). However, these processes are generally energy expensive and has complex mechanisms involved for transforming pollutants into by-products while treating wastewater. In this context, nanotechnology which is an interdisciplinary field covering a wide range of streams including the frontier of chemistry, physics, materials, medicine and biology provides an efficient solution for photocatalytic degradation of pollutants (Ratner & Ratner 2003, Yang 2003). NCs possess a high surface to volume ratio, large area and small sizes, and have a strong adsorption reactivity and capacity pollutants (Ratner & Ratner 2003, Yang 2003). Various types of NCs, including carbon

nanotubes, zerovalent metal NCs, semiconductor NCs, metal oxide NCs, nanocomposites and heterostructures have been reported worldwide for the disintegration of bacteria, emerging pollutants, organic pollutants, and inorganic anions (Pruden & Ollis 1983, Horikoshi & Serpone 2020). Semiconductor NCs based photocatalysts operating in ambient conditions is a cost effective and green technology which can degrade organic pollutants present in wastewater into CO₂ and other small molecules, and reduce or oxidise inorganic pollutants into harmless substances (Pruden & Ollis 1983, Horikoshi & Serpone 2020, Li et al. 2019). Metal oxide semiconductor NCs which are low cost, highly abundant and nontoxic are promising for heterogeneous photocatalysis of both organic and inorganic pollutants (Naseem & Durrani 2021). The metal oxide NCs possess a wide bandgap which permits both oxidation of water and reduction of protons which is the main helpful factor to enhance the photocatalytic activity (Naseem & Durrani 2021). Also, metal oxide NCs display excellent light absorption properties, outstanding charge transport characteristics, which are suitable in the photocatalytic system for the treatment of wastewater (Naseem & Durrani 2021). Among various semiconductor NCs, oxide semiconductor NCs like ZnO, TiO₂ are the most investigated photocatalysts because of their electronic band structure, photostability, chemical inertness and commercial availability (Schneider et al. 2014). However, the metal oxide photocatalysis is restricted due to the poor quantum efficiency and the fact that it could only absorb the UV light of the solar spectrum. The developing directions of photocatalysis need catalysts with higher catalytic performance, which includes doping, heterojunction formation, alloying, composite formation and so on (Naseem & Durrani 2021).

In this review article, we overview the development and advances of oxide NCs in photocatalytic removal or degradation of several common categories of water pollutants. In this article, we have reviewed the current research progress on oxide-based nano photocatalysts, designing, and structural modifications. We have also discussed the insight of photocatalytic mechanism, intermediates formation and designing of photocatalytic reactors. Through this article, we hope to provide forward-looking ideas and prospects for the future development of more advanced photocatalysts useful for water waste treatment.

2. Discussion

2.1. Nanocrystals

Nanoscience and nanotechnology related to the materials that have dimensions in nanometers or one-billionth (10⁻⁹) of a meter, at minimum, one external dimension is in the range of 1-100 nm are called NCs. NCs show superior chemical, biological, mechanical, electrical, magnetic and optical properties which are often significantly different from their corresponding bulk counterparts (Schneider et al. 2014). All these properties depend on the size, shape, composition, defects and interface which can be tailored by proper design and synthesis process (Rao et al. 2004). Semiconductor NCs have different energy bands called valence and conduction bands. The energy gap between the top of the valence band and the bottom of the conduction band is called the bandgap. The electronic states in crystals are different from the isolated atom. (Figure 1a) Semiconductor materials can be elemental or compound type. They

are mainly composed of periodic groups of IV (e.g. Si and Ge), II-VI (e.g. ZnO, CdS and CdSe), III-V (e.g. InP and InAs), IV-VI (e.g. PbS, PbSe, SnS, SiO₂) combination (Rao et al. 2004, Zhao et al. 2004, Wu & Zelenay 2013, Rowland et al. 2014). Elemental semiconductors like Si and Ge have four valence shell electrons. In II-VI, III-V and IV-VI compound semiconductors there are eight valence shell electrons shared by two pairs of nearest atoms. The elements belonging to the II, III and IV groups are more electropositive whereas V and VI group elements are more electronegative. So, because of the electronegativity difference between the constituent elements, the covalent character is predominant in III-V and IV-VI semiconductors whereas II-VI semiconductors have more ionic character (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003).

2.2. Quantum confinement effect

When the length scales of material are below the de-Broglie wavelength of an electron, the electron gets confined in a spatial dimension resulting in new unique properties which are different from the bulk (Figure 1a). Semiconductor NCs show unique optoelectronic properties due to the restricted motion of electrons i.e., quantum confinement effect (Ioannou & Griffin 2010). Upon absorption of a photon, an electron gets excited from the valence band of the semiconductor to the conduction band leaving a positively charged hole in the valence band (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003). Due to the coulomb attraction between the electron and the hole, they form a loosely bonded pair known as an exciton. The separation distance between the electron and hole pair in an exciton is termed as exciton Bohr radius (Ratner & Ratner 2003, Yang 2003).

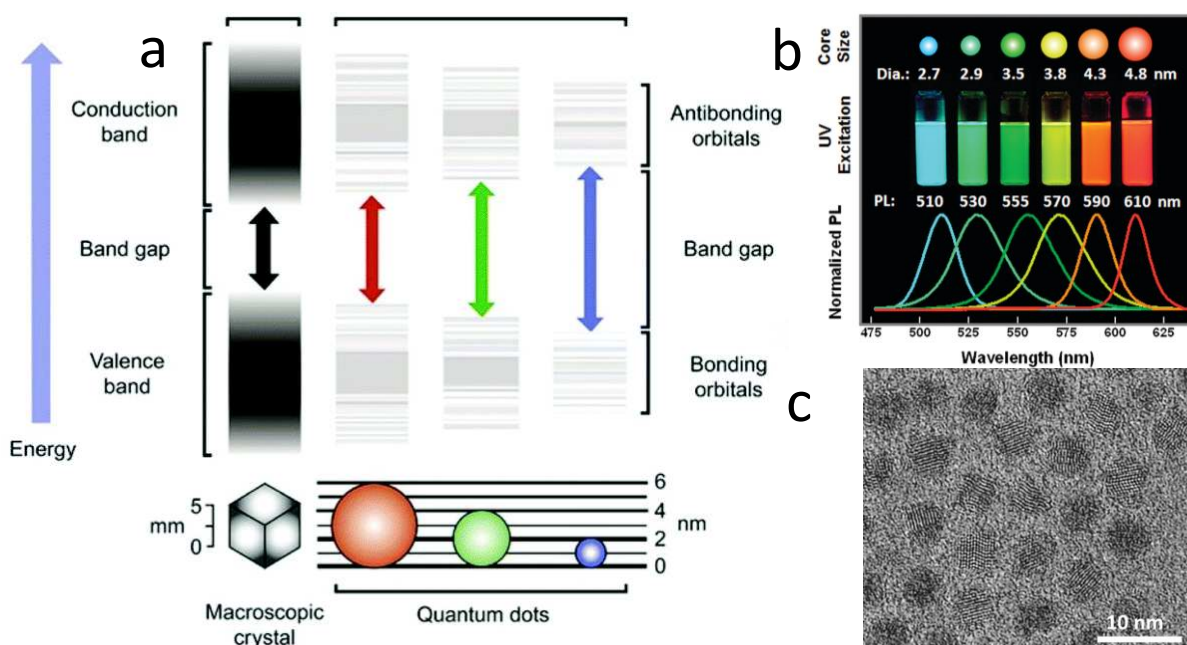


Figure 1. (a) Comparison of the energy band of bulk and nano semiconductor materials due to effect of quantum confinement. Electronic states in a bulk semiconductor and quantum dots (QDs) made of the same material with different diameters (Ioannou & Griffin 2010). Reproduced with permission from Informa UK Limited, copyright 2010. (b) Schematic, photograph, and photoluminescence (PL) spectra illustrating progressive color changes of CdSe/ZnS with increasing nanocrystal size. The larger band-gap energy of smaller QDs of the same material leads

to lower PL wavelengths (large QDs are red and small QDs are blue) (Algar et al. 2011). Reproduced with permission from American Chemical Society, copyright 2011. (c) Transmission electron micrograph of CdSe/ZnS QDs (Talapin et al. 2001). Reproduced with permission from American Chemical Society, copyright 2001.

Dielectric constant of the semiconductor materials reduces the strength of Coulomb attraction (Ratner & Ratner 2003, Yang 2003). Thus, smaller exciton binding energy implies a larger spatial separation of electron and hole and eventually has a larger excitonic Bohr radius (Ratner & Ratner 2003, Rao, et al. 2004). Semiconductor NCs in nanometer length scale where charge carriers are confined in all three spatial dimensions are called Quantum dots which display unique optoelectronic properties and immense applications in the field of science and technology (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003). Figure 1b shows the fluorescence colour of the highly luminescence CdSe/ZnS quantum dots upon excitation of UV light (Algar et al. 2011). This photoluminescence colour originated from the recombination of the exciton. The transmission electron microscopic image of the quantum dots is shown in figure 1c (Talapin et al. 2001).

2.3. Tuning the properties of the NCs

The most fascinating property of semiconductor NCs is the modulation of electronic structure as a function of size. As the size of the semiconductor crystals decreases from the bulk size to nanometer regime, the electronic structure is altered from the continuous electronic bands to discrete or quantized electronic levels and therefore the size of the NCs defines the optoelectronic properties of the NCs. (Figure 1) In semiconductor NCs both linear and non-linear properties arise as a result of transitions between electron and hole quantum size levels. Other ways of tuning of NCs properties includes changing shape, composition, formation of heterojunction, doping etc. which will be beyond our scope to discuss in this short overview (Ratner & Ratner 2003, Rao, et al. 2004, Yang 2003).

3. Photocatalytic application

Catalysis refers to a process that influences the rate of a chemical reaction using a substance (catalyst) that remains unconsumed at the end of the reaction. A catalyst participates during a reaction and only alters the activation barrier for the transition state and thus, influences the rate of the reaction. A positive catalyst accelerates the chemical transformation, while a negative catalyst retard the process. A catalyst does not change the overall value of the equilibrium constant and the overall free energy for the reaction when compared with the analogous uncatalyzed reaction (Cotton et al.1994). Depending upon the phase of the catalyst compared to the reactant, the catalysts can be classified as homogeneous or heterogeneous catalyst. In homogeneous catalysis, the reactant and the catalysts are in the same phase whereas in the heterogeneous catalysis, catalysts are in a different phase with respect to the reactants (Pagni 2001). A nanomaterial-based catalyst is an example of heterogeneous catalysis. Here, catalysts can be easily separated from the reaction mixture by means of physical or chemical methods. NCs with smaller size have high surface area with available surface- active sites with high interfacial charge carrier transfer rates leading to higher catalytic activities compared to

their bulk counterpart. Photocatalysis, where photons are used for catalytically activating chemical reactions on the surface of photosensitized catalysts, remains one of the leading hubs of research for harvesting solar light (Teoh et al. 2012). Efficient separation of exciton leads to greater photocatalytic efficiency. Metal semiconductor heterostructure or semiconductor-semiconductor heterostructure and composite of semiconductor material have shown efficient charge separation ability and hence better photocatalytic efficiency (Yang 2003, Lijuan et al. 2012, Ren et al. 2021). However, in this short review, we have little scope to cover the photocatalytic activity of all these systems. We will discuss mostly the photocatalysis reaction of oxide-based NCs specially ZnO and TiO₂.

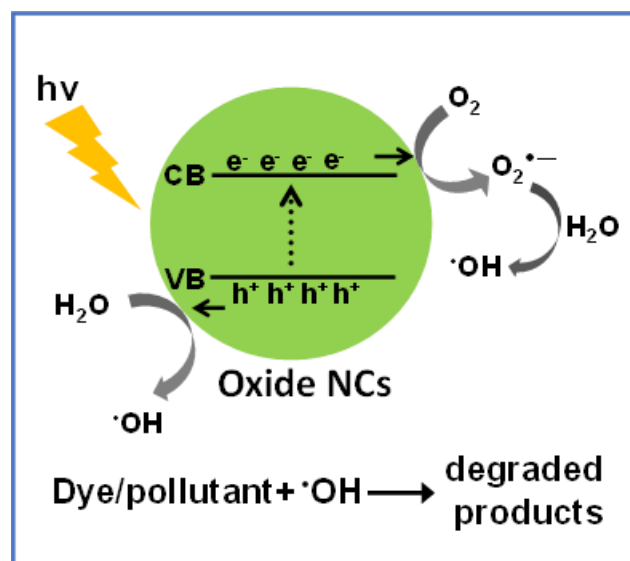
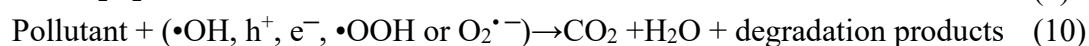
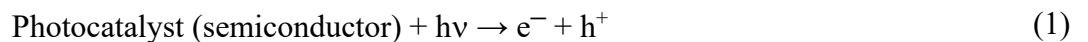


Figure 2. Schematic illustration of the photocatalytic degradation of pollutant by oxide NCs with details reactions pathways.

3.1. Photocatalytic reaction mechanism

Semiconductor materials possess an energy bandgap (E_g) which is an important parameter for photocatalysis reaction. Bandgap of the semiconductor NCs is tuneable by changing the size, shape and composition. On excitation of light, electron (e^-) from the valence band (VB) of the semiconductor excite into the conduction band (CB), leaving holes (h^+) in the valence band (Figure 2). For bulk materials, these photogenerated electron-hole pairs (i.e., exciton) are difficult to separate from each other and undergo recombination easily (Ratner & Ratner 2003, Yang 2003). However, for materials at nanoscale dimension, it becomes easy for the separation of electron holes. Photogenerated electrons and holes undergo various surface reactions to generate active oxidative radicals which are responsible for the photodegradation of pollutants (Ratner & Ratner 2003, Yang 2003, Lijuan et al. 2012, Ren et al. 2021) (Figure 2). Photogenerated electrons are widely considered as reductants for directly reducing some heavy metal ion pollutants. Also, photogenerated electrons can react with dissolved oxygen in water to produce superoxide radicals ($O_2^{\cdot-}$) which undergo further reactions to produce $\cdot OH$ radicals. On the other side, photogenerated holes react with water or hydroxyl ion (OH^-) to produce hydroxyl ion ($\cdot OH$) and can also participate directly in the oxidative decomposition of the

pollutants (Lijuan et al. 2012, Ren et al. 2021) (Figure 2). For heterogeneous photocatalysis using NCs, pollutants first adsorb on the surface of the NCs. Then upon photoexcitation electron-hole pairs are generated in NCs which also benefit charge mobility and enhance its redox ability. Then the charge carrier undergoes a series of chemical reactions with the active species generated by the NCs and pollutants to obtain degradation products (Lijuan et al. 2012, Ren et al. 2021). All the redox reactions discussed above are listed below (equation 1-10).



3.2. Photocatalytic degradation of pollutants in waste water

3.2.1. Removal/degradation of organic pollutants (Dyes, phenol, pharmaceuticals)

There are different types of organic pollutants found in wastewater. These pollutants can be classified as hydrocarbon, dyes, phenolic compounds, surfactants, organohalides, organonitro compounds etc (Lijuan et al. 2012, Ren et al. 2021). These organic pollutants are chemically stable, toxic and carcinogenic (Wang et al. 2014). Carey et al reported the catalytic degradation of polychlorinated biphenyls by TiO_2 under UV light which laid the foundation stone for the research of photocatalysis (John et al. 1976). Semiconductor NCs based photocatalysts have been widely investigated for degrading a wide range of organic pollutants in which the photocatalyst degrades organic pollutants into readily biodegradable compounds or less toxic molecules which are further mineralized into CO_2 and H_2O .

Thousands of dyes are available in the market which are used in industrial processes for the synthesis of wide range of products ((Lijuan et al. 2012, Wang et al. 2014, Ren et al. 2021). Among which methylene blue (MB), Methyl orange (MO), Rhodamine B (RhB), Methyl red (MR) are most common and all are water soluble, not readily biodegradable and harmful for the ecosystem. During oxide NCs based photocatalysis, photogenerated holes (h^+) and H_2O react to form highly oxidising hydroxyl radicals whereas photogenerated electrons react with oxygen to form superoxide ions which further react with H_2O to generate hydroxyl radicals (details in the photocatalysis reaction mechanism). These radicals with potent oxidising power react with dye pollutants to degrade into CO_2 and H_2O or less harmful small chemical compounds (Lijuan et al. 2012, Ren et al. 2021). Zhao et al. reported ZnO microstructures of different morphologies like twining-hexagonal prism, twining-hexagonal disk, sphere and flower-like respectively (Zhao et al. 2013).

Table1: Photocatalytic degradation of organic pollutants

Type of waste water	Classified/characteristic	Pollutants/chemicals	Catalysts	References
Dye waste water	Dye: Water-soluble, not readily biodegradable, harmful to the ecosystem	Methylene Blue	NiO, ZnO, ZnTiO ₃ , TiO ₂	Jayakumar et al. 2017, Petrovicová et al. 2021
		Methyl orange	ZnO, TiO ₂	Raliya et al. 2017
		Rhodamine 6G, Rhodamine B	TiO ₂ , ZnO, AgZnO	Abdullah et al. 2011, Doina et al. 2012, Majumder et al. 2020
		Anthraquinone dye	TiO ₂	Routoula et al. 2020
		Azo dye	ZnO	Chen et al. 2017
Phenolic wastewater	Highly soluble in water, acutely toxic, biologically recalcitrant	Phenols Phenols BPA	Cu-NiO CuO-TiO ₂ TiO ₂ -x @ZIF-67	Ethiraj et al. 2020, Çinar et al. 2020, Tang et al. 2020
Pharmaceutical wastewater	Anti-biotics: Water-soluble, not readily biodegradable, harmful to the ecosystem Anti-inflammatories High polarity, hydrophilicity, the absorption coefficient	Sulfamethazine	ZnO	Yi et al. 2018
		Amoxicillin	TiO ₂	Emad et al. 2010, Varma et al. 2020, Balarak et al. 2021
		diamyl phthalate, butyl benzylphthalate, methyl p-hydroxybenzoate ibuprofen	ZnO TiO ₂	Emad et al. 2010, Vela et al. 2018, Khalaf et al. 2020
		Cloxacillin	TiO ₂	Emad et al. 2010, Ana et al. 2010
		Oxolinic acid, Diclofenac	TiO ₂	Emad et al. 2010, Ana et al. 2010
		Cephalexin, and Oxytetracycline	ZnO, TiO ₂ , Fe ₃ O ₄	Blady et al. 2011

	Lipid regulators	Metformin Amoxicillin metformin	TiO ₂ -ZrO ₂ TiO ₂	Chinnaiyan at al. 2018, Carbuloni et al. 2020
Pesticide wastewater	Toxicity, biological resistance	Kappa furan, carbofuran pesticides, melathion	TiO ₂ , ZnO	Emad et al. 2010, Blady et al. 2011, Khan et al. 2020
		Dieldrin, Deltamethrin	TiO ₂	EL-Saeid et al. 2021
		Armour mix phosphorous	TiO ₂	Wang et al. 2010
		Organophosphorous pesticides	TiO ₂	Doong & Chang. 1997
Explosive waste water	Contains highly toxic nitroaromatic compounds, hazardous to environment, animal and human	TNT	TiO ₂ , WO ₃ /Fe ₃ O ₄	Lee et al. 2002, Reza at al. 2021
		RDX	TiO ₂	Lee et al. 2002
		HMX	TiO ₂	
Chlorine hydroxybenzene waste water	Compared to phenol, chlorophenolic compounds are more toxic and have more bioaccumulative potential, very low biodegradability.	Chlorinated phenol	TiO ₂ , ZnO	Dionysios at al. 2000, Elkady et al. 2017
Nitrobenzene waste water	Toxic to microorganism and environment	Nitrobenzene	TiO ₂ , Ag-Cu ₂ O	Wang et al. 2010, Chen et al. 2021

They showed that flowerlike ZnO exhibited higher photocatalytic activity due to its morphology, surface defects, bandgap and surface area. In 2020, Saifuddin et al reported the photocatalytic degradation of organic pollutants by MFe_2O_4 ($M = Co, Ni, Cu, Zn$) catalyst (Gupta et al. 2020). These photocatalysts are highly suitable for the remediation of dye-contaminated wastewater. They have demonstrated that dye degradation mechanism in the UV/ H_2O_2 /ferrite system was primarily driven by the formation of $\bullet OH$ radicals and holes, which was confirmed by scavenger studies and fluorescence spectroscopy (Figure 3). Table 1 demonstrates photodegradation of organic pollutants by metal oxide NCs such as ZnO, TiO_2 , doped metal oxide and composite system.

Petroleum hydrocarbon pollutants are persistent important pollutants containing alkanes, olefins and polycyclic aromatic hydrocarbons (Douglas et al. 2012). It is well known that marine environments are the ultimate and largest sink of petrochemical pollutants and has become a critical issue to effectively treat hydrocarbon pollutants in the aquatic environment (Varjani 2017). In this line, NCs based photocatalysts are promising candidates for the photodegradation of petrochemical hydrocarbons. Younesi et al reported that TiO_2 NCs in zeolite matrix works as efficient photocatalysts for the removal of organic pollutants from petrochemical refinery wastewater (Ghasemi et al. 2016). Two-dimensional g- C_3N_4 nanosheet reported having good efficiency for photocatalytic removal of petroleum hydrocarbon in water (Yang et al. 2020).

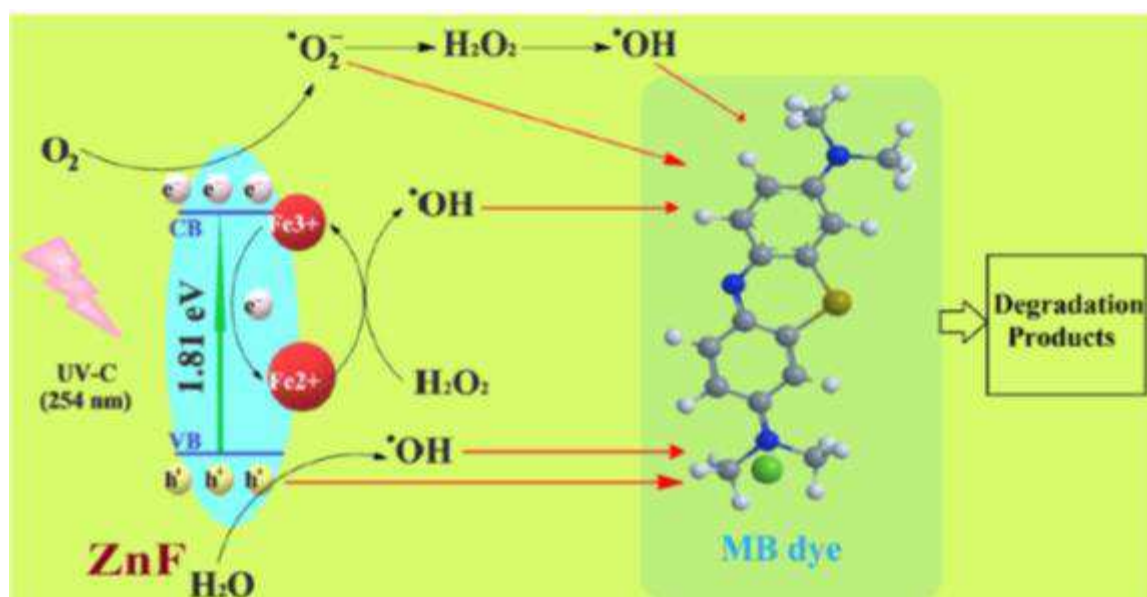


Figure 3. Schematic illustration of the photocatalytic degradation process of MB dye onto Zn ferrite photocatalyst (Gupta et al. 2020). Reproduced with permission from Springer Nature Limited, copyright 2020.

Phenolic compounds are reported to be highly soluble in water, carcinogenic, acutely toxic and biologically recalcitrant. Phenol in wastewater is introduced via a large number of industrial processes such as petroleum production, refineries, manufacturing of paints, pharmaceuticals and pesticides (Maszenan et al. 2011). It is reported that photocatalytic degradation of 4-nitrocatechol produces benzoquinone, hydroquinone and some organic acids (Ahmed et al. 2010). The synergistic effect of hydroxyl radical and superoxide radical leads to the

degradation of phenol. Also, p-n heterostructure of CuO-TiO₂ with band alignment and efficient charge separation ability exhibit good efficiency towards photocatalytic degradation of methylene blue as well as 4-nitrophenol under visible light irradiation (Çinar et al. 2020). Fe₃O₄ NCs with magnetic properties also exhibit high efficiency for photocatalytic removal of phenolic compounds as adsorption sites of the phenolic compounds are provided by the defect state of the Fe₃O₄ NCs (Bui et al. 2020). TiO₂ NCs demonstrate high activity for photocatalytic degradation of biphenyl compounds (Tang et al. 2020).

In modern day, anti-inflammatory drugs have been widely used for many physiological treatments. TiO₂ nanoparticle was reported to be a very effective catalyst for photodegradation and mineralization of dichlofenac in aqueous solution (Achilleos et al. 2010, Günel et al. 2019). TiO₂ nanocatalyst can also be effective for the removal and destruction of ibuprofen which is used to relieve pain and rheumatism (Khalaf et al. 2020, Akel et al. 2020).

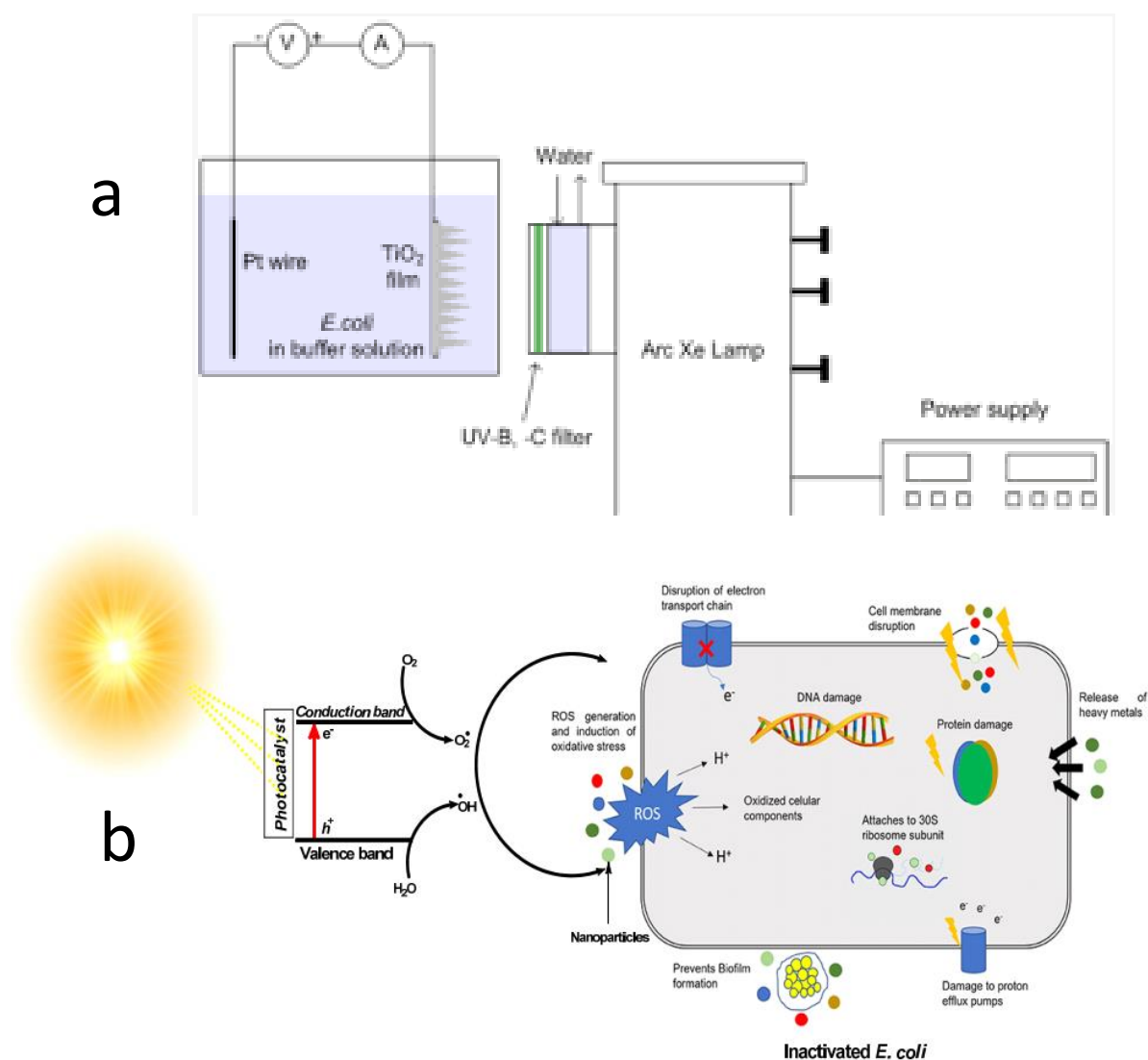


Figure 4. (a) Photoelectrochemical and photocatalytic *E. coli* inactivation set-up (Park et al. 2013). Reproduced with permission from MDPI, copyright 2013. (b) Mechanism of photocatalytic inactivation of *E. coli* (Ajiboye et al. 2021). Reproduced with permission from MDPI, copyright 2021.

Metformin drug is commonly used for hyperglycemia and type-2 diabetes. This drug can enter into the environment through various sources and create pollution to marine and other water resources. Carbuloni et al. reported that TiO_2 and $\text{TiO}_2\text{-ZrO}_2$ photocatalyst exhibit high efficiency for photocatalytic removal of metformin in sewage and water (Carbuloni et al. 2020). TiO_2 nano photocatalysts were also effective for degradation of amoxicillin and metformin (Prashanth et al. 2021).

3.2.2. Removal of Pesticides

Pesticides are one of the major sources of water pollution. All pesticides are carcinogenic and have toxic effects on living organisms, ecosystems and human health even in trace amounts. Semiconductor NCs based photocatalysis technology has been widely investigated for the photodegradation of pesticides. Oxide NCs such as TiO_2 , ZnO are reported to be very effective for the photodegradation of pesticides (Taghizade et al. 2020). Ce-doped TiO_2 nanoparticle was reported for photocatalytic degradation of triazophos and profenofos pesticides (Liu et al. 2019).

3.2.3. Inactivation and degradation of microorganisms

Verities of microorganisms present in the wastewater cause fatal diseases to living organisms and human health. Microorganisms like enterovirus cause different gastrointestinal diseases, adenoviruses cause respiratory diseases, salmonella causes colitis, dysentery and meningitis. TiO_2 photocatalysts could kill bacteria in water through the generation of reactive oxygen species (ROS) (Wu et al. 2010). Since then, ROS mediate water treatment technology through the destruction of toxic microorganisms has become the focus of research. The ROS on microorganisms acts in the following ways: ROS destroys the coenzyme A on the cell membrane, reduces or inhibit cellular respiratory or ROS from entering the cell further to oxidize nucleic acid, proteins and eventually cause cell death (Wu et al. 2010). Apart from the laboratory standard photocatalytic reaction, instruments are also available for the photocatalytic treatment of waste water and the production of safe drinking water. In a recent review article, Onwudiwe et al. demonstrated the photocatalytic inactivation method of E. Coli from water. Different photocatalysts for effective inactivation of E. coli and the mechanism involved are discussed in detail (Ajiboye et al. 2021). A portable and easy to use photocatalytic reactor design has also been reported based on the TiO_2 nanotube as photocatalysts (Park et al. 2013, Ajiboye et al. 2021). Using this reactor can inactivate 5-log of E. coli within 10 seconds. A rechargeable battery is used as source of energy for the LED fitted into the reactor light source and TiO_2 nanotube is used as photocathode. The design of this novel photoreactor is shown in Figure 4.

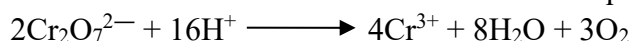
Table 2: Photocatalytic degradation/removal of inorganic pollutants from wastewater

Type of waste water	Classified/characteristic	Pollutants/chemicals	Catalysts	Mechanism	References
As containing waste water	As: carcinogenic and highly toxic	As(III)	Fe-BF/H ₂ O ₂ ZnO TiO ₂ /C	Photooxidation Photooxidation Photooxidation	Yao et al. 2012, Rivera-Reyna et al. 2013, Wei et al. 2022,
Heavy metal ion containing waste water	Cr: Carcinogens, harm human skin and internal organs; Hg: High toxicity, tendency to bioaccumulate Pb: Toxicologica, fatal	Mn(II)	TiO ₂	Photooxidation	Li et al. 2003
		Ti(I)	TiO ₂	Photooxidation	
		Hg(II)	TiO ₂ α -Fe ₂ O ₃ / g-C ₃ N ₄	Photoreduction Photoreduction	Khalil et al. 2002, Kadi et al. 2020
		Cr(VI)	ZrO ₂ , TiO ₂ -ZrO ₂ , Mn ₃ O ₄ @ ZnO/Mn ₃ O ₄	Photoreduction Photoreduction Photoreduction	Botta et al. 1999, Li et al. 2017, Yan et al. 2020
		Pb(II)	TiO ₂ Fe ₃ O ₄ @ C@TiO ₂	Photoreduction Photoreduction	Murrini et al. 2008, Bi et al. 2019
CN ⁻ containing waste water	interfere with cellular respiration, inhibition of cytochrome oxidase	CN ⁻	TiO ₂	Photooxidation	Hidaka et al. 1992
NO ₂ ⁻ containing waste water	Toxic to human and animals, causes blue baby syndrome	NO ₂ ⁻	Fe ³⁺ /TiO ₂ /SiO ₂	Photooxidation	Jin et al. 2001

3.2.4. Removal of heavy metals and toxic anions

Accumulation of heavy metals with high concentration leads to the toxicity in living system. Different types of heavy metals with large quantity are produced due to development of metallurgy, mining, nuclear and chemical manufacturing. Heavy metals can modify the gene of living organism by binding with nucleic acids, protein and metabolites leading to destruction of living cell and fatal health problems. As heavy metals are not biodegradable, it actually gets enriched in the living organism through food chain and drinking water (Wang et al. 2020). Hence, it is very much essentials to remove these heavy metals in waste water before release into the ecosystem. Photocatalysis is an alternate way to remove such heavy metal ions from water where photocatalysts reduces toxic high valent heavy metal ion into lower-valent ions or zero-valent metals ions.

Higher valent chromium (Cr) is ions are carcinogenic, which directly harm human skin and internal organs (Wang et al. 2020). Chromium ions are introduced into the ecosystem either as oxyanions (e.g., CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^-) or cations (Cr^{3+}). Higher valent chromium Cr(VI) present in the oxyanions form reduces into Cr^{3+} in acidic or neutral aqueous solution.



Different nano photocatalysts have been widely investigated for the reduction and removal of Cr(VI) into lower valent Cr(III) (Table 2). In 2017, Liu et al reported the synthesis of $\text{BiVO}_4\text{-Fe}_3\text{O}_4$ heterostructure photocatalytic system using a solvothermal method and adopted it as a photoreduction catalyst to the removal of Cr(VI) in water under visible light irradiation (Chen et al. 2021). BiVO_4 system itself showed a potential method for the economic-friendly removal of high valence metals with easier separation in the water (Figure 5).

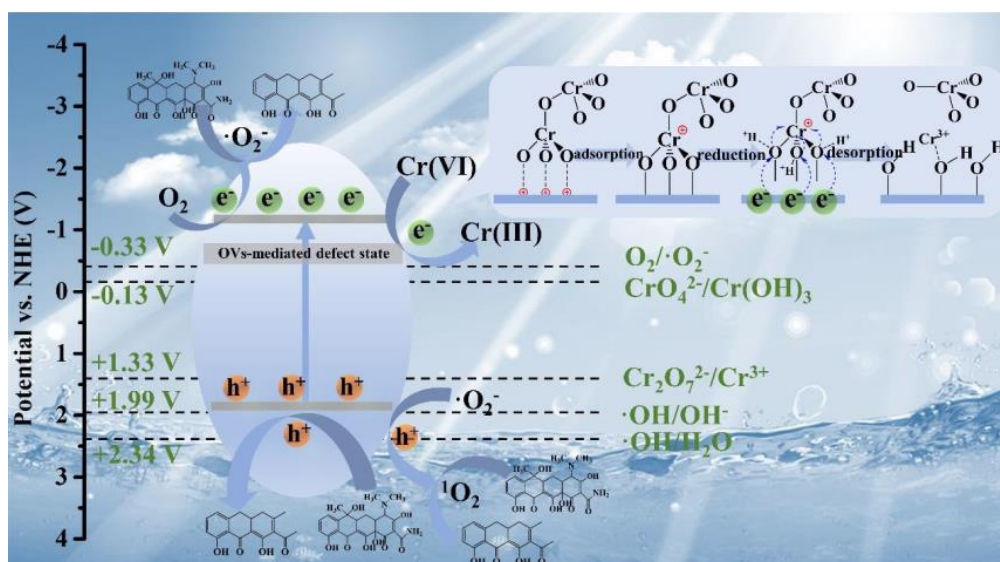
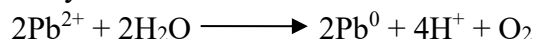


Figure 5. Proposed oxygen vacancy induced charge transfer mechanism on BiVO_4 semiconductor and photo-reduction of Cr(VI) in waste water under visible light irradiation (Chen et al. 2021). Reproduced with permission from American Chemical Society, copyright 2021.

Lead imparts several toxicological effects on human health and even leads to fatal health problems. Lead pollution in the ecosystem come from municipal sewage, mines and chemical production. The Photocatalysis method was reported to be an effective method for the removal of Pb(II) from aqueous solutions (Murrini et al. 2008, Peter et al. 2017, Hosseini & Mohebbi 2020). The possible photocatalysis reactions are as follows:



Magnetic $\text{Fe}_3\text{O}_4@\text{C}@\text{TiO}_2$ oxide heterostructure system showed potential for capturing and removing of Pb(II) (Peter et al. 2017, Bi et al. 2019). $\text{TiO}_2/\text{Al}/\text{Fe}$ NCs magnetic composite system reported to be very effective for removal of a variety of heavy metals ions including Cr(III), Cu(II) and Pb(II) (Peter et al. 2017, Wang et al. 2020).

Mercury (Hg) can damage human health through inhalation of mercury vapour or organic mercury ingestion through aquatic organisms such as Minamata Disease (Hadi et al. 2015). Most of the mercury contamination comes from industrial wastewater mainly from industrial discharge such as a chlor-alkali, plastics, batteries, electronics, and used medical devices. Hg(II) ion can be deposited into mercury metal by the following equations:



Many photocatalysts have been widely investigated for the photoreduction of mercury ions till date. $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanocomposite system showed a high photocatalytic reduction of mercury compared to pure Fe_2O_3 NCs and $\text{g-C}_3\text{N}_4$ nanosheet (Kadi et al. 2020). In addition to the above-mentioned ions, others heavy metal ions such as Arsenic (As), Uranium (U), and cadmium (Cd) are also difficult to biodegrade, quickly accumulate in living organisms and are highly toxic even at very low concentrations (Table 2). $\text{Fe}_2\text{O}_3/\text{C}$ nanocomposite system showed a higher capacity for the photooxidation of As(III) to As(V) which is easy to remove by adsorption (Liu et al. 2019). Chowdhury et al. demonstrated that Y-sensitized TiO_2 photocatalysts can be very effective for the removal of Cd(II) ions (Chowdhury et al. 2017). The pH of the solution is an important factor for photocatalytic reaction efficiency. Metal oxide NCs like TiO_2 , Fe_2O_3 is proven to be very effective for the removal or degradation of these toxic anions from the wastewater (Table 2).

3.2.5 Design of photocatalytic Reactors

The rational designing of photocatalytic reactors plays an extremely important role for the photocatalytic treatment of wastewater in an industrial scale (Sacco et al. 2020). At present, most photocatalytic reactions are limited to the experimental stage and difficult to put into practice in the industry. So, the development of a new and efficient photocatalytic reactor is a crucial factor to accelerate the application of photocatalysis in practical industrial-scale applications. In 2021, in a minireview article, Enesca et al described the parameter for designing of a photocatalytic reactor and its operating parameters (Enesca 2021). In this article, two main aspects have been considered such as photoreactor geometries (cylindrical and rectangular), and analyses the correspondence between the photoreactor concept characteristic

(working regime, volume and flow rate), irradiation scenarios (light spectra, irradiation period and intensity) and the photocatalytic process parameters (photocatalyst and doses, pollutant type and concentration, removal efficiency) (Figure 6). Cylinder photoreactor consist of TiO_2/WO_3 heterostructure exhibit high efficiency for the photocatalytic removal of different organic pollutants (phenols, pharmaceutical active compounds, dyes etc.) (Enesca 2021). On the other side, a rectangular reactor allows a higher versatility of the irradiation source orientation and photocatalyst can be immobilized on the reactor wall. Rectangular photoreactor allows maximum production of oxidative species required for degradation of organic pollutants (Figure 6) (Enesca 2021). It is worth mentioning that for designing an efficient photoreactor several parameters such as pH, temperature, oxygen concentration, the concentration of ion scavenger need to monitor critically. However, the development prospect of photocatalytic water treatment is promising and efficient reactor with an optimized model are worth exploring.

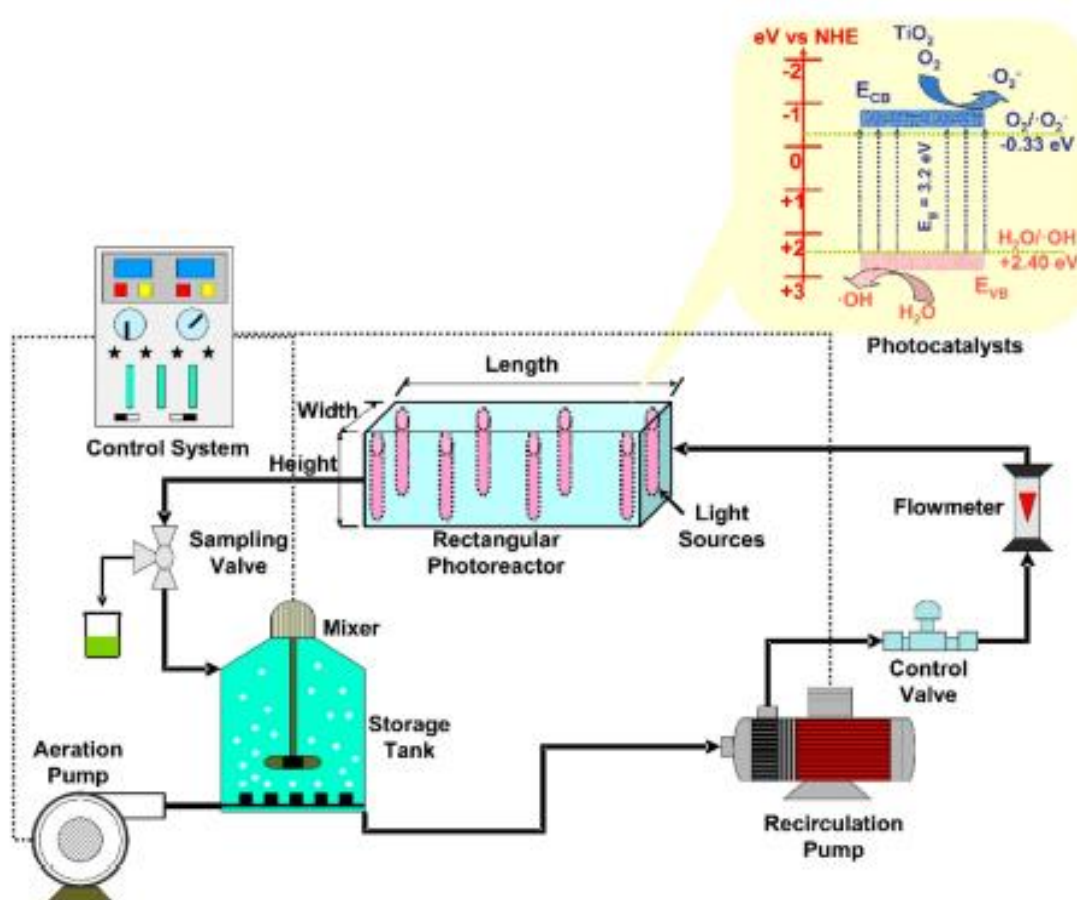


Figure 6. Schematic presentation of a rectangular photoreactor components using TiO_2 photocatalysts (Enesca 2021). Reproduced with permission from MDPI, copy right 2021.

4. Summary and future perspective

In summary, this review article summarized the progress and perspective of NCs based photocatalysis technique for the application of wastewater treatment. Firstly, the prospect of NCs for the photocatalytic reaction was discussed. Then mechanism of the photocatalytic reaction process was introduced. After that, recent advances in photocatalytic removal of

several common categories of water pollutants were explained in detail using examples of some oxide NCs. Also, strategies to improve photocatalytic performance such as composite and heterostructure formation were discussed. To realize photocatalytic treatment of pollutants in wastewater, many aspects of the photocatalysis must be considered. For better understanding of the photocatalysis mechanism requires theoretical and computational study for investigation of surface transformation and chemical changes at molecular level during the photocatalytic degradation. Also, experimental finding and theoretical calculations should be combined to provide better reaction mechanism at the interface. Utilization of advance characterization techniques like mass spectroscopy, NMR are found to be useful for exploring these reaction intermediates and better understanding reaction pathways and degradation mechanism of various water pollutants. From analysing of all the factors, it may point out that although there is promising advancement in synthesis and efficiency of the photocatalyst, most of the photocatalytic experiments reported are performed in laboratory conditions whereas photochemical treatment of industrial waste water or natural wastewater involves large degree of complexity. Hence, further development of photocatalytic system is essential including designing of efficient photoreactor with optimization of photocatalyst concentration and recycling.

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Plant *in vitro* cultures for phytoremediation of heavy metals

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Abstract: *Environmental contamination/pollution is one of the major global problems in the present times faced by urbanized and developing countries. It is caused by natural processes like geological erosion or anthropogenic activities like industrialization as well as agricultural practices. Contaminants or pollutants can be in the form of chemicals released by these processes or in the form of energy such as heat, light, radioactive waves etc. Polluted environment can lead to contamination of groundwater reservoirs, imbalances in the food chain and therefore poses a major threat to the very existence of living beings! Among the different contaminants present are the heavy metals, which are chemical elements with relatively high atomic weights and atomic numbers. Common examples of concern which are hazardous to plants, animals and human beings include cadmium (Cd), mercury (Hg), lead (Pb), arsenic (As). Some others like copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn) can be classed as essential for the normal biochemical and physiological processes when present within limits. Mostly these metals originate from various activities such as industrial and agricultural processes. Heavy metals cannot be degraded by any physical or biological processes; therefore, these metals remain in the environment and can enter the human body through the food chain via crops, causing a plethora of diseases. Thus, appropriate remediation measures are to be taken to prevent these heavy metals from contaminating the environment. Although several physical and chemical methods have been applied for eliminating contaminants from the environment, these are costly and have other drawbacks. Phytoremediation or the use of plants for environmental remediation, is an eco-friendly, cost-effective, scientific alternative to the traditional methods of environmental clean-up. The method is based on the natural ability of plants to uptake chemicals from the air, water and soil and to metabolize a number of these chemicals in their tissues. In vitro plant cell and organ cultures are convenient laboratory tools for phytoremediation research. Plant tissue culture is a technique used for the aseptic culture of plant cells, tissues, organs and their component parts (explants) under defined physical and chemical conditions. Unlike field grown plants, these cultures can be maintained indefinitely under aseptic conditions, free from geographic and seasonal barriers. Also, being grown in sterile conditions, these cultures are free from microbial contamination and can therefore be used easily to discriminate between the responses of plant cells grown in presence or absence of microorganisms which are normally present in the rhizosphere or plant tissues. The present review gives a brief idea about heavy metals, phytoremediation and the potentiality of plant in vitro cultures for the phytoremediation of such metals.*

Keywords: Contaminant, environment, phytoremediation, pollutant

1. Introduction

Environmental pollution is a serious global issue affecting the wellbeing of all living beings. Pollutants, either organic or inorganic, are released into the environment as a result of natural geological processes (erosion, saline seeps) or from extensive anthropogenic activities (agricultural practices, urbanization, industrialization etc.) as a result of the rise in global population (Cherniwchan 2012, Wu et al. 2016a). Among the pollutants are radionuclides,

agrochemicals, heavy metals and metalloids, organic compounds, oil spills etc. (Hu et al. 2010, Sunitha et al. 2012, Prakash et al. 2013, Ron & Rosenberg 2014, Su et al. 2014, He et al. 2015, Malik et al. 2017). These pollutants are either non-biodegradable or degrade very slowly, resulting in their accumulation in the ecosystems, which can ultimately be deleterious for the survival of the entire living world. Thus, a lot of effort has been given for developing remediation strategies for environmental clean-up. Although various traditional techniques like incineration, irradiation, soil washing, pump and treat, surfactant flushing, activated carbon adsorption or extraction have been used for remediation of environmental pollution (Bedmohata et al. 2015, Gautam & Gotmare 2016, Nidoni 2017), in most cases their applications are limited by high costs, requirement of huge labour, safety hazards and threats to the environment (Doran 2009, Ali et al. 2013). Therefore, research was focussed on the development of other efficient and reliable biological techniques to clean-up the environment and phytoremediation appeared to be an attractive alternative. Plant tissue culture has emerged as an efficient tool for phytoremediation research. The present review gives a brief idea about heavy metals, the process of phytoremediation and the application of plant tissue culture techniques used for the phytoremediation of such metals, which are hazardous.

2. Heavy metals and their adverse effects on the living world

Heavy metals (HMs) are a group of chemical elements which are metallic in nature, have relatively high atomic weights and atomic numbers (Yan et al. 2020). HMs may be formed naturally because of paedogenic weathering, erosion, volcanic activities (Kordrostami et al. 2019) or through anthropogenic activities like industrialization and urbanization. Addition of fertilizers and pesticides in agriculture, sewage sludge consumption, metal mining and smelting, electroplating, medical applications, burning of fossil fuels etc. are some of the factors contributing to the contamination of the environment by heavy metals (Muradoglu et al. 2015, Iqbal et al. 2016, Hamzah et al. 2016, Chen et al. 2016, Shi et al. 2018). Depending on their biological role, HMs are classified as essential [required for normal physiological and biochemical processes within the plant body, namely, copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn)] and non-essential [lead (Pb), arsenic (As), cadmium (Cd), mercury (Hg), with no defined function in the plant body] (Cempel & Nikel 2006, Fasani et al. 2018). Both of these groups of HMs at higher concentrations are toxic to the living beings, affecting cell membranes, DNA structure, enzyme properties, cell function or may be even carcinogenic (Wu et al. 2016b, Mishra et al. 2019, Shakya & Agarwal 2020). These HMs cannot be degraded by any biological, chemical or physical process and persist in the environment for long periods of time, posing a threat (Wuana & Okieimen 2011, Suman et al. 2018). The common HMs/metalloids found in contaminated areas include Cd, cobalt (Co), Hg, Pb, As, Zn, Cu, Ni, and chromium (Cr) (Dubey et al. 2018). These metals enter and bioaccumulate in the animal and human body through the food chain via the crops, finally affecting human health (Rehman et al. 2017, Rainbow 2018). Ingestion of food crops contaminated with HMs can cause a plethora of serious complications in the human body such as the reduced intelligence and learning ability, mental retardation, fatigue, anaemia,

depression, cardiovascular problems and damage to nervous system due to Pb exposure (Kazemipour et al. 2008; Singh & Kalamdhad 2011, Grover & Jhanda 2017; Santa Maria et al. 2019), Itai-itai disease due to chronic Cd exposure (Pan et al. 2010); kidney dysfunction and anaemia due to Zn (Duruibe et al. 2007); corrosion of mucosa, hepatic system failure, damage of kidney and central nervous system due to Cu (Singh & Kalamdhad 2011, Karim 2018) etc. Some other maladies include skin irritation and nervous system complications due to Ni (Argun et al. 2007); abortion, nervous breakdown and skin rashes due to Hg (Duruibe et al. 2007); cancer due to Cr and cancer and immune system dysfunction due to As (Duruibe et al. 2007). Apart from these, HMs also cause other diseases such as neurological disorders (Parkinson's disease, Alzheimer's disease, schizophrenia), nutrient deficiency, hormonal imbalance, obesity, respiratory and skin disorders, brain damage, various types of allergies and asthma, endocrine disorders, chronic viral infections, enzyme dysfunction, metabolic changes, infertility, nausea and vomiting, headache and dizziness, irritability, gene degradation, premature aging, memory loss, anorexia, joint inflammation, hair loss, osteoporosis, insomnia and even death (Mishra et al. 2019; Pirsheeb et al. 2016; Wasana et al. 2017).

HMs can also have adverse effects on plants. Although not directly involved, forms of these elements absorbed by plants can affect their growth and development (Rostami & Azhdarpoor 2019). These metals can inactivate proteins and enzymes and disrupt metabolism of sugar (Kordrostami et al. 2019). Plant cells are stressed and injured by the production of oxygen-free radicals (Liang & Yang 2019) mainly in the chloroplasts and mitochondria. Oxidative stress cause oxidative damage to lipids, proteins, nucleic acids (Kordrostami & Mafakheri 2021). Important physiological processes in plants like photosynthesis, respiration and growth are affected (Mishra et al. 2006). Pb, a common HM contaminant, has been found to inhibit seed germination, root elongation, development of seedling, plant growth, transpiration, chlorophyll production (Kumar et al. 2017). Another HM, Hg, has been reported to inhibit plant growth, affect nutrient uptake (Patra & Sharma 2000) and the photosynthetic system (Patra et al. 2004).

So, the presence of HMs in the environment beyond standardized limits is not desirable. Vegetation is affected causing extinction of species, human health is seriously affected as well as soil fertility is affected, causing soil erosion. So, it is extremely important to prevent HMs from entering our environment and to remediate sites already contaminated with these pollutants.

Generally, soils contaminated with HMs can be remediated by non-biological methods such as excavation, extraction or stabilization of polluting ions or other physical and chemical methods. But as mentioned earlier, these methods are not only expensive and limited by other factors, but might also destroy the physical and chemical properties of soil (El Rasafi et al. 2017). So alternative biological remediation methods using plants have been used for

removal of HMs from contaminated areas because of cheapness and simplicity of the methods (Osman 2018) and phytoremediation using plants is one such method.

3. Phytoremediation

Phytoremediation is a solar energy driven technique where plants' natural ability to uptake chemicals and convert them into nontoxic, readily harvestable forms in their tissues is being utilized to clean up pollutants from contaminated water, air or soil (Doty 2008, Doran 2009). It is an inexpensive and eco-friendly process as plants are used to contain, sequester and detoxify pollutants from contaminated areas (Ashraf et al. 2019). Plants are autotrophs, capable of absorbing a variety of allelochemicals and xenobiotic compounds through their roots. Once inside the plant body, the harmful compounds can be volatilized, metabolized or mineralized, generating simpler compounds. In fact, 'xenome' or a biosystem has been defined which can detect, transport and detoxify xenobiotic compounds in the plant cell (Edward et al. 2005). A wide variety of plants, both monocots and dicots, can uptake, sequester and metabolize pollutants from polluted areas of land and water (Ashraf et al. 2019). Ideally, there are certain criteria to be fulfilled by a plant species to be chosen for phytoremediation – it should be high biomass producing, should be tolerant to the toxic effects of the pollutants, should be easy to cultivate and hardy in nature, should have high absorption capability and should be non-attractive to herbivores (Adesodun et al. 2010, Sakakibara et al. 2011, Shabani & Sayadi 2012). Removal of contaminants from polluted sites (phytodecontamination) and their stabilization, thus preventing their movement and harmful effects, are the key aspects of this technique (Sadowsky 1999).

Plants utilize diverse mechanisms (*viz.* phytoextraction, phytodegradation, phytostabilization, phytovolatilization, rhizodegradation, phytofiltration) to degrade, remove or immobilize the contaminants. Phytoextraction refers to the process of absorption of contaminants by plant roots and their subsequent translocation to aerial parts or in other words, plants are used to extract contaminants from the soil (Doty 2008, Jacob et al. 2018). This method is considered to be the most applicable phytoremediation strategy for the recovery of HMs and metalloids from contaminated soils (Ali et al. 2013, Sarwar et al. 2017). Plants used for phytoextraction should be highly tolerant to the toxic effects of HMs, should be able to extract and accumulate high concentrations of HMs in their aboveground parts, should be fast growing with abundant shoots and highly developed root systems (Seth 2012, Ali et al. 2013). Mention may be made of two categories of plants which are especially suited for phytoextraction of HMs from contaminated sites. Plant species with the capability to accumulate very high amounts of HMs in their aerial parts without any phytotoxicity are known as hyperaccumulators (Rascio & Navari-Izzo 2011; van der Ent et al. 2013). Under identical conditions, hyperaccumulators can accumulate metals at 100-fold higher levels than that of non-hyperaccumulating species (Rascio & Navari-Izzo 2011). At present, more than 450 plant species from about 45 angiosperm families have been classified as hyperaccumulators (Suman et al. 2018). Examples include *Thlaspi caerulescens*, the Zn

hyperaccumulator, *Sedum alfredii* hyperaccumulating Zn, Pb, Cd, *Pteris vittata* hyperaccumulating As, Cr, Cu, *P. cretica*, *P. biaurita* hyperaccumulating Pb, different species of *Alyssum* accumulating Ni to a large extent, *Medicago sativa*, *Brassica juncea*, *B. nigra*, the Pb hyperaccumulators etc. (Assunção et al. 2001, Srivastava et al. 2006, Bani et al. 2010, Kalve et al. 2011, Koptsik 2014). The second category of plants suitable for phytoextraction include the high biomass producing crops, such as *Helianthus annuus*, *Cannabis sativa*, *Nicotiana tabacum* and *Zea mays* (Herzig et al. 2014). Grasses such as *Trifolium alexandrinum*, with a short life cycle, high growth rate, high rate of biomass production, high stress tolerance are also suitable for phytoextraction of HMs such as Cu, Pb, Cd and Zn (Malik et al. 2010, Ali et al. 2012).

Organic pollutants (*viz.* chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, herbicides, pesticides etc.) are phytodegraded either by plant endogenous enzymes or enzymes which are secreted (Suresh & Ravishankar 2004, Doty 2008). Plants suitable for this process are *Blumea malcolmii*, *Phragmites australis*, *Pontedaria crassipes* etc. (Kagalkar et al. 2011, He et al. 2017, Gong et al. 2019).

In phytostabilization or phytosequestration, plants stabilize the polluted soil to check its movement to the surroundings, instead of eradicating the pollutant from such site (Sadowsky 1999). This strategy uses metal-tolerant plant species to immobilize or inactivate contaminants such as HMs or organic contaminants under the ground and decrease their bioavailability. Thus, the contaminants fail to migrate into the ecosystem (Marques et al. 2009, Kafle et al. 2022). Plants with a fast growth rate capable of producing large biomass and dense rooting system are especially suited for this strategy as roots play a crucial role in immobilizing pollutants, stabilizing the structure of the soil and preventing soil erosion (Yan et al. 2020). Plant species specifically used for phytostabilization include *Eupatorium cannabinum*, *Solanum nigrum*, species of *Salix* etc. (Gonzalez et al. 2019, Yang et al. 2019, Li et al. 2019).

In yet another mechanism, known as phytovolatilization, harmful compounds after being taken up by the roots are converted into less toxic volatile forms and released into the atmosphere by the process of transpiration through the stomata of the leaves (Mahar et al. 2016). Organic pollutants and HMs like Se, Hg and As can be removed through this process (Mahar et al. 2016). Examples of plant volatilisers include *B. juncea*, *Juncus effuses*, *Phragmites australis* etc. (Banuelos et al. 1997, Wiessner et al. 2013, San Miguel et al. 2013). However, through this technique, pollutants will continue to contaminate the ambient air as pollutants are only transferred to the atmosphere from the soil in the volatile form.

In cases where the contaminants cannot be degraded by plants only, association with rhizosphere colonizing bacteria has been proposed to augment the process of phytoremediation *explanta* (outside the plant body) (Ontañón et al. 2014). This process is called rhizodegradation. The contaminant degrading microbes get nutrients and energy from

the plant root exudates. The method is mostly applicable for removing organic contaminants. Plants known to utilize rhizodegradation include *Cynodon dactylon*, *Rubus fruticosus*, species of *Cucurbita* etc. (Alagić et al. 2016, Ely & Smets 2017, Nguemté et al. 2018).

Phytofiltration is the eradication of pollutants from aquatic environment by terrestrial and aquatic plants like, *B. juncea*, *Setaria italica*, *Pistia stratiotes*, *Salvinia auriculata*, *S. minima*, *Azolla filiculoides*, *Carex pendula*, *Platanus mexicana*, *Solanum diversifolium*, *Asclepius curassavica*, etc. (Arthur et al. 2005, review by Kristanti et al. 2021). Such plants have high tolerance towards HMs and fast growth rates. Rhizofiltration (use of roots), caulofiltration (use of shoots) or blastofiltration (use of seedlings) are some of the strategies used for the removal of contaminants from polluted surface water, ground water or waste waters (Mesjasz-Przybyłowicz et al. 2004, Kristanti et al. 2021). Contaminants like HMs are either absorbed by or adsorbed onto the root surface during rhizofiltration to clean up contaminated ground or surface water resources (Kafle et al. 2022). The pH of the rhizosphere is changed by the root exudates, causing precipitation of HMs on the plant roots, thus further inhibiting the movement of these contaminants to the ground water (Javed et al. 2019).

Yet another technique is phytodesalination, where salt-tolerant plant species are used to extract excess amounts of salts from the soil; an excessive amount of salt in the soil affects normal plant physiology, inducing salt stress in plants (Kafle et al. 2022). Halophytic plants are mostly used for this purpose.

Further details about these processes have been discussed previously (Majumder & Jha 2012). One or more of these mechanisms may be used by plants to eradicate pollutants from polluted site, depending upon the chemical nature of contaminant present, contaminated environment or the plant species used (Kafle et al. 2022). For instance, heavy metals get accumulated in plant tissues after uptake, whereas organic pollutants are mostly degraded (Mahar et al. 2016, Saleem et al. 2020). Contaminated ground water can be remediated through methods like phytodegradation, phytovolatilization, rhizofiltration, rhizodegradation and phytodegradation whereas surface and wastewater contaminations can be treated by rhizofiltration, phytodegradation or rhizodegradation. Contaminations in soil, sediments or sludges are remediated through phytoextraction, phytodegradations, phytostabilization, rhizodegradation or phytovolatilization (Kafle et al. 2022). To enhance the efficacy of phytoremediation, various aids like biochar, ethylene diamine tetraacetic acid (EDTA), endophytic bacteria or arbuscular mycorrhiza are added, which either reduce the toxicity or increase the availability of pollutants or promote the growth of plants, thereby assisting in the phytoremediation process (Kafle et al. 2022).

Being a less expensive, passive, solar driven and eco-friendly process, the method is advantageous over other conventional non biological strategies used for environmental clean-up and is gaining popularity and wide acceptance by society and regulatory agencies. Soil fertility is also improved because of the release of various organic matters to the soil (Wuana

& Okieimen 2011; Jacob et al. 2018). The rhizosphere also harbours microbes which beneficially degrade and detoxify toxic substances (Doty 2008). However, as the method is based on plants for decontamination, it is time consuming, taking several growing seasons to clean up a contaminated site. The method may also be dependent on species, season and on the plant age, with young plant roots displaying greater absorption capacity compared to older plants (Tangahu et al. 2011, Song et al. 2019). Also, contaminants present beyond the reach of plant roots cannot be eradicated using this method (Doran 2009). Another limiting factor is the inhibition of plant growth by high concentration of contaminants (Tangahu et al. 2011). Also, there are chances of contamination through the food chain as animals may feed on plants which have accumulated toxic compounds. Other advantages and limitations of phytoremediation have been discussed elaborately previously (Majumder & Jha 2012).

4. How do plants defend themselves from HMs?

Plants have the capability to accumulate and excrete HMs (Kordrostami et al. 2019). According to Edelstein & Ben-Hur (2018) there are basically three groups of plants depending on how they grow in soils contaminated by HMs - (a) plant species preventing the entry of HMs in their aerial parts; (b) species where metals are accumulated in the aerial parts and returned back to the soil; and (c) species concentrating HMs in their aerial parts at concentrations much higher than that in the soil. Due to the presence of well-organized metal transfer systems, plants can absorb metals from the soil and transfer and store them in their aerial parts, as indicated by the higher levels of metals found in the shoots as compared to the roots (Kordrostami & Mafakheri 2021).

A series of complicated processes such as mobilization of HMs, uptake by roots, xylem loading, transport from root to shoot, cellular compartmentation and sequestration etc. are involved in the accumulation of HMs in plant tissues (Yan et al. 2020). Mostly present in the insoluble form in the soil, which plants cannot absorb, HMs are made bioavailable to the plants through the release of root exudates by plants which alter the pH of the rhizosphere, thus increasing metal solubility (Dalvi & Bhalerao 2013). This metal enters the root cells, where the ions can form complexes with chelators like organic acids. These complexes are then immobilized either in the extracellular or intracellular spaces (Ali et al. 2013). The metal ions subsequently translocate to the shoots and are finally distributed in the leaves where these are sequestered either in cell walls or vacuoles (Tong et al. 2004). Different types of complexing agents and metal ion transporters are involved in the uptake and translocation of HMs in plants (Yan et al. 2020).

To implement phytoremediation successfully, detoxification of HMs is essential (Thakur et al. 2016). Plants adopt two defence strategies, i.e., avoidance and tolerance, to cope up with the toxicity of HMs accumulated in the plant body (Hall 2002). Avoidance, considered the first line of defence, is a strategy through which plants can control the uptake of HMs and can restrict the movement within the plant body (Dalvi & Bhalerao 2013). The second strategy is

tolerance, considered the second line of defence. It is carried out through various mechanisms such as inactivation, chelation and compartmentalization of heavy metal ions (Dalvi & Bhalerao 2013). Also, the anti-oxidative defence system of plants plays an important role in response to heavy metal stress (Yan et al. 2020).

5. A brief idea about plant *in vitro* culture:

Plant *in vitro* culture or plant tissue culture (PTC) is a technique of aseptic culture of cells, tissues, organs and their component parts under defined physical and chemical conditions *in vitro* (Street 1977). Theoretically, a plant body can be cut into small parts known as 'explants' and under appropriate conditions, each of these explants can develop into a whole new plant. The two main aspects of the concept, first developed by Austrian botanist Professor Gottlieb Haberlandt, are *in vitro* proliferation of a single plant cell and development of a new plant from the proliferated tissue. In fact, each cell of the plant body has the capability to give rise to a new plant (cellular totipotency).

In vitro culture of plant parts requires some basic prerequisites, of which, an aseptic or sterile environment for the cultivation process is of primary importance, as the technique of PTC aims at fast production of pathogen-free plants. Being nutrient rich, PTC media support the growth of bacteria and fungi which outgrow the cultured plant tissue, ultimately destroying the culture. Also, the toxic wastes produced by these microorganisms inhibit the growth and development of plant cells and tissues. Sterilisation of explants, glasswares, plasticwares, instruments, nutrient media, transfer areas and culture rooms are therefore important in PTC practices and is carried out using various methods suitable for the purpose. The second prerequisite is a culture medium containing the nutritional components (macro- and microsalts, vitamins, carbon source, organic nitrogen) indispensable for the growth, development and maintenance of the cultured cells, tissues or organs. Different types of PTC media are in use. Various kinds of plant growth regulators (PGRs) are often added to the culture media to obtain the desirable results. Physical factors like photoperiod, temperature, relative humidity are also tightly controlled for the proper growth, development and maintenance of the cultured tissue. The success of any PTC protocol depends on the proper coordination of all these factors and on the type of explant selected, age, physiological condition of the donor plant etc.

As defined, PTC refers to the *in vitro* culture of either whole plants or any plant part (viz. organs, seeds, embryos, anthers, single cells which may be dedifferentiated, protoplasts etc.). Accordingly, there can be various types of cultures such as seed culture, embryo and endosperm culture, meristem culture (culture of shoot apical meristems), anther and pollen culture, protoplast culture (culture of cells without cell walls), culture of differentiated organs like roots, shoots, buds etc. Another interesting form of PTC is the culture of clumps of disorganized, undifferentiated cell masses called 'callus', formed when mature plant cells revert to a meristematic state by dedifferentiation. Callus cells can be totipotent, capable of

regenerating complete plants or can differentiate organs like roots, shoots or embryos by redifferentiation. Theoretically, any kind of living plant tissue can be transformed to callus masses depending upon the origin and physiological state of the explant, the genotype of the donor plant, the environmental condition in which the donor plant is cultivated and a balance between two PGRs – auxin and cytokinin. Apart from other applications, callus cultures are important sources of a wide variety of economically important phytochemicals (review by Halder et al. 2021). Single cell populations, small groups of cells and larger aggregates of cells are often grown in a liquid medium under agitation and aeration. Such cell suspension cultures are most commonly initiated from friable callus masses and also from cells isolated from plant materials through mechanical or enzymatic methods.

Yet another very interesting form of culture is that of the ‘hairy roots’. In higher plants, the hairy root syndrome is characterized distinctly by the development of adventitious roots with profuse root hairs at or next to the site of infection by a soil borne bacterium known as *Agrobacterium rhizogenes* (Sevon & Oksman-Caldentey 2002). Following infection of wound sites in plants by *A. rhizogenes*, certain genes (the transferred DNA or T-DNA genes) are transferred from the bacterium to the plant, which get stably integrated in the plant genome and are expressed, resulting in the development of the hairy root phenotype. These roots are highly branched, plagiotropic, capable of rapid growth on phytohormone free culture medium, remain genetically and biochemically stable over extended periods (Sevon & Oksman-Caldentey 2002). Often referred to as ‘phytochemical factories’, these roots can biosynthesize higher or analogous amounts of compounds which are naturally produced by the roots of the mother plant (Lorence et al. 2004). Presently, hairy roots are being used for producing economically important plant secondary metabolites, for expressing genes for the production of foreign proteins to be used for therapeutic purpose (antibodies, vaccines, cytokines), enzymes, molecular farming, elucidation of biosynthetic pathways, phytoremediation research as well as for the biotransformation of exogenous substrates (Häkkinen 2014, Gharari et al. 2020, Perotti et al. 2020).

6. The role of plant *in vitro* cultures in phytoremediation studies

The technique of plant tissue culture has emerged as a useful tool for phytoremediation research. In contrast to field grown plants, which have a limited lifespan, plant *in vitro* cultures can be propagated indefinitely, free from seasonal and geographic barriers and are easily available on demand (Doran 2009). Thus, the time required for any experimental investigation is considerably reduced. *In vitro* culture has been used as model plant systems to study plant cell responses to toxic compounds, the metabolic processes involved in their degradation and the end products formed (Majumder and Jha 2012). As tissue cultured plants are grown under aseptic conditions in the laboratory, free of any pathogens, responses of plant cells can be easily distinguished from the responses of microorganisms residing within the plant body or in the rhizosphere (Van Aken & Schnoor 2002). Also, since callus and plant cells in suspension lack various barriers (viz. leaf wax, bark, cuticle, epidermis etc.) which

otherwise regulate the penetration of compounds in whole plants, *in vitro* culture can result in greater and uniform uptake of compounds than whole plants (Lucero et al. 1999). Plant tissue culture has emerged as an excellent approach for studying the responses of plants to contaminants without the interference of other factors. Studies can be carried out under controlled conditions which are not possible for field grown plants (Doran 2009). Large quantities of contaminants can be fed to *in vitro* cultures otherwise unavailable from the soil, allowing the recovery of amounts of metabolites suitable for analytical studies for further research (Laurent et al. 2007). Isolation of the products of reaction and purification of such products are easier in cultured cells compared to whole plants due to the presence of less amounts of starch, chlorophyll and other pigments in cultured plant cells (Schmidt 2001). Also, plant tissue culture represents a vital technology for the incorporation of foreign genes into plants for the development of transgenic plants with improved phytoremediation capabilities. Being organized structures, hairy roots are analogous in structure and property to the organs in whole plants, thus offering clear ideas about the biological behaviour of roots in nature (Doran 2009). Other advantages and disadvantages of plant *in vitro* cultures in phytoremediation research have been discussed in details in the previous review (Majumder and Jha 2012). Few examples of plant *in vitro* cultures employed successfully for the accumulation of heavy metals are tabulated below (Table 1).

7. Conclusion

HMs are environmental pollutants having serious impacts on the wellbeing of living organisms including human beings. Phytoremediation is a cost-effective, environment-friendly approach which utilizes plants to remediate environmental contaminants through diverse mechanisms such as phytoextraction, phytostabilization, rhizofiltration, phytovolatilization, phytodesalination, phytofiltration etc. The present review highlights how plant *in vitro* cultures play a crucial role in phytoremediation research, particularly for the accumulation of heavy metal contaminants. These *in vitro* cultures act as supplementary model systems, providing a better understanding of the consequences of contaminants inside the plant body; the information obtained thereof can be used for field plant trials.

Table 1: Heavy metal accumulating *in vitro* cultures of some selected plant species

Plant species	Family	Type of culture used	HM accumulated	Reference
<i>Solanum nigrum</i> L.	Solanaceae	Hairy roots	Zn Cd	Subroto et al. 2007 Ye et al. 2020
<i>Ailanthus altissima</i> (Mill.) Swingle	Simaroubaceae	<i>In vitro</i> grown shoots	Cu, Zn, Mn	Gatti 2008
<i>Alyssum murale</i> M. Bieb.	Brassicaceae	Hairy roots	Ni	Vinterhalter et al. 2008
<i>Armoracia rusticana</i> G. Gaertn.	Brassicaceae	Hairy roots	U (uranium)	Soudek et al. 2011
<i>Brassica juncea</i> (L.) Czern.	Brassicaceae	Hairy roots	Zn, Ni	Ismail & Theodor 2012
<i>Prosopis laevigata</i> (Humb. & Bonpl. Ex Willd.) M.C. Johnst.	Fabaceae	Cell suspension	Pb	Maldonado-Magaña et al. 2013
<i>Nicotiana tabacum</i> L.	Solanaceae	Hairy roots	As	Talano et al. 2014
<i>Alyssum bertolonii</i> Desv.	Brassicaceae	Hairy roots	Ni	Ibañez et al. 2016
<i>Hyptis capitata</i> Jacq.	Lamiaceae	Hairy roots	Cu	Malik et al. 2016
<i>Bacopa monnieri</i> (L.) Wettst.	Plantaginaceae	<i>In vitro</i> cultures	Cr, Cd	Jauhari et al. 2017
<i>Limnocharis flava</i> (L.) Buchenau.	Alismataceae	Callus	Pb, Mn, Cd, Fe	Wardani et al. 2017
<i>Dittrichia viscosa</i> (L.) Greuter	Asteraceae	Micropropagated plantlets	As	Guarino et al. 2018
<i>Lemna minuta</i> Raf.	Araceae	Hairy roots	Cr	Paisio et al. 2018
<i>Brassica oleracea</i> L.	Brassicaceae	Callus	Pb	Sadeghi et al. 2019
<i>Lantana camara</i> L.	Verbenaceae	Callus	Cr, Pb, Cd	Tahtamouni et al. 2020
<i>Brassica napus</i> L.	Brassicaceae	Hairy roots	Cr	Perotti et al. 2020
<i>Verbascum phrygium</i> Bornm.	Scrophulariaceae	<i>In vitro</i> germinated seedlings	Zn	Akin 2021
<i>Armeria maritima</i> Girard ex Boiss.	Plumbaginaceae	<i>In vitro</i> multiplied shoots	Cd, Mn, Pb, Zn	Purmale et al. 2022

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Clay-based cleaners and disinfectants: A back to basic approach for cleanliness and sanitisation

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Abstract: *With the widespread dispersal of pathogens, toxins and all sorts of harmful chemicals throughout the globe, the demand for suitable cleaners, hand sanitisers and surface disinfectants are increasing day by day. Most of the conventional sanitisers are alkali-based, like the soap cakes, liquid soaps, and detergents; or alcohol-based liquids, gels, or sprays. The recent pandemic situation led to an unprecedented rise in the production and use (as well as overuse) of such disinfectants. But all of them have certain detrimental effects on human health and also on the environment.*

Since reducing the use of disinfectants is not possible in the present scenario, the only solution is to find out a better alternative that can effectively clean a surface without causing any harm. The natural clays, owing to their unique physical and chemical properties, can remove from a surface a wide variety of viruses, bacteria, grease and dirt. In some cases, clay minerals assist in the bactericidal actions of cations like Fe^{2+} , Cu^{+} etc. In contrast to the alcohols and alkalis, the clays don't have any significant detrimental effect on human health – instead of damaging the skin, the clay-based disinfectants may contribute to skin nourishment. Furthermore, clays are readily available everywhere, and their purification processes are also simple and less expensive. This makes them suitable for large-scale production of low-cost skin sanitisers and surface disinfectants, thus helping the developing economies to meet the challenges of the ever-increasing demands for these products.

This contribution explains the correlation between the internal structures, chemical compositions and properties of clay minerals that make them suitable as cleaners and disinfectants, and discusses the present situation and future prospects of the clay-based sanitisers.

Keywords: clays, clay minerals, hand sanitisers, disinfectants, cation exchange capacity, adsorption

1. Introduction

Clays occur in almost all the inhabitable places on Earth, and primarily form by weathering of rocks. Their easy availability and a number of unique properties facilitate their application as one of the earliest materials to be used by the human civilisation: even the most primitive cultures utilised it for different purposes. The applications of clays have always been many and varied, ranging from pottery, masonry, production of tools and equipment, medicines for topical and oral uses etc. Among all these, the application of clays as cleaners and disinfectants are of utmost importance – very few natural substances can match the clays in this field. It is one of earliest cleaning agents to be used by man, and was possibly the most widely used one until the large-scale industrial production of alkali-based soaps in 19th – 20th Centuries. The use of alcohol-based sanitisers started much later and was initially restricted

among the medical professionals. It is only during the recent global pandemics of 21st Century that the use of alcohol-based sprays and hand-rubs greatly increased, though their relatively higher prices make them less popular than the alkali-based cleaners among the masses.

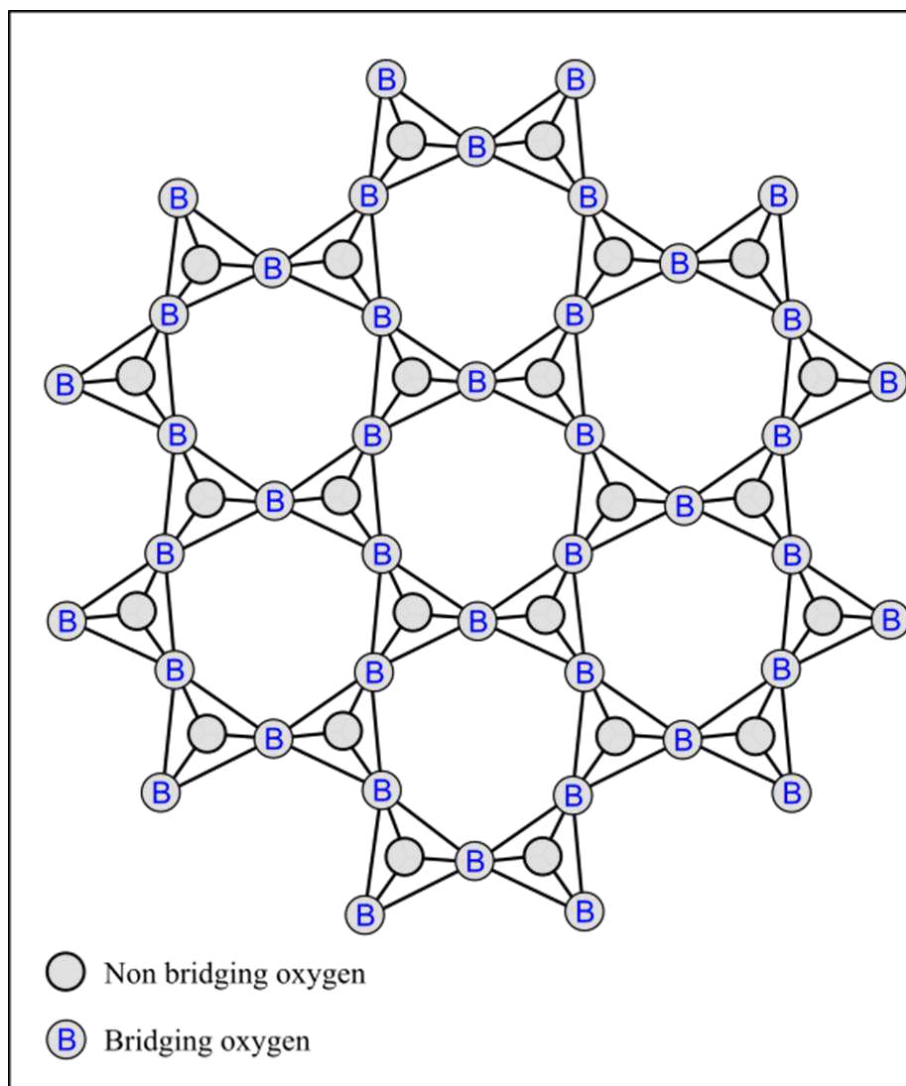
However, the conventional sanitisers, both the alkali-based and the alcohol-based ones, have certain detrimental effects on human health and also on the environment (see Chapter 6, Section 6.2 of Ghosh & Chakraborty 2022 for a comprehensive explanation). Moreover, some sections of the masses may not afford these sanitisers in sufficient quantities, especially in the developing countries. This contribution suggests a ‘back-to-basic approach’ for sanitisation that involves manufacture of more effective but less expensive disinfectants from clays. Meeting the requirements of an interdisciplinary volume, a brief description of clays, clay minerals and clay derivatives are given in Section 1, which may help the readers of different disciplines to understand the subsequent sections. Sections 3 and 4 explain the mechanisms of the protective actions of clay minerals against viruses and bacteria respectively. Production of different types of clay-based disinfectants have been described in Section 5. The advantages of the clay-based sanitisers over the other commonly used sanitisers, and their future prospects are discussed in Section 6. Finally, the article has been concluded with some recommendations for the future.

2. A brief overview of clays, clay minerals and their properties

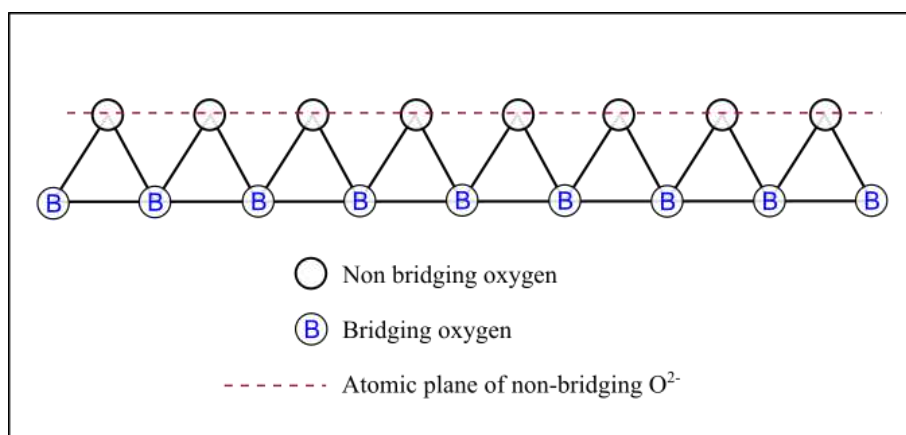
2.1. What the clays actually are

The term **clay** refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim & Martin 1995, 1996). Kaolin, china clay, bentonite, bleaching earth, ball clay, fire clay, refractory clay etc. are the common types of clay that satisfy the above definition.

The essential constituents of clays are the clay minerals, associated minerals, and some non-mineral matters or associated phases. The **clay minerals** are a number of mineral species belonging to the phyllosilicate subclass of silicate class, which impart plasticity to clays, and harden upon drying or firing (Guggenheim & Martin 1996). The clay minerals are therefore responsible for the distinctive physical properties of the clays. It is important to note that all the phyllosilicate minerals present in clay are not clay minerals. The **associated minerals** are the minerals generally present in a natural clay that are not plastic when wet and do not harden by drying or firing. They include some phyllosilicates (like talc, muscovite, chlorite etc.), other silicates (such as quartz and feldspars), and minerals of other classes (like corundum, gibbsite, boehmite, diaspore, magnetite, hematite, etc.). The **associated phases** are the amorphous constituent of clay, like allophone, imogolite, particles of peat, humus etc. A detailed discussion on clays and their constituents is given in Ghosh (2013).



[A]



[B]

Figure 1: A. Schematic diagram showing the arrangement of SiO₄ tetrahedra in clay minerals, in **apical view (plan view)** where the observer faces the non-bridging apical oxygen of each tetrahedron. It may be noted that there are three bridging oxygens in each tetrahedron, thus forming a layered

structure. All the minerals of phyllosilicate subclass have the same internal arrangement of tetrahedra. Not to scale.

B. Schematic diagram showing the arrangement of SiO_4 tetrahedra in clay minerals, in side view (elevation). All the minerals of phyllosilicate subclass have the same arrangement. It may be noted that all the non-bridging oxygens are facing the same direction. Not to scale.

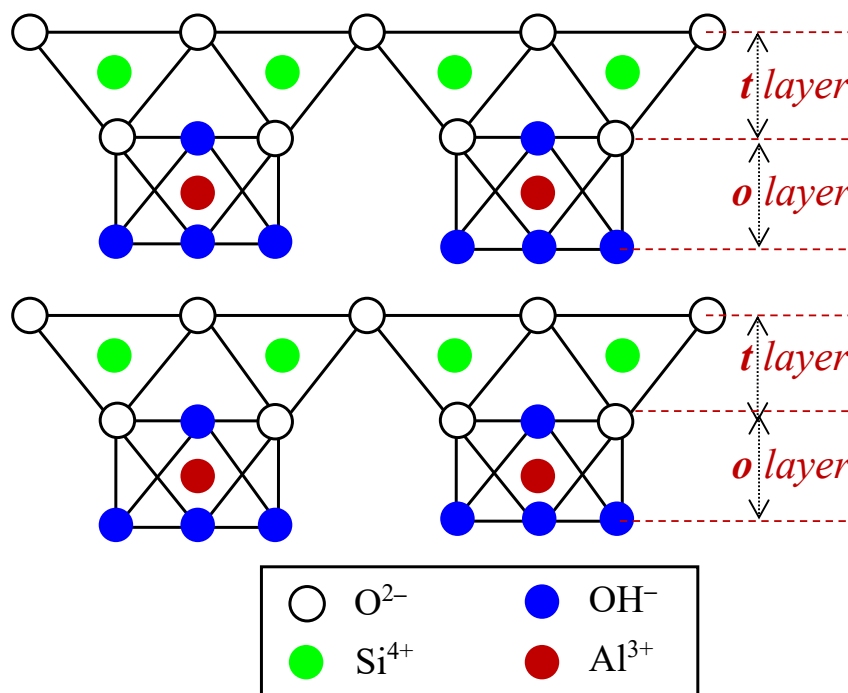
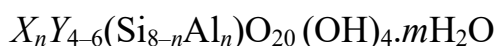


Figure 2: Schematic side view of clay minerals with $t - o$ structures, showing the internal arrangement of anions and cations in the tetrahedral and octahedral layers in side view. Minerals of kaolinite group have this structure. Not to scale.

2.2. The composition and structure of clay minerals

The clay minerals, like all other minerals, are essentially natural, inorganic solids. Each of them has a definite composition and a fixed, distinctive internal structure. They belong to the phyllosilicate subclass in the silicate class, and are categorized into six groups based on their compositions and structures: kaolinite, illite, smectite, vermiculite, palygorskite-sepiolite, and mixed layer clays. All of them consist of the anionic group $[\text{SiO}_4]^{4-}$ where one Si^{4+} is surrounded by four O^{2-} , to form a $[\text{SiO}_4]^{4-}$ tetrahedron. The general chemical composition of all the clay mineral groups can be expressed with the following structural formula. One formula unit comprises eight $[\text{SiO}_4]^{4-}$ tetrahedra.



X = K, Na or Ca at 12-fold coordination sites.

Y = Al, Mg, or Fe at octahedral coordination sites.

n = number of Si^{4+} substituted by Al^{3+} in each formula unit of eight tetrahedral coordination sites. $n = 0$ in the clay mineral species with no substitution of Si^{4+} by Al^{3+} at the tetrahedral site.

m = number of H₂O molecules in each formula unit of eight tetrahedral coordination sites. In some clay mineral species, there is no H₂O molecule; i.e., $m = 0$.

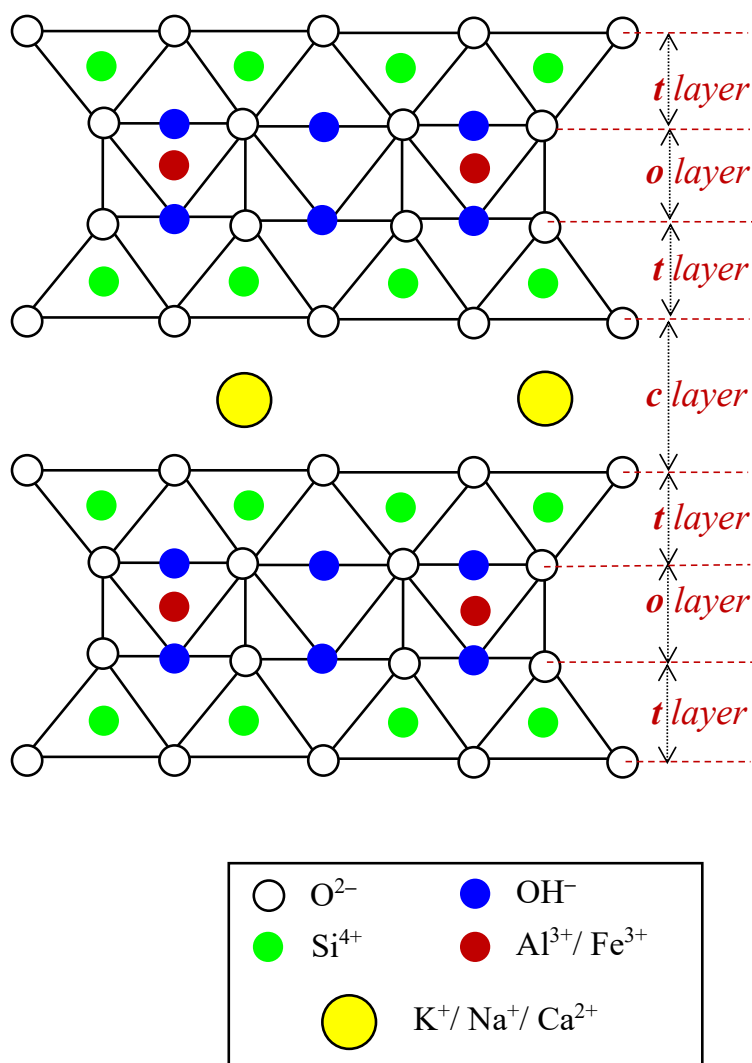


Figure 3: Schematic side view of clay minerals with **dioctahedral** $t-o-t-c$ structures in side view, showing the array of anions and cations in the tetrahedral and octahedral layers. $2/3^{\text{rd}}$ of the octahedral sites in each $t-o$ layers are filled up with trivalent cations, and the remaining $1/3^{\text{rd}}$ are vacant. Not to scale.

It may be noted that if $n = 0$, then $X = 0$, i.e., no cation at 12-fold coordination sites. Talc has this composition: $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$. The mica group minerals, on the other hand, have substitution in their tetrahedral sites and consequent inclusion of monovalent cations (e.g., muscovite and biotite) or divalent cations (e.g., margarite). Both compositional types are found among the clay minerals.

All the minerals of phyllosilicate subclass, including those belonging to the six clay mineral groups, have a **layered structure**; i.e., each tetrahedron is connected to three other tetrahedra by sharing three apical O²⁻, thus forming a continuous layer of $[\text{SiO}_4]^{4-}$ tetrahedra or t -layer (Figures 1A, 1B). Each tetrahedron in the t -layer thus comprises three **bridging O²⁻**, which

connect it to three other adjacent tetrahedra; and one **non-bridging** O^{2-} , which is not shared with another tetrahedron. All the non-bridging O^{2-} are on the same side of the t -layer of a phyllosilicate mineral, thus forming a continuous atomic plane of non-bridging O^{2-} in the t -layer (Figure 1B).

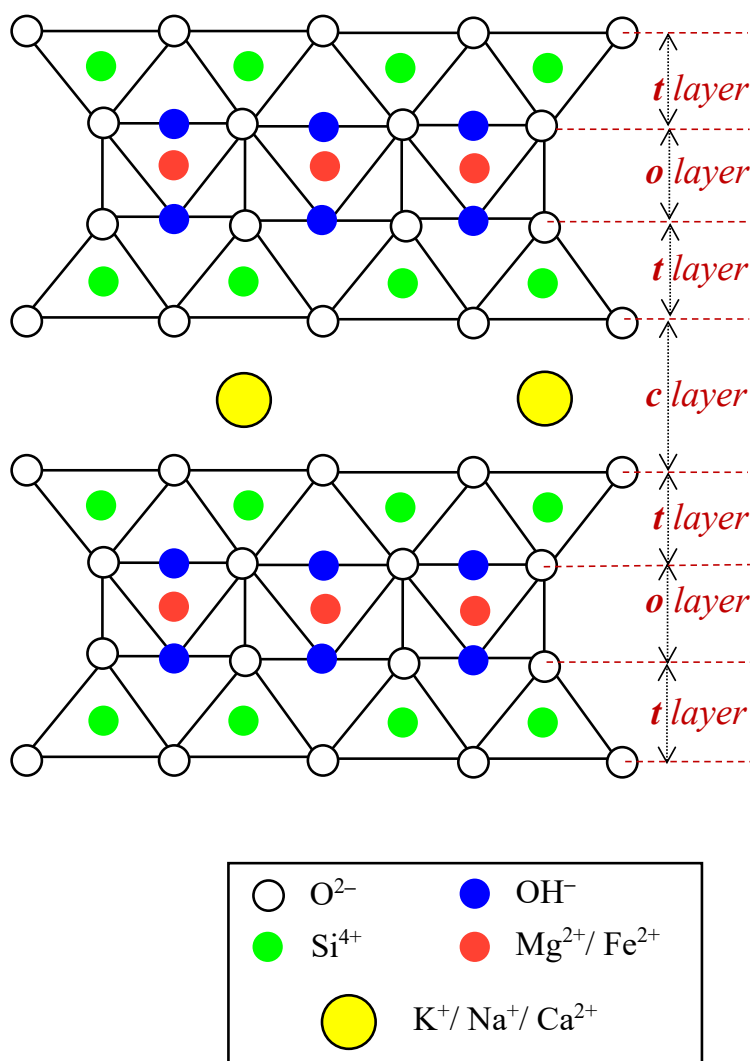


Figure 4: Schematic side view of clay minerals with **trioctahedral** $t-o-t-c$ structures, showing the array of anions and cations in the tetrahedral and octahedral layers in side view. All of the octahedral sites in each $t-o$ layer are filled up with divalent cations, and site is vacant. Not to scale.

The non-bridging O^{2-} and the hydroxyl groups in a t -layer are coordinated with bivalent or trivalent cations (commonly Mg^{2+} , Fe^{2+} , Al^{3+} etc.) in octahedral coordination sites. Those octahedra form a continuous layer of octahedra or o -layer parallel to the t -layer.

The minerals of kaolinite group have one t -layer connected to one parallel o -layer, forming a structural unit comprising $t-o$ layers (Figure 2) that are bonded together by weak van der Waals force.

In the minerals of illite, smectite, and vermiculite groups, there are two parallel *t*-layers with one *o*-layer in between them. In most of these minerals, a number of tetrahedral Si^{4+} are substituted by Al^{3+} , resulting in a charge imbalance. The excess negative charge is balanced by inclusion of monovalent or bivalent cations in between two *t* – *o* – *t* layers, thus forming a *t* – *o* – *t* – *c* structure where *c* represents the **interlayer cations**. If the octahedral cations are trivalent like Al^{3+} , then two-third of the octahedral sites in the *o*-layers are filled up and one-third are vacant. Such clay minerals are called **di-octahedral** (Figure 3). In contrast, the **tri-octahedral** minerals (Figure 4) have their octahedral sites occupied by divalent cations like Mg^{2+} or Fe^{2+} , thus all the octahedral sites are filled up.

In the clay minerals of palygorskite-sepiolite group, the cation-centred octahedra are linked together in linear array to form long chains. These octahedral chains, with much vacant spaces in between them, are connected to the *t*-layers.

2.3. Properties of clay minerals that are important in their anti-pathogenic actions

In most cases, the clay minerals disinfect a surface by removal of viruses and bacteria from that surface through adsorption (see Section 3 and 4.1). Adsorption is a process in which a gas, liquid, or solid (an adsorbate) is held on the surface of a solid adsorbent (after Skoog et al. 2014). The unique internal structures and chemical compositions of the clay minerals enable them to adsorb a wide range of metal ions, organic molecules, and microbes. The capacity of a clay mineral to adsorb a certain substance depends largely on the following factors (Ghosh & Chakraborty 2022, Chapter 1, Sections 1.5, 1.6, 1.7 and the references therein).

- (i) **Specific surface area:** The total surface area of a solid per unit mass is its specific surface area (SI unit: m^2 / kg), which depends largely on its shape. A thin, flat particle (having length \approx breadth \gg thickness) has much greater specific surface area than an equidimensional particle (having length \approx breadth \approx thickness) of the same material.

The clay minerals have a layered internal structure, with very weak bond between two successive *t* – *o* – *t* layers. As a result, they can break very easily along the interlayer spaces (i.e., in between two *t* – *o* – *t* layers), forming very thin grains known as **clay flakes** with very high specific surface area. This provides greater surface area for adsorption per unit mass, thus enhancing their adsorption capacity.

- (ii) **Cation exchange capacity (CEC):** In the clay minerals of illite, smectite and vermiculite groups, some of the tetrahedral Si^{4+} are substituted by Al^{3+} . Some octahedral cations may also be substituted by other cations of lower charge. These substitutions produce a net negative charge on their *t*–*o*–*t* layers, which is balanced by the interlayer cations like K^+ , Ca^{2+} , Na^+ , and Mg^{2+} . But these cations are easily are

replaced by the heavy metals, like Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} etc., when the clay flakes are in contact with a liquid containing these cations. This phenomenon is known as **cation exchange** between the clay minerals and the surrounding liquid, and the **cation exchange capacity** (CEC) of a clay mineral is the number of moles of positive charge it can absorb per unit mass (after Raymond & Brady 2016). Its SI unit is Milli equivalents per 100 grams (meq/100 g).

- (iii) **Surface roughness of clay particles and size of the adsorbates:** A smooth adsorbent surface provides nearly equal area for the adsorption of small and large adsorbate particles. But on an uneven adsorbent surface, the smaller particles will have greater area for adsorption. The viruses and the smaller bacteria are therefore readily adsorbed by clay flakes.

The larger bacteria may not be removed by adsorption, but some of them are destroyed by the clay-induced bactericidal processes (see Section 4.2).

3. Protective actions of clays against viruses: Virus adsorption and removal

The clay minerals cannot destroy the viruses – they can only remove the viruses from a surface through adsorption and flocculation (Carlson et al. 1968).

In the mineral world, the clay minerals have the distinctive ability of adsorbing a wide range of microorganisms, metals, and organic molecules, which largely facilitate their application as cleaners and disinfectants. The process of adsorption involves the adhesion of particles to the surface of a solid. As the size of the viruses are very small, they are readily adsorbed by clay flakes in an aqueous medium.

But many viruses do not lose their abilities of infection and causing harm to human health even when they are adsorbed on the clay surfaces. It is therefore essential to remove the adsorbed viruses from the system. The clay particles suspended in an aqueous system, in presence of electrolytes, have the tendency to form **coagulates** or **flocs**. The floc, being heavier than water, settles at the bottom of that aqueous system, and can thus be removed easily by decantation or filtration.

The protective action of clays against the viruses therefore depends largely on processes of adsorption and flocculation (coagulation), which are briefly explained in this section.

3.1 The mechanism and controlling factors of virus adsorption on clay surface

The virus adsorption on clay is favoured by the cation concentration in the system. Other factors remaining same, the virus removal from a system increases with the total concentration of cations. But different types of cations are not equally effective. In a given experimental condition (Carlson et al. 1968), the virus removal capacities of kaolinite,

montmorillonite and illite were found to be greatest in presence of Na^+ (99%), less with Al^{3+} (98%), and still less with Ca^{2+} (89% to 96%). It has been inferred that the viruses are attached to the clay surfaces by formation of a **clay-cation-virus bridge**. Just as a bridge connects two separate landmasses, the cations connect the viruses the surfaces of a clay particle.

The major controlling factors of the virus adsorption mechanism of clay minerals are described below.

- (i) **Cation Exchange Capacity:** The CEC of the clay mineral is an important controlling factor – those having higher CEC were reported to show greater capacity of virus removal from a solution. The ability of montmorillonite to adsorb greater quantity of virus than kaolinite in an experiment was attributed to the higher CEC of montmorillonite (Lipson & Stotzky 1983).
- (ii) **Nature of interlayer cations:** The natural clay minerals are generally heteroionic, i.e., they contain different types of cations in their interlayer spaces. **Homoionic** clays, having only one type of interlayer cation, are prepared to compare the virus adsorption capacities of different cations, e.g., homoionic Na^+ kaolinite. Comparing different types of homoionic kaolinites having Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Al^{3+} , the following sequence was established in order of decreasing adsorption of virus (Lipson & Stotzky 1983, Sykes & Williams 1978):
$$\text{Na}^+ > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+.$$
- (iii) **Van der Waals bond and hydrogen bond:** Some workers suggested that the attraction causing the aggregation of clay and virus was the combined effects of weaker interactions (van der Waals bonding and H- bonding) than the strong electrostatic forces (Greenland et al. 1965, Stotzky 1980, Lipson & Stotzky 1983, Block et al. 2016).
- (iv) **Other possible factors:** Electrophoretic mobility of the clay particles, and the zeta potential of the clay minerals in a solution are the other factors that may affect virus adsorption on clays (Carlson et al. 1968). Certain organic molecules like proteins, if present in the system, impeded the virus adsorption. These proteins possibly occupied some adsorption sites on the clay surfaces, thus reducing the number of adsorption sites available for the viruses.

The adsorbed viruses are strongly attached to the surface of clay, and are not easily separated. Transmission electron microscopy studies revealed that the bonds that link the viruses to the clay cause some shape distortion of the viruses – they become flattened with increased surface area at their contacts with clay (Block et al. 2016). This increased contact surface may further strengthen the bonding between them.

Though the shapes of the adsorbed viruses may change, their internal structures generally remain intact. The viruses are therefore still infectious after adsorption, and must be removed from a surface for disinfecting it. This can be done by the following two ways.

- (i) A semisolid mixture of clay and water, like a clay pack or clay poultice, may be rubbed on a surface or left on it for some time to adsorb the viruses from it. Then the mixture is

to be washed with clean water, to remove the clay along with the viruses. This process was prevalent in many parts of the world for hand sanitisation, disinfecting utensils, kitchenware etc. before the large-scale industrial production of soaps, and is still practised in some rural areas of our country.

- (ii) An aquatic system may be cleared of viruses by adding clay particles in sufficient quantity. These particles remain suspended in water for certain time, then form flocs, and settle slowly at the bottom. The viruses entrapped on the surfaces of the clay particles in that floc can be removed from the system by decantation or filtration.

The viruses are so small that they cannot be separated from a liquid medium with the finest bacteria filter. They can remain suspended in a liquid for such a long time that it is not practicable to separate them by decantation as well. But those adsorbed on the surfaces of clay particles in a floc can be separated easily by both methods. The process of flocculation has been described in the next subsection.

3.2 Removal of the viruses through flocculation

Flocculation (agglomeration or coagulation) is the process by which particles suspended in a liquid adhere to one another, to form a large cluster of particles. In many cases, the clay particles have a **net negative charge** on their surface. Cations, if present in the solution, are electrostatically attracted by the clay particles. These cations may create a positively charged layer on the clay surface, and hold together two or more clay particles like a bridge. In the presence of these cations, the clay particles thus connect together to produce the flocs (after Chibowski 2011).

The cations with higher valences have greater flocculation powers, e.g., Al^{3+} , Ca^{2+} , and Na^{+} have successively less flocculation powers. Also, increase of cation concentration in a system brings about faster flocculation.

Some laboratory investigations indicate that virus adsorption on the clay particles takes place first, and the flocculation of the particles occurs later. There is no significant amount of virus entrapment during or after the flocculation (Schaub and Sagik 1975, Lipson and Stotzky 1983).

4. The protective actions of clays against bacterial infections

The clays can remove several types of bacteria from a system by adsorption. They also assist in the bactericidal actions of some metals, which destroy some bacteria species in a series of chemical reactions. These two protective actions of clays are described briefly here.

4.1. Removal of bacteria from a surface by adsorption

Some types of bacteria, especially the relatively smaller forms, can adhere to the surfaces of clay particles by **electrostatic attraction** to form biofilms (Calvaruso et al. 2006, Freebairn et al. 2013). The edges of the ultrathin clay particles are generally positively charged, while the surfaces of some bacteria are negatively-charged. Such bacteria are linked to the positively-charged edges of the clay minerals by electrostatic attraction. In case of kaolinite, bacteria are largely attached along the positively charged edges of the octahedral sheets and tetrahedral sheets. In addition to the edges, the basal surfaces of a few clay minerals contain a feeble positive charge, which may also contribute in the adsorption of some bacteria to a lesser extent (Wu et al. 2011, Kang et al. 2013, Tuson & Weibel 2013, Cygan & Tazaki 2014, Wu et al. 2014, Huang et al. 2015).

Another possible mechanism may be the formation of a **clay-cation-bacteria bridge**, connecting the negatively charged bacteria cells to the clay surfaces by the interlayer cations like Na^+ , Ca^{2+} , etc. (Perdrial et al. 2009, Warr et al. 2009), similar to the clay-cation-virus bridge (see Section 3).

Some workers have suggested a few other factors that possibly contribute to the adsorption of bacteria on clay surfaces, such as the **hydrophobic attraction** (van Oss 2008, Poorni & Natarajan 2013), the **Lewis acid-base interaction** (Sharma & Hanumantha 2003, Bayoudh et al. 2009), and the **combined effects of van der Waals forces and electrical double layer forces** (Kim et al. 2010). The definitions and brief explanations of these factors are given in Section 2.2.2 of Ghosh & Chakraborty (2022).

The adsorption of bacteria on clay surfaces is largely controlled by the ionic concentrations and pH of the system; and the surface properties of bacteria like their protein covers, extracellular polymeric surface covers, hydrophobicity, and charge characteristics (Hong et al. 2012).

The electrostatic attraction between bacteria surfaces and clay particles decreases in mildly to strongly alkaline condition, and is highly favoured in acidic condition (Hong & Brown 2006, Castro & Tufenkji 2007, Jia et al. 2011, Cai et al. 2013, Hong et al. 2014, Zhang et al. 2015). At low level of ionic concentration ($<0.01 \text{ mole L}^{-1}$ of MgCl_2), the adsorption of certain bacteria forms on kaolinite and montmorillonite is found to increase when ionic strength increases. But bacterial attachment on clay surfaces decreased significantly when the salt concentration is higher than 0.01 mole L^{-1} (Hong et al. 2014).

Although the true mechanisms for adsorption of bacteria by clay minerals are yet to be fully understood, it is quite evident that if a surface is cleaned with a mixture of clay and water, some types of bacteria will adhere to the clay flakes and will be removed from that surface.

4.2. Bactericidal processes activated by clay minerals

Clays cannot destroy bacteria by themselves. But some types of clays, known as the **bactericidal clays**, enable the metal ions like Fe^{2+} to penetrate into certain bacteria and destroy them, through a series of chemical and biochemical reactions. It has been suggested that Cu^+ and Al^{3+} present in the bactericidal clays may also contribute in the destruction of bacteria. While copper has multiple toxic effects on bacteria cells, aluminium possibly killed them by impeding the inflow of cell nutrients and the outflow of wastes (Warnes et al. 2011, Williams et al. 2011).

Table 1. Some common bacteria species that can be destroyed by the bactericidal actions of clays, as reported by Haydel et al. (2008), Cunningham et al. (2010), Williams et al. (2011).

Bacteria Species	Diseases Caused
<i>Escherichia coli</i>	Enteric diseases
<i>Mycobacterium marinum</i>	Causes a tuberculosis-like illness in fish. Can infect humans when injured skin is exposed to a contaminated aqueous environment (Akram & Aboobakar 2022).
<i>Mycobacterium smegmatis</i>	A non-pathogenic bacteria used in scientific researches, though in some rare cases it is suspected of causing tuberculosis (Reyrat & Kahn 2001).
<i>Pseudomonas aeruginosa</i>	It is a multidrug-resistant bacteria that can cause pneumonia, septic shock, infections in urinary tract and gastro-intestinal tract etc. (UK Standards for Microbiology Investigations 2022, Diggle & Whiteley 2020).
<i>Salmonella enterica</i>	Salmonellosis, which is a food-borne disease causing diarrhea, fever, abdominal cramps, and vomiting.
<i>Serovar typhimurium</i>	It causes gastroenteritis in humans.
<i>Staphylococcus aureus</i>	Causes pulmonary infections (e.g., pneumonia and empyema), gastroenteritis, meningitis, toxic shock syndrome, urinary tract infections, skin and soft tissue infections such as carbuncles, cellulitis etc. (Tong et al. 2015). Multi-drug resistant strains developed from it (Taylor & Unakal 2022).
<i>Staphylococcus epidermidis</i>	Generally infects through healthcare-associated infections, entering the bloodstream during device insertions in patients. It accounts $\sim 1/5^{\text{th}}$ of bloodstream infections in ICU patients, and prosthetic valve endocarditis infections (Otto 2009).

The bactericidal actions of Fe^{2+} can destroy *Escherichia coli*, which is a major cause of enteric diseases in humans, along with a few other common bacteria listed in Table 1.

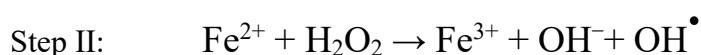
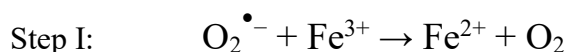
A comprehensive description of the bactericidal actions of Fe^{2+} is given in Ghosh & Chakraborty (2022), Section 2.2.1, p. 37 – 42. A brief outline is given here.

- (i) The bacteria cells contain enzymes that catalyse oxidation-reduction reactions. These redox enzymes may produce H_2O_2 and superoxide ion ($\text{O}_2^{\bullet -}$) inside the cells (Messner & Imlay 1999, 2002).

- (ii) The penetrated Fe^{2+} reacts readily with H_2O_2 , to produce Fe^{3+} , hydroxide (OH^-) and hydroxyl (OH^\bullet) radical, as described in the **Fenton reaction** (Fenton 1894).



- (iii) Inside the bacteria cells, Fe^{3+} can also synthesize OH^\bullet by reacting with the intracellular superoxide, as described in the **Haber – Weiss reaction** (Haber & Weiss 1934).



- (iv) The OH^\bullet thus produced can damage the bacterial DNA by reacting with the sugar and the base moieties, leading to sugar fragmentation, strand scission, and base adducts (Imlay and Linn 1986, Hagensee and Moses 1989, Park and Imlay 2003). This causes the destruction of the bacteria.



The exact role of clay in this process, however, is yet to be fully understood. They presumably assist in the bactericidal actions of Fe^{2+} in the following two ways.

- The iron-rich clays act as the sources of Fe^{2+} .
- Fe^{2+} is soluble in water and can penetrate into the bacteria cells only at a certain pH and oxidation state. The clay minerals, when present as suspension in water, act as a buffer to maintain the required pH and oxidation state.

These two roles of clay minerals are discussed in the next two subsections.

4.2.1 Clay as a source of Fe^{2+}

The bactericidal clays are more iron-rich than the other clays (Williams et al. 2008, 2011, Cunningham et al. 2010). Iron is present in the constituent clay minerals, associated minerals and associated phases of these clays, in fully reduced state (Fe^{2+}) or partially reduced state (mixture of Fe^{2+} and Fe^{3+}). Some of common iron-bearing constituents of bactericidal clays are listed in Table 2, which may release Fe^{2+} in a clay-water mixture and initiate the bactericidal process.

4.2.2 Clay minerals acting as buffers in the bactericidal reactions of metals

In a chemical system, a **buffer solution** resists changes in pH when it is diluted or when acids or bases are added to it (Skoog et al. 2014). A buffer also tends to resist the change of other chemical properties related to pH, like its oxidation–reduction potential (Eh), concentration of certain ions etc. When all these chemical factors are within a certain range, a system is favourable for some chemical, biochemical and geochemical reactions.

The bactericidal process of Fe^{2+} in a water-clay mixture involves the successive formation of a number of short-lived compounds in a series of chemical reactions. The pH and oxidation state of the reaction system are the two most important factors to make these reactions possible. Clay minerals present in the system act as the buffers to maintain the pH and Eh favourable for dissolution of Fe^{2+} and Cu^+ , and maintain the stability of these cations in the solution. Furthermore, the anaerobic condition created by the clay minerals is favourable for penetration of Fe^{2+} and other metals into the bacteria cells (Williams et al. 2011).

Table 2. Some common Fe^{2+} -rich constituents of clays, including clay minerals, associated minerals, and associated phases. (After Velde 1995, Chapter 2 and Bergaya et al. 2006, Chapter 1).

Mineral Species	Chemical Composition
Montmorillonite	$(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe})_4[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4.n\text{H}_2\text{O}$
Diocahedral vermiculite	$(\text{Ca}, \text{Na})_{0.6-0.9}(\text{Mg}, \text{Fe})_6[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4.m\text{H}_2\text{O}$
Illite[1]	$(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Fe}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2.\text{H}_2\text{O}$
Chamosite [2]	$(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{O})_8$
Biotite	$\text{K}(\text{Mg}, \text{Fe})_3(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$
Hornblende	$\text{Ca}_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$
Hematite	Fe_2O_3
Maghemite	Fe_2O_3
Goethite	FeOOH
Lepidocrocite	FeOOH
Pyrite	FeS_2

Mineral compositions:

[1] <http://webmineral.com/data/Illite.shtml>. (See Internet Resources No. 5).

[2] <http://webmineral.com/data/Chamosite.shtml>. (See Internet Resources No. 6).

5. Application of clays and their derivatives as sanitisers and surface disinfectants

Natural clays of various types have been used as hand sanitisers and cleaners long before the discovery of the microbes. The systematic study of the internal structures of minerals (including phyllosilicates) started in the early part of 20th Century, and the relation of the structure and composition of the clay minerals with their antimicrobial actions were studied much later than that. But since the onset of human civilisation, the common people learnt from their experiences that the natural clays have the unique property of cleaning surfaces from toxins, dirt and greases. The ancient medicine men and the medieval chemists also observed that the clays can heal infections and resist some diseases. In almost all the ancient cultures, clay is one of the ingredients of traditional medicines. In the present age, however, the scientific knowledge acquired about the clay minerals and their actions on the pathogens have facilitated the formulation of more effective disinfectants from the clays and their derivatives. This section gives a brief overview of the application of clays and clay-based formulations as hand washes (used with water), dry hand sanitisers and disinfectant hand gels (used without water), and surface disinfectants that can substitute detergents.

5.1 Natural and purified clays as hand wash

There is a common belief that soaps are better disinfectants than clays or other natural substances. But several surveys carried out on adults and children showed that post-defecation scrubbing of hands with soil, ash, and soap were equally effective in reducing the levels of faecal coliforms. Hoque & Briend (1991) carried out an empirical study in the slums of Dhaka, Bangladesh with a group of twenty volunteers, aged 18 to 35 years, for five consecutive days. The volunteers were divided into five groups. The members of three groups used soap, mud and ash for post-defaecation washing, the fourth group used plain water, and the fifth group, designated as the 'control group', did not wash their hands. An orange-yellow coloured mud of pH = 6.5, collected in those slums, was used in the study. It was sterilized by heating for 3 hours at 110 °C before handwashing, for removing any pre-existing pathogens. The fingertips of each volunteer were sampled for faecal coliform bacteria after each defecation. The result of this study showed that 60% (12 out of 20) of the samples collected from control group were contaminated, while soap, mud and ash reduced bacterial contamination to 20%. It proved that mud was equally effective as soap in reducing the coliform counts. For this reason, the workers suggested not to promote any expensive or less available washing agents whose superiority to traditionally used mud have not been established.

A number of subsequent surveys showed similar results. In Bangladesh, 32.1% of urban population and 55.5% of rural population were found to use soil or mud for post-defecation handwashing, but no significant difference was reported between them and the soap-users in terms of coliform infection (Hoque et al. 1995a, 1995b, 2003, Baker et al. 2014).

Bangladesh Demographic and Health Survey (2007) also suggested that clean and dried soil should be promoted for handwashing, because it can effectively resist many infectious and parasitic diseases. Citing the result of this survey, Bloomfield and Nath (2009) stated that a large population of Bangladesh belonging to the low-income group cannot afford soaps; and if washing hands with mud (and other traditional substances) is actively discouraged, that may deprive these people from any hand hygiene.

It is important to note here that in most of the above studies, natural soil or mud was used for washing hands. A standard sample of soil contains only 45% clays (clay minerals + other minerals + non-mineral substances), and the remaining 55% are organic matters, water and gases (see Ghosh 2013 and references therein for details). Clays in purified form are expected to be much more effective as hand sanitisers. Some commercial houses have claimed to produce bath soaps with kaolinite clay that can purify the skin and nourish it as well (Internet Resources No. 1).

Bentonite is a natural clay composed predominantly by montmorillonite. Das & Tadikonda (2020) suggested a technique for hand sanitisation using bentonite paste (a thick mixture of bentonite and water) to prevent the transmission of viruses and bacteria through dermal

contacts. When applied topically on hand or any other part of the body, the ultrathin montmorillonite flakes of this paste are expected to bind strongly to the pathogens, and remove them from the skin surface when the paste is washed with water.

5.2 Clay-based dry sanitisers and hand gels to prevent infection without causing skin desiccation

All types of hand washes are needed to be rinsed and wiped off after rubbing them on skin, therefore always require a sufficient supply of water, which restrict their use in certain situations. That also makes the process of hand sanitisation more time consuming, hence inconvenient for medical professionals who need frequent hand washes. The ‘dry’ sanitisers are preferred in such cases, which are applied on the hand and can be rubbed lightly until dry, without needing to be washed off the hand with water. Most of such dry sanitisers are alcohol-based, though some commercial houses claim manufacturing some clay-based formulations. One such product prepared by mixing natural green clay and eucalyptus oil has been claimed to eliminate 99.9% of common germs on rubbing gently on hand. It becomes dry and can be dusted off the hand without rinsing and washing (Internet Resources No. 2). Some mixtures prepared by infusion of essential oil and clay have been claimed to clear the skin and also hair (Internet Resources No. 3).

Disclaimer: The efficacy of the commercial products cited in this section, or their side effects (if any), have not been tested or verified in the present work.

Frequent use of hand washes and hand sanitisers makes the skin dry, which may lead to skin irritation and some types of skin diseases. The gel-based sanitisers keep the skin moisturised and protect it from drying. A clay-based sanitiser gel was suggested by Hoang et al. (2021), composed of zinc amino-clay and the extract of a desert plant *Opuntia humifusa*. The ZnAC present in this formulation can effectively sanitise the skin, while *O. humifusa* extract is found to prevent skin desiccation caused by frequent washing. Moon et al. (2020) described the other beneficial effects of *O. humifusa* extract on human skin.

Hoang et al. (2021) claimed that the sanitiser prepared by them is much more preferable than the conventional ones due to their highly effective disinfectant power, very little or no toxic effect, and prevention of skin dryness and irritation even after frequent uses.

5.3 Clay-based surface disinfectants and detergents

Da Silva-Valenzuela et al. (2014) studied the applicability of different types of clays for the production of detergents, and inferred that purified bentonite was the most appropriate material for this purpose. Purification was recommended for the removal of associated minerals and associated phases from the detergent, which may contain Fe^{2+} and other transition elements and may put undesirable stains on the objects. Furthermore, the impurities like quartz grains may scratch and tear the clothes during washing. According to these

workers, the swelling capacity, pH, high CEC, and rheological properties (i.e., viscosity, elasticity, stress-strain relation, response to force etc.) of montmorillonite present in the purified bentonite make it suitable for the production of liquid detergents.

Application of bentonite-water mixture has also been suggested for washing and sterilising the medical gears and other surfaces infected with viruses (Das & Tadikonda 2020). Bentonite slurry may be sprayed on those surfaces, and then washed with water. This sanitisation process is expected to prevent the infection of the SARS-CoV-2 and other highly infectious pathogens through different sources of surface-to-hand transmissions.

It may be added that the clay minerals of smectite and vermiculite group are very much effective antimicrobial agents, but their use in the clay-based detergents are restricted owing to the presence of Fe^{2+} and other transition elements as octahedral cations. The transition elements have a strong property of imparting colours, which may stain or decolourise the clothes. Better suited for this purpose are kaolinite, illite, and other white clay minerals, which do not contain the transition elements as essential constituents. Some commercial laundry soaps prepared with kaolinite have been claimed to be effective for cleaning clothes without any change of colour (Internet Resources No. 1). A list of clay-based detergent liquids and powders are given in the Internet Resources No. 4.

Disclaimer: The commercial products cited in this section have not been tested in the present work to verify or confirm their efficacy as disinfectants or their side effects, if any.

6. Discussions: Future prospects of clay-based sanitisers and surface disinfectants

6.1. Harmful effects and drawbacks of the conventional sanitisers

The following four categories of common sanitisers that are widely used now-a-days are referred to here as conventional sanitisers.

- (i) Alkali-based bath soaps and liquid hand washes
- (ii) Alcohol-based hand rubs
- (iii) Alcohol-based surface sprays
- (iv) Alkali-based detergent powders and liquids

All the above have some detrimental effects on human health and environment, which are briefly explained below.

The alkali-based soaps and liquid hand washes have a high pH, ranging from 9.01 to 10 (Tarun et al. 2014), and their frequent use may increase the skin pH, damage of the protective acid mantle of the skin, dehydrate the skin, and cause irritability. Damage of the acid mantle can worsen the conditions of patients already suffering in skin diseases like acne, eczema, dermatitis, and rosacea (Pahr 2018). In addition, increase of skin pH causes long term skin

infections like acne vulgaris, owing to the rapid growth of the bacteria *Propionibacterium* (Baranda et al. 2002, Korting et al. 1987, Prakash et al. 2017).

The alcohol content in the alcohol-based hand rubs is 70% by weight, while that in the surface sprays vary from 30% – 60% (Alhmidi et al. 2017, Jiang et al. 2021). During their application, some amount of alcohol evaporates quickly and mixes in the surrounding air, which is inhaled by the users and all the people in the immediate vicinity (Bessonneau & Thomas 2012). The surface sprays possibly release more alcohol vapour in the air than the hand rubs, but the latter is bound to cause some alcohol intake through dermal absorption (Institut National de Recherche et de Sécurité 2007). Recent investigations revealed that frequent use of ethanol-based disinfectant sprays may significantly change the indoor air quality through release of volatile organic compounds and nano-sized particles, thus causing serious human health risk (Jiang et al. 2021). All these unintentional alcohol intakes, if continues for a long time, may lead to a number of serious health issues, including irritation of eye, nose, and throat; damage of the mucus membrane; nerve disorders, nausea, dizziness, and in extreme cases, abnormal decrease of body temperature and blood pressure (Tonini et al. 2009, Bessonneau et al. 2010, MacLean et al. 2017).

Although the detergents increase the skin pH to a lesser extent than the alkali-based soaps, their frequent uses may cause dermatitis and increase of the skin permeability, leading to adsorption of toxic materials through the skin (Gfatter et al. 1997, Nielsen et al. 2000). The surfactants and bleaching agents used in the detergent can cause skin and eye irritations and if ingested, may damage the endocrine system. Some chemicals present in common types of detergents, like nonylphenol ethoxylates, are reported to be carcinogens.

Phosphate-containing detergents, transported to water bodies from the washing areas, may cause eutrophication that leads to continual oxygen depletion, thus affecting the natural ecological balance in those water bodies (Effendi et al. 2017, Cohen and Keiser 2017). Surfactants like Sodium Lauryl Sulphate present in the detergents, when mixed with the water in ponds and lakes, are detrimental to the fishes as well as the people consuming them (Borah 2022). Other harmful effects of the detergents include reducing the growth of the bacterial population in sea water (Effendi et al. 2017), and damaging the gills and the protective mucus covering of the fishes (Lenntech 2022).

A few other disadvantages of the conventional sanitisers are given below.

- (i) **High expense and less availability:** Good quality alkali-based soaps and liquid hand washes, which cause less harm to the skin, are generally expensive. The alcohol-based hand rubs are even costlier, which make them inaccessible to a large section of the society. If the people of low-income group are prohibited from using the traditional cleaning agents, and compelled to use the conventional ones, many of them will be deprived from any sort of hand hygiene (see Section 5.1 for details).

Furthermore, large scale production of high-quality conventional disinfectants require long, complex industrial procedures, and it is difficult to increase their production abruptly within a short time due to economic and technological constraints. Therefore, during the last pandemic situation, these products were not available in sufficient quantities even to those who could afford them.

- (ii) **Problems of large-scale production:** Large factories of soaps and detergents may pollute soil and water, thus causing serious threat to the surrounding environment. The water bodies near the waste-disposal sites of many such plants have exceptionally high pH of water.

The raw materials necessary for the large-scale production of the alkali-based and alcohol-based cleaners may not be available everywhere. Some countries may therefore require to import the raw materials to set up the industries, or purchase the finished products, which will reduce the accessibility of these essential commodities to the inhabitants of those countries, especially in the latter case.

- (iii) **Other factors:** Using bar soaps and liquid handwashes need a supply of sufficient quantity of water and access to basin etc., which make them difficult to use in many situations, e.g. for the travellers on the move.

The alcohol-based sanitisers, in contrast, do not require water. But although they can effectively disinfect the hands, they cannot clean them from dirt and grease. This restricts their uses as handwashes under many situations, e.g., after fixing a car, having a traditional Indian meal, or working in a garden with mud, dirt and manures.

The next section explains how the limitations of the conventional sanitisers can be overcome with clays and clay-based formulations.

6.2. Advantages of clay-based sanitisers

A major concern for the pharmacists is the ability of the pathogen to evolve into drug-resistant strains. Most anti-microbial drugs use some chemical processes to destroy the pathogens, which may be useless against the newly evolved forms. The anti-microbial actions of clays, in contrast, largely depend on adsorption which is a physical phenomenon, with the exception of assisting in the bactericidal actions of metals (explained in Section 4.2). The clays are therefore effective against newly introduced mutant varieties as well.

From the economic point of view, the clays are readily available almost everywhere, and are less expensive than the raw materials of the commonly used sanitisers. For hand washing purposes, the natural clays do not need any complex purification processes; as established from the studies carried out in Bangladesh (described in Section 5.1). The abundance and

ubiquity of clays facilitate large scale production of clay handwashes anytime and anywhere, and no hefty investment is needed for establishing such production plants.

The therapeutic and economic advantages described above undoubtedly brighten the prospect of clays as the sanitising agent of future. It has, however, a few other edges over its competitors, as stated below.

- (i) Owing to their unique internal structures, the clay minerals can bind easily to a wide variety of organic and inorganic substances in their interlayer spaces, which enable the preparation of better-quality hand sanitisers and disinfectants (e.g., those described in Sections 5.2 and 5.3).
- (ii) Instead of causing any harm to the skin, the clay minerals can actually nourish the skin. The pH of clay-water mixture is similar to that of the skin (Pan-on et al. 2018). Thus, the clay facial masks do not disturb the normal skin pH. Topically applied clay masks have drying effects on the skin. This adsorbs the excessive sebum, oil, bacteria, and metabolic toxins from the skin pores that cause lesioned skin, acne and other skin issues. (Ducrotte et al. 2005, Herrera et al. 2000, Meier et al. 2012). The clay packs can also increase the blood flow and supply of oxygen in the skin, thus making the skin healthy (Poensin et al. 2003). Other health benefits of clay masks include skin cell contraction to reduce wrinkles, exfoliation of dead skin cells, and retaining skin moisture (Carretero et al. 2006, Pan-on et al. 2018).
- (iii) Being one of the basic components of the environment, clay is not generally harmful to the environment. When mixed with the soil, they enrich the soil. They can also purify the water in natural water bodies by adsorption of microbes, heavy metals, and harmful organic molecules. The clay purification plants or the factories of clay-based sanitisers are therefore not a serious threat to the environment, excepting a few situations described in the next section.

6.3. On the flip side

When the clays are used for handwashing in the traditional ways, a small amount of it is taken from nature, purified, and the desired cleaning agents were prepared. The quantity of the raw materials and products involved in this process is so small that it does not cause any significant health hazards or environmental pollution, even in local scale.

But the large clay-based industries necessitate extraction of huge amounts of clays from the mines. Clay flakes, being exceedingly fine, are easily airborne, thus increasing both PM_{2.5} and PM₁₀ in significant quantities in the air. The clay particles are mainly released in the air during the excavation and blasting operations, and through wind erosion of the exposed clay beds after mining operations. The clay particles in the overburden dumps may also contribute to the air pollution. The large clay mines are therefore potential sources of air pollution in varying degrees.

The large factories of all the clay-based products may dump a large amount of clay in their waste disposal sites. If not properly managed, these sites can also release particulate matters in the air.

Prolonged exposures to the particulate matters may create respiratory troubles like shortness of breath, cough, pneumoconiosis etc. in humans and animals. In a few cases, the asbestos associated with some clay minerals were reported to cause lung cancer. Particularly prone to these diseases are the workers of clay-based industries and the inhabitants in the immediate vicinity of the factories (Wagner et al. 1987, Gibbs 1990, Wagner 1990, Gibbs et al. 1992, Gibbs & Pooley 1994, Wagner et al. 1998).

It may be added here that unlike many other air pollutants, the airborne clay flakes are not toxic or poisonous; and can create health issues only in very high concentrations and by prolonged exposure (Wagner et al. 1998), which may be avoided by adopting the proper remedial measures.

7. Conclusion

This contribution, within its limited scope, has attempted to provide an overview of the anti-microbial actions of clay minerals, their present uses as disinfectants – both per se and combined with other substances, their advantages over the other disinfectants, and the few drawbacks of their large-scale utilisation. With this discussion in the backdrop, the following recommendations may be put forward.

- (i) Clay minerals, owing to their unique internal structures and consequent properties, should be used in the production of hand sanitisers, surface disinfectants, and detergents.
- (ii) There should be further investigations to understand the interrelation between the internal structures, compositions, properties, and the antimicrobial actions of the clay minerals, for their better utilisation in this field.
- (iii) Further researches are recommended to formulate clay-based disinfectants by combining clay minerals with different types of antibacterial and antiviral substances, which will be more effective than pure clays.

For preparation of better-quality hand-gels, clay minerals may be infused with natural moisturisers like plant extracts. Finding the correct materials, their correct proportions, and the appropriate procedures for preparation also require extensive studies, like the one performed by Hoang et al. (2021) described in Section 5.3.

- (i) The residues of all the cleaners and disinfectants, after their applications, finally go to the nature in some form or other. Some antimicrobial metals, such as copper, zinc etc., may bring about soil and water contamination. It may be anticipated that if these metals are used in clay-based disinfectants, their residues may cause some environmental issues. Some plant-based ingredients, like the extracts of *Aloe vera*, rosemary, grape seed, olive

leaves, green tea and sage have antibacterial actions, and have been reported to destroy various gram positive and gram negative bacteria (Klančnik et al. 2010, Fani & Kohanteb 2012). These plant extracts may be combined with the clay minerals to produce more effective clay-based disinfectants, which are expected to be environment-friendly as well.

- (ii) Some antibacterial plant matters also have moisturising and anti-inflammatory properties, like *Aloe vera* leaves. The hand rubs prepared by combining their extracts with the clay minerals are expected to protect the skin from infections and also nourish it. Further investigations are required in this field.
- (iii) Site selection for a new industrial plant is based on a number of factors, and the easy availability of raw materials is one of the most important among them; for example, an iron and steel plant cannot be established in a desert area rich in iron ores, if there is no proximal source of water and coal. The easy availability and ubiquity of clays facilitate the establishment of factories of clay-based handwashes anywhere required. The simple, inexpensive procedures for purification of natural clays enables setting up small, low investment purification plants. Smaller establishments will use less quantity of raw materials, and will release less amount of particulate matters in the air.

De-centralised industrial production of clay-based sanitisers is therefore highly recommended, in small manufacturing units spread all over a country, instead of large factories concentrated at certain places.

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Disclaimer: Some information have been gathered from a few websites of commercial products, the web addresses of which have been given in the **Internet Resources No. 1 to No. 4**. The effectiveness of these products, as claimed in those web pages, have not been tested in the present work, and this article has no intention to promote any of such products.

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Internet Resources

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The Art of ‘Organic’ Living: Lessons from Apatani Women in Ziro Valley of Arunachal Pradesh in Northeast India

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Abstract: *The Apatani of Ziro valley, Arunachal Pradesh, stand out as an indigenous community of settled agriculturists in the ecocultural landscapes of the Eastern Himalaya. Their biocultural heritage is an ingenious hill farming system of fish cultivation in paddy fields, integrated animal husbandry and with social forestry. This progressive hill farming system produces two staples in one agricultural plot to accomplish balanced diet at the source itself. This is economically viable and ecologically sound. This advanced ‘organic’ farming system sustainably uses, manages and conserves local resources to balance agriculture and the biodiversity underlying the functioning of the food production system. Their ‘green’ and ‘clean’ agricultural practices promote harmonious coexistence of people and their environment. Like other tribes of Northeast India, the Apatani people are poised at the crossroads of tradition and modernity. Both men and women are involved in the traditional rice-fish farming. However, like other patriarchal milieus, these women are excluded from the decision-making process. The world’s tribal and rural women often engage in multiple livelihood strategies, and along with their domestic chores silently perform monotonous agricultural work which necessitates insight into local plant resources, and the Apatani women are no exception to this. This is an endeavour to relook at the Apatani agricultural heritage as a model green farming system that promotes organic living, and focuses on the ‘silent’ role played by these women with their knowledge-based innovations in an attempt to understand their contributions in advancing solutions to the critical global issue of ensuring food and nutritional security while protecting the environment.*

Keywords:

Agricultural heritage, Apatani, ecological sustainability, traditional knowledge, women

1. Introduction

The term ‘sustainability’ implies a compromise between the human aspiration for a better quality of life on the one hand, and the limits of nature on the other hand (Kuhlman & Farrington 2010). During the course of its long history from the Neolithic revolution to the scientific and industrial revolution and beyond, agriculture emerged among nomadic hunting-gatherings and evolved throughout with the innovation of shifting cultivation and sedentary farming, to culminate into intensive agriculture. The human concern for preserving natural resources for posterity is a perennial one. In the hunting-gathering stage, the worry was about annihilation of game. In the agrarian phase the anxiety was of losing soil fertility. In the industrial age the apprehension is of environmental holocaust. Early cultures, nearly 12,000 years ago, domesticated plants and animals to ensure a reliable food production system that

buttressed the growth of the early cities and civilization. The Colombian exchange, about 500 years ago, triggered the globalization of plants and animals. The industrialization of agricultural production in the last 300 years allowed the skyrocketing of human population. However, intensification of food production and poverty elevation are linked (Mozumdar 2012). The turbulent first half of the last century triggered a technological response in the form of the so-called ‘green’ revolution in its second half. Food grain yields doubled in only 40 years for the first time in history (Khush 2001). However, this also drastically altered traditional farming practices at a global scale within a span of only a few decades (Shiva 1991). Soon, the ambivalence so typical of technology manifested itself with undesirable ecological, and even social consequences (Pingali 2012). The bumper harvests from high-input monocultures that relied on high-cost, energy-inefficient and more-polluting external resources such as modern crop varieties, intensive irrigation, farm mechanization and agrochemicals were deleterious to the health of humans and the environment (Evenson & Gollen 2003). Today, the global food production system faces the dual challenge of meeting the food and nutritional security for an ever-growing world population on one hand, and maintaining the productive health of the ever-shrinking global agroecosystems on the other hand. In this century, the effort was to reverse this trend and grow food through biodiverse farming with minimum use of irrigation, farm machinery, mineral fertilizers, and synthetic chemicals. These sustainable agricultural practices adopted alternatives as low-input polycultures with low-cost, energy-efficient and less-polluting local resources to provide greater resilience in the face of economic, environmental and social challenges (Jackson et al. 2007). The need for replacing high-risk ‘dirty’ technologies with low-risk ‘clean’ technologies has led to the adoption and diffusion of ‘green’ agricultural practices as the emerging trend in global agriculture (Rogers 1983). The ‘green’ technology is an umbrella term for environment-friendly practical solutions from production to usage of a product, that promotes economic development as well as ensures the long-term health of people and the environment. ‘Organic’ farming has been defined in multiple ways, and in essence refers to a self-reliant agricultural production system that relies more on management of the wider ecosystem itself, rather than outside support. Traditional societies, unlike modern ones, relate to nature in terms of custodianship (Verschuuren et al. 2010). Their resource management practices have been well-documented worldwide among diverse cultures and environments (Berkes 1999; Berkes et al. 2000). Traditional agricultural systems have co-evolved with local natural and cultural systems, exhibiting social and ecological rationale manifested in their traditional knowledge-based sustainable resources utilization practices. These, as an intermediate between hunting-gathering traditions providing local subsistence, and modern farming technologies supporting global mass-production, have achieved the critical balance between exploitation and conservation of natural resources (Jeeva et al. 2006). Reviving them would be the true ‘green’ revolution that would restore this harmony of agroecosystems with ecological principles that underlie all food production systems. This art of ‘organic’ living among the world’s traditional communities are model food production systems that, in the context of inter-generational equity, espouses care for the environment not only because of its intrinsic value, but also in to preserve the assets for future generations. Gender roles in

traditional and modern agriculture is a recurrent theme of study as these shed light on the role of women in agrarian and even industrial societies. Women, the most important workforce engaged in exhausting tasks, form the backbone of global agriculture. Dictated by social norms to manage daily domestic chores as daughters, wives and mothers, they also pursue multiple livelihood strategies as farmers, gardeners, herbalists, plant gatherers, plant breeders, seed custodians to manage local plant resources as food and medicine to ensure the wellbeing of their family. However, in rural settings, their hard work and key role as producer of food, earner in household economy, and custodian of intangible cultural heritage, remain largely unacknowledged by society at large. Furthermore, despite their key services, customary laws limit their participation in decision-making processes at home, and in the field, plantations and marketplaces, thus increasing the level of inequality vis-à-vis their partners. However, empowered women farmers are in the best position to lead their communities in the conservation, even revival, of the traditional sustainable 'green' practices of their 'organic' farming heritage.

2. Apatani People of Ziro Valley

Northeast India with its incredible blend of diverse ethnicities, is home to small and diverse ethnic groups with distinctive historical, geographical, cultural and social attributes (Ali & Das 2003). The Apatani people are native to the secluded Ziro valley (22°34'N, 88°24'E) in Lower Subansiri district of Arunachal Pradesh in North-east India. This miniscule (1,058 km²) hilly terrain (1,524 – 2,738 m) is hidden in the sub-tropical ranges of Eastern Himalaya – a part of the Himalaya Biodiversity Hotspot. Although they belong to the Tani tribal group of central Arunachal Pradesh, the Apatani language, beliefs and customs are distinct from all the others. They belong to the Mongoloid stock (Goswami & Das 1990) and speak a Tibeto-Burmese dialect of the Tani language group (Post & Kanno 2013). They (traditionally) adhere to the shamanistic Tani religion called Donyi-Polo (Blackburn 2010). Their 60,000 population is largely concentrated in seven traditional villages (*lemba*), and their satellite hamlets, as well as increasingly in the towns of Hapoli and Old Ziro located at the two ends of the Ziro valley (Kani 2012). They are endogamous, and socially organized into 78 exogamous clans (*Halu*) and sub-clans (*Tulu*) among them (Blackburn 2010). The tribal council (*buliang*) comprising of clan elders dispenses their traditional self-governance (Elwin 1988). The Apatani people are the custodians of a rich intangible cultural heritage which profoundly reflects their close relationship with their physical environment (Chaudhuri & Chaudhuri 2016). Like the myriad other tribes of India's Northeast, this indigenous micro-culture is now poised at the crossroads of tradition and modernity.

3. Agricultural Heritage of the Apatani People

The traditional agriculture of the indigenous communities in Northeast India ranges from shifting to sedentary agriculture (Majumder et al. 2011). This region, with climatic and ethnic diversity, harbours genetic resource in Asian rice (*Oryza sativa*) as local staple. Unlike the

slash-and-burn (*jhum*) cultivation of their neighbours (Karthik et al. 2009), the Apatani people are settled agriculturists whose cultural landscape confirms to the paradigm of harmony between nature and humans. Their agroecosystems are extensive terraced rice fields (33 km²) surrounded by forested mountains (288 km²), drained by Kale and its tributaries (Rai 2005). Based on their traditional agroecology moulded by their environment, the Apatani people have adopted a plethora of 'green' practices to sustain their rich but fragile agroecosystems along with its biodiversity, to support their traditional way of life. This 'organic' lifestyle is in tune with the now popular idea: reduce, reuse and recycle. The centrepiece of their agricultural heritage is the sedentary farming perfected over centuries in the form of paddy-cum-fish cultivation, linked with animal husbandry and social forestry, to form a 'circular' economy. This exemplifies a highly diverse, well-integrated and noticeably advanced indigenous farming system. Among the disparate methods of fish farming practiced in ubiquitous rice agroecosystems of Northeast India, the Apatani people are the best exponents of mountain valley rice-fish farming (Das 2002). Their *jebi-aji* agriculture, an integrated farming system, concurrently farms rice and fish in the same plot. On the terraced slopes (Figure 1a), native cultivars of japonica rice (*O. sativa* var. *japonica*) or *pyapin* (Dollo et al. 2009) are grown with the exotic common carp (*Cyprinus carpio*) or *aji-ngiyi*, in the plots (*aji*), and finger millet (*Eleusine coracana*) or *sarse* on earthen bunds (*agher*) separating them. Other exotic and native fish-species are also stocked (Nimachow et al. 2010). Farming the primary crop (rice) along with a secondary crop (fish), and even a tertiary crop (millet), is not only an economically viable (Rahman et al. 2012), but also an ecologically sound (Noorhosseini-Niyaki & Bagherzadeh-Lakani 2013) practice. Along with these cereals, a host of other native food crops and wild edibles adds up to an amazing agrobiodiversity (Sundriyal & Dollo 2013). These terraced paddy fields are also the natural habitats of indigenous hill-stream fishes (Nimachow et al. 2010). Their animal husbandry consisting of rearing livestock, including *mithun* (*Bos frontalis*), a semi-domesticated regional bovine of cultural significance (Rai 2005). Their social forestry is centred on bamboo plantations and pine groves (Rechlin & Varuni 2006).

4. Apatani Women as 'Organic' Farmers

The Apatani women traditionally have distinctive nose plugs and face tattoos, a tradition of 'uglification' to save themselves from abduction in the past (Bharadwaj & Boruah 2020). In Apatani society, monogamy is a rule (Kani 2012). The social order is patriarchal, patrilocal and patrilineal, and inheritance rule is primogeniture (Hazarika 2011). The tribal council elders are all men (Elwin 1988). Therefore, women in general, are marginalized and silenced across their social, legal and administrative spheres. Ursula (1953) first reported the role of Apatani women in agriculture and crafts. Haimendorf (1962) documented their hard work in doing monotonous farm jobs alongside daily domestic chores. These women follow a traditional agricultural calendar for maintaining optimum agricultural productivity (Dutta 2015). Each farming activity is linked with festivals in their natural and social settings. The male tribal council administers the integration of land units and utilization of limited

resources of the Ziro valley (Rai 2005). Traditionally, women work alongside men in the fields, gardens and plantations (Kani 1993). However, with distinct gender roles, women till, sow, transplant and harvest the crops, as well as maintain and repair bunds, trails, fences and drains, (Figures 1b-d). All daily and seasonal agricultural activities involve communal labour of traditional farmer groups called *patangajing* (Dollo et al. 2009). Although administered by the male tribal council, women are key members of all these groups. They lead the farm work in the rice terraces, except those operating in the forested periphery. Overlooked in most studies on this agricultural heritage is the pivotal role of the Apatani women. These women farmers, intimately interacting with their environment as part of their daily work, not only hold traditional ecological knowledge (Yamang & Singh 2021), but also transmit them across generations. The oral tradition of the Apatani people is the *miji-migung* (Blackburn 2010). The *miji* represents complex ritually chanted verses of male shaman priests (*Nyibu*) during agrarian festivals to communicate with the ‘spirit’ world of ancestors for wise council in determining the agricultural almanac. Possibly, their shamanic state of trance involves access and retrieval of cultural memory from the subconscious mind for the practical purposes of social coordination in pre-scientific cultures (Joralemon 2001). However, these further exclude women from decision making in agricultural activities. In contrast, the *migung* consists of myths, legends and tales about the origin of crops, livestock and human social order, spoken in ordinary conversational prose as part of daily activities, usually narrated by grandmothers, mothers and older siblings to the youngsters to assume the didactic function of cultural transmission of traditional knowledge, including those related to agriculture, in this pre-modern society with no traditional writing system in the past (Bouchery 2016). In their myths, Ayo Diilyang Diibu the first wife of Abotani, the forebear of humankind, is the ideal women and an epitome of hard work bringing bountiful harvests. It is a belief that women who follow her footsteps would never face starvation (Dinsu 2018). One story about Abotani’s devious second wife Tiinii Rungya reveals her indolence. Pretending to work hard in the rice paddy she demands bamboo tools for weeding, but keeps them idle. Soon, the rice field turn into a grassy wasteland. There was no grain left even for planting the next crop. Therefore, in their unique agricultural heritage, men may decide when to work, but it is the women as informal educators who infuse how to work. These women as ‘organic’ farmers play a vital role in agricultural operations as a bulk of the workforce, often as leaders, and this is well-integrated with their practical knowhow of local plant and other resources. All round the year, on a rotational basis, women farmers as workers or leaders are singlehandedly involved in ingenious approaches to the management of agronomic resources such as land, water, nutrient and forests, as well as innovative solutions to agronomic problems such as weed and pest infestations, using their ‘clean’ and ‘green’ solutions. The following sections highlight the ‘green’ technology of these women as ‘organic’ farmers, with the details of their traditional knowledge-based management practices in these agroecosystems to sustain their indigenous food production system along with the substructure of the local biodiversity.



Figure 1: Rhizipisciculture of Apatanis women in Ziro valley, Arunachal Pradesh. **(a)** View of the agroecosystems in May. **(b)** Rice transplantation in May. **(c)** Rice harvesting in October. **(d)** Rice threshing in October.

4.1. Land Management Practices

The Ziro valley is a mosaic of settlements (*ude*) among human-modified and natural habitats. The key to the successful agriculture by Apatani women is their diversified land-usage pattern (Dollo et al. 2009) that links rice terraces (*aji-ager*) with houses (*ude*), gardens (*ballu* and *yollu*), pastures (*polang*), pig pens (*alyigiiri*), granaries (*nesu*), burial grounds (*nendunenchang*), plantations (*bije* and *sansung*), forests (*moorey* and *myodi*) and sacred groves (*ranthii* and *sarosani*). Integrated rice-fish farming allows optimal use of limited land resources (Frei & Becker 2005). Paddy fields, as agriculturally-managed lentic wetlands, can be used for fish culture under wet conditions, although these are not primarily designed for fish farming (Halwart & Gupta 2004). The agroecosystem of Apatani women perfectly blends wet rice farming with aquaculture with four physical modifications that favour pisciculture: raised bund height to retains more water, fish pits provide refuge in dry conditions, drainage system controls water level, and fish screens prevent their escape. The terraces are levelled and small (250 to 3,000 m²) plots are separated by high (0.2 to 0.5 m) earthen bunds fortified with bamboo, cane or timber chips from their plantations. The ideal levelling of plots and presence of bunds reduce soil erosion. The finger millet on the bunds

fortifies them, functions as soil binder, and prevents soil erosion. Weeds such as *Houttuynia cordata* or *siya-haman*, are not weeded out on the bunds and performs the same function. The contiguous natural woodlands and human-made plantations also check soil erosion (Rechlin & Varuni 2006). The bunds are repaired at the beginning of the farming season (late January), marked by the Murung festival as a fertility rite. The *aji-lenda* farmers group often led by a woman entitled *lenda-kagenee*, constructs and repairs bunds. In plots near forests, crops are protected from wildlife damage with fencing (*narung*) made with bamboo, cane and timber from their plantations. This is done after the farming season (late November). Women of the *sulu-sikhii* farmer group build and mend fencings. In February, rice and millet seedlings are raised in nurseries (*miding*) in the most fertile plots. *Huta*, a wooded trowel is used. The *tanser-patang* farmer group led by a woman *patang-ahtoh* prepares seed beds and sows seeds stored by women as expert seed collectors from their previous harvest. In March, paddy fields are levelled and prepared, denoted by the Myoko festival celebrating kinship. Each paddy field has a small (25 – 35 cm deep) trench as fish pit (*siikho*). The *konchi-patang* farmer group led by a woman *patang-ahtoh* prepares the fields. *Sampeyee*, a wooden shovel is used. In April, rice transplantations begin and fingerlings raised in spawn ponds (*ngyi super*) are first released into the pits. The *halying-patang* farmer group led by a woman *patang-ahtoh* transplants rice in the plots (Figure 1b). Holes are made for planting rice in the plots with *kdu*, a wooden stick with metal tip, and millet on the bunds with *dum*, another wooden stick with sharp tip. During monsoons, the fish moves into waterlogged fields and feeds on the naturally available food and nutrients of this wetland ecosystem. No additional feeding is done. The water is drained out during fish harvest after two-three months. *Takhung*, a funnel-like bamboo trap ensnares the fishing at water outlets. The remaining fish retreats into the pits where they are caught with *tajer*, a conical bamboo net. Sometimes fish is also captured in paddy field itself with *barju*, a basket-like bamboo net, or *ngiyi-pakhe*, a tray-like bamboo trap. The harvested fish is transported live to the market in *ajii-piiwa*, a finely-woven, conical basket made of bamboo or cane. The Apatani women successfully manage their diverse farmlands with early and late ripening rice landraces (Dollo et al. 2009). Early-maturing low-yielding ones e.g., *Ahreh Emmo* are grown in remote plots facing greater risk of wildlife intrusion, inferior fertility and poor irrigation. These are harvested in July. Late-maturing better-yielding ones e.g., *Hatii Emmo* are planted in nearby plots with favourable conditions. These are harvested in October. Terraces with early-maturing rice produce only one fish harvest, while late-maturing ones allow up to three. The rice fields are classified and managed based on water retention capacity of the soil. The *jebi* has clayey soil and high water-retention capacity compared to *ditor* with sandy soil. In the soft field, less fish is stocked than the hard ones to reduce risk of damage to the paddy. Crops such as millets and maize are also cultivated in drier uphill plots (*yaapyo*). In July, the principal agricultural festival of *Dree* is celebrated with rituals for plentiful harvest. The *enthee-patang* farmer group often led by a woman *patang-ahtoh* harvests the crop (Figure 1c), followed by *in situ* threshing (Figure 1d) and transfer to granaries. *Taggi*, a small metal sickle, is used to harvest rice, millet and maize. *Yapyo*, a large tray, is used for winnowing the grains. This rhizipisciculture is a model food production system for developing societies with the

simultaneous production of low-cost plant carbohydrate and animal protein in an agricultural plot to accomplish a balanced staple at the source itself. Therefore, with these ingenious 'green' practices, the Apatani women efficiently manage their limited land-resources of their agroecosystems.

4.2. Water Management Practices

In the Ziro valley, like indigenous farming systems of other tribal communities of northeast India, wet rice cultivation is essentially rain-fed. Integrating rice and fish culture allows optimal use of the water resources as well (Frei & Becker 2005). The rhizipisciculture of the Apatani women involves careful management of the seasonally-available rainwater. Paddy fields are classified as *jebi*, *aane* and *ditor* depending on the increasing need for irrigation (Rai 2005). Kiiley and its tributaries provide limited water supply for irrigation. The rice terraces receive enough water through a complex system of rainwater harvesting and its efficient management. Each rain-fed stream (*kley*) in the adjoining forests is channelized into a series of irrigation canals running along the edges of the valley. Each terrace level receives enough water supply through a network of carefully designed primary channels (*siikho*), secondary channels (*pakho*) and tertiary channels (*hehte*). In each rice field, continuous inflow of water from an earthen feeder channel (*siigang*) takes place through wooden or bamboo pipes (*hubur*). The continuous outflow of excess water from higher to lower terraces involves a ditch (*muhgo*) with a similar pipe. All water inlets and outlets are blocked with bamboo screens to prevent fish escape. Blocking or reopening a connecting pipe with mud and grass allows draining and flooding of plots at a desirable depth. During transplantation, 1-2 cm water level is maintained. This is later gradually raised to about 15 cm. This ensures inundation of rice fields, especially for late ripening rice varieties. Paddy fields are drained during weeding cycles and harvesting. Bamboo fences and plantations along the embankments of canals and streams hold the soil together. Pegs and pebbles are placed in the earthen channels of canals as energy dissipaters. Soil binding reeds such as *Phragmites karka* or *pepu* is grown on these beds. These traditional measures control soil erosion. During the long fallow season centred on December, the *jebi* plots are kept dry but the *ditor* plots are kept inundated. The canals and trenches are also repaired along with the bunds before the farming season (late January). The women in the *bogo* farmers group are engaged in constructing and repairing the irrigation works. In August, the peak season for rice cultivation, the women perform the *Yapung* ritual for adequate rainfall. Therefore, these innovative 'green' practices of the Apatani women ensure efficient management of the limited water resources available in their agroecosystems.

4.3. Nutrient Management Practices

The agroecosystems of the Ziro valley, like any other wet rice farming system in the world, suffer from nutrient washout. However, the Apatani women farmers maintain soil fertility by 'organic' means only, and that essentially includes recycling of natural nutrient and waste.

Integrated rice-fish farming improves soil fertility through nutrient recycling (Frei & Becker 2005). The fish plays a key role. They feed on soil detritus, planktons, periphytons, benthos and other aquatic biota of paddy-fields. These habitats in Arunachal Pradesh are conducive for plankton growth (Saikia & Das 2008). Fish excreta added to the soil is an organic fertilizer. The feeding activities of the common carp, a benthic feeder, loosens the soil to increasing dissolved oxygen that accelerates microbial activity at the water-soil interface and improves mineral availability for the crop (Giap et al. 2005). In comparison to rice monocultures, integrated rice-fish farming exhibits higher mineral content of the soil and faster plant biomass accumulation (Duanfu et al. 1995). The paddy fields also receive natural nutrient washout from the surrounding hills. Houses and granaries built on higher elevations supply decayed and decomposed waste drained out to the fields below. *Azolla*, an aquatic fern capable of nitrogen fixation, grow in water-logged paddy fields as biofertilizer. The Himalayan alder (*Alnus nepalensis*) or *rwme*, a non-leguminous tree capable of nitrogen fixation, is planted as agroforestry to enrich the soil (Rai 2005). Panicle harvesting is practiced. Threshing is done in the field. Local rice cultivars are tall with high straw yield. These agricultural wastes are left to decay in the fallow fields. During land preparation, decomposed straw (*liisii*) is added to enrich the soil. Undecomposed materials are incinerated on dry terraces and the ash (*muyuo*) fertilizes the soil. The Apatani women also integrate rice-fish farming with animal husbandry (Rai 2005) and social forestry (Rechlin & Varuni 2006). All local organic wastes are recycled to replenish the humus in the farm soil. The women dump household waste as well as rice chaff (*piinang*), firewood ash (*mubu*), pig excreta (*alyi-ekha*), poultry droppings (*paropai*), cow dung (*sii-ekha*), weeds (*tamih*) and leaf litter (*ankho*) into the rice fields near the villages during fallow season for replenishing the soil fertility. After harvest, cattle graze on the terraces and their dung gets naturally recycled. This fallow season itself also help to regain the depleted soil nutrients. Plant biomass is recycled into compost by traditional method of dumping and covering with a thin layer of soil for decomposition. Measures taken to control soil erosion help conserve soil fertility. The choice of the rice cultivars depends on nutrient status of the soil. In March, the *Myokung* ritual is performed for soil fertility. Thus, these novel 'green' approaches of the Apatani women, include recycling household and farm wastes, help them successfully manage, by organic means, the soil fertility of the agroecosystems.

4.4. Weed Management Practices

The agroecosystems of the Ziro valley, like any other paddy farming system, face the problem of weed infestation. Weed management below the threshold level in agroecosystems is important for sustaining productivity (Singh et al. 1996). Nutrient-rich paddy fields are easily infested with algae and herbaceous weeds that compete with the crop for light, water and nutrients. Commonly weeds in the upland paddy fields of northeast India are *Echinochloa crus-galli* subsp. *crus-galli* and *Cyperus iria* (Chanu et al. 2010). The Apatani women employ only 'organic' means for weed management. The *konchi-patang* farmer group led by a woman *patang-ahtoh* is engaged in weeding (*ahru-hodo*) the paddy fields.

Kele, a long-handled bamboo hoe with sharp metal tip is used for weeding during tillering (May-June) and flowering (September). The short metal-tip *pale* is used in gardens. Surplus free-floating aquatic weeds such as *Azolla* are fished out. Manual weeding loosening the soil to causes water turbidity detrimental to fish growth. These women farmers avoid this problem by draining their paddy fields during weeding and the fish retreats into the refuge pits. Paddy fields biodiversity helps in the biological control of weeds (Hajek 2004). Finger millet growing on the bunds suppresses weeds. Fish farming is now an important element of integrated weed and pest management in rice monocultures (Berg 2002). Water-depth in paddy fields stocked with fish inhibits the growth of paddy field weeds in general (Manna et al. 1969). Microphytophagous (algivorous) and macrophytophagous (herbivorous) fish control algae and weeds in the paddy fields (Piepho & Alkamper 1991). The common carp is an opportunistic omnivore in the paddy fields. While foraging on benthic organisms, it incidentally feeds on epiphytic algae (Saikia & Das 2008) and roots, buds, leaves and stems of weeds (Piepho & Alkamper 1991). As bottom feeders they also indirectly reduce weeds by uprooting plants, making the water turbid for photosynthesis (Moody 1992) and devouring seeds (Chapman & Fernando 1994). Hence, these inimitable ‘green’ practices of the Apatani women allow efficacious management, by organic means, of weed infestation in their agroecosystems.

4.5. Pest Management Practices

The agroecosystems of the Ziro valley, like the other rice farming systems in the world, also face the problems of pests and pathogens. The Apatani women farmers again cope with this by ‘organic’ means only. The fish again plays a key role. The common carp feeds on numerous potential rice pests like zooplanktons, zoobenthos and small aquatic fauna such as molluscs and insects (Saikia & Das 2008). The efficacy of fish as a biocontrol agent of pests depends on their position in this habitat. In flooded paddy fields, if the fish pit as not more than 10% of the area, the common carp frequents the rice plants rather than their refuge (Halwart et al. 1996). This carp is the best-known biocontrol agent of the golden apple snail (*Pomacea canaliculata*), a polyphagous herbivore that attacks rice plants across Asia (Teo 2006). The diet of this benthophagic fish in paddy fields significantly comprises of molluscs (Ardiwinata 1957). It predaes on juvenile snails which are small enough to fit into the opening between their pharyngeal teeth, crushes the shell, ejects shell fragments, and consumes the flesh (Halwart et al. 2014). This carp is also useful against insect pests of rice such as plant hoppers, stem borers and leaf folders (Yuan 1992). The fish predaes on the neonate larvae which, after hatching, often suspend themselves from the rice leaves. Indirectly, the fish also feeds upon aquatic weeds in paddy fields which act as hosts for rice pests. Halwart (1994) concludes that the presence of fish in flooded paddy fields reinforces the natural, well-balanced pest-predator interactions in the natural ecosystem. Rice ear-head bug (*Leptocoris oratorius*) is a common rice pest in northeast India (Chanu et al. 2010). This is ingeniously managed by the Apatani women by fixing short wooden or bamboo sticks in the paddy fields with impaled frogs, crabs or salted fish captured from the rice paddy

itself, to distract the adult bugs away from the crop (Singh & Bag 2002). Furthermore, the common carp is known to reduce anopheline (*Anopheles* spp.) and culicine (*Culex* spp.) larval populations (Halwart & Gupta 2004). Fish, in general, can also indirectly reduce incidence of fungal diseases by aerating the soil and accelerating the decomposition of organic remains. The common carp strips diseased leaves near the base of the rice plants that are sources of fungal inocula. This also improves air and light availability making the microclimate unfavourable for fungal growth (Guang-Ang 1995). In April, the *Tamu* ritual, and in July, rituals of the *Dree* festival, are done to protect crops from pests. Therefore, again with the help of these pioneering ‘green’ practices, the Apatani women commendably manage, by organic means, pest influx in their agroecosystems.

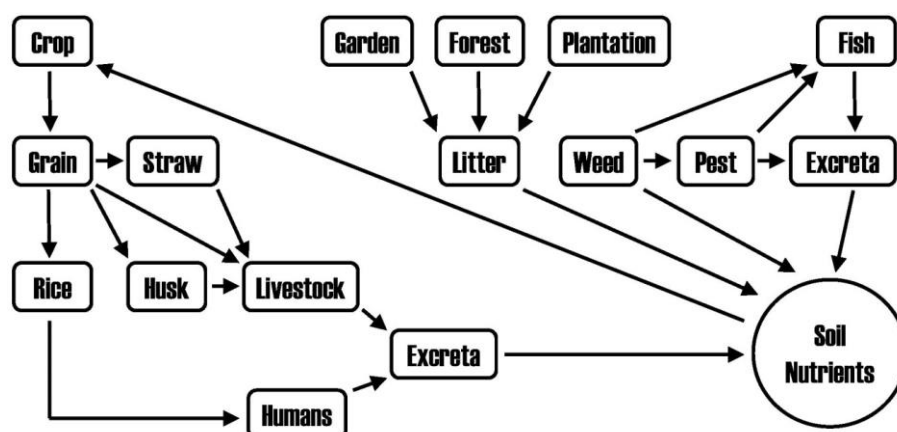


Figure 2: Resource recycling system in the organic farming model of the Apatani women in Ziro valley, Arunachal Pradesh.

5. Conclusion

The intangible cultural heritage of the less technologically-advanced communities, are shaped by their natural environment. Their reverence for nature, entrenched in their way of life, permeates into every facet of their language, culture and wisdom. In traditional agriculture, the environmental stewardship of autochthonous societies is reflected in their beliefs and practices, knowledge and skills, aiming at the conservation of bioresources and biodiversity in natural and modified ecosystems as the foundation of their food production systems. These subaltern cultures emphasize upon harmony, rather than subjugation, in defining their relation with nature. Today, biodiversity of agroecosystems is receiving global attention due to the role in its functioning. This agrobiodiversity is becoming increasingly endangered by changing farming practices with the shift to monocultures, modern cultivars, intensive irrigation, farm mechanization, toxic agrochemicals, and destruction of natural refuges. There is growing global awareness about adopting the ‘green’ practices of ‘organic’ farming that puts greater reliance on ecological goods and services for sustainable food production, and less damage to the environment, biodiversity and human health. The Apatani women farmers of northeast India, with traditional knowledge-based management practices based on biodiversity, as well as lore and beliefs that underlie them, are a good example of a traditional

agricultural society practicing environment-friendly strategies to ensure food, health and livelihood security for the community. This enviable ‘art’ of organic living of these marginalized and silenced women engaged in rice-fish farming is a model system for promoting the idea of ‘green’ biodiversity-based agricultural practices elsewhere. These women shun ‘dirty’ external modern inputs to espouse ‘clean’ local traditional inputs from their limited natural resources through the sustainable use, management and conservation of their agricultural resources, and effective management of problems in agriculture. Agricultural inputs are minimal, with no profligacy. These are inexpensive, safe and easily-available. No monoculture is practiced. Polyculture is the rule. No modern cultivars are used. Local landraces are nurtured. No farm machinery is used. All agricultural operations are manually performed with indigenous tools and implements. Even draught animals are not employed. Human labour is a major input. No agrochemicals such as inorganic fertilizers, synthetic algicides, fungicides, herbicides, insecticides or molluscicides are used. Compost, biofertilizers and green manure are used to manage soil fertility in their fallow agriculture. Biological control is employed to manage incidence of weeds and pests. Nothing goes to waste. Everything gets recycled (Figure 2). These women with multiple livelihoods as farmers, homemakers, gardeners, planters, foresters, fully explore all the three key features of ‘green’ technology, viz. reduce, reuse and recycle, in their ‘organic’ farming. From the Apatani women, the ‘daughters of the soil’ in a neglected corner of the biodiversity-rich Eastern Himalaya, the key lessons draw from their economically viable, ecologically bearable, socially equitable food production system are about insightful and engaging ways and means of living in harmony with nature and sparingly, but diligently, using her assets to promote economic development without compromising on environmental protection and public health.

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Organic Waste Recycling

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Abstract: *Organic wastes contain materials which originated from living organisms. There are many types of organic wastes and they can be found in municipal solid waste, industrial solid waste, agricultural waste, and wastewaters. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments. Present paper on Organic waste recycling in which discussed on Organic wastes, Organic waste recycling, Methods of organic waste recycling, Process (General Steps / Mechanism) of organic waste recycling, Significance of organic waste recycling and Barriers and Challenges of organic waste recycling.*

Key Words: Waste recycling

1. Introduction

Organic wastes contain materials originated from living organisms. There are many types of organic wastes, and they can be found in municipal solid waste, industrial solid waste, agricultural wastes, and wastewaters. Organic wastes are often disposed of with other wastes in landfills or incinerators, but since they are biodegradable, some organic wastes are suitable for composting and land application. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. Because of recent shortages in landfill capacity, the number of municipal composting sites for yard wastes is increasing across the country, as is the number of citizens who compost yard wastes in their backyards. Some of the organic materials in municipal solid waste are separated before disposal for purposes other than composting. The organic fraction of industrial waste covers a wide spectrum including most of the components of municipal organic waste, as well as countless other materials. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments.

2. Organic wastes

Solid organic waste is primarily understood as organic-biodegradable waste, and it contains about 80-85% moisture content. The most common sources of organic wastes include agriculture, household activities, and industrial products. Green waste like food wastes, food-soiled paper, non-hazardous wood waste, landscape waste, and pruning wastes are some of

the examples of biodegradable or organic wastes. Recently, however, the concept of organic waste management and recycling has been introduced and implemented.

Organic wastes have been an important source of pollution in the environment. Some of the common types of organic wastes usually found in nature include the following:

2.1 Cattle wastes. Cattle manure and fodder constitute organic wastes in the form of cattle wastes. Besides, poultry wastes and piggery wastes also add the number of organic wastes of animal origin. Cattle waste is also an important soil fertilizer that provides a high concentration of micro and macronutrients for crop growth and soil fertility. Cattle wastes are animal wastes that are of animal origin and act as good resources of organic matter.

2.2 Food wastes. Fruit and vegetable canning industries, frozen vegetable industries, and fruit drying industries, along with residential areas and hotels or restaurants, are the major producers of food waste. Some of the examples of food waste include peelings, cores, leaves, fruits, twigs, outer skins, and sludge. Food wastes account for about 30% of total organic waste in nature via natural and artificial means.

2.3 Municipal solid wastes. Municipal solid wastes include the more common wastes that are generated in our daily life in the form of product packaging, grass clippings, furniture, clothing, bottles, food scraps, appliances, paint, newspapers, and batteries. These wastes are generated from residential areas, schools, hospitals, and businesses.

3. Organic waste recycling

Organic waste recycling is the process of organic waste management where organic wastes are recycled or converted into useful matter by different recycling methods.

Biological treatments are among the most convenient and effective alternatives for treating organic waste. The excess moisture content increases the volume of waste while lowering their incinerator temperatures, causing an overall load of waste disposal. The need for organic waste recycling has increased over the years as waste management has become an emerging issue in most metropolitan cities. The primary objective of organic waste recycling is to maintain a sustainable cycle where the biodegradable fraction of organic waste is converted into useful organic manure or fertilizer through various recycling techniques.

4. Methods of organic waste recycling

There are different methods of organic waste recycling, each of which can be used for a particular group of waste to produce some form of useful organic matter. Some of the common methods are described below:

4.1 Anaerobic digestion. Due to the negative impacts of land filling and incineration, anaerobic digestion has been proposed due to the cost-effective technology for renewable energy production and treatment of high moisture and energy-rich material. The biogas

produced by anaerobic digestion includes gases like methane, carbon dioxide, and a trace amount of hydrogen and hydrogen sulphide.

4.2 Animal feed. Feeding organic waste to animals is a simple and easy method of waste recycling. However, the direct feeding of organic waste to animals might result in some health issues in such animals. One of the most common and efficient ways of recycling organic waste is by giving agricultural and food waste to cattle and other animals as food. This also helps the farmers as they do not have to buy extra animal feed and eventually, helps the economy.

4.3 Composting. Compost bins are most suitable for use in houses to compost simple kitchen waste and garden cuttings. Composting is an aerobic process that takes place under correct conditions of moisture and biological heat production. Even though all organic matter can be composted, some materials like woodchips and paper take much longer to compost than food and agricultural wastes. Large scale composting is conducted in large reactors with an automated supply of oxygen and moisture to generate large tons of compost for industrial applications. There are different composting systems ranging from simple, low-cost bin composting to highly technical high-cost reactor systems.

4.4 Immobilized enzyme reaction. Enzymes like esterase's can be used to esterify oils to form biodiesel. Immobilization of enzymes also supports the reuse of biocatalysts for multiple processes which then reduces the cost of chemical and enzymatic processes. The use of enzymes over chemical catalysts in the treatment of wastewater and other similar waste products reduces the formation of by-products and significant energy inputs. The use of immobilized enzymes during organic waste recycling allows the degradation activity even under non-ideal environments as not exactly right for a particular purpose, situation, or person no ideal circumstances. All of these processes allow for a more economical and efficient way of waste management.

4.5 Rapid thermophilic digestion. A rapid thermophilic digester works six to ten times faster than a normal biodigester. Enzymes like esterase's can be used to esterifies oils to form biodiesel. Immobilization of enzymes also supports the reuse of biocatalysts for multiple processes which then reduces the cost of chemical and enzymatic processes. Rapid thermophilic digestion is the process of rapid fermentation of organic wastes by activating fermenting microorganisms at high temperatures. The process of thermophilic digestion is an exothermic process that maintains a thermophilic condition at 55-65°C. The use of enzymes over chemical catalysts in the treatment of wastewater and other similar waste products reduces the formation of by-products and significant energy inputs. The use of immobilized enzymes during organic waste recycling allows the degradation activity even under non-ideal environments. All of these processes allow for a more economical and efficient way of waste management.

4.6 Rendering. Rendering is the process of conversion of waste animal tissues into stable and usable forms like feed protein. Rendering, however, has some disadvantages like it cannot

completely degrade waste products like blood. Some cases of non-animal products can also be rendered down to form pulps.

5. Process (General Steps/Mechanism) of organic waste recycling

The overall process of organic waste recycling begins with the collection of waste materials which are then passed through various steps to obtain a usable form of organic matter. The general steps/ mechanism of organic waste recycling can be explained as below:

5.1 Collection. The first step in the organic waste management of recycling is the collection of waste materials which can either be on a small scale in a kitchen or on a large scale in industries. A sufficient amount of waste matter needs to be collected in appropriate bags so that they can be moved to the site of recycling. In the case of composting, the organic waste is collected in a pit, whereas that in a digester is collected in the digester.

5.2 Decontamination. An important step in organic waste recycling is the decontamination of waste in order to avoid its harmful effects. This step is particularly important while dealing with organic waste from industries. Besides, any non-biodegradable substance like glass, plastic, and bricks, if present, should be removed during this step.

5.3 Preparation. Before the organic waste is added to a recycling system, it should be prepared. Some methods might even require a period of stabilization prior to recycling, in which case, the time should be designated. The method of preparation employed depends on the type of recycling method chosen. For, e.g., composting requires shredding and stacking of organic waste, whereas an immobilized enzyme system requires immobilized enzymes.

5.4 Recycling process. Depending on the nature of the organic waste and desired end products, an appropriate method of recycling should be adopted. Human wastes like sewage and faecal wastes should be recycled via anaerobic digestion whereas sewages can be treated with thermophilic digesters.

5.5 Screening and grading. The obtained residues or compost are then screened into different sizes to be used for different purposes. Depending on the application of the end products, grading and screening are essential.

6. Significance of organic waste recycling

Organic waste recycling has multiple advantages that help prevent the problems that arise with the accumulation of waste products in nature. Some of the common advantages or significances of organic waste recycling are:

Some compost prepared with appropriate substrate work as bio control agents to prevent and control plant diseases. The separation of organic and inorganic wastes also improves the efficiency of non-organic recycling. The generation of bio fertilizers by recycling process improves the quality of soil, which then increases soil fertility and plant growth. Landfills

tend to increase the emission of greenhouse gases, and the recycling of such wastes into less harmful wastes decreases such emissions. Recycling of organic wastes also reduces the concentration of waste remaining for less efficient processes like landfill and incineration. Organic matter recycling increases the organic content of the soil, which improves soil fertility and provides essential nutrients to plant, increasing crop yield.

7. Barriers and Challenges of organic waste recycling

Even though organic waste recycling is a novice and important method of waste recycling, there are some challenges that limit the use of recycling methods. Some of the most prominent barriers or challenges of organic waste recycling are: Microbial degradation of organic waste might result in the formation of airborne microorganisms or bioaerosols, which may pose potential risks like respiratory disorders on the plant workers and adjacent residents. Recycling process like composting generates odours which might cause air pollution or discomfort. Air pollution is a mixture of solid particles and gases in the air. Car emissions, chemicals from factories, dust, pollen and mold spores may be suspended as particles. Water pollution is the contamination of water sources by substances which make the water unusable for drinking, cooking, cleaning, swimming, and other activities. Pollutants include chemicals, trash, bacteria, and parasites. Some selected groups of persistent organic pollutants like chlorinated dioxins, polycyclic aromatic hydrocarbons, and organochlorine pesticides are accumulated in solids during the treatment process.

8. Conclusion

Present paper on Organic waste recycling in which discussed on Organic wastes, Organic waste recycling, Methods of organic waste recycling, Process of organic waste recycling, Significance of organic waste recycling and Barriers and Challenges of organic waste recycling. Organic wastes contain materials which originated from living organisms. There are many types of organic wastes and they can be found in municipal solid waste, industrial solid waste, agricultural waste, and wastewaters. Organic wastes are often disposed of with other wastes in landfills or incinerators, but since they are bio degradable, some organic wastes are suitable for composting and land application. Organic materials found in municipal solid waste include food, paper, wood, sewage sludge, and yard waste. Because of recent shortages in landfill capacity, the number of municipal composting sites for yard wastes is increasing across the country, as is the number of citizens who compost yard wastes in their backyards. Some of the organic materials in municipal solid waste are separated before disposal for purposes other than composting. The organic fraction of industrial waste covers a wide spectrum including most of the components of municipal organic waste, as well as countless other materials. A few examples of industrial organic wastes are paper mill sludge, meat processing waste, brewery wastes, and textile mill fibres. Waste managers are continually experimenting with different “recipes” for composting industrial organic wastes into soil conditioners and soil amendments.

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Urban Solid Waste Pollution in India: Its Impact and Management

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Abstract: In recent decades high population density in major cities and metropolis of India has resulted into large quantities of solid waste generation. The ever-increasing materialistic demands of city bound people has increased municipal solid waste disposal manifold. Improper management of both domestic biodegradable as well as non-biodegradable wastes in urban cities and metropolises causes environmental pollution of that area disrupting the environmental hygiene. Since personal protective equipments are the primary line of defense against COVID-19, the pandemic and post-pandemic periods have increased the use of plastics and disposable items manifold imparting serious threat to environment and diversity. Its improper management causes environmental pollution and decline of environmental health. Moreover, ground water pollution due to industrial effluents and municipal waste is becoming an ever-increasing concern in many cities of India. Some major causes include runoff from poorly treated waste water, leakage from underground storage and old landfills, and industrial waste dumps near aquifers. Hence, the present study attempts to analyze the effects of variable solid wastes generated in India using data from print and electronic media.

Since solid waste management is an important factor for maintaining environmental health and hygiene, municipal waste management in India needs more attention in present scenario. Its management requires more effectiveness by increasing manpower, spreading awareness, timely collection of bins, and reducing financial issues. Dumping of solid waste in many cities and towns due to lack of proper space has become an emerging problem in India. The expansion of municipal solid wastes and biomedical wastes are further endangering the habitats and organisms. An urban solid waste management strategy includes integrated management system having three main components viz. source reduction, recycling and disposal.

Keywords: Municipal solid wastes, plastics, face mask, ground water, Solid waste management, COVID-19.

1. Introduction

The urbanization, industrialization, significant rise in population growth, and high population density is contributing to the generation of large quantities of solid waste in the country. Due to lack of proper space solid waste are being dumped in open area in many cities and towns. The roads and tourist places are being found littered with vivid plastic bottles and bags in most cities and metropolises. In India, high population growth and economic development are contributing many serious environmental issues. The most important environmental influence is the urban solid waste pollution associated with landfill leachate causing contamination of groundwater and surface water. Poorly managed landfill causes leachate migration to groundwater resource. Since disposal of municipal solid waste through open dumping has been the most common waste disposal method in

India, it is posing environmental and human health risk. One of the major threats to ground water quality deterioration is the disposal of municipal solid waste in non-engineered landfill (Kamboj & Choudhary 2013, Rathod et al. 2013, Maiti et al. 2015). This may lead to contamination of drinking water supplies through contaminated aquifers or surface supplies (Singh & Mittal 2011, Mishra et al. 2018). The population living in the vicinity of dumping sites are prone to severe health problems such as respiratory illness, eye irritation, and stomach problems (Singh et al. 2021). One of the most common problems associated with ill designed landfills and poorly managed solid waste is attraction of large number of vectors causing vector borne diseases like Dengue fever (Vidyavathy 2018). The non-hazardous solid waste routinely collected from a city, town and village, and being transported to a disposal site is the municipal solid waste (MSW). Municipal solid waste includes all trash or garbage from home and commercial places, such as food, paper, glass, metals, plastics, leather, sanitary and other wastes. The improper management of municipal solid waste disposal and the by-products like leachate and gaseous products arising from it is posing hazardous effect to human beings and other organisms as well. Hence, for maintenance of environmental health and hygiene, urban solid waste management needs attention in India. According to 2016 estimate of World Bank, India produces 277.1 million tonnes of municipal solid waste every year, which is expected to touch 387.8 million tonnes in 2030, and 543.3 million tonnes by 2050 (TOI 2020). The ever-increasing population and fast urbanization have made solid waste management a challenge in India. As per current government estimates, there is about 65 million tonnes of waste generation annually in India, and over 62 million tonnes of it are Municipal Solid Waste (MSW). Only about 75-80 percent of the total municipal waste is collected, and out of this only 22-28 percent is deposited at dump yards (Pavithra 2021).

The collection and disposal of solid wastes is under the control of Municipal Corporation. Composition of municipal solid waste varies in different seasons both qualitatively and quantitatively depending on several parameters like locations, climatic conditions, and habits of the people in the vicinity (Agarwal et al. 2013). The seasonal changes in composition influence the quality of recyclable and residual wastes. This in turn affects the quality of emissions from landfills, and the quality of incineration residues as well. The solid wastes in the form of domestic biodegradable as well as non-biodegradable wastes include both combustible and non-combustible types. Combustible wastes include paper, wood, plastics, textiles, rubbers, and garden wastes, while non-combustible include metals, glass, stones, ceramics etc. The composition of urban solid waste varies greatly depending upon its source, locality and activities, which include domestic wastes, commercial wastes, institutional wastes, construction wastes, burning ashes, animal waste, industrial solid waste, biomedical waste, agricultural solid waste, and sewer cleaning sludge. Biomedical waste includes anatomical waste, pathological waste, infectious waste, hazardous waste, and other waste generated from hospitals, clinics, nursing homes, health care units, medical labs, and research laboratories that require specific handling. They include plastic disposable syringes, needles, blades, blood bottles, catheters, expired drugs, empty medicine bottles, surgical masks, liquid wastes etc. In developing countries like India, the biomedical waste generated during pandemic period has added to the already existing solid

waste management issues. According to the Central Pollution Control Board (CPCB), India generated nearly 146 tonnes of biomedical waste every day related to COVID-19 treatments. Further, India produced 45,308 tonnes of COVID-19 biomedical waste between June 2020 and May, 2021, which was an addition to the 615 tonnes of biomedical waste a day being produced before COVID-19 (HT 2021).

During COVID-19 pandemic period human health and the healthcare materials were given more emphasis as compared to environment. Since plastics are flexible, lightweight and easily available, it became the most preferred raw material by several industrial sectors including the healthcare sector. The healthcare materials included in PPE kit are medical gloves, face shield, head cover, hand sanitizers, face masks, whole body aprons, and shoe covers. The type of plastic used in manufacture of various PPEs is polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC) (Klemes et al. 2020). The face mask production in highly accelerated rate, and its daily uses are resulting into increased sources of COVID-19 associated waste generation. The increase in COVID-19 associated waste and its improper management practices is increasing the potential risk of food chain contamination. Finally, the lack of awareness of environmental pollution, people negligence, and improper management of municipal wastes are the prime causes of solid waste pollution issues (Kothari et al. 2021).

2. Ground Water Pollution Through Municipal Solid Waste Landfill: Impact of Leachate

Municipal solid wastes are generated from household, offices, and commercial units containing paper glass, plastics, metals, and organic matter. Ground water pollution due to municipal solid waste leachate is of great concern in many cities and metropolises like Delhi and Kolkata (Kamboj & Choudhary 2013, Maiti et al. 2015, Singh & Mittal 2011). Though, the disposal is done commonly through a sanitary landfill, the problem is arising with the older landfills where the pollutants are percolating down to the groundwater aquifers. After the waste being deposited at the landfill, percolation of leachate takes place to the porous ground surface, where contamination of associated aquifers occurs making it unfit for domestic water supply and other uses.

Some of the major causes of groundwater pollution in urban areas due to MSW are, industrial waste dumps above and near aquifers, leakage from underground storage containing hazardous substances, seeping out from the bottom of old landfills, and poorly designed and maintained septic tanks. Since in many cities there is no segregation of waste at the source point, and no separate landfills for different type of wastes, a common landfill site receives all kinds of wastes such as debris, chemical materials, biomedical wastes, PPEs, liquid wastes, agricultural wastes, oil products etc. In majority of cases pre-treatment is not being practiced for all MSWs or hazardous waste before dumping. Moreover, the landfills remain uncovered at the sites. The characteristics of leachate from an active landfill vary due to age, type of wastes dumped, and the climatic conditions.

Very often the leachate is drained directly into the surface water, thereby reaching the groundwater aquifer. Various studies have reported contamination of groundwater resources by MSW landfill particularly from uncontrolled and unmanaged landfills (Mor et al. 2006, Jhamnani & Singh 2009, Kamboj & Choudhary 2013, Mishra et al. 2016). Several investigations have been carried out on impact of landfill leachate on surface and groundwater quality in metropolitan cities like Delhi and Kolkata from time to time. A case study of Okhla landfill, Delhi revealed the presence of potentially high pollution levels in both old and fresh leachate (Singh & Mittal 2011). The leachate samples collected from different time periods of the year showed variability in its characteristics in terms of age and dumping locations. Data depicts significant rise in physiochemical parameters, showing high concentrations of Total Dissolved Solids (TDS), high values of Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), and ammonia in both fresh and old leachates, which were significantly higher than municipal sewage, indicating potential threat to adjacent water resources and groundwater quality. Heavy metals like Pb, Cd, Mn, Cr, Fe, and Ni were found to be several times higher in all leachate samples than drinking water standards as prescribed by the US EPA. This indicates the disposal of refuse solid wastes like fluorescent light bulbs, waste batteries, food cans, materials made of iron, metal alloys, electronic objects, construction debris etc. Similar studies were carried out at various locations in Gazipur area, New Delhi on landfill leachate and its impact on ground water quality (Kamboj & Choudhary 2013, Alam et al. 2020). The grab samples of leachate and ground water samples were collected and analysed as per standard procedure. Higher value concentrations of various physiochemical parameters were recorded depicting unsuitability for household purposes. Moreover, the leachate proved to be highly toxic for the fishes which may be due to the synergistic effect of the combination of complex pollutants.

Based on another case study carried out in a closed landfill site of Dhapa, Kolkata, West Bengal, the characterization of leachate and its impact on surface and ground water quality was found to be exceedingly high in accordance to related studies (Maiti et al. 2015). According to study, leachate was highly contaminated with organic matters having high values of TDS (8994.16 ± 6239 mg/l), COD (4191.66 ± 2282 mg/l), Cl^- (4356.65 ± 1304 mg/l), and two heavy metals viz. Pb (0.56 ± 0.33 mg/l) and Hg (0.42 ± 0.44 mg/l) exceeding their respective standards as specified in “Municipal Solid Wastes (Management and Handling) Rules, 2000” for disposal of treated leachates (MPCB (MEF-GOI) 2000). In surface water samples, TDS and concentrations of Hg and Pb were above their respective permissible limits. In case of ground water samples, Total Hardness (TH), TDS value, and Cl^- concentrations were above the permissible limits recommended by Bureau of Indian Standards (BIS 2012).

3. Plastic Pollution and Environmental Challenges

One of the major components of ‘Municipal Solid Waste’ is plastic, especially single-use products chocking land and ocean. In recent years, plastic wastes have become a universal

pollutant all over the world due to its demand, rise in production, and improper solid waste management. Much of the plastic produced each year is being discarded after single-use, some of which are dumped in landfills and some find their way to aquatic ecosystems. According to a report of 'The Economic Times' released on April 05, 2022, India is generating about 3.5 million tonnes of plastic waste annually, and the per capita plastic waste generation has almost doubled over the last five years (ET 2022).

Plastics, in the form of macroplastics and microplastics are causing toxic effect to human and other organisms both in land and water bodies (Cole et al. 2011, De-la-Torre 2020). They either remain as large plastic debris, called macroplastics or breakdown into minute pieces less than 5 mm in size in the form of microplastics. Microplastics are widely distributed in soil, air, and freshwater ecosystems in the form of primary and secondary microplastics. Primary microplastics are microscopical that are manufactured, whereas secondary microplastics are created from the degradation of larger plastic products like water bottles, soda bottles, fishing nets, plastic bags etc. The major sources of microplastics are sewage treatment plants, cosmetic industry, textile industry, manufacturing industries, packaging and shipping industry. The large macroplastic debris is often ingested by birds, reptiles, and mammals causing premature death (Wilcox et al. 2018). Recent data depicts that both macroplastics, and microplastics whose size is less than 5 mm, are found to be ingested by variety of animal species like fishes, sea birds, sea turtles, marine mammals, and even smallest plankton (Garcés-Ordóñez et al. 2020, Zheng et al. 2021). Hence, through sustainable solid waste management, the consumption of single use plastic products could be reduced and avoided, along with increased rate of recycling at the same time. In this context, the Ministry of Environment and Central Pollution Control Board has recently launched several green initiatives for plastic waste management (PWM), and to beat plastic pollution.

4. Impact of Covid-19 Associated Waste (CAW) on Human and Environment

In recent years the challenging impacts of COVID-19 pandemic on human and environment is the generation of huge quantities of healthcare waste. The production and consumption of PPEs has been increased drastically with increased use of plastics and disposable items resulting into increased sources of CAW generation (Ranjan et al. 2020). Off PPEs, single use face masks like surgical masks and N95 masks are imparting an environmental risk due to their improper management. Since face masks are the primary line of defence to protect from COVID-19 as per guidelines of W.H.O., its production and utility has increased enormously all over the world. Based on a report of 'Centre for Science and Environment', June 2021, there was a significant increase in COVID -19 related biomedical waste generation during second wave in India. In April 2021, India generated 139 tonnes of biomedical waste, which escalated to 203 tonnes per day indicating an increase of 46 percent (CSE 2021). According to Central Pollution Control Board (CPCB), India generated 47200 tons of COVID-19 associated waste between

August, 2020 and June, 2021, which includes face masks, gloves and other medical items (Krishnan 2022). Also, the government of India has made obligatory in wearing face masks in public places. Face masks are made up of non-woven materials incorporating polypropylene (PE) and polyethylene (PE) plastic, which can take as long as 450 years to decompose according to experts. After being discarded, the PPEs are thrown away as municipal solid waste, of which some makes its way into fresh and marine water bodies. The presence of enough face masks on the seashore indicates the lack of awareness and mismanagement practices, leading to harmful effects to the aquatic life. A survey was carried out in six beaches of Tamil Nadu along the coast of India for the presence of PPE, particularly face masks and gloves (Gunasekaran et al. 2022). Result depicts the presence of face mask (98.39 %) as the most abundant type of PPE.

The disposable masks, gloves, and other medical wastes in significant amounts are making their way to garbage piles across cities, posing challenge to its collection and disposal. Microplastics formed by the degradation of plastic products used in PPE's pose disastrous impacts on human and environment. The use of face masks unprofessionally is creating severe problem in the environment both as a solid waste open dump, and as microplastic pollution in the marine as well as freshwater ecosystems. Since face masks are easily ingested by fishes and aquatic microorganisms, the microplastics get easily incorporated into the food chain affecting the humans (Aragaw 2020). Under environmental conditions these face masks break down into smaller sizes less than 5 mm particles, and contribute to microplastic pollution. Experiments were carried out artificially to estimate the release of microfibrils by a surgical mask dumped in marine environment. Results depicted that a single surgical mask might release upto 173000 fibres a day. (Saliu & Lasagni 2021).

5. Sustainable Solid Waste Management and Practices

As because of fast urbanization and rapid population growth, developing countries like India is less able to tackle projected waste disaster issues and its management. Solid waste management is being offered by local government which includes complete process of collection, transportation, treatment, analysis, and disposal of waste. But municipal authorities often dispose the solid waste to an open dump yard in the vicinity of city. Since in India, the infrastructure and technology for waste management are not much advanced, the open dumping practices should be replaced by engineered landfills in order to prevent soil contamination. However, solid waste management practices can minimize the amount of solid wastes with further reduction in its amount in landfills. Avoidance and reduction in the amount of waste generation can be achieved by maximizing efficiency, and reducing consumption. Moreover, the residual waste could be converted into a useful resource. For recycling the material is collected from consumers, remanufactured, and once again sold to consumers, thus conserving the resources, and reducing the volume of refuse to be disposed. Due to scarcity of proper land filling areas across cities, various methods are adopted to reduce the volume of wastes. Incineration could be done to reduce the volume of wastes to 20% to 30% of the original volume. Again, by the process of Pyrolysis, which

is combustion in the absence of oxygen, volume of wastes could be reduced, and the residues are economically important. Further, biomedical solid wastes are discarded after proper treatment, which includes incineration, deep burial, autoclaving, chemical disinfections, shredding, and disposal in municipal landfills.

Sustainable solid waste management consists of a sequence of steps comprising waste minimization and resource reduction, reuse, recycle, and safe disposal (Thomas and Leon 2020). Its management steps include collection, storage and recovery of recyclable materials, transportation, treatment, and disposal. Some of the important sustainable waste management practices to make our lifestyle sustainable, and more environment friendly are-

- (i) Managing degradable and non-degradable wastes.
- (ii) Replacing single-use products with reusable ones.
- (iii) Household waste recycling.
- (iv) Recycling biodegradable wastes and e-wastes.
- (v) Reducing plastic products in daily use.
- (vi) Going for paperless practices.

6. Conclusion

The developing countries like India are already facing the challenges of solid waste management, due to high population density, lack of awareness in rural areas, accelerated urbanization as well as recently overcome severe pandemic situation. The insufficient and improper waste management practices are posing potential risk to humans and other organisms of terrestrial and aquatic life with severe risk of food chain contamination. The COVID-19 pandemic has changed the types and amount of waste being generated in the last two years. The recycling part of waste management sector still needs innovation, especially after post pandemic period to overcome the surge in biomedical waste. There is great need of sustainable utilization of COVID-19 associated products and sustainable management of COVID-19 associated wastes. For maintaining health and hygiene, municipal solid waste management needs more attention in India. Finally adopting sustainable solid waste management system, which focuses on avoidance, reduction, reuse, recycling, treatment and disposal, resources could be utilized efficiently.

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Green Audit and Sustainable Development

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Abstract: *Worldwide anthropogenic factors have contributed to environmental and ecological degradation and catastrophes in an alarming rate since the inception of civilization. Over the last few centuries, increase in population, urbanization and industrialization in an unplanned manner has worsened the situation. Today we are more concerned about the quality of environment we are handing over to our future generations. Thus, means of organic living has percolated into all human activities although a lot is yet to be done. Much of the organic practices have stemmed from the policy-oriented research on sustainable development involving its three pillars – social, economic and environmental approaches. Although several policies related to sustainable development have been drafted, there is a need for periodic assessment, measuring and accounting of ecological components to govern the implementation of policies. Green audit undertaken by organizations primarily ensures that human activities are in sync with environmental policies. ‘Green’ symbolises eco-friendly or not being harmful to the environment. Acronymically it stands for “Global Readiness in Ensuring Ecological Neutrality” (GREEN). According to ISO 14000, green audit is a systematic and documented verification evaluating environmental impact of human activities. “Green Auditing”, an umbrella term, also called as ‘Environmental Auditing’. This chapter highlights the objectives, protocols, scopes and authorities concerned with green audit. Activities involved in pre-audit, on-site audit and post-audit stages are outlined. The points analysed in the green audit gives a guideline to daily organic practices to be adopted in daily lives. Water conservation, biodiversity preservation, planting trees, use of bio fertilizers, waste management, going plastic free, switching to alternative energy comes under the preview of green audit. Abiding to these guidelines also overcomes the effects of hazardous environment on human health. Historical man-made disasters have triggered the need for cautionary and preparedness measures to be followed by organizations. Every level of the society holds responsibility towards environmental conservation. Calculating the total carbon footprints at individual and organizational level must be made into a mandatory practice in order to protect the environment and sustain human health. Methodical advancement keeping in mind the all-round benefits of present and future stakeholders come within the interest of green audit. The green audit was first put into use in USA in the early 1970s. Even after five decades, several shortfalls are noticeable. Lack of awareness and enforcement, cumbersome data retrieval, absence of Standard Accounting policy and intangible outcomes restricts the proper execution and its implied benefits. Focused and dedicated implementation shall definitely benefit both the planet and its inhabitants in the long run. Often it has been realized that traditional and indigenous practices when amalgamated into urban lifestyle paves way for sustainable use of natural resources. The aim of this chapter is to draw the readers’ attention towards environmental deterioration, need for sustainable development and effectiveness of green audit. In this respect, a confluence of traditional knowhow and technological advancement is prophesied.*

Keywords: Sustainable development, Green audit, Organic living

1. Introduction

The environment directly affects the survival of diverse biological organisms on this planet. Human beings have made use of scientific innovations to better the quality of life. This has however gone overboard to an extent that irreversible damage has been done to the environment. As the world copes with environmental hazards, environmental sustainability and implementation of eco-friendly approaches have become important issues. A vast majority of the global population have come within the prerogative of increasing population, civilization, industrialization and urbanization (Patil et al. 2019). This in turn has led to a lifestyle far removed from the organic way of living by our ancestors which was less deleterious to the environment. At this junction the only possible solution is bringing about a balance in the use of development-oriented technology while preserving the environmental quality. Environmental scientists and policy makers introduced 'sustainability' into the mainstream in the 1980s (Purvis et al. 2019). In order to save the planet, a thorough assessment is needed to make 'sustainability' from concept to reality. Measuring individual and organizational carbon footprint, Environmental Impact Assay, meeting Sustainable Development Goals and Green Auditing are such monitoring mechanisms. Here the relevance of Green Auditing in Sustainable Development is discussed. Practices like tree plantations, organic manuring, efficient waste management, use of renewable energy and reduction in consumption of non-renewable energy have been identified as some of the green measures to reduce environmental pollution. Thus, blending traditional way of living and technological advancement can save the earth we inhabit.

2. Why the concern?

Natural calamities and climate changes have threatened human survival and socio-economic stability several times in the past. Irrational human activities have been, and still continue to be the primary reason behind such threats. Unless mankind adopts efficient natural resource management strategies, the existence of our future generations will be endangered (Klarin 2018). Development must cater to our current needs without compromising on what we hand over to the coming generations.

3.1. Concept of sustainable development:

Sustainable development stands upon the Triple bottom line concept:

- i. Environmental sustainability - maintaining the environment while supporting human life and activities
- ii. Social sustainability – maintaining human rights and dignity
- iii. Economic sustainability – maintaining financial resources for supporting life and living standards

Hence equal emphasis is laid on development and sustainability although the two terms appear to be contradictory to each other (Sharpley 2000). Sustainability literally means “a

capacity to maintain some entity, outcome, or process over time” (Jenkins 2009) and performing activities without exhausting the resources on which that capacity depends. Development on the other hand implies advancement in infrastructure, political power and economic policy (Klarin 2018). According to UNDP 2015, the most valid development indicator Human Development Index (HDI) takes into account different categories of socio-cultural, economic, ecological and political growth. Thus, long term benefit can only be attained by blending sustainability and development as far as practicable. The holistic nature of Sustainable Development was highlighted by the Brundtland report as inclusive of protection of ecology, heritage and biodiversity (WCED 1987). A number of organizations and institutions participated in the implementation of the concept of sustainable development. The foundation of United Nations (UN) in 1945 with headquarters in New York (UN 2015) marked the first step. In 1968 the Activities of United Nations Organizations and Programmes Relevant to the Human Environment was framed which laid the groundwork for the establishment of the world’s leading environmental authority, United Nations Environment Programme (UNEP). In 2022, UNEP completes 50 years of its service to mankind in terms of improving life quality while preserving nature for the future. The time frame for evolution of sustainable development is intricately woven with the progress of civilization itself as outlined in Figure 1, 2. Till today, the world tries to abide to the 17 Sustainable Development Goals as formulated by the UN.

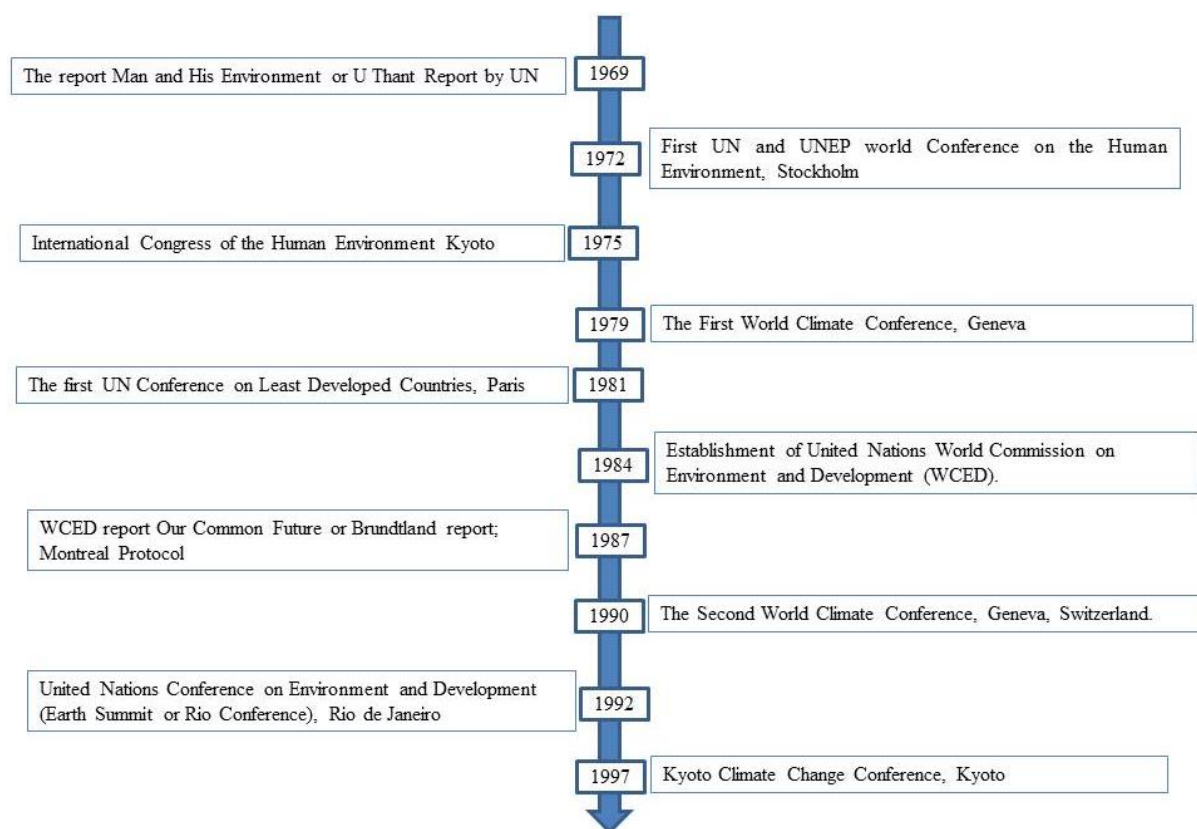


Figure 1: Time frame for progress in Sustainable Evolution during the 20th century

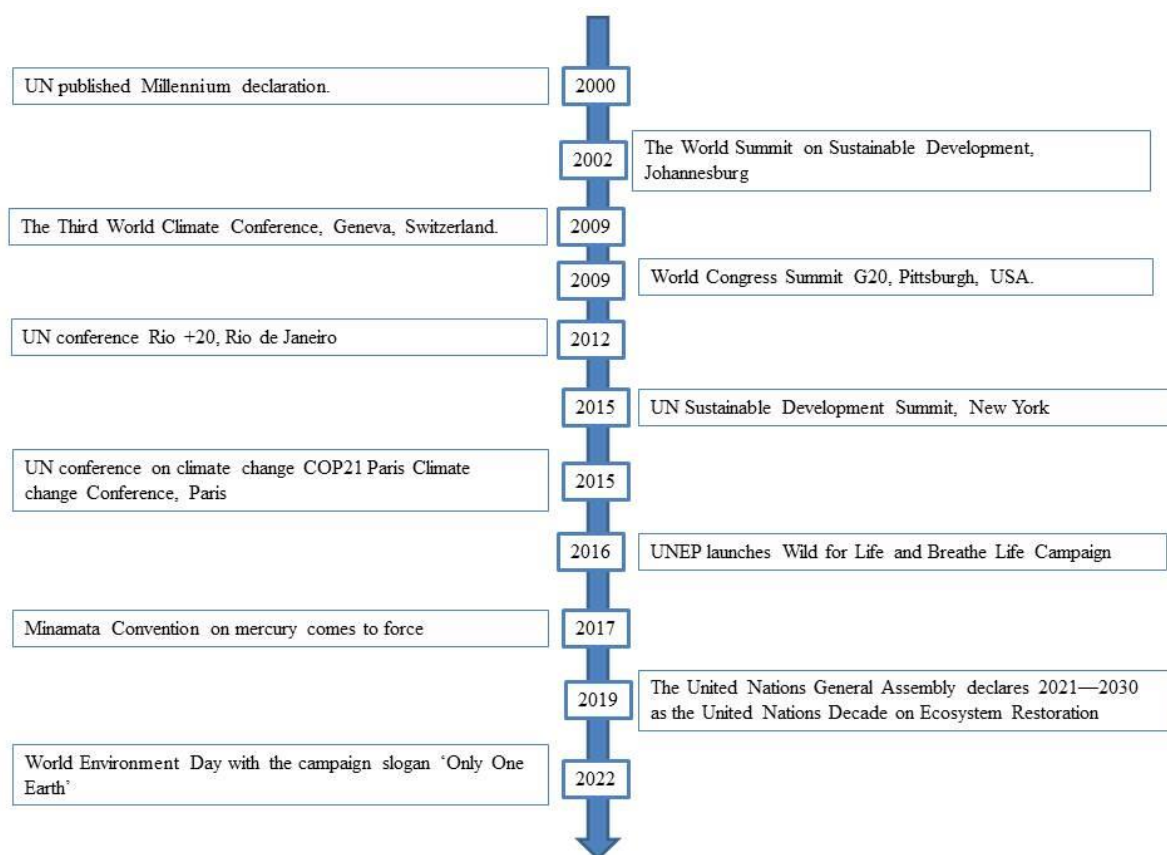


Figure 2: Time frame for progress in Sustainable Evolution during the 21th century

3.2. Challenges towards Sustainable Development:

Environmental opportunities and constraints largely influence holistic development. Impact of degradation of nature is manifested through poverty, hunger and shelter destruction. Such detrimental effects on basic human needs have sabotaging effects on quality of human beings, their intellectual and creative potentialities. Thus, future oriented development goes hand in hand with preservation of ecology. Human development must be considered in relation to global carrying capacity, as exhaustion of natural resources is an absolute natural restraint (Holden et al. 2014). Non-renewable resources are more vulnerable as no amount of effort can replenish these. Sustainable development indicators (SDIs) are aimed at measuring, monitoring and assessing the sustainable development. Although there has been involvement of several government agencies, national and international NGOs, social scientists, environmentalists and workers; universal applicability of the indices is under realized. Another hindrance is the inaccessibility of data for the calculation of indicators (EEA 1999, 2003, 2005, European Commission 2001ab, 2005, 2007, 2009, 2012; Eurostat 2012, 2013, 2014, 2015, OECD 2000, 2001, UNCSD 1996, 2001, UNDESA 2007). The Brundtland report pointed out that the concept of sustainable development is somewhat restricted to western techno-centric development as opposed to human development in relation to environmental sustainability as proposed by the International Union for Conservation of Nature (Sharpley

2000). Poverty eradication without harming the environment is also neglected (Lele 1991). Enhanced need of crop productivity prompted the need for chemical fertilizers and pesticides which has uncontrollably affected the environment leading to lowering of productivity and availability of fertile land. The Earth Summit +5 (New York 1997), and the World Summit on Sustainable Development or Rio +10 in 2002 revised certain agenda of the 1992 Rio Conference. In spite of certain positive outcomes, the problem of global implementation remained. The Rio +10 conference held in Johannesburg noted greater natural degradation and widening of the gap between developed and underdeveloped countries (UN 2002). Subsequent conferences have analysed the progress and problems in the past period of assessment. In 2012 the 20th anniversary of the World Summit in Rio, was observed in Rio entitled '*From Rio to Rio +20*' which adopted the resolution *The future we want* (UN 2012, UNEP 2012). In 2022, Sweden hosted World Environment Day with the campaign slogan '*Only One Earth*'. Accordingly, the focus in the coming days is '*Living Sustainably in Harmony with Nature*'.

4. Green Audit – a step towards living sustainably:

“Green Auditing” or ‘Environmental Auditing’ is an umbrella term used for assessing ecological impact of human activities. Green or sustainable accounting was first brought into common use by economist Professor Peter Wood in the 1980s. ‘Green’ epitomizes eco-friendly or not being environmentally harmful. Acronymically it stands for “Global Readiness in Ensuring Ecological Neutrality” (GREEN). According to ISO 14000, green audit is a systematic and documented verification evaluating environmental impact of human activities. Its scope spans a systematic, documented, periodic and objective review of practices in accordance to environmental requirements. It aims to inculcate environmentally safe practices such as effective waste management, use of alternative energy sources, tree plantation, and ensuring carbon neutrality. Evaluating our own activities constitutes a basic step towards organic living.

4.1. Perspectives of Green auditing:

1. Preliminary survey on existing green practices with relation to waste management, conservation of biotic and abiotic resources and effective utilization strategies
2. Identifying areas where implementation of green measures is needed
3. Developing green policy framework
4. To inculcate environmental awareness among people
5. Measuring and reporting the environmental impact of undertaken activities at a site
6. Analysis and troubleshooting of problems pointed out by Audit Report

4.2. Methodology of Green auditing:

Green auditing can be primarily classified into three types depending on the nature of assessee:

1. Environmental compliance audits review the company's or site's legal compliance status
2. Environmental management audits provide guidance to comply to environmental performance standards
3. Functional environmental audits measure the impact of a particular activity

The phases of auditing are categorized as pre-audit, audit and post-audit steps. The components of each phase are outlined in Figure 3.



Figure 3: Protocol followed during Green Auditing

5. How Green audit sustains development?

Green audit monitors environmental protection while considering cost-cutting strategies such as waste minimization and management. This approach befits the three pillars of sustainable development namely environmental, social and economic sustainability. It empowers organizations to frame a better environmental performance. As academic institutes nurture the future generations, it is now imperative for them to submit green audit report as a part of the corporate social responsibility of the institutions. Scientific innovations have eased life at the cost of harming the environment we live in. This in turn has taken a toll on human health and quality lifestyle. Thus awareness, conscious living and periodic self-assessment are much needed. The audit presents guidelines, methods and implementation strategies for environmental protection. It must be undertaken by any industry, organization, institute and housing complex. It thus ensures safety of stakeholders and while aiming to minimize disasters.

6. Conclusions

The world has witnessed several manmade disasters which has jeopardized the very existence of life in the affected areas. The Bhopal Gas Tragedy (Bhopal 1984), the Chernobyl Catastrophe (Ukraine 1986), the Exxon-Valdez Oil Spill (Alaska 1989), Jilin Chemical Plant Explosion (China 2005) and the Deepwater Horizon Oil Spill (Mexico 2010) are some of the frightening ones. Green auditing conceptualized in the early 1970s aims at inspecting organizational activities having the potentiality of environmental degradation beyond permissible limit. Abiding by the auditing regulations enables reduction in environmental contamination which in the long run has adverse effect on human health and wellbeing. Organizations need to take responsibilities for periodic assessment through competent authorities for sustaining quality living for the present and the future generations. Ensuring the implementation of relevant rules and regulations, improving procedures and material capability, analysing potential duties, and determining cost reduction strategies (Shelke 2022) are looked into. These in turn help to meet the wider goal of sustainable development adopted by the UN. Interestingly, the solution to the problem of environmental degradation can be largely overcome by adopting traditional way of life while enjoying the benefits of technological advancements. Awareness on our part today shall ensure the world to be a liveable place for the coming generations.

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Rukmani in her Garden: A View of an Organic Living in Nectar in a Sieve

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Abstract: *Literary representation of 'organic living' often trespasses into the boundaries of sciences. However, it is also possible to relocate and reinvestigate some literary texts in order to unveil the close relationship between these two realms. Kamala Markandaya's text 'Nectar in a Sieve' remains pertinent to the context of depicting interrelationship between woman and her organic farm which has provided her sustenance. The text uniquely posits a response to the forces of urbanization which threatens this relationship. This paper endeavours to contextualize Markandaya's text from the perspective of a negotiation between two lives- one lived in sync with nature and another which is away from it. Woman in her garden also incites readers to reinvestigate the interrelationship between indigenous women and nature-a key concept that has been explored in ecofeminism. The paper will also explore how the protagonist's retreat to the life of her choice at the end of the novel emphasizes her intrinsic relationship with the land.*

Keywords: Ecofeminism, urbanization, organic farm

In an age of increasing technological development that often undercuts the narrative of sustainability, it is imperative to look back to the kind of life that is lived in sync with nature. In literature one is reminded of the idyllic life evoked in the pastoral in which nature is very much a part of our living realm. However, it can also be observed that in the capitalized society nature is often seen as a commodity and designed for pleasure. Michael Bunce posits that country retreat often alters the meaning of the rural landscape as it provides 'pleasure rather than economic sustenance. It becomes a private landscape controlled by the power' (qtd in Gaard, 56). Living in sync with nature remains therefore, problematical because it interrogates dual aspects of preserving nature-one is preserving nature for its own sake and the other is restoring it as a space for capital gain. Our relationship with nature which is often described as 'the other' in cultural discourse remains, therefore, a contentious issue which requires critical investigation. Eminent ecofeminist Vandana Shiva in her book 'Staying Alive' has described Prakriti as an embodiment and manifestation of the 'feminine principle' which nurtures creativity, and ensures inter-relationship of all beings. Coining the term 'maldevelopment' she posits that the process of development 'is the violation of the integrity of organic, interconnected and interdependent systems, that sets in motion a process of exploitation, inequality, injustice and violence' (Shiva, 5). Women's biological alignment with nature has been, however, under critical investigation because it draws the flaw of essentialism. It is also observed that women share a close relationship with nature based on

their lived experiences which have been either systematically omitted or devalued in cultural discourses. Bina Agarwal has observed that third world women, as a heterogeneous entity, share multiple relationships with nature and this relationship should be based on the material reality of their lived experiences over any ideological construct. Poor women need to collect fodder, food, water from their surroundings in order to provide sustenance for their families. Ironically their narratives remain primarily absent in the development discourse. This paper intends to focus on Kamala Markandaya's fiction 'Nectar in a Sieve' which registers this absence and analyses the relationship of Rukmani, the central character in the novel, with her land.

Kamala Markandaya (1924-2004) occupies a unique position among Indian novelists. A.K Bhatnagar observes that her novels represent reality 'in a natural way' and her characters 'follow their minds and face life as a natural man should do'. It is this quality which makes her works intrinsically different from other novelists such as R.K. Narayan, Bhabani Bhattacharya, Mulk Raj Anand and Raja Rao (Bhatnagar, 3). *Nectar in a Sieve* (1954) was Markandaya's first novel for which she was internationally acclaimed. Her other novels - *A Handful of Rice* (1966), *The Coffers Dams* (1969), *Two Virgins* (1973), *The Nowhere Man* (1972) and *Bombay Tiger* (1982) - poignantly portray themes of east-west encounter, displacement and intricacies of human relationships. Writing about the 'ambivalent relationship' between women and the environment, particularly depicted in the writings of postcolonial women authors, Gurpreet Kaur observes that writers like Kamala Markandaya, Anita Desai, Gita Mehta, Arundhati Roy have retained the social issues a key part of their writing (Kaur, 388). Markandaya's text *Nectar in a Sieve* as an early response to these issues underpins the conflict of rural life and industrialization. This novel which came out in 1954, has been widely discussed from various perspectives. On one hand it deals with themes of hunger and degradation, on the other hand it also shows how one's connection with the land and belief in traditional values negotiate with forces of modernity which causes urbanization and industrialization.

The novel pivots around the character of Rukmani, a village girl who gets married to Nathan at the age of twelve. Her father as the headman of the village has lost his affluence because of the new centralization of power, hence she gets married to an ordinary peasant unlike her sisters who are married off to wealthy husbands. The small, thatched mud house with its doorway decorated with a garland of mango leaves symbolizing happiness and good fortune is her new home. The blue sky and tender trees greet her and the gentle brook soothes her soul. Rukmani treasures this memory till the rest of her life. Rukmani shared an intimate relationship with the river- as a bride of only a week she followed it to find a suitable place for washing. She walked for nearly an hour to find a wide stretch of water and a beach. With her saree tucked up above her knees, she stood in water, washing clothes using a little of washing powder. She feels immensely contented as she lives amidst nature with a loving husband taking care of her – in her words 'While the sun shines on you and the fields are green and beautiful to the eye, and your husband sees beauty in you which no one has seen

before, and you have a good store of grain laid away for hard times, a roof over you and a sweet stirring in your body, what more a woman ask for?' (9). The text locates Rukmani in her surrounding and shows how she strives to maintain a symbiotic relationship with her land. When she builds her home in a new place she finds the land as a means of sustenance. It yields whatever she needs – 'The soil here was rich, never having yielded before, and loose so that it did not require much digging. The seeds sprouted quickly, sending up delicate green shoots that I kept carefully watered, going several times to the well nearby for the purpose' (10). The garden that she tends yields lustrous vegetables – pumpkin, brinjals which she sells in the market and earns for the family. Her gardening skill drew admiration from her husband who now adored her as a 'clever woman'. Rukmani was much pleased though she 'tried not to show her pride'. Gradually from a simple village girl she becomes confident and ambitious – 'I planted beans and sweet potatoes, brinjals and chillies, and they grew well under my hand, so that we ate even better than we had done before' (11). Rukmani's garden not only provides sustenance for her family but also fills her with a sense of wonder.

'Now that I did not work in the fields I spent most of my time tending my small garden: the beans, the brinjals, the chillies and the pumpkin vine which had been the first to grow under my hand. And their growth to me was constant wonder' (14).

Planting and getting crops evokes a kind of pastoral life which is primordial in its essence. Her relationship with the land, garden in particular, has been investigated from ecofeminist perspectives by the critics. Dana C Mount has observed that 'Rukmani experiences her own physical, emotional, sexual and psychological development through her work in the garden and the growth of vegetables,' (Mount, 3). She also posits that her relationship with her land is mediated through labour and this relationship is also vulnerable as Rukmani has to fight against vagaries of nature to survive. She is aware of the uncertainty of nature- "that sometimes we eat and sometimes we starve ..." (132) and yet it is the source of sustenance for her. She gradually becomes a mother of several children and lives a very simple life with little demand for any extravagant need. Thus, in Rukmani's narrative Markandaya records how lives of rural women are embedded in nature. In their simple way of living Rukmani and Nathan celebrate the birth of their son with utmost pleasure and happiness. But Rukmani's relationship with her land places her in a very curious interdependent survival mode which is not only peaceful and fulfilling but also susceptible to nature's whims. Thus, Markandaya writes that 'Nature is like a wild animal that you have trained to work for you. So long as you are vigilant and walk wearily with your thought and care, so long as will it give you its aid; but look away for an instant, be heedless or forgetful, and it has you by the throat.' (42) The kind of challenges that this way of life encounters is also threatening. Nathan and his family starve due to drought and storm for a long period of time. Yet nature also regenerates and provides prosperity. After the hardship the family is able to survive – crops are grown, a new hope of survival assures them all.

The text records how the process of urbanization leaves its deep impact not only on the environment of the concerned village but also on the socio-economic orientation of the villagers whose lives are intrinsically dependent on the place where they live, particularly the poor peasants. Rukmani's own sons, Arjun and Thambi, are not willing to join their father on the farm on the ground that they do not own the land. There are people like Kunthi, Kali, Janaki and others who are ready to reconcile with their changing fate but Rukmani 'stood in pain, envying such easy reconciliation and clutching in my own two hands the memory of the past, and accounting it a treasure' (32). She fails to accept the gradual encroachment of the new regime even when her husband. Nathan advises her to '.. Bend like grass that you do not break'. She is deeply affected when children cannot play in the playground, market prices become too high and there are crowds with full of clamours. She felt how they are going to be ousted from the land of their own- 'In our maidan, in our village he stood, telling us to go.' Cement, sheets of tin and corrugated iron, coils of rope and hemp were placed in the village and invaded the country with clatter and din. Rukmani, ridiculed as a village girl mourns for the absence of birds who '... have forgotten to sing, or else their calls are lost to us' (31). The tranquillity of the village life is forever lost and young girl like Ira cannot move freely but has to get married too early. The encroachment of the tannery is a threat to their existence as it tries to engulf the land. The basic simple life of the farmers changes as they are now choosing the lives of a tannery labourer. Finally, the owner of their land sells the land to the tannery and Rukmani and her husband are bound to leave the country. They move to the city where they are forced to work as labourer in a stone factory.

While the first section of the novel reflects a symbiotic life lived in harmony with nature, the second part records Rukmani's struggle in an alien land which threatens to register her survival strategies. Dispossessed of their land Rukmani and her husband fall prey to hunger and degradation in the city. Rukmani works as a letter writer and a reader but later she starts working in the quarry. The description of the quarry which mutilates the body of nature by blasts using gunpowder reminds one of the tanneries that transformed the rural environment. Though the quarry was on a hillside, it was not the calm and pleasant hill with which Rukmani was familiar. It was 'an enormous irregular crater strewn with boulders and lined with jagged rocks, its side pitted with holes of varying size' and the sharp, vertical falling of the land shows the violation wrought on the body of the hill (176). Nathan accustomed to work on the field succumbs to the extreme stress and hazardous existence. Rukmani after losing her husband decides to go back to the village with a newly found orphan Puli who has provided help in the city.

In the village she is united with her daughter and son with whom she renews her life. Her decision to cling to what Dana C. Mount describes as the 'land-based community ethic' is an assertion of her inextricable relationship with her land. Rukmani's choice to be back to the organic farm where she experienced self sufficiency and happiness also reflects how one's symbiotic relationship with nature ultimately wins over technological development which fails to include poor village woman like Rukmani in its narrative. In her choice to go back to

the village which remains vulnerable to industrial progress, Rukmani defies the forces by embracing the values of love and care. It is true that this retreat does not guarantee her peace but the touch of her land rejuvenated her spirit – ‘I looked about me at the land and it was life to my starving spirit’ and this nearness to her land made her forget the suffering she had. Her son’s assertion not to get worried because ‘We shall manage’ may not sound convincing, yet it is an assertion of their bond based on love and affection, an assurance of their spirit to fight against all odds when they are near to their land.

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Back to Basics: A Multidisciplinary Approach to Organic Living and Waste Management

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