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Emerging Contaminants

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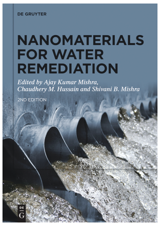

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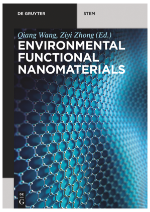

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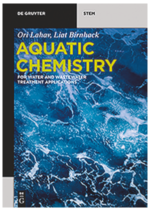

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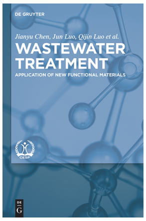

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Rameshwar Yadav Hiranmai* and Murugesan Kamaraj

1 Occurrence, fate, and toxicity of emerging contaminants in a diverse ecosystem

Abstract: Activities that were developed for better/modern living conditions of humans are the primary source of contaminants to the natural ecosystem. Some of the compounds involved in urbanization and industrialization are termed emerging contaminants (ECs) or contaminants of emerging concern. ECs are either chemical or derived from natural sources which environmental concerns and public health have been raised in recent years. ECs enter wastewater treatment systems and migrate from here to different ecosystems as direct or by-products. They are persistent and also stay for a long duration due to their less biodegradation and photodegradation nature. Also, ECs accumulated in living cells and transformed through trophic levels. Technological developments and their application/utility in daily life led to the production of various components that are being added to the natural ecosystem. The treated/untreated wastewater enters into fresh/marine water bodies and gets accumulated into fauna, flora, and sediments. These pollutants/contaminants that are getting added on an everyday basis bring about changes in the existing ecosystem balances. ECs have been found in almost every country's natural environment, and as a result, they became a global issue. The present review discusses the route and transport of selected ECs into the terrestrial ecosystem through water and other means and how they influence the natural process in an ecosystem. The ECs such as personal care products, pharmaceuticals, polyaromatic hydrocarbons, endocrine disruptors, nanoparticles, and microplastics are highlighted in this review.

Keywords: anthropogenic activities; emerging contaminants; food web; occurrence; terrestrial ecosystem; toxicity.

1.1 Introduction

Anthropogenic activities have exerted large stress on the ecosystem. The addition of pollutants throughout environmental matrices changes the ecological condition of a

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given region. Due to the developmental activities, a large number of pollutants in trace amounts are added to the air, water, and soil daily. There is a wide range of undetected contaminants that are being added are of environmental concern. These are also found in biological tissues and quantified by various methods. Emerging pollutants encompass a range of manmade materials added to the environment [1]. Uncontrolled human activities have added a range of pollutants that are in everyday use by modern society and are becoming a part of life. It includes pesticides, personal care, pharma products, and many others included in a part of regular use materials. Emerging pollutants are divided into three categories: Compounds introduced into the environment recently. Compounds have been introduced into the environment for a considerable amount of time but have been detected for a short period. Compounds with well-known adverse effects on ecosystems and human health are identified and measured over time [2]. These emerging pollutants are introduced into the ecosystem through various industries, municipal wastes, and agriculture activities and produces. The sources, occurrence, environmental behavior, and fate of emerging contaminants (ECs) are diverse from conventional contaminants. In advanced research, the pathway of emerging pollutants from source to target is an essential part as their behavior is unpredictable in the environment. The molecular pathway can be detected through genomics to understand the behavior and route of ECs into organisms. Molecular biomarkers can be designed and used to assess the bioavailability of ECs that will also help in environmental biomonitoring and remediation [3].

Agrochemicals, personal care products (PCPs), pharmaceuticals, polyaromatic hydrocarbons (PAH), nanoparticles (NPs), and microplastics (MPs) are the primary emerging pollutants. In addition, many pollutants such as endocrine disruptors, hormones, pesticides, industrial and household chemicals, metals, surfactants, micropollutants, industrial additives, and solvents are also included in the emerging pollutants category. These components are a large group of synthetic or naturally occurring chemicals that have recently appeared in the environment and are not commonly monitored. They enter the environment and cause known or suspected adverse ecological and/or human health effects. Among emerging pollutants, pharmaceuticals are highly stable in chemical structure and possess pronounced biological activity that could be observed through organic chemistry, molecular biology, biotechnology, and pharmacology of the compound. In open ecosystems, they are potentially dangerous, entailing environmental consequences [4].

Reduction of pollutants at source and substitution of toxic compounds can help to reduce/remove them from the environment. In addition, traditional wastewater treatment techniques are not designed to remove or decompose these compounds, so new treatment techniques need to be designed for the reduction of risks and removal opportunities. Examination of wastewater treatment plants (WWTP) and quality of released treated effluent assures the reduction in contaminants in the aquatic system. Water monitoring and the use of new analytical techniques help to detect the contaminants in very small quantity also. The ECs and their associated environmental problems are received much attention in recent years worldwide. Several studies have reported the impacts of various ECs and remediation techniques. Scopus database analysis for the research output in the keyword of “Emerging contaminants” for the period of 2012–2021 is illustrated in Figure 1.1. Though the ECs receive worldwide attention, the systematic review is most needed to highlight the current progress in the ECs occurrence and toxicity on the ecosystem. Hence, the present review aimed to discusses the occurrence, fate, and toxicity of selected ECs in a diverse ecosystem. Although there are several chemicals categorized as under ECs, the current review highlights an overview of agrochemicals, pharmaceuticals, PAH, NPs, and MPs as model ECs and their fate, occurrence, and toxicity on the diverse ecosystem are covered in cumulative aspect instead of covering in a detailed manner.

1.2 Sources and fate of ECs

The environmental fate and potential effects on the environment, their distribution in the environmental compartments (water, soil, and air), and its degradation processes are of concern in the scenario. ECs and their metabolites can enter the environment through a variety of point or diffuse sources, and then enters the water bodies (surface water, groundwater, and marine water), soil, and atmosphere via a variety of routes or mechanisms that are largely determined by ECs properties (persistence, volatility, polarity, and so on) and environmental compartment characteristics [5]. The outflow of WWTP in urban, industrial, and agricultural areas is a major pollution point source for treated municipal and industrial wastewater. Water bodies become a primary contact source of ECs due to the discharge of insufficiently treated effluents from WWTP. ECs can pass through several treatment processes due to their high solubility, low volatility, and – for many of them – low degradability. Because surface waters are the direct receivers of effluents from WWTP and residence durations in surface waters are shorter than in groundwaters, the range and concentrations of ECs observed in surface waters are usually larger than those reported in groundwaters. The ECs enter the soil by the usage of treated effluents for irrigation and the application of chemicals as a fertilizer, herbicides, weedicides, etc. Many ECs, particularly medicines and PCPs, are regarded as key point sources in households (e.g., natural hormones, synthetic steroids). The expired or unused pharmaceuticals are typically disposed of in household solid trash or flushed down the toilet. Excretion in human and animal urine and feces, flushing of unwanted medications, home uses, and bathing are all examples of point sources [6].

The life-cycle distribution of ECs from sources to receptors viewpoint is summarized in Figure 1.2. The spatial distribution of emerging pollutants in ground and surface water was observed with a wide range of contaminants (emerging and organic) that pose threat to water quality [7]. The presence of contaminants is also influenced by sources, hydrogeography, and inherent properties. The physicochemical properties and release into the environment play a significant role in the occurrence of

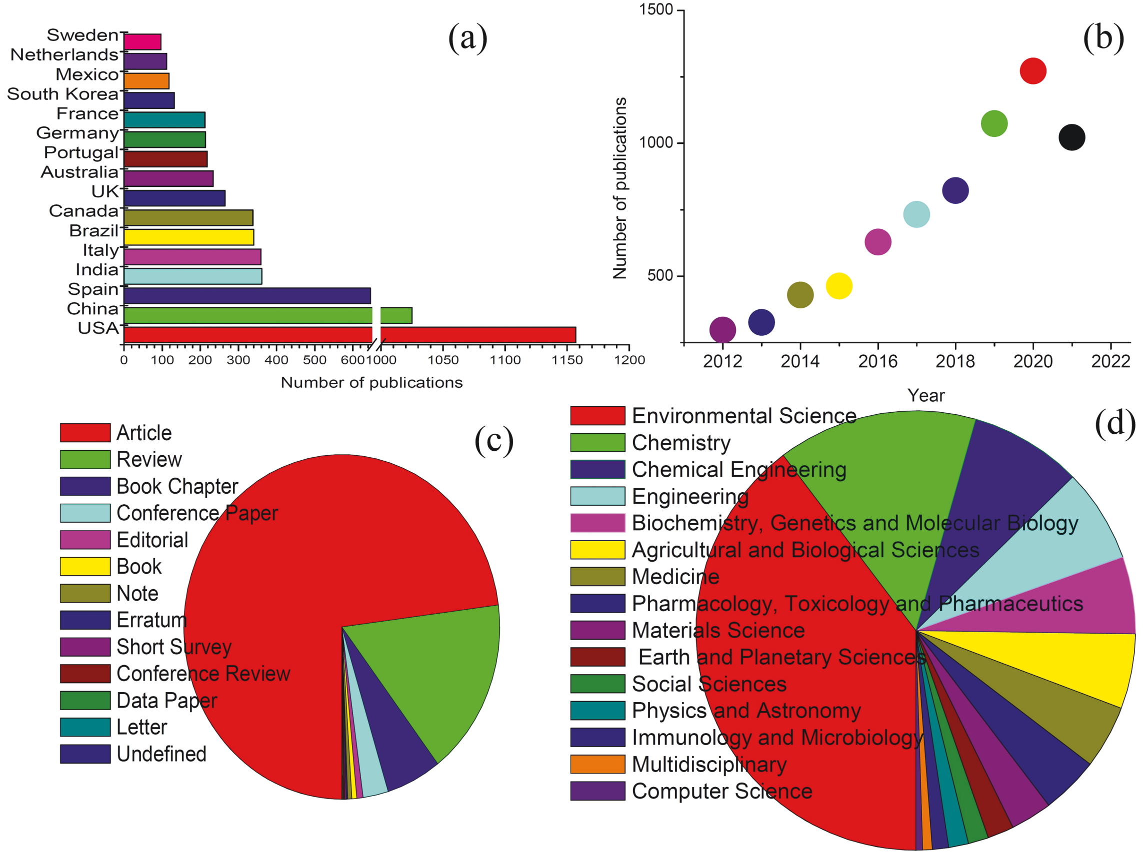

Figure 1.1: Scopus database analysis for the research output in the keyword of “Emerging contaminants” for the period of 2012–2021 (Scopus database as on 18/06//2021). (a) Documents by Top 15 country/territory, (b) documents for year-wise, (c) documents by type, and (d) documents by Top 15 subject area.

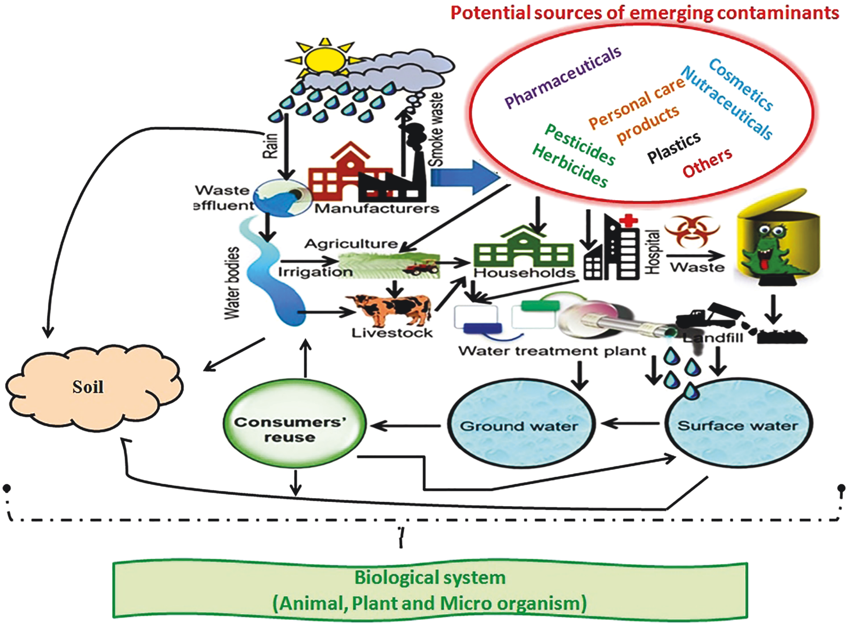

Figure 1.2: Life-cycle distribution of emerging contaminants from sources to receptors viewpoint. (reproduced after modification with permission from Rasheed et al. [73] Copyright © 2019 Published by Elsevier Ltd.)

contaminants. However, these ECs are hydrophobic and cannot be removed by these traditional treatment techniques. ECs are typically detected in waters downstream of sanitary discharge points at concentrations ranging from 0.15 ng L^{-1} to 2.0 g L^{-1}. However, this concentration can be high in wastewater flowing through the hearts and regions of large cities where many ECs are been utilized [8].

Due to their endurance, they can (bio)accumulate in sediments and river flora and fauna, as biodegradation, chemical degradation, and photodegradation (in the absence of light) can all occur at very low rates. Hence, their disappearance from the environment is almost trifling. Certain microbial populations, however, are able to overcome ECs biocide action and potentially change them, speeding up their disintegration rate. Few kinds of research have looked into the natural biodegradation of ECs like hormones, detergents, and medicines. Typically, these investigations are conducted in the laboratory, but there is no guarantee that the experimental systems accurately reflect the real-world environment, and the application of these findings on a wide scale has yet to be determined [5]. As a result, the development of research for finding the impact of natural microbial systems and sunlight-mediated photodegradation on different type of ECs or their transformed product is a task with great perspective to identify their fate in various environments.

1.3 Occurrence and Impacts of EC

1.3.1 Agrochemicals

The consumer products in daily life include biocidal active substances, insecticides, and repellents. Biocides are used in the food industry as disinfectants and food preservatives. Drinking water is treated with biocides to eliminate any harmful micro-organisms. Agrochemicals are used for plant protection and enhancing crop production. The selected examples of ECs of Environmental Protection Agency (EPA) contaminant candidates are listed in Table 1.1. In agriculture, pesticides are used that are now detected in water sources. Various pesticides are taken up by algae, daphnids, and catfish that accumulate and pass through aquatic food chains. Sanchez-Bayo [9] documented that herbicide application adversely affects plant biomass and biodiversity, arthropod communities ultimately lack food for birds and amphibians that lead to their community reduction. Earth's ecosystems are adversely affected by human activity in agriculture and development. The application of pesticides also affects nontarget organisms in agricultural land and surrounding landscapes.

Meena et al. [10] reported the negative effect of agrochemicals on soil fauna and flora, food safety, and sustainable agriculture and influences nutritional value and health of consumers. Beneficial microbial community gets changed in their population and diseases in plants become common. Agrochemical's potential to cause adverse health effects either acute and persistent damage to the nervous system, reproductive organs, lungs, immune and endocrine system, birth defects, and cancer are reported in laboratory experiments [11]. Bio-magnification and the persistent nature of pesticides pose high risks to living organisms and they also pollute the ecosystem [12]. Bhagat et al. [13] reported from a review study that fungicide azole is used in antifungal products that are used in the plant, animal, and human beings for treatment. They are found in the environment and accumulated in aquatic organisms and cause several detrimental effects on fish. Due to the toxic nature agrochemicals are handled and stored with regulations and used for crop production but adversely affect the environment. The utilization of agrochemicals also leads to groundwater contamination with nitrate and surface runoff of fertilizers to aquatic bodies results in increased algal growth that adversely affects the life cycle of aquatic organisms [14]. Lushchak et al. [15] have stated in their review on pesticides that they possess high persistence and pervasiveness. Their biotransformation permits them to stay long in an environment in a living organism. Fungicides inhibit protein and ergosterol biosynthesis and mitochondrial respiration. Growth of seedling, photosynthesis, amino acid, and lipid biosynthesis is inhibited by herbicides in addition to disrupting the cell membrane. Growth, development, and energy production are affected by insecticides.

Table 1.1: Example emerging contaminants on the EPA contaminant candidate list (CCL) [75].

Chemical contaminant	CASRN[a]	Use
17-Alpha-estradiol	57-91-0	It is an estrogenic hormone found in some pharmaceuticals.
2-Methoxyethanol	109-86-4	It is used in a number of consumer products, such as synthetic cosmetics, perfumes, fragrances, hair preparations, and skin lotions.
2-Propen-1-ol	107-18-6	It is used in the production of other chemicals.
3-Hydroxycarbofuran	16655-82-6	It is a pesticide degradate, the parent, carbofuran, is used as an insecticide.
4,4′-Methylenedianiline	101-77-9	It is used in the production of polyurethanes foams, glues, rubber, and spandex fiber.
Acephate	30560-19-1	It is an insecticide.
Acetaldehyde	75-07-0	It is a disinfection byproduct from ozonation; it is used in the production of other chemicals.
Acetochlor	34256-82-1	It is an herbicide for weed control on agricultural crops.
Acrolein	107-02-8	It is used as an aquatic herbicide, rodenticide, and industrial chemical.
Bensulide	741-58-2	It is an herbicide.
Benzyl chloride	100-44-7	It is used in the production of other substances, such as plastics, dyes, lubricants, gasoline, and pharmaceuticals.
Butylated hydroxyanisole	25013-16-5	It is used as a food additive (antioxidant).
Captan	133-06-2	It is a fungicide.
Chlorate	14866-68-3	Chlorate compounds are used in agriculture as defoliants or desiccants and may occur in drinking water because of the use of disinfectants such as chlorine dioxide and hypochlorites.
Chloromethane (methyl chloride)	74-87-3	It is used as a foaming agent and in the production of other substances.
Clethodim	110429-62-4	It is an herbicide.
Dimethipin	55290-64-7	It is an herbicide and plant growth regulator.
Equilenin	517-09-9	It is an estrogenic hormone used in hormone replacement therapy.
Equilin	474-86-2	It is an estrogenic hormone and is used in hormone replacement therapy.
Erythromycin	114-07-8	It is used as an antibiotic.
Estradiol (17-beta estradiol)	50-28-2	It is an isomer of estradiol found in some pharmaceuticals.
Estriol	50-27-1	It is a weak estrogenic hormone used in veterinary pharmaceuticals.
Estrone	53-16-7	It is a precursor of estradiol used in veterinary and human pharmaceuticals.
Ethinyl estradiol (17-alpha ethynyl estradiol)	57-63-6	It is an estrogenic hormone and is used in veterinary and human oral contraceptives.
Ethoprop	13194-48-4	It is an insecticide.

Table 1.1: (continued)

Chemical contaminant	CASRN[a]	Use
Mestranol	72-33-3	It is a precursor to ethinylestradiol used in veterinary and human pharmaceuticals.
Methamidophos	10265-92-6	It is an insecticide.
Methyl bromide (bromomethane)	74-83-9	It has been used as a fumigant and fungicide.
Metolachlor	51218-45-2	It is an herbicide for weed control on agricultural crops.
Nonylphenol[b]	25154-52-3	The main use of nonylphenol is in the manufacture of nonylphenol ethoxylates, which have been used in a wide range of industrial applications and consumer products including laundry detergents, cleaners, degreasers, paints and coatings, and other uses. Several other CASRNs are associated with nonylphenol due to varying chemical structures including 104-40-5, 84852-15-3, 91672-41-2, and 139-84-4.
Norethindrone (19-Norethisterone)	68-22-4	Norethindrone is a synthetic hormone used in oral contraceptives and for hormone replacement therapy.
Permethrin	52645-53-1	It is an insecticide.
Profenofos	41198-08-7	It is an insecticide and an acaricide.
Quinoline	91-22-5	It is a component of coal tars and used in the production of other substances, and as a pharmaceutical (antimalarial).
Vinclozolin	50471-44-8	It is a fungicide.
Ziram	137-30-4	It is a fungicide.

[a] Chemical Abstract Service Registration Number (CASRN#) - Chemical abstracts service registry numbers are used in reference works, databases, and regulatory compliance documents by many organizations around the world to identify substances with a standardized name. [b] Selected from the full list at https://www.epa.gov/ccl/chemical-contaminants-ccl-4

1.3.2 Personal care products (PCPs)

PCPs used for cleaning, protecting, and keeping body surface in good condition enter the wastewater – sewage plant – receiving water route, - aquatic environment. PCPs are found in different environmental compartments and exert adverse effects on living organisms. They are observed in water, sediments, and biota of any aquatic system. Commonly PCPs occur in human and veterinary medicine and are continuously released into the environment. Environmental fate depends on the physicochemical properties and efficiency of microbes in sewage treatment plants, surface waters, and soils for their biological degradation [16]. PCPs are released through effluents and get bioaccumulated in fish tissues. The use of microbeads in cosmetic and personal care (toothpaste, skin cleansers, shaving cream, etc.) are reaching public water reservoirs and natural environments as they are used in personal hygiene by communities upstream of rivers, lakes, and seas [17]. They remain in the aquatic system and get into the food web slowly through a transfer at different levels. PCPs enter soil through sludge land application or landfill, use of livestock wastes as fertilizers, and reclaimed water irrigation.

Bioactive compounds used as PCPs (UV filters, synthetic musk fragrances, disinfectants, food additives, biocides, preservatives, and cosmetics) to improve life quality are of concern due to their accumulation in the environment. They are continuously released into the environment through wastes and affect terrestrial and aquatic organisms. Some PCPs, such as polycyclic musks, organic UV filters, and plasticizers, are chiral compounds [18]. PCPs that are used topically are discharged through water and enter into the ecosystem based on their application methods. In wastewater treatment, they are not removed completely and get discharged into water bodies. The PCPs sorbed onto biosolids of treatment plants gets ultimately into agricultural fields during irrigation and get amended to soil and from there to crops and ultimately to animals and humans [19]. Urban runoff and atmospheric deposition are also routes of entry of PCPS into the environment and there it gets transformed. Volatile PCPs are also released into the atmosphere during spray application. If not frequently changed there are chances of its accumulation in swimming pools [20].

A large number of ECs enter water systems from various sources (sewage, disposal, leeching from landfills, drain water, or from industries) and occur in surface waters, and create pressure on wastewater treatment works for their effective removal [21]. There are three main transport pathways that transportation of the compounds into the cells, which are apoplastic (moving between cell walls), symplastic (moving through cells via plasmodesmata), and transmembrane (moving through cells via cell membranes). The ecological-level effects include effects on biodiversity and community composition, habitat structure, nutrient, and food web dynamics, and disease dynamics. PCPs pollution-induced changes in community composition studied in macroinvertebrates (freshwater fish and macroinvertebrates) exhibited ecosystem-level interactions and bioaccumulation [22].

1.3.3 Pharmaceuticals

The group of ECs and pharmaceuticals are released into the environment through industrial discharges. Due to the universal use of these active pharmaceutical ingredients and their disposal to the aquatic environment, they modify the characteristics of the water body. They also bring about changes in aquatic organisms. Only limited content is removed in wastewater treatment units. A considerable amount of them reaches the aquatic environment and enters the biodiversity. Transformation of drugs occurs due to various factors that are drained to water bodies. Surface water bodies of most countries contain varying concentrations of animal and human drugs as treated effluents are released by industries. Exposure of aquatic organisms to such chemicals continuously can lead to bioaccumulation and changes in their natural characteristics. Hence, the production of more pharmaceuticals for saving lives also emerged as a new contaminant to the environment. Many of them exert acute effects or chronic effects on organisms indirectly. The examples of adverse effects of selected ECs on different biological sources are summarized in Table 1.2. Their presence is recorded in surface, ground, and wastewater, and soils that reach from various sources. Various treatment methodologies are unable to remove them completely in WWTP. The effluent from pharma industries needs specific treatment before their discharge.

Wastewater discharges from the treatment unit carry pharmaceutical residues to water bodies and thereby enter into aquatic animals that are being consumed [23]. The pharmaceuticals in the contaminated environment get into an exposure route through the prey and predator. They also observed that fishes are more prone to human drugs compared to other organisms like algae or zooplankton. The type of pharmaceutical decides the magnitude of contamination and effects on the organism [24]. World 1/3rd population lives in the coastal region and annually the population is increasing that ultimately leads to the release of more compounds like PPCPs and is expected to increase further every year [25]. Variation in climatic patterns changes the precipitation and movement of PPCP into ground and surface waters that further exerts synergistic stress effects on marine organisms and ecosystems. Researches have shown that there is an accumulation of pharmaceuticals in aquatic invertebrates and from them, it gets into predators of these invertebrates and further to the food chain. As increases in the use of pharmaceuticals are inevitable their concentration in the aquatic ecosystem and food web also increases [26].

According to Maldonado-Torres et al. [27], depending on solar radiation and soil characteristics PCPs undergo various transformations. These secondary residues can pose risk to the environment as their toxic effects are different from parent compounds. They made a study with ibuprofen and clofibric acid to identify the degradation and its toxicological effect on selected microbes. It was observed that the transformed products could interact with other PCPs in water sources. Ebele et al. [28] observed that PPCPs are found in surface, ground, and drinking water samples in Lagos state, Nigeria during two different seasons. Most prevalent was amoxicillin recorded as 1614 ng L^{-1} in surface water, 238 ng L^{-1} in groundwater, and 358 ng L^{-1} in drinking water. In addition acetaminophen, nicotine, ibuprofen, and codeine were also found. The concentration of glyburide, caffeine, naproxen, and diclofenac concentrations were significantly ($p < 0.05$) higher during the dry season, while Nicotine and Codeine levels were higher during the rainy season.

Table 1.2: Adverse effects of selected ECs on different biological sources (reproduced with permission from Gogoi et al. [76] Copyright © 2018 Published by Elsevier Ltd.).

Chemical	Adverse effect
Pharmaceuticals	
Diclofenac (nonsteroidal anti-inflammatory drug)	Renal lesions and gill alterations of rainbow trout (*Oncorhynchus mykiss*)
Carbamazepine (antiepileptic drug)	Oxidation stress of rainbow trout (*Oncorhynchus mykiss*)
Gemfibrozil (blood lipid regulator)	Growth inhibition of algae (*Anabaena* sp.)
Penicillin, sulfonamides, tetracyclines (antibiotics)	Cause resistance among bacterial pathogens, that lead to altered microbial community structure in nature and affect the higher food chain
Roxithromycin, clarithromycin, tylosin (antibiotics)	Growth inhibition of algae (*Pseudokirchneriella subcapitata*)
Caffeine (stimulant drug)	Endocrine disruption of goldfish (*Carassius auratus*)
Propranolol (β-blocker)	Reduction of viable eggs of Japanese medaka (*Oryias latipes*)
HHCB (synthetic musk)	Oxidation stress of goldfish (*Carassius auratus*)
Fragrances (musk)	Carcinogenic to rodents, easily absorbed by human skin and may damage the nervous system
Endocrine-disrupting compound	
Bisphenol A (BPA)	Proven to have estrogenic effects in rats and hormonal effects which increase breast cancer risk in humans Reported to act as anti-androgen that causes feminizing side-effects in men.
Estrone and 17-β estradiol (steroidal estrogens) and 17-α ethynylestradiol (synthetic contraceptive) – contained in contraceptive pills	Feminization in fishes mimics as estrogen hormone to nontargets
Preservatives	
Parabens (alkyl-phdroxybenzoate) – (used for antimicrobiological preservatives in cosmetics, toiletries, and even foods)	Shows weak estrogenic activity
Disinfectants/antiseptics	
Triclosan (used in toothpaste, hand soaps, and acne cream)	Acts as toxic or biocidic agent and cause of microbial resistance

1.3.4 Polyaromatic hydrocarbons (PAHs)

In nature, PAHs are spread as heavy and light benzene ring aromatic compounds and are considered major environmental carcinogens [29]. Their hydrophobicity and electrochemical stability get increased as the size and angularity of a PAH molecule increase. PAHs are part of many dietary ingredients and are assessed by bioaccessibility. Natural (volcanic eruptions, natural forest fire, and moorland fire caused by lightning flashes, as well as anthropogenic (industrial, mobile, domestic, and agricultural emission sources) emission, adds pollution by PAHs [30, 31]. PAH pollutants are ubiquitous, found equally in aquatic and terrestrial ecosystems as well as in the atmosphere, and are observed to be highly toxic, mutagenic, carcinogenic, teratogenic, and immune-toxicogenic to various life forms [32, 33]. PAHs have higher hydrophobicity and low aqueous solubility so they are deposited in soil and sediments and adsorb on them easily. They get accumulated in soil and are slowly transported to water and plants [31]. Through plants, they enter the food chain. PAHs are entering living organisms (mammals) through inhalation, ingestion, and dermal contact. They strongly influence humans as well as other organisms and adversely affect health [34].

Soil and atmospheric deposition lead to contamination of edible parts of the plants that further get into the food system. Atmospheric deposition, as well as industrial processes, adds PAHs into the most favored beverages tea and coffee that are detected in instant tea and coffee [35]. The black clayish carbon particles and coal tar are entrapped to reduce the bioavailability and natural plant-soil-microbes interaction could be utilized to reduce contamination risks [33]. The high content of PAHs in the soil is toxic to terrestrial invertebrates and they lead to developmental changes and affect reproduction. PAH uptake by plants through root and translocation to different plant parts highly depend on soil type, availability, and concentration. PAHs were expected to be high in fish and shellfish that can lead to biomagnification.

Uptake, transport, distribution, and accumulation of PAHs in the environment and living organisms are determined by their solubility. Volatility is a factor for their transportation in the atmosphere. Its chemical reactivity influences adsorption to organic material or degradation. These all factors favor their presence in the food chain. The lipid tissue of plants accumulates more PAHs compared to the high water content part and limits their transfer to other plant parts. PAHs get adsorbed onto the surface of waxy vegetables. Through surface water, PAHs are transferred to fresh water and the marine ecosystem. There it gets adsorbed onto surfaces. Organisms in these regions get exposed to the PAH and it gets biotransformed and gets into the aquatic food chain. Mussels and oysters accumulate comparatively large quantities as they filter water and possess low metabolic capacity [36]. Benthic organisms such as lobsters, muscles, and clams are exposed to PAHs in sediments and pore water and they are directly consumed by predators (squid and fish) and further by humans.

1.3.5 Nanoparticles (NPs)

NPs are generally considered with a diameter of 1–100 nm. Engineered NPs come in a variety of forms, and more are predicted to emerge in the future. Most contemporary nanomaterials in the environment can be classified into four categories for such as (i) metal-based materials, (i) carbon-based materials (iii) composites, and (iv) dendrimers [37]. Nanomaterial manufacturing facilities' wastewater may contain a wide range of

NPs. Long-range atmospheric transport, as well as movement in saturated and unsaturated subsurface regions, may result in nanomaterials being transferred to the water. Nanomaterials are most likely discharged into the atmosphere during manufacturing and are eventually found in the effluent of storm runoff [38]. Metal-based NPs tend to disrupt beneficial interactions more forcefully and trigger toxicity due to their unique physicochemical features, such as surface charge, increased surface area and reactivity, and very small size [39]. Colloidal, gas-phase, vapor deposition, and attrition are the four basic types of NP formation processes, all of which can lead to exposure through inhalation, cutaneous, or gastrointestinal routes [37]. When NPs are inhaled or swallowed into the human body, they are frequently thought to be harmful. They get deep into the lungs, where their sheer numbers overwhelm the body's defense mechanisms. They can then be delivered to essential organs via the bloodstream or lymphatic system. Exposure to NPs in soil includes intentional release by soil and water treatment techniques, potential agricultural use industries such as water and fertilizers mentioned above, and inadvertent discharge to air, water, and sludge as the result of various activities [38].

The emission of metal-NPs initiated from the production of raw material, product manufacturing, use, and waste management. The shape of nano-Ag is considered to be spherical for the sake of comparison throughout the literature [39]. This literature summarizes the concentration of nano-Ag in air emissions ranged from 6×10^{-8} to more than 6.9×10^{-4} mg L^{-1} air. Wide ranges of concentrations are reported as above and below the existing industrial exposure limit of 2×10^{-6} mg L^{-1} air. Similarly, for Ag-NPs enabled product manufacturing, the data in the range of 2×10^{-8}–2.4×10^{-7} mg L^{-1} air, 4.4×10^{-4} mg L^{-1} air, and 7.9×10^{-6}–5.5×10^{-5} mg L^{-1} air concentrations. The emission of Ag-NPs in wastewater effluents was found in the range of 0.1–1.3 mg L^{-1} during waste management practices, and 3.8 ± 0.7 mg L^{-1} concentrations were reported during landfilling activities. The toxicological ramifications of these released levels in the environment are unknown. Furthermore, a lack of understanding of NPs' physicochemical properties prevents the development of systematic methodologies for analyzing NPs in complex environmental media [39].

Canesi and Corsi [40] summarized the impacts of NPs on marine invertebrates, which have been identified as important NP targets. The digestive tract and gills are the primary sites of NP accumulation, and the majority of data is available for polychaetes, bivalves, and echinoderms. Immunomodulation, oxidative stress, and embryo damage are the main physiologic reactions. Biomolecule interactions with NPs (e.g., polysaccharides, proteins, and colloids) can alter their aggregation and bioavailability. When the NPs enter inside the organism they have the ability to interact with plasma protein and form a protein radiance that can alter the uptake and toxicity. Current overview of key properties of silica NP (SiNP) (physical and chemical properties, applications, and emissions), latest scientific output related to SiNP, biometric analysis, key toxic mechanisms, and aquatic organisms (knowledge of the ecological toxicity of SiNPs for marine and freshwater) and the main vulnerabilities of ants. The recognition of the toxicity of SiNP from an environmental point of view has been reported by [41]. Bjorkland et al. [42] reported low bioaccumulation of carbon nanotubes in plants, invertebrates, and nonmammalian vertebrates. Among various metal NPs, silver (Ag) is still the predominant one due to its widespread application. The trophic availability of AgNPs in the food chain using conventional and biodynamic methodologies, the processes that control AgNP trophic transfer, and the toxicological effects of AgNP trophic transfer are all being investigated by [43]. Direct investigation of the *in vivo* fate of AgNPs in the food chain, including the discrimination of ions and NPs, as well as the localization of NPs at the subcellular level, will greatly enhance a mechanistic understanding of AgNP trophic transfer and its toxicological consequences, according to this study. These investigations are found to be dependent on the quantification and localization of NPs in biological samples.

There is a potential risk of groundwater pollution as the NPs are transported through the soil. Little is known about the behavior, migration, and fate of NPs in soil [38]. NPs in the soil are a major concern because of their toxicities with a subsequent threat to soil, the environment, and the human community. These contaminants may badly influence soil ecology, crop production, or product quality, groundwater purity, and human health. Research initiatives are focused on understanding the impacts of manufactured NPs on the human being, soil and formulate combat mechanisms to mitigate the adverse consequences of nanocontaminants on human health and soil quality. While this attempt signifies an exclusive chance for soil scientists to investigate these highly potential technologies, it also emphasizes on foremost challenges to a field of research that has great scope to predict the consequences of nano contaminants on soil ecology and animal health [44]. Metal NPs' continuous deposition, low biodegradability, and extended persistence in soils have a negative impact on the population of soil beneficial bacteria and fungus. Based on multiple toxicity endpoints, the research implies that NP-fungi and NP-bacteria interactions are harmful [39]. Accumulation of zinc, copper, and cerium ions and NPs in carrots is reported by Ebbs et al. [45]. In the sand where the carrots were grown, the NPs and metal ions were mixed separately. Surprisingly, the NPs were no more hazardous than the metal ions, and they accumulated less in the carrot's edible portion.

Selck et al. [46] published EU–US opinions on the status of the ecotoxicity study, research priorities, and future challenges. It covers key topics for future research include characterization of NPs in the environmental matrix, alternative methods for toxicity, exposure assessment, the impact of exposure scenarios on bioavailability, and toxicity have was developed on realistic bioassays for the environment and absorption, internal distribution, and NPs depletion. In recent years, several studies on the fate, transport, and toxicity of nanomaterial contaminants are reported. Engineered nanomaterials (ENMs) face complex fate and transport in aquatic ecosystems due to multiple dynamic interactions between the physical/chemical properties of ENMs and complex environmental conditions. Man-made nanomaterials combine with other materials in water or become by-products. ENM combines with suspended particles, colloids, and Dissolved Organic Carbon (DOCs) to deposit suspended particles at the bottom of rivers, lakes, and estuaries. Suspended particles can be deposited and buried in sediments, or deposited in water columns, depending on the hydrodynamics. ENM is biologically available to plants which induces nutrient transfer and plant biochemistry [47]. ENMs may accumulate and/or increase concentrations of the component metal or carbon nanomaterials in the fruits/grains of crops, have detrimental or beneficial effects on the agronomic traits, yield, and productivity of plants, induce modifications in the nutritional value of food crops, and transfer within trophic levels [48].

The molecular properties of the accumulated NP are also not well understood. However, a multi-modality-based approach should reveal not only isolated experimental parameters but also the molecular characteristics of the integrated pathway leading to transfection-induced toxicity. A more complete understanding of the link between exposure to the food chain and toxicity outcomes will allow us to predict how ecosystems will respond to AgNP exposure. Comprehensive AgNP risk assessment results accelerate the development of AgNP-related nanotechnology while reducing risk to wildlife and humans [43]. Considering the structural and functional toxicity of NPs to biodiversity, measures for safe NP disposal in the environment have been advocated, and safe by design approaches to reduce NP contact have to be developed. Agro-nanotechnology solutions should be tailored to specific target applications.

1.3.6 Microplastics (MPs)

Fragmentation of larger plastic (secondary MPs) leads to the production of debris below 5 mm in size (primary MPs) that represents the MPs and that of size between 1 and 100 nm forms nano plastics. MPs are even commonly reported in seafood, honey, beer, and table salt. They are produced by domestic and industrial sources or human activities that are found all over the world in rivers, oceans, soil, and other environments. Those small produced as microbeads are added to toothpaste and exfoliants. Some are produced as larger plastics are broken down in the environment. As they reach the aquatic system through different means are eaten up by organisms [49]. Plastics are used in packaging and when food is heated in it becomes harmful releasing chemicals like bisphenols and phthalates that are endocrine disruptors. In an experiment with mice, MPs were found to be accumulated in the liver, kidneys, and intestine. The MPs can move from the intestine to other parts of the body carried by the blood and are toxic to the brain. *In vitro* studies have shown that human lungs contain plastics as the small particles are present in the air and they produce inflammatory chemicals. Repeated consumption of food packed in plastic can lead to health hazards.

Due to their threat to soil and aquatic ecosystems, MPs are grouped as ECs. Guo et al. [50] made a literature study to observe the MPs in soil and their trophic transfer in food chains and adverse effects on the functioning of ecosystems, microbes, and animal and human health. Similarly, Zhou et al. [51] reported adverse effects of MPs. MPs interact with different properties of soil and it determines their rate and migration in soil. Its presence interferes with the normal functioning of plant-microbe-soil interactions. They form biofilms on microbes and get transported. Nanoplastics are produced during the fragmentation of MPs debris and arise from the engineering materials used for various industrial processes e.g. water, and air used for cleaning of machines, processing aids, equipment, and textiles. The literature for the in-depth understanding of nano plastics occurrence and fate is very limited, hence it's required much research attention. Browne et al. [52] observed MPs in the circulatory system of mussels. Organisms in the marine ecosystem that live near the bottom line of the food chain also accumulate MPs. It enters the food web by consuming plastic-contaminated fish [53]. In addition to this feeding of MPs facilitates the transport of invasive microbes [54].

MPs are also found in natural sediments and soils. As particles sink to the bottom sediment becomes a source and gets into organisms living there and on beaches [55]. Transported through various segments, plastic debris remains in the environment for centuries and it gets into the ecosystem through various sources [56]. MPs are distributed through air, water and are found in many places. Water currents carry them through and accumulate in different parts and are taken up by flora and fauna of the ocean [57]. In this way, MPs enter food directly or indirectly by trophic transfer or between prey and predator. In urban regions air is inhaled in the industrial area, especially textiles contain MPs that get into living tissues while speaking or eating in these areas [58]. Sea birds, mammals, fishes, and bivalves are studied for MP in their meat and found in chicken gizzards among terrestrial organism that is commonly consumed [59] and more than 690 marine species (edible and nonedible) are reported to contain micro/nano plastics [60].

Seawater contains MPs in a suspended form that is easily entering marine organisms as plankton-eating fish in North Pacific Gyre ingest due to their size [61]. Estuarine catfish in Brazil also contained MPs in their stomach. Benthic zone organisms including crustaceans and polychaetes take up MPs from sediment surface and subsurface layers. Trophic level transfer between species was reported to have more accumulation in the upper trophic level. Edible marine organisms (fish, bivalves, crustaceans, and turtles) contained MPs in their gastrointestinal tract, and in bony fishes, it was found in the stomach and guts [62].

In 2016, the European Food Safety Authority published an overview on the presence of MPs and nanoplastics in food, with a particular focus on seafood [49]. According to their report common mussel, bivalves, shrimps and fish ingests MP. Browne et al. [52] reported that the gut of *Mytilus edulis* contains polystyrene microspheres and they get translocated to the circulatory system. It is also evident by Li et al. [63] that MP is present in mussels used in UK coasts and supermarkets. As the MPs are small in size fishes are unable to distinguish between them and food particles. It gets easily ingested by fish and leads to their entry into the marine food chain. Pollution due to MPs are high in marine habitat and indicator species are identified to be mussels as they are distributed across varying marine regions and adapt to various changes in surroundings. MP influences ecological and human risks. The MPs' persistence in the marine ecosystem and aquatic life, their trophic transfer via the food web, and the identifications of seafood species as suitable indicators have become a research priority [64]. Heterogeneous distribution and high concentration of MPs are related to oligotrophic subtropical gyres. The concentration depends on the motility of organisms, their feeding habit, and detection capacity. Setälä et al. [65] observed ingestion, inhalation, entanglement, and trophic transfer of MPs in the marine food web. Organisms like filter feeders have also detected, ingested, processed, and rejected MPs. Lipid metabolism and behavior of fish are affected and weight loss, the triglycerides: cholesterol ratio in blood serum, and the distribution of cholesterol between muscle and liver were also influenced by ingestion of NPs.

1.3.7 Endocrine disruptor chemicals (EDCs)

EDCs are of concern to many scientists and water quality authorities. EDC is a ubiquitous, toxic, and persistent biologically active chemical that mimics or blocks hormone activity in humans and animals, resulting in reproductive function in both men and women. Alternative increases the incidence of breast cancer causes abnormal growth patterns and alters immune function Neurodevelopmental retardation in children. Wastewater may contain tens of thousands of individual EDC and their degradation products, and the net effect of these mixtures can be synergistic or antagonistic (i.e., context-dependent), making it difficult to understand and predict how organisms will respond to them or how to manage them. Vieira et al. [66] summarized the occurrence of some EDCs found in wastewaters and surface waters in several countries which are detected through various analytical methods.

The EDCs are reported in the concentration level of ng L^{-1} in wastewater as follows Estrone-79 (USA), 20 (Canada), 71.2 (France); 17β-estradiol-147 (USA), 20 (Canada), 20.4 (France); estriol-1661 (USA), 297 (France); 17α-ethinylestradiol.-230 (USA), 421 (Brazil); Bisphenol A-2550 (USA), 84 (Brazil); Triclosan-39.8 (Spain); Atrazine-36 (Spain). Furthermore, secondary product degradation is still widely disregarded in bioremediation research. These, on the other hand, might be distinguished by higher concentrations or toxicity levels, or by increased reactive and nonspecific toxicity compared to the parent chemical [67]. EDCs affect the human gut microflora and lead to the development of metabolic disorders due to the induction of xenobiotic pathways. Different EDCs bind to the same hormone receptors and results in combined effects [68]. EDCs in pesticides cause gonad cancer and dysfunction in many animals. Similarly, humans exposed to these were also reported to be at risk of dysfunction of gonads based on their use [69].

1.4 Toxicity of ECs

EPs' toxicity has resulted in an increase in environmental and human health hazards. EPs are considered very dangerous because nanogram per liter (ng/L) doses can cause hormonal interference in fish, genotoxicity, carcinogenicity in lab animals, endocrine disruption, and immunological toxicity in humans and aquatic creatures [5]. Exposure to these xenobiotic compounds triggers biochemical alterations and develops diseases. The study related exposure to pesticides and relative risk of cancer and observed gonadal diseases (ovarian and testicular cancer and dysfunction). Globally there is an increased consumption of materials containing ECs and it occurs naturally as phytoestrogens, in plasticizers, or industrial substances. Humans are exposed to them in higher or lower concentrations and they are persistent compounds. They mimic estrogenic hormones and interfere with them triggering pathways that result in diverse responses in the biological system [70]. They can bioaccumulate in organisms and induce hazardous health effects. Global pollutants reported to be a part of the food chain involve drugs, industrial chemicals, PCPs, and antimicrobials. Few of them come under the category of endocrine disruptors that are proved by *in vitro* and *in vivo* tests. The overview of common major consequences and adverse effects of ECs of high concern on human health is illustrated in Figure 1.3. The toxicity of ECs is critically reviewed by Stefanakis and Becker, [6] and it reported that the daphnid fish and algae were susceptible to pharmaceutical compounds, with antibiotics and sex hormones being the most dangerous substances for human health and aquatic life. Besides, it's been reported that many chemical pollutants can interfere with the normal function of the endocrine system of many aquatic and terrestrial animals, making them more vulnerable to the presence of ECs in water than humans. Reproductive dysfunction, reduced fertility, and population decline are some of the negative effects of this interference on organisms' well-being.

Literature has found pyrethroids and their metabolites to contain estrogenic activity compared to parent compounds [71]. ECs involve a range of consumer products, natural compounds, persistent pollutants, pesticides, etc. The food chain is a major route of exposure to the population as they enter through living components. ECs are found in food packaging and have a toxic effect on consumers. The materials leach to food from the packaging materials and might cause chronic illness. These are unintentionally added products that migrate through food to the environment and need toxicological characterization for their effects on biodiversity. The endocrine system and its normal functioning can be affected by various compounds that in turn influence hormonal function. They ultimately get into the food chain through various means. Pesticides used in the agricultural field and plant-based products like phytoestrogen also show such effects. The application of pesticides, food contact materials, and fertilizers is a cause of their entry into the food chain. Lipid-rich foods containing polychlorinated and polybrominated chemicals are a source of EDCs. Multiple residues

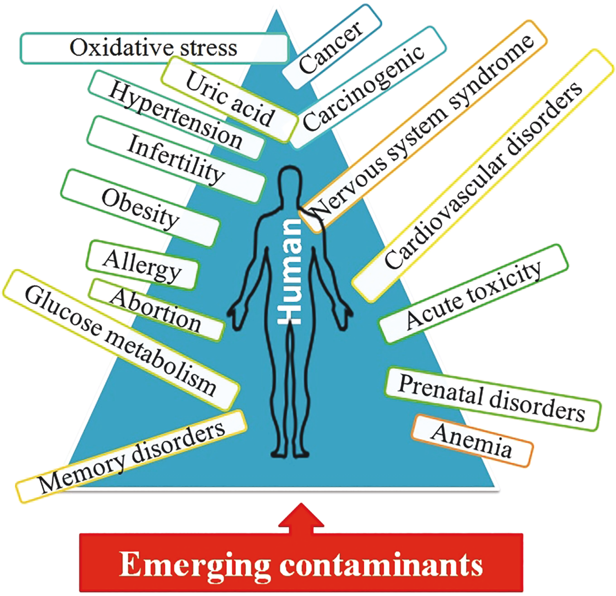

Figure 1.3: Major consequences and adverse effects of ECs of high concern on human's health [73, 74].

of various compounds in the food materials at different levels need to be assessed to reduce the long-term risks through the food chain [72]. ECs that appear at different concentrations have a negative impact on different organisms including exerting adverse effects on soil and water life and thereby on human beings. Because estimating and evaluating the risk for each of the thousands of chemical compounds and pharmaceuticals that have been identified in the environment is almost difficult, the focus should be on those substances that are known to cause harm. Hence, environment-friendly technologies need to be developed and adopted for the efficient removal of ECs from nature.

1.5 Conclusion

The great majority of studies available and reported several chemicals as emerging pollutants could be bioaccumulated and hazardous to the various ecosystem. However, our in-depth knowledge about their real environmental occurrence, fate, and toxicity is still limited. The ECs are detected in various concentrations in various ecosystems at present can be overwhelmed in a near future. The toxicological effects of ECs on various life forms are still caution for their negative impacts and most of the findings are just the output of a single contaminant effect. Due to our incapacity to predict the effect (direct and indirect) of mixed contaminants on natural communities and in a specific ecosystem, extended research in this is high in demand. The best approach to overcome these issues is likely to act on preventions based on the evidence already available and to build cognitive research. The strong policy implementation is highly recommended to promote the derivation of predicted no-effect concentration for emerging pollutants. Intensive ecotoxicological studies based on standard protocols and analyzing very sensitive endpoints to create a relevant data set are highly necessary for protecting the environment. Generation of real impacts of ECs in the various ecosystems and their mode of mechanism, detection, and determination of occurrence, fate, and persistence is highly recommended to overcome the issues associated with the ECs.

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2 Techniques for the detection and quantification of emerging contaminants

Abstract: In recent years, the diverse industrial practices and human inputs widely disseminated emerging contaminants (ECs) throughout environmental matrices, which is of great concern. Even at low concentrations, ECs pose major ecological problems and threaten human health and the environment's biota. Consequently, people's interest and concerns on the widespread dissemination of environmentally connected ECs of great concern as developed due to their scientific understanding, technical innovation, and socioeconomic awareness. Increased detection of contaminants may occur from climatic, socioeconomic, and demographic changes and the growing sensitivity of analytical techniques. Hence, this article reviews the determination of ECs in ecological specimens, from aquatic setup (river water, marine water, and wastewater), sludge, soil, sediment, and air. Sample collection and the quality measures are summarized. The preparation of samples, including extraction and cleanup and the subsequent instrumental analysis of ECs, are all covered. Traditional and recent extraction and cleanup applications to analyze ECs in samples are reviewed here in this paper. The detection and quantification of ECs using gas chromatography (GC) and liquid chromatography (LC) linked with various detectors, particularly mass spectrometry (MS), is also summarized and explored, as are other possible techniques. This study aims to give readers a more excellent knowledge of how new and improved approaches are being developed and serve as a resource for researchers looking for the best method for detecting ECs in their studies.

Keywords: chromatography; detection; emerging contaminants; extraction; mass spectrometry.

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2.1 Introduction

Emerging contaminants (ECs) are a wide-ranging group of compounds that typically do not include under conventional detection and regulatory programs but maybe the entrant for imminent regulation after additional information pertaining to their harmfulness and health impacts becomes available [1]. The term “emerging” is often misapprehended to mean that a substance’s occurrence in the environment is new when it means that the EC has only recently piqued the attention of regulatory and scientific forums owing to advancements in the monitoring protocols or tools and a better elucidation of its harmful impact [2].

The ECs are being released to the environment at elevated quantity as additionally persistent or hazardous contaminants as a result of growing domestic, industrial, and agricultural use due to rapid urbanization; thus, they can enter all possible compartments through volatilization, wet and dry deposition for soil matrix, and diffusive exchange, or aerosol formation process for atmosphere [3]. A considerable number of research articles have been evaluated worldwide on the presence and fate of ECs in aqueous and terrestrial ecosystems [4]. Currently, an enormous amount of chemicals are in use all over the world. All compartments and, by extension, the connected ecosystems are affected by the unavoidable influx into the environment. Organic micro pollutant’s transformed residuals and metabolites can also impart an upsurge in the quantum of ECs that reach the environment and trigger harm, but they remain uncontrolled, and their fate, behavior, and prospective consequences are unknown [5]. Their altered products and metabolites must also be scrutinized owing to the reason that their harmfulness may be analogous to or greater than the parent chemicals. For these reasons, identifying and quantifying the types of ECs present is the first move to consider the possible biological impact of ECs in the environment.

Innovative sampling techniques must be combined with analytical methodologies to confirm known and unknown compounds in complex environmental samples at trace amounts. Research in this sector is hectic because of the public’s interest in environmental issues, with many papers published every year. Similarly, numerous reviews in the literature cover various aspects of environmental investigations, such as the development of new extraction techniques, rapid chromatographic methods, the exploit of mass spectrometry (MS) for target-specific and nontarget analysis, and stratagems for identifying transformed or by-products of ECs [6]. The research on detection ECs in environmental samples is in continuous progress and receives worldwide importance. The thematic map (Figure 2.1) was generated from 619 articles found in the Scopus database for 2012–2012 to identify the most interacted keywords and technologies in detecting ECs from various matrices. The thematic map indicates the incidence of some connections between the type of sample, different ECs, extraction procedures, chromatography, and MS for quantification of ECs specified for the study sequence. The selection of appropriate measures and procedures is crucial for detecting ECs to understand their wide occurrence and distribution better. Hence, the focal point of this review is set to discuss general techniques which can be used to deal with the issues of sampling, extraction, and detection of ECs, in diverse environmental samples.

2.2 Quality assurance/quality control (QA/QC) in sampling

The sampling processes directly impact the value of analytical results; procurement of a sample at the source of attention is frequently disregarded but a critical part of every monitoring process. Malfunction to gather a sample properly can nullify any later consequences. The sample should be typical of the natural domain (water, sediment, air, biota, etc.) and devoid of contamination that may have occurred during sample procurement and transportation to the diagnostic facility. These topics were covered in-depth in a prior assessment of legacy and new ECs, which haven't changed in a long time [7].

Figure 2.1: Thematic map generated from the 619 articles found on Scopus with the keyword 'quantification of emerging contaminants'.

A complete plan and established protocols are required for a successful sampling strategy. The following questions should be appropriately answered while scheduling the procurement trip: 1) selecting the sampling technique which is most fit to collect a characteristic sample, 2) determining the adequate sample quantity required for the analytical methods, 3) determining the QC measures to be taken care to avoid or minimize any predisposition occurred by the sample collection. The sample size criteria and the compounds to be tested in the sample must be defined in the study plan based on the analytical methods which planning to be performed for quantification. The need to preserve samples, which can vary between chemical classes, usually necessitates the need for preservatives in samples but could be circumvented for most ECs [2].

Due to the prevalence of ECs in the diagnostic tools, equipment, and indoor air; blank contamination is a significant issue to consider during the sample preparation procedure once in the lab. To avoid or limit blank contamination, apply the strategies such as pre-extraction of materials, minimize surface contact during sample handling, reduce the usage of plastic materials, and before using the nonvolumetric material, rinse it, heat it, and wrap it in aluminum foil [8]. The replacement of some elements with others, constructed with different types of materials, and incorporating a trap are the preferable options to mitigate instrumental contamination. During the extraction, cleanup, and evaporation operations, time and procedure steps must be reduced. Direct injection is another option for water samples to avoid contamination caused by sample laboratory processing. However, while direct injection method, matrix effects may be worse, affecting sensitivity and precision significantly [9].

Grab or spot sampling is the most popular method for obtaining surface water samples, as this may engage collecting a single or a composite sample envoy of width- and depth-integrated profile. Bailers or thief samplers are frequently used to collect samples in deeper water, such as lakes and reservoirs [10]. Pore water samples are crucial for determining the toxicity of pollutants to benthic invertebrates and determining the possibility for trophic transmission. Pore water can also be a sign of chemicals that have been discharged into the water column above. In the laboratory, centrifugation, squeezing, and vacuum filtering can collect pore water from sediment samples. The usage of vacuum filtration is maintaining the samples are not exposed to air; hence the pore water properties are preserved, and volatile chemical loss is reduced. Chemical exposure is often determined using time-weighted average values, an essential aspect of chemical stressors' ecological risk assessment process [11]. Passive sampling devices are an alternative to grab sampling that overcomes many of the drawbacks of traditional methods. Solid-phase microextraction (SPME), polar organic chemical integrative samplers (POCIS), Semipermeable membrane devices, polyethylene strips, polymers on glass, and devices, and Chemcatchers are some of the passive samplers available [2].

The atmospheric samples are collected with active samplers equipped with a pump that impel air through a filter (for atmospheric particulate matter) and/or a solid adsorbent (for organic pollutants [OPs]). The air sampler, such as polyurethane foam disk, is one of the most often used passive air samplers. The consistently porous polyurethane in these devices allows gaseous compounds to pass through while keeping OPs [4]. Depending on the kind and distribution of pollutants, a representative sample plan for soil may comprise two or more sampling methodologies: random sampling, stratified random sampling, systematic grid sampling, systematic random sampling, search sampling, and transect sampling [12]. The sediment samples acquired with a grab sampler (dredgers, shovels, scoops, etc.) are the most common sediment samples reported to assess ECs [8]. To ensure data validity during the analysis of ECs, QA/QC was vital from sampling to quantification. The general procedure workflow for the detection of ECs is depicted in Figure 2.2. ECs occurrence is studied critically in an array of environmental matrices; water and wastewater [13], soil [14], sludge [15], atmosphere [4], marine sources [5], plants [16], and food products [17], etc.

2.3 Extraction and cleanup techniques for ECs

The advancement and progression of robust and uniform analytical protocols and machinery that can be effortlessly shifted to laboratories pan-globe is the prime impediment imparted on the analytical community. While today's technicians can

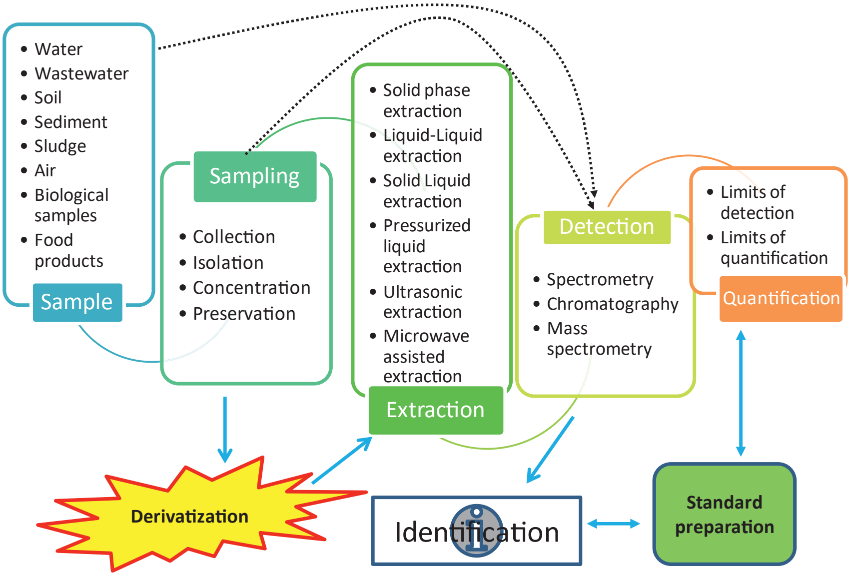

Figure 2.2: Overview of general workflow for the analysis of ECs.

perceive pg L^{-1} and ng L^{-1} dosage-levels in a variety of ECs (e.g., perfluorooctanoic acid [PFOAs], perfluorooctanesulfonic acid [PFOSs], nonyl- and alkyl-phenol ethoxylates, steroids, hormones, pharmaceuticals, and their metabolites) in a variety of sample matrices (e.g., surface waters, wastewaters, and groundwater), appropriate analytical approaches required. The samples may be cross through to a pretreatment step before being analyzed. This procedure is required because it enables further extraction and eliminates matrix elements that interfere with instrumental detection. Water removal (solid samples such as soil and sewage sludge) or concentration (water and wastewater) is the first step before extraction to ensure optimal interaction between the solvent and the matrix in the extraction process [18]. Depending on the substances that need to be examined, various techniques are employed to eliminate or minimize water in samples. Some researchers use centrifugation and decantation as an alternative to air-drying or heating to separate suspended particulates from wastewater before additional water removal. While air-drying is uncommon, samples can also be heated in an oven [19]. Lower temperatures would be required for analytes that degrade at particular temperatures, implying a longer time to concentrate/remove water from the sludge [18]. As a result, most researchers choose to lyophilize their samples since it is a straightforward, time-saving process that prevents analytes from evaporating or degrading [15]. An efficient extraction method is required to acquire effective extraction and purification of the target ECs from the sample as a priority. In terms of conventional extraction, there are two types: those that utilize a tiny quantity of sorbent constituent (sorbent-built absorptive micro-extrication) and those that engage the least volume of solvent (solvent-entrenched absorptive micro-extrication) (solvent-based micro-extraction). The quantity of appliances has expanded dramatically in total research domains to date, with environmental chemistry occupying a unique niche.

2.3.1 Liquid-liquid extraction (LLE)

The extraction method of choice has traditionally been LLE. However, it is a time-consuming, labor-intensive, and costly technique frequently followed by the cleaning and pre-concentration process. It also necessitates significant amounts of organic solvents and is labor-intensive to automate. This methodology has been used to examine polybrominated diphenyl ethers (PBDEs) and endocrine disruptor compounds (EDCs) [20]. Because they are nonpolar and volatile, PBDE is the most commonly extracted chemical by LLE. However, because of their hydrophobic nature and low concentration, especially in water samples, a considerable volume of samples is required (up to 1 L needed for enrichment). The final extract must also be evaporated to reduce the method's Limits of detection (LOD)/Limit of quantification (LOQ) and increase sensitivity. The formation of emulsion in sewage water samples may interfere with PBDE extraction with LLE. The solvents utilized for PBDE extraction with LLE are dichloromethane (DCM), n-hexane (HEX), and combinations of DCM-HEX (1:1, v/v). It is uncommon to employ LLE for the investigation of additional pollutants such as estrogenic chemicals or xenobiotics. DCM was used to extract estrogenic chemicals, which were then cleaned and derivatized with anhydrous pyrene and bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing 10% trimethylchlorosilane (TMCS). These tests were carried out using gas chromatography (GC) and high-resolution mass spectrometry (HRMS). Depending on the analyte, different solvents were utilized to extract xenobiotics [13].

LLE is an aqueous two-phase system (AqTP) generally formed by two phases, in which one is water containing target samples and another composed of water, solvent, polymers, electrolytes, etc., even sometimes both phases have been the same liquid group. When the system's composition is polymer + electrolyte + water, the ATPS typically has a top phase (TP) rich in the polymer (extract phase) and a bottom phase (BP) rich in the electrolyte under specified thermodynamic circumstances. The AqTP is created by obtaining the composition of the two-phase system using a rectangular phase setup that expresses the TP and BP concentrations in mass percentage percent (w/w) and, as a result, the tie line length is used to express the difference between the phases' intensive thermodynamic properties. The polymer and salt composition values in the TP and BP are used to compute this parameter. This technique has already been employed in several analytical procedures to extract and/or partition a wide range of analytes, including proteins, DNA, nanoparticles (NP), dye, metals, and, more recently, ECs [21].

2.3.2 Solid-phase extraction (SPE)

The SPE is a classic approach for extracting trace pollutants from water sources, and it is the most often used technology. It enables multi-residue analysis and can be utilized offline or online and in conjunction with chromatographic analysis. Because the technique is ideally suited for compounds with a wide variety of polarity and physicochemical characteristics, SPE has been broadly employed to analyze EDCs, PBDEs, and pharmaceutical and personal care products (PPCPs). These approaches have been used to determine polycyclic aromatic hydrocarbons (PAHs), UV filters, pesticides, medicines, and alkylphenols (APs) in natural and wastewater samples [13].

This strategy is adaptable and can be tailored to the features of the analyte. Because PFASs are negatively charged at ambient pH, weak anion-exchangers such as Oasis WAX and Strata-X are commonly used as sorbents [8], whereas C18 columns are also used in some studies. Oasis HLB and Strata-X are examples of polymeric reversed phases or hydrophilic-lipophilic sorbents. SPE might be done with sample quantities ranging from 100 to 1000 mL. These sorbents have also been used to extract various organic contaminants from natural water samples, including APs, Bisphenol-A (BPA), herbicides, pesticides, and other EDCs, including nitrosamines and drugs of abuse. The downsizing of solvent employment is one key trend in sample extraction framed in the ideas of “green analytical chemistry”.

SPME is a simple, effective, and environmentally friendly testing and test readiness technique that combines inspection, detachment, and progression into a single step, reducing or even eliminating the use of solvents [22]. Because it is an equilibrium-based phase transfer method that requires a unique equilibrium to be attained during extraction, it is critical to improving the fundamental elements that influence extraction balance and energy, such as sample ionic strength, temperature, pH, and extraction time. SPME is a newly developed test design technique that combines examination, extraction, fixation, and test presentation into a single stage. It has gained widespread acceptance in various research domains, including the assurance of endogenous mixtures [23].

The SPME process, which offers several advantages such as one-step pre-concentration, extraction, greenness, and simplicity, has sparked much attention. The direct immersion method (DISPME) and the headspace (HS-SPME) approach are two fiber-based SPME methods. The fiber is simply drenched in a small volume of the sample arrangement containing the analytes of interest in the DISPME method. Under optimum working circumstances, such as pH, stirring, temperature, and time, the target analytes are focussed on the fiber covering. Finally, the SPME fiber is injected into a warmed Gas Chromatography inlet for warm desorption or into a suitable desorption solvent for the subsequent high-performance liquid chromatography (HPLC) analysis [24]. The higher versions of SPE are available such as matrix solid-phase dispersion (MSPD) and microextraction by packed sorbent (MEPS). MSPD is a rarely utilized extraction technique, but still, it is an excellent technique for dealing with complex matrices [25]. MSPD has been utilized to determine EDCs and PPCPs in sewage sludge. MSPD has also been used to remove synthetic and natural estrogenic chemicals, parabens (PBs), triclosan (TCS), triclocarban (TCC), BPA, and certain medicines such as nonsteroidal anti-inflammatory drugs (NSAIDs), UV-filters, and chlorinated azoles. MMEPS is a novel miniature SPE that may be coupled with liquid chromatography (LC) or GC online. Since its introduction in 2004, this technique has been regarded mainly as a viable alternative to existing sorptive microextraction techniques [26].

2.3.3 Solid-liquid extraction (SLE)

The most prevalent method for extracting ePOPs from solid matrices such as sediment, sewage sludge, soil, and SPM is SLE. Traditional procedures, including mechanical agitation and soxhlet extraction and modern techniques like ultrasound aided extraction (USE) and pressurized liquid extraction (PLE), are used in SLE. The choice of solvent system and the number of solvent cycles will be decided as per the type of target ECs. In a few research works, traditional approaches such as mechanical shaking and stirring (such as hand-agitation, orbital shaker, or vortex) have been documented to extract EDCs from solid samples. A recent review by Martin-Pozo et al. [15] summarized that the analytes extracted by mechanical shaking include PBDE congeners, APs, benzotriazoles UV filters, BPs, PBs, and their metabolites, antibiotics, benzothiazoles, and benzophenones, etc. Their review also reported that for the determination of APs, some pentachlorophenol (PCP) products (TCC), benzotriazoles UV-filters, nonsteroidal anti-inflammatory drugs (NSAIDs), BPA, and PBs, solvents such as MeOH, pure or mixed with water, acetone-hexane (1:1, v/v), cyclohexane, and acetonitrile (ACN) with 1% acetic acid had been employed. Mechanical shaking has also been mentioned as a method for determining NPs in several studies. A modified community bureau of reference sequential extraction technique with end-to-end shaking was used for Zn-, Pb-, Fe-, Ti, and Sn-containing NPs [27].

Although Soxhlet is an efficient method for extracting these chemicals from solid matrices, it requires extensive extraction durations and significant amounts of solvent. Despite these drawbacks, sewage sludge has been used to extract some EDCs (mainly flame retardants). It has also been used to determine organophosphorus complex using dichloromethane-ethyl acetate (DCM-EtAc), other flame retardants such as decabromodiphenyl ethane (DBDPE) and 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), PBDE congeners, and other EDCs such as nonylphenols, PBs, and TCS [28]. As a result of the extraction, cleanup conduct such as silica gel and alumina SPE is frequently necessary. Nonetheless, alternative equally effective procedures, such as ultrasonic-assisted extraction (UAE) and PLE, have gradually supplanted Soxhlet extraction in recent years, requiring less time and solvent extraction.

2.3.4 Ultrasonication assisted extraction (UAE)

The increased collision of ultrasonic energy in liquid medium is due to sound cavitation, an effect that produces many bubbles, causing solids to erode mechanically and particles to burst. UAE is becoming more popular as a substitute for Soxhlet extraction. Although both procedures use identical solvents, UAE is thought to lower the extraction solvents and extraction time. The most accessible and affordable source of ultrasound irradiation is an ultrasonic bath. Despite this, a more efficient technique is presently employed to sonicate samples: a robust cylindrical probe [29]. Regueiro et al. [30] were the first to develop ultrasound-assisted emulsification microextraction (USAEME), which is based on the emulsification of organic solvent which is in small volume as the extractant to extract target content in an aqueous sample using ultrasound radiation, followed by centrifugation to separate the two liquid phases. The cavitation action of ultrasonic radiation reduces the extraction time required in traditional extraction procedures dramatically [31]. As a result, because USAEME is an efficient, simple, low-cost extraction, and pre-concentration procedure for GC analysis, it is a suitable method for determining analytes in water samples at the trace level. This extraction method was originally used to determine phthalate esters, synthetic musk scents, and lindane from natural water samples, with LODs ranging from 7.4 to 133 pg mL^{-1} with excellent sensitivity [31]. It has also been used to identify numerous PBDE congeners (BDE – 47, 99, 100, and 153) with low LODs in the 1–2 pg mL^{-1} range [32] and β-sitosterol with the LOD and LOQ values of 0.013 and 0.04 μg mL^{-1}, respectively, from selected dietary supplements and food products [33].

2.3.5 Pressurized liquid extraction (PLE)

PLE is considered an elevated level extraction method due to its merits over traditional extraction methods. PLE employs solvent extraction at high pressures and temperatures, always beneath their fundamental focuses, to keep the solvent in a liquid condition throughout the extraction process. High-pressure solvent extraction, subcritical solvent extraction, pressurized fluid extraction, pressurized hot solvent extraction, high-pressure high-temperature solvent extraction, and accelerated solvent extraction are some extended terms used to describe this method [34]. Whereas, in pressurized hot water extraction (PHWE), water is employed as the extraction solvent at high pressure and temperature, eliminates the need for organic solvents. This extraction approach is based on the same principles as PLE [35]. Variables including extraction temperature, pressure, number of cycles, and flush volume are studied in PHWE, just as they are in PLE. When analytes have acid-based characteristics, the pH of the water can also affect extraction effectiveness. Martin-Pozo et al. [15] critically reviewed the extraction technique of PLE to determine a broad range of target EDCs such as BPA, Bisphenols (BPs) congeners, APs, chlorinated flame retardants, and flame retardants such as brominated flame retardants (BFRs), hormonal steroids, antimicrobials, and PBs from sludge samples.

2.3.6 Microwave-assisted extraction (MAE)

MAE, also acknowledged as microwave-assisted solvent extraction (MASE), has become a popular alternative to traditional procedures in recent years due to significant advantages in sample production, such as requiring the least solvent volume, reducing extraction time, and allowing the preparation of a large number of tests at once [36]. It is an automated green extraction method with many advantages, including a reduction in extraction time and solvent use, the ability to separate up to 40 samples, and an increase in solvent throughput. The primary advantage of MAE is its ability to rapidly warm the sample solvent combination, allowing it to be used for the rapid extraction of analytes, particularly those that are thermally unstable [37].

Successful extraction of EDCs such as BPA, hormonal steroids, TCS, quinolone antibiotics, PBDEs, chlorobromo derivatives, UV filters, PBs, NPs, OPs, and their corresponding ethoxylates has been documented in the literature [15]. Because the extraction solvents employed for MAE must have the capability to absorb microwaves (solvents with persistent dipole leading effect), their number is restricted. Regardless, the combination of solvents with and without dipoles allows for a wide range of solvent mixes [28]. Water is commonly used to dilute the extracts to a 5% content of organic solvent. The resulting solutions are then processed as liquid samples and cleaned before being analyzed. According to the bibliography [23, 37], MAE coupled with SPE for cleanup is the most extensively used method for preparing solid samples. In most cases, acid digestion is carried out with HNO_3, either alone or in combination with H_2O_2, H_2O, or hydrogen fluoride (HF), as detailed in the literature.

2.3.7 QuEChERS (quick, easy, cheap, effective, rugged, and safe) method

New extraction methods aim to limit organic solvents to obtain more environmentally friendly, less expensive, and less polluting approaches. The QuEChERS extraction method, and its miniature counterpart, micro-QuEChERS, are two of the more extensively used extraction methods for versatility and good results [38]. QuEChERS replaced traditional LLE and SPE methods. An induced liquid-liquid partitioning follows a SLE with an organic solvent with an appropriate salt mixture in the QuEChERS method. As a cleanup method, dispersive-solid phase extraction (d-SPE) is commonly used. Because of its adaptability, this technique has recently been used to extract ECs from solid ecological possessions such as agricultural soils and crops watered with recycled water, sediments, manure, and sludge [39]. Pharmaceuticals, benzotriazoles, benzothiazoles, benzenesulfonamines, hormonal steroids (natural and manufactured), and additional PCP classes such as BPA, TCC, PBs, and benzophenones have all been successfully determined using this method with recoveries ranging from 15% to more than 100% [15].

2.4 Instrumental analysis of ECs

2.4.1 Chromatography and Spectrometry (MS) analysis

Conventional fractionation and separation entail preparative column chromatography, followed by GC or HPLC are the most frequent instrumental technique for detecting diverse substances in any material. The separation of multiple families of compounds is possible using a combination of extraction and derivatization procedures with either LC or GC. GC is used to determine volatile, nonpolar, and thermostable ECs (such as pesticides, flame retardants, and filters), whereas LC is used to determine polar, nonvolatile, and thermolabile ECs.

GC frequently necessitates the attachment of a derivatization procedure to advance the analytes' chromatographic appearance while also boosting selectivity, sensitivity, and peak separation [40]. A derivatization reaction is not required in the majority of flame retardant approaches employing PBDE congeners. The manufactured and natural hormones, pharmaceuticals, and phenolic substances, on the other hand, have been routinely characterized using GC the following silylation with N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA) or N, O-bis (trimethylsilyl)trifluoroacetamide (BSTFA) to form methoxylated trimethylsilyl derivatives, and MSTFA-Iodotrimethylsilane-1,4-Dithioerythritol (MSTFA-TMIS-DTE) is used to derive the androgens and progesterone, such as testosterone. The anti-inflammatory and estrogenic compounds were derived using BSTFA with pyridine/TMCS or both [15]. The use of acylation (typically acetylation), alkylation, or silylating reagents is common in derivatization techniques [41].

Derivatization processes are commonly utilized and well established for everyday labor, despite the fact that they are time-consuming and have some limits. In reality, *in situ* derivatization was developed as a substitute for preparative processes in order to speed up reaction speeds and reduce evaporative losses. When compared to manual derivatization, this process provides a better chromatographic response, uses fewer reagents, and takes less time to prepare the sample. However, *in situ* derivatization has the drawback of requiring a large volume of a reagent to be infused into the instrument, which impairs the chromatographic column's recital over time [42, 43]. On the other hand, derivatization is a time-consuming process with many drawbacks, including compound losses and unanticipated oxidation, incomplete derivatization, lower derivative stability, and incomplete extraction.

In the recent decade, GC or LC coupled to MS or MS/MS has been the most often used method for ECs detection. Because ECs demands high selectivity and fewer LODs, the most commonly reported technique for sludge samples is GC to MS or MS/MS, as these techniques meet the needs for determining these substances. Depending on the sort of ionization mode used, the MS detector can give excellent selectivity and sensitivity. MS/MS spectral libraries, which contain enhance product ion (EPI) spectra collected at various collision energy for the analytes of interest, aids identification based on EPI spectra [44]. Furthermore, LC-MS/MS is commonly used for analytical assessments involving trace amounts of medicines. The matrix effect is complex in investigating PPCPs and EDCs using electrospray ionization as a resource in this scenario. However, GC combined with electron impact ionization MS (GC-MS) can be used to analyze these chemicals without a matrix effect. It is also less expensive and necessitates fewer operations than LC-MS/MS.

On the other hand, ultra-high-performance liquid chromatography (UHPLC) uses sub-2 m diameter particles to conduct separations 5–10 times faster than regular HPLC. With peak widths of 1–2 s, this provides for improved separation efficiency. During data transfer from conventional UHPLC to MS equipment, the possibility of misidentifying peaks is reduced. Mass analysis, on the other hand, necessitates the use of ultra-fast MS detection capabilities. UHPLC/MS necessitates a higher sampling rate, which necessitates faster scan and polarity switching speeds. As the quantity of data points declines, so does the sensitivity, which has a negative impact on repeatability [45].

However, due to the complexity and vibrant range of the samples and the enormous integer of compounds that can be present, identifying nontarget compounds that were not included *a priori* in the instrumental technique offers significant hurdles in environmental analysis. Full-scan LC-HRMS systems are the best option for identifying nontargeted chemicals in actual samples because they overcome the limitation of analytical reference standards. In addition, nontargeted analyte detection does not need to be planned and can be done retrospectively after capture. The use of various nontarget screening procedures with LC-MS has yielded some encouraging findings (Table 2.1). The use of accurate mass measurements and multiple-mass fragmentations (MS/MS) are suggested in reviews on the topic, both of which are dependent on the use of equipment with full-scan high sensitivity and library searching. LC–complete scan HRMS opens up new opportunities and methodologies for environmental water analysis and introduces new obstacles. For manual inspection of extracted ion chromatograms, the number of analytes detected is relatively considerable. As a result, the molecular feature extraction software application must automatically extract the analytes of interest from the raw data [45].

In this scenario, there is an apparent need for high-quality information on ECs and their transformed products (TrPs), which can be obtained in two ways: (1) target analysis of several compounds using wide-scope screening methods and (2) development of rapid and proficient screening methods for determining unknown or nontarget (TrPs) compounds (Figure 2.3). Both techniques necessitate technological advancements to develop sensitive and selective procedures for reliable identification, confirmation, and quantification of these substances. MS, primarily in conjunction with LC, has contributed to these advancements by extending its applicability to more polar chemicals and metabolites. The substantial literature on LC-MS use in environmental analysis now accessible demonstrates that this is the most often utilized approach for this purpose [56]. In recent years, several analyzers have been invented and/or modified, enhancing the approaches’ capabilities and performance. The advancement of the development of HRMS with Orbitrap, time-of-flight (TOF), and quadrupole-TOF (QTOF) mass spectrometers is becoming more popular, has been a watershed moment in recognition of unknown chemicals. The advent of tandem MS systems, such as triple quadrupole and quadrupole-linear ion trap (QLIT-MS/MS), on the other hand, has improved the qualitative and quantitative performance of target analysis [44].

A diode identification method based on supercritical-fluid chromatography was established and validated for seven ECs, including two medical substances (glyburide and carbamazepine [CBZ]), three endocrine disruptors (bisphenol A, 17-Ethinyl estradiol, and 17-estradiol), one bactericide (TCS), and one pesticide (diuron) The findings were confirmed with recoveries of more than 94% identification and LOQ of 0.10–1.59

Table 2.1: Summary of selected ECs detection using different versions of LC-MS.

Type	Form/Source	Specimen pre-treatment	LC-MS	Column	Salvages	LOD/LOQ	Reference
19 biocidal compounds	Ecological waters, sediments soil, and sludge	SPE (liquid), solid-liquid extraction + SPE (solid)	UHPLC-ESI-QqQ (Dual-polarity)	Zorbax SB-C18 (100 × 3 mm; 1.8 μm); T_{column} = 40 °C; F = 0.3 mL min^{-1}	70–120%	LOQs = 0.03 to 5.31 ng L^{-1} (surface water), 0.07–7.48 ng L^{-1} (influent), 0.01–3.90 ng L^{-1} (effluent), 0.01–0.45 ng g^{-1} (sediment), 0.01–6.37 ng g^{-1} (sludge), and 0.01–0.73 ng g^{-1} (soil)	[46]
81 pharmaceutic cum residuals	Surface and treated wastewaters	SPE (Oasis HLB)	UHPLC-ESI(±)-QqQLIT (MRM and IDA procurement); procured separately positive and negative ion	Acquity HSS T3 (50 × 2.1 mm; 1.8 mm) for the samples analyzed under ESI(+); F = 0.5 mL min^{-1}. Acquity BEH C18 (50 × 2.1 mm; 1.7 mm) samples analyzed under ESI(–); = 0.6 mL min^{-1}	12–174%	LOQs = 0.2–140 ng L^{-1}	[44]
50 antimicrobials counting sulphonamides (SAs), tetracyclines (TCs), fluoroquinolones (FQs), macrolides (MLs), ionophores (IPs), b-lactams, lincosamides, diaminopyrimidines, aminocoumarins, polypeptides, and chloramphenicol derivatives	Ecological waters, sludge, sediments, and manure	SPE (Oasis HLB) (liquid), solid-liquid extraction + SPE (SAX HLB) (solid)	Rapid resolution LC-ESI(±)-QqQ; two separate procurement	Agilent Zorbax XDB (100 × 2.1 mm; 1.8 μm); F = 0.3 mL min^{-1}	50–150%	LOQs = 0.52–5.88 ng L^{-1}, 2.36–65.8 ng L^{-1}, 1.73–20 ng L^{-1}, 1.42–9.52 ng L^{-1}, 0.64–6.67 ng g^{-1}, 1.33–17.4 ng g^{-1}, and 1.50–28.6 ng g^{-1} in surface water, lagoon effluent, influent, effluent, sediment, manure, and sludge.	[47]

Table 2.1: (continued)

Type	Form/Source	Specimen pre-treatment	LC-MS	Column	Salvages	LOD/LOQ	Reference
26 insecticide and their residuals	Sediments	Pressurized liquid extraction + SPE (Oasis HLB)	UPLC-ESI(±)-QqQ (dual polarity)	Purospher STAR RP-18e column (125 × 2 mm; 5 μm); $F = 0.2$ mL min^{-1}	65.5–118%	LOD < 80 ng g^{-1}	[48]
Bisphenols (S, F, A, B, and AF), tetrachlorobisphenol A, tetrabromobisphenol A	Environmental waters, sediments, and sludge	Water samples: SPE (Oasis MAX); solid samples: ultrasonic liquid extraction þ SPE	UPLC-ESI(±)-QqQ	Acquity BEH C18 (2.1 × 100 mm; 1.7 μm); $F = 0.4$ mL min^{-1}	57–114%	LOQs = 0.05–4.35 ng L^{-1}	[49]
41 pharma compounds and 21 endocrine disruptors	Freshwater invertebrates	SPE (Oasis HLB)	UPLC-ESI(±)-QqQLIT acquisition in positive and negative ion mode was carried out separately, HPLC-LTQ Orbitrap (for discrimination of an isobaric interference of diclofenac)	Acquity HSS T3 column, $F = 0.5$ mL min^{-1} for pharmaceuticals analysis in positive ionization mode. Acquity BEH C18 column, $F = 0.6$ mL min^{-1} for pharmaceuticals analysis in negative ionization mode and for EDCs analysis at $F = 0.4$ mL min^{-1}	34–125%	MDLs = 0.06–4.3 ng g^{-1}	[50]
122 chemicals	Atmospheric particles	SPE, Waters SunFire C18 (30 m × 4.6 mm i.d., 3.5 lm)	LC-MS/MS	Waters SunFire C18 (30 m × 4.6 mm i.d., 3.5 lm)	–	LOD = 0.121–121 ng L^{-1}	[51]

Table 2.1: (continued)

Type	Form/Source	Specimen pre-treatment	LC-MS	Column	Salvages	LOD/LOQ	Reference
E1, E2, EE2, NP, OP, and their metabolites (counting MeTCS)	Sludge and suspended solids (China), 2016	– LSE (phosphate buffer, pH2, and ACN, twice; ACN, once) – Rotary evaporation and diluted with water – SPE (HLB)	LC-QqQ-MS-selected ion monitoring mode (SIM)	–	40.2–89.4%	MQLs: 0.5–20 µg kg^{-1}	[52]
398 ECs	Wastewater	SPE (200 mg Oasis HLB, 150 mg Isolute ENV+, 100 mg Strata-X-AW, and 100 mg Strata-X-CV)	PLC-QTOF-MS/MS-DIA mode	Acclaim RSLC C18 column (2.1 × 100 mm, 2.2 µm)	–	0.14 ng L^{-1}–431 µg L^{-1}	[53]
172 ECs (pharmaceutics and cosmetics, illicit drugs, organophosphate flame retardants, and erfluoroalkyl substances)	Municipal wastewater	SPE	LC-HRMS	–	>70%	<1 ng L^{-1}	[54]
107 ECs, (pharmaceuticals (58), antibiotics (16), and pesticides (33))	Urban treated wastewater	SPE (QuEChERS method)	LC-QqLIT-MS/MS	Kinetex C18 core-shell analytical column	70–120%	5–500 ng L^{-1}	[39]
27 OPs	Agriculture soil sample	SPE (QuEChERS method)	HPLC-QqQ-MS/MS with an ESI source	Zorbax Eclipse Plus C8 of 1.8 µm × 2.1 mm × 100 mm	30–87%	0.05–50 ng g^{-1}	[55]

DIA, Data-independent acquisition; HSS, High strength silica; IDA, Information-dependent acquisition; LTQ, Linear trap quadrupole; MDLs, Method detection limits; MRM, multiple reaction monitoring; QqLIT, Quadrupole-linear ion trap; QqQ, triple quadrupole; UPLC, Ultra performance liquid chromatography.

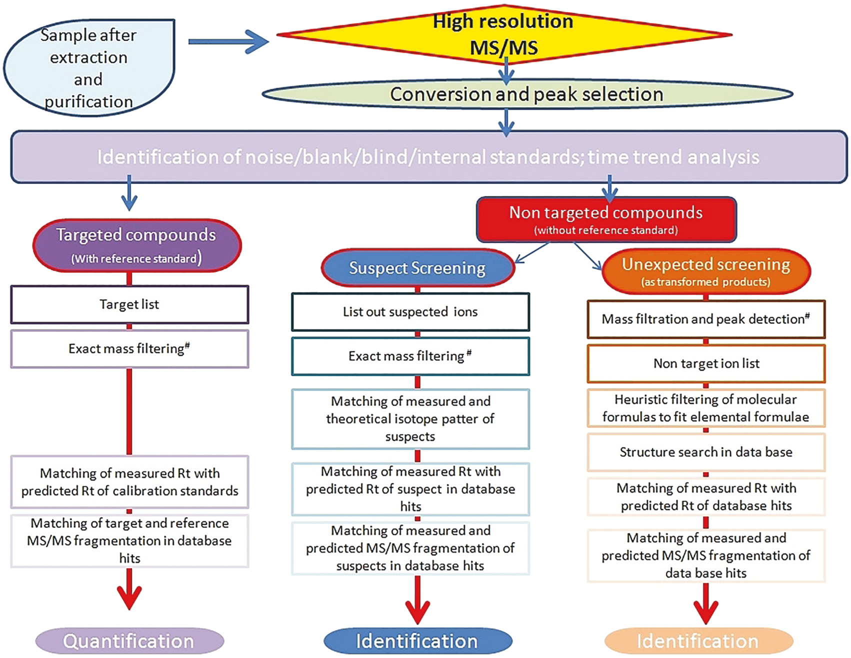

Figure 2.3: Comparison of systematic workflows for contaminant analysis using HR-MS. (Adapted from Krauss et al. 2010 [57]).
(#Consider that the m/z range of the extraction window for the exact mass filtering hinge on the mass precision and the resolving capability of the mass spectrometer used).

and 0.31–4.83 g L^{-1} [58]. Over 400 ECs have been discovered in the examination of surface water and wastewater, according to Robles-Molina et al., including flame retardants, medications, pesticides, lifestyle goods, drugs of abuse, and plasticizers compounds. The use of LC with time-of-flight mass spectrometry (TOFMS) has resulted in high-resolution data derived from retention time data, characteristic insource fragment ions, and accurate target ion masses [59]. In the study of Gago-Ferrero et al. [53], a comprehensive quantitative target approach based on LC-HRMS/MS was established to measure 2316 EPs in water. Pesticides, medicines, illicit narcotics, industrial chemicals, doping compounds, and numerous TrPs were targeted as analytes.

2.4.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is one of the most perceptive techniques for analyzing trace metals in a variety of elemental samples. The main merit of this technology is its high precision, cheap cost, concurrent analysis of the majority of elements (even at mixed conditions), and isotopes in the periodic table in just a few minutes. For most elements, ICP-MS also has exceptionally low LODs, ranging from a few parts per billion (ppb) to a trillion (ppt) [60]. In comparison to inductively coupled plasma-atomic emission spectroscopy

(ICP-AES) and graphite furnace atomic absorption spectroscopy (GF-AAS), it has a quick scanning capability of multi-element over a wide range of masses with lower LOD. Furthermore, the use of ICP-MS in conjunction with chromatographic techniques is critical in depicting and detecting impurities, TrPs, and speciation studies. It contains helpful information on profiling the impurity of drugs and pharmaceuticals. It is quickly becoming the preferred method for QA and QC in the pharmaceutical industry. A variety of chromatographic methods, including capillary electrophoresis, ion chromatography, supercritical fluid chromatography, gel permeation chromatography (GPC), GC, and HPLC, have been combined with ICP-MS for speciation [43, 61]. A GC-ICP-MS study was carried out by Novak et al. [62] to detect the six PBDEs congeners in environmental water samples. These PBDEs are part of a group of BFRs, one of the ECs found in various industrial products.

Single-particle inductively coupled plasma mass spectrometer (SP-ICP-MS) can study NPs at environmentally relevant concentrations concerning size, elemental composition, physicochemical conditions, and particle concentrations. Initially, the SP technique was used for airborne particles, but currently, due to its ability to detect ion pulses on a “particle to partition” basis, the SP technique is more relevant to ICP-MS devices. The ability to detect ion pulses from individual particles is based on the acquisition speed of instruments which is a combination of the time of residence and adjustment [61]. Tou et al. [27], used a single particle inductively coupled plasma mass spectrometer (SP ICP-MS) to quantify the abundance of metal NPs in the fractions of waste sludge samples from across the mega-city of Shanghai, China using a sequential extraction procedure combined with SP-IC-MS. Their study reported that most observed sludges with high concentrations of Cr, Cu, Cd, Ni, Zn, and Pb, exceeded the maximum allowed levels in China under the national acid soil application standard.

2.4.3 Other techniques

Fourier transform near-infrared (FT-NIR) spectroscopy is a technique which recently developed to overcome the disadvantages of traditional Fourier transform infrared (FTIR) spectroscopy. This technique does not provide reagents, nondestructive characteristics, enable sample reuse after measurement, quick technology, and the ability to monitor online. The combination of FT-NIR and chemometrics has been developed to identify the pharmaceuticals (β-estradiol, CBZ, ethinylestradiol, sulfamethoxazole, and ibuprofen) of wastewaters by Quintelas et al. [63].

Biosensors are good tools for monitoring micropollutants in the environment because they are selective, sensitive, easy to handle, and quick. However, compared to other fields of relevance, such as medicine, their growth in environmental analysis is slower. Long-term firmness of biomolecules, cross-reaction with structurally similar substances, and matrix effects with multifaceted environmental samples are the key obstacles. The improvement of multiplexed assays, spurred by parallel breakthroughs in nanotechnology and microfluidics, has been a major step forward. The usage of NPs has improved sensitivity and robustness by increasing signal transduction.

Nonetheless, significant progress has been made in terms of miniaturization. There have been some instruments that have been mainly utilized to build systems that can detect and measure ECs, and/or their toxicological effects, in the aquatic environment among the various combinations such as immunosensors and whole-cell biosensors with optical or electrochemical transduction [5]. The River ANAlyzer and Automated Water Analyzer Computer Supported Systems [64] were two projects financed by the European Commission more than 25 years ago that initiated this area of research [65].

These immunosensors used solid-phase fluoroimmunoassays in combination with a total internal reflection fluorescence optical transducer on a chip that was chemically customized with an analyte derivate. The systems were initially designed to identify developing toxins in rivers, but they served as the foundation for further developments applied to marine systems. The River ANAlyzer system, for example, was utilized to identify testosterone traces in natural river water samples without sample pretreatment, with a recovery rate of 70–120% and LOD of 0.2 ng L^{-1} [5]. Surface plasmon resonance (SPR) was used in an added group of ultrasensitive biosensors to quantify ECs in environmental samples. SPR uses plasmon polaritons (i.e., surface electromagnetic waves) to probe communications between an analyte in solution and SPR sensor surface where biomolecular recognition elements are immobilized. Without any sample treatment, a plasmonic enzyme-linked immunoassay was employed to assess diclofenac in seawater. The LOD for this chemical as an ECs in seawater was 1 ng L^{-1}, which was one order of magnitude lower than that recommended by the first European Union's watch list [66]. Sanchis et al. [67] developed a fluorescent multiplexed microarray platform capable of detecting and quantifying a wide range of pollutants, including CECs. A sulfonamide and chloramphenicol antibiotics, triazine pesticide, PBDEs, 17β-estradiol, and domoic acid were chosen as model analytes to evaluate the system (a marine biotoxin). However, because of the cross-reactivity of the immunoreagents used, the platform can detect a greater range of chemicals.

Immuno-analytical approaches may benefit the treatment of organic contaminants, as these involve only small sample preparation, are very accurate, and are less costly than chromatographic and mass-spectrometry tests. However, the specificity of the immunoassay antibiotic makes it unsuitable for the concurrent analysis of different chemical classes of reactive [68]. For the quantification of ECs, enzyme-linked immunosorbent assays (ELISA) appear to be a viable option. Even though ELISA has some drawbacks, such as; single-analyte technique, the higher cost (antibody production), and the cross-reactivity effects with nontarget compounds with structural similarity to the target analyte; still, ELISA has been used to quantify ECs in the aquatic environment with great effectiveness [69]. Silva et al. [70] ELISA technique was used to monitor 17-estradiol (E2) and 17-ethinylestradiol (EE2) (natural and synthetic hormones, respectively), cetirizine (CET) (antihistamine), CBZ (antiepileptic), and caffeine (CAF) (stimulant) in water matrices with varying salinity and organic matter contents. This study quantifies the referred pollutants in the central part of Portugal's aquatic environment, with values (ng L^{-1}) ranging from 5 to 87, 17, 10 to 1290, 10 to 190, and 62 to 6400 for E2, EE2, CBZ, CET, and CAF, respectively. The selected studies on the determination of ECs in different samples are listed in Table 2.2.

Table 2.2: Selective studies on the determination of ECs in diverse samples.

Specimens	Abstraction approaches	Apparatus	ECs	Reference
Wastewater samples	QuEChERS	GCxGC-TOF-MS	Pesticides, organohalogens	[71]
Water samples	Rotating-disk sorptive extraction (RSDE)	GC-MS with derivatization	Parabens, hormones, anti-inflammatory drugs, triclosan, bisphenol A	[72]
Seawater	Disk-based SPE and UAE	GC-MS/MS	Polycyclic and nitro-aromatic musks, brominated, chlorinated flame retardants, methyl triclosan, chlorobenzenes, organochlorine-pesticides, poly-chlorinated biphenyls	[73]
Surface water, wastewater, suspended particulate matter, sediments	SPE	UHPLC-HRMS	Pharmaceutic-compounds, herbicides, stimulants, illegal-drugs, preservatives	[74]
Wastewater	SPE	LC-Orbitrap-MS	Pharmaceutic-compounds	[75]
Surface water and wastewater	SPE	LC-TOF-MS	Pharmaceutic-compounds, cosmetics, illegal-drugs, pesticides, nitrosamines, flame retardants, plasticizers, perfluorinated compounds	[59]
Lakewater	SPE	LC-QTOF-MS	Endocrine active compounds	[76]
Tap water	SPE	UHPLC-Q-Exactive Orbitrap MS	Pesticides, drug residues	[77]
Wastewater samples	SPE	UHPLC-Q-Orbitrap-MS	Pharmaceutic-compounds and cosmetics	[78]
Surface water, wastewater, suspended particulate matter, sediments	SPE	UHPLC-HRMS	Pharmaceutic-compounds, herbicides, stimulant, illicit drugs, preservative agent	[79]
Wastewater	SPE	LC-Orbitrap-MS	Pharmaceutic-compounds	[75]
Surface water and wastewater	SPE	LC-TOF-MS	Pharmaceutic-compounds, lifestyle products, drugs of abuse, pesticides, nitrosamines, flame retardants, plasticizers, perfluorinated compounds	[59]

Table 2.2: (continued)

Specimens	Abstraction approaches	Apparatus	ECs	Reference
Lakewater	SPE	LC-QTOF/MS	Endocrine active compounds	[76]
Tap water	SPE	UHPLC-Q-Exactive Orbitrap MS	Pesticides, drug residuals	[77]
Crude wastewater, final effluent, and river water	MAE	UHPLC-MS/MS	PCPs, pharmaceutic-compounds and illegal-drugs	[79]
Aquifer sediments	MASE	UHPLC-Q-Orbitrap	Antibiotics	[80]
Water samples	HFLPME	LC-MS/MS	Pesticides, pharmaceutic-compounds, PCPs, industrial products, lifestyle products	[81]
Treated wastewater	Direct injection	UHPLC-QqLIT-MS/MS	Pharmaceutic-compounds, transformation products, pesticides	[82]
Freshwater sediments	Soxhlet extraction	UHPLC-QTOF-MS	Pharmaceutic-compounds	[83]
Water samples	SD-DLLME	LC-MS/MS	Pharmaceutic-compounds, cosmetics, pesticides	[84]
River and seawater	Online-SPE	HPLC-ICP-MS	Mercury	[85]
Water samples	LLE	GC-ICP-MS	Flame retardants	[62]
Atmospheric and lake water samples	Microwave-assisted digestion	ICP-MS	Trace metals	[60]
Soil samples	–	ICP-optical emission spectroscopy (ICP-OES)	Heavy metals	[86]
Seawater	Cross-flow ultrafiltration and LLE	ICP-MS	Colloidal trace metals	[87]
Wastewater	–	FT-NIR	Pharmaceutic-compounds	[63]
River water	–	ELISA	Hormone, pharmaceutic-compounds	[70]
River water	–	Biosensor	Hormones	[64]

2.5 Conclusion

The desire to extract and analyze the greatest number of ECs possible at the same time has led to the development of simple, quick, and generic sample treatments in recent years. Because of the low concentration levels, varying chemical characteristics, and complexity of the matrix, a practical sample preparation step is required to achieve acceptable sensitivity and robust analysis in the sample. The goal of this review was to provide a comprehensive overview of the approaches utilized to detect ECs in various situations. The handling of samples, extraction techniques, and instrumental analysis to quantify ECs are all thoroughly examined. Through the review process, it was found that the concentration levels of different kinds of ECs in various environmental matrixes may be due to their abundance in usage and different molecular structural characteristics.

Sample preparation is a leading step that has concentrated on several important developments in recent decades: simplification, miniaturization, speed, automation, safety, cost reduction, and waste diminution. The methodologies devised were either common and inclusive to meet the large-scale studies or highly particular to meet the needs of targeted quantification. New materials and extraction methods are constantly being developed, and rapid advancements are projected, particularly in nanostructured sorbents and their organization in more beneficial shape. d-SPE decreases stationary phase waste and minimizes sorbent clogging (triggered by suspended particles/matrix compounds) compared to cartridge-based SPE since a slighter amount of adsorbent may be cleaned and reused more times. The key objectives were to save time, money, and labor. Handling "dirty" extracts and accepting low recoveries is an unavoidable trade-off, especially if the goal is to isolate multi-class contaminants encompassing distinct physicochemical attributes.

Conversely, green processes devoid of solvents, have been the unique mode to augment aqueous medium restraining insecticides and pharmaceuticals that are particularly polar and hydrophilic (lyophilization coupled with evaporation or dilute-and-shoot tactics in low-pressure settings). The expansion of some mobile phase filling materials and/or accompaniments/supplements is so new that the quantum of appliances in the environmental-research sector remains meager, nonetheless is predicted to grow dramatically in the future. In comparison to HPLC, UPHLC instrumentation offers superior sensitivity, resolution, swiftness, and superior throughput. When large-scale LC-MS screening is required, these are valuable qualities; however, the direct consequence of highly narrow peaks is the requirement of MS detectors with a high scan rate (and thus higher costs) to accumulate good data throughout the LC peaks for precise elucidation and replicability.

After focusing on merits such as mass precision and acuteness, the most recent advances in MS detection have been concentrated on achieving extensive instrumental discernment. Indeed, the intricacy of ecological matrices is a decisive attribute for efficacious quantitative analysis and accurate documentation. The hunt for transformation products of ECs has become a common trend in environmental study, particularly in the previous decade. As a result, the use of HRMS platforms has increased dramatically. When combined with an excellent data-mining strategy, all-in-one data capture has the potential to save much time when it comes to metabolite screening and identification. The hunt for such an instrument will continue in the coming years to incorporate the required desirable characteristics in a single MS. In the coming years, a significant expansion of HRMS utilization in the environmental domain will be unavoidable.

While encouraging outcomes have been reported in the literature search and appear to be realistically suited for dealing with most emergent items, more thorough research on the magnitude of EC in this environment is required, given that they are relatively new and hence have received little attention. In this regard, the advancement of analytical tools and testing procedures to assess the incidence and effect of additional EC in the environment and their collective effect is urgently needed. Large-scale worldwide programs that are well-coordinated can successfully raise overall levels of knowledge and, ultimately, the quality of our lives.

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3 Advances in biopolymer composites and biomaterials for the removal of emerging contaminants

Abstract: Domestic, agriculture, and industrial activities contaminate the waterbodies by releasing toxic substances and pathogens. Removal of pollutants from wastewater is critical to ensuring the quality of accessible water resources. Several wastewater treatments are often used. Researchers are increasingly focusing on adsorption, ion exchange, electrostatic interactions, biodegradation, flocculation, and membrane filtration for the efficient reduction of pollutants. Biopolymers are a combination of two or more products produced by the living organisms used to give the desired finished product with a unique attribute. Biomaterials are also similar to traditional polymers by having higher flexibility, biodegradability, low toxicity, and nontoxic secondary byproducts producing ability. Grafting, functionalization, and crosslinking will be used to enhance the characteristics of biopolymers. The present chapter will illustrate some of the important biopolymers and its compos that will impact wastewater treatment in the future. Most commonly used biopolymers including chitosan (CS), activated carbon (AC), carbon-nanotubes (CNTs), and graphene oxide (GO) are discussed. Finally, the opportunities and difficulties for applying adsorbents to water pollution treatment are discussed.

Keywords: biodegradation; biopolymers; composites; metal ion; pollution control; wastewater treatment.

Abbreviations

CS	Chitosan
AC	Activated Carbon
CNTs	Carbon Nano Tubes
GO	Graphene Oxide
EPS	Extracellular Polymeric Substances;
TFC	Thin Film Composite

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CS/MIL-100(Fe)	Chitosan/MIL-100(Fe)
G-PDA-BSA	Graphene-Polydopamine-Bovine Serum Albumin
PVA/SA/ZSM-5	Polyvinyl Alcohol/Sodium Alginate/Zeolite Socony Mobil-5
MW-CNTs	Multiwall-Carbon Nano Tubes
CuI-RGO	Copper Iodide-Reduced Graphene Oxide
COD	Chemical Oxygen Demand.

3.1 Introduction

Water is essential for survival, humans continue to pollute it. About 80% of the world's wastewater is discharged, mostly untreated, directly into waterways, polluting rivers, the atmosphere, and the ecosystems [1]. The global population has increased from 6 billion in 2000 to 7.85 billion in 2021 (*World Population Dashboard | UNFPA – United Nations Population Fund*, 7.7.21) [2]. The exploitation of freshwater bodies has been caused by increasing development, industrialization, global warming, urbanization, and a lack of adequate water supply management. Water contamination is a major environmental concern that has gained a huge consideration recently, owing to the growth of the industry and agriculture. These industries generate effluents that contain a variety of pollutants including metals, dyes, pharmaceuticals, herbicides, phenols, phosphates, and nitrates [3, 4]. These pollutants are poisonous and have a negative impact on animals when the permissible concentrations are exceeded. As a result, removing these pollutants from drainage is imperative. Sorption process, ion exchange, membrane isolation, electrochemical transformation, and biodegradation are indeed a few of the methods used to treat ecological pollutants [5].

Water contains a variety of organic and inorganic contaminants, some of which are generally complex, carcinogenic, toxic polymers, polychlorinated biphenyls, phenols, polycyclic aromatic hydrocarbons (PAHs), pesticide residues, insecticides, and polybrominated diphenyl ethers [6]. The toxic metals include cadmium (Cd), arsenic (Ar), chromium (Cr), lead (Pb), and mercury (Hg), as well as nutrients like PO_4 and NO_3, is principal inorganic contaminants. Various methods have been developed to remove toxins from effluent and preserve water sources [7, 8]. Traditional electrodialysis, ion-exchange, adsorption, electrolysis, coagulation, reverse osmosis, and chemical precipitation are all demonstrated to remove pollutants from wastewater [8, 9]. Among these techniques, adsorption is receiving significant research due to its higher effectiveness, relatively inexpensive, ease of processing, and wide availability of various adsorbents [1].

Biopolymers are generated by living creatures and are formed when enzymes bind together basic components like sugars, amino acids, or hydroxy fatty acids to form large macromolecules. Bacteria could indeed produce a variety of such biopolymers, including polysaccharides, poly phosphates, polyesters, and polyamides [25, 26] (Figure 3.1). List of various biopolymers and its composites and its application in treatment of various pollutants are tabulated in Table 3.1.

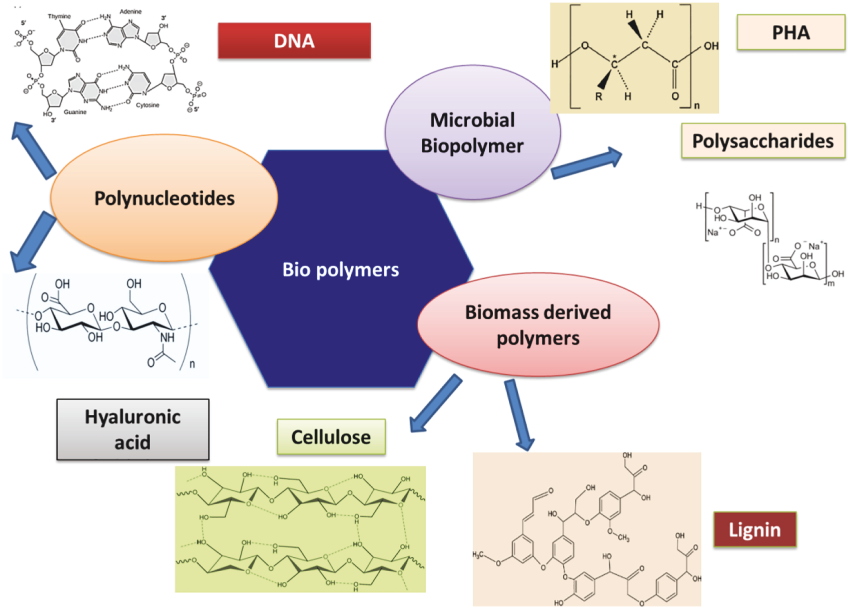

Figure 3.1: Chitosan@Graphene Oxide-Hap composite.

The primary constraint on the use of bioflocculants is the expenditure of flocculants and its manufacture. With lower production costs, the economically feasible synthesis of the biopolymers can indeed be done with wastewater sludge. Carbon, nitrogen, and other nutrients are easily available in sewage sludge, which is incredibly cheap. Bacteria can consume carbon, nitrogen, phosphorus, and micronutrients that are accessible in wastewater from both industrial and municipal systems [6]. Several bacterial strains have the ability to produce extracellular polymeric substances when they were grown in the sludge medium and effectively remove the N and P concentration of waste sludge [27]. A lack of carbon and nitrogen in the growth media and culture conditions determine the biosynthesis of extracellular polymeric substances by microbial cells. When it comes to getting the most out of the carbon and nitrogen in the reaction mixture, different organisms vary according to their preferred carbon and nitrogen source consumption, minerals, temperature, and pH, which seem to be the major determinants for extracellular polymeric substances formation. It is necessary to have a thorough understanding of the metabolic, physiological, and biological parameters of the EPS-producing microbes as well as the various chemicals and antimicrobial agents with which they might be exposed in wastewater sludge to have a good grasp of its extracellular polymeric substances-producing ability [25].

This chapter is a current overview of the use of various natural biopolymers and its composites in wastewater treatment, including preparation and alteration processes

Table 3.1: List of various biopolymers used in wastewater treatment.

Name of the biopolymer and its composites	Type of wastewater or pollutant	References
Chitosan-CNTs humic acid induced biomass	Phenol	[10, 11]
Magnetic multiwall CNTs modified with chitosan biopolymer	Endocrine disrupting factors	[12, 13]
Carbon nanotubes/Chitosan nanocomposite	Picric acid	[13]
CS/MIL-100(Fe)-nanofiltration membrane	Anionic, cationic textile dyes and mixture of salts	[14]
Feather keratin derived sorbents	Wastewater produced during energy generation processes	[15]
3D printed graphene-biopolymer aerogels (graphene-polydopamine-bovine serum albumin [G-PDA-BSA] aerogel)	Cr^{6+}, Pb^{2+}, methylene blue, Evans blue, n-hexane, n-heptane, and toluene	[16]
Alginate–CS hybrid adsorbent		[17]
Extracellular polymeric substances (EPS) producing freshwater *Cyanothece* sp. strain	Micro- and nano-plastics	[18]
EPS	Turbidity removal of river water, municipal wastewater and brewery wastewater	[19]
Poly(acrylic acid) embedded CS & biochar composite	Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, and Cr^{3+}	[20]
Superoleophobic membrane by crosslinking konjac glucomannan on pristine fabrics	Oil–water separation polyaromatic dyes and heavy metal ions	[21]
Porous carbons synthesized from wood-based biopolymers	CO_2 sorbents	[22]
Surfactant-clay (organo-clay) and chitosan biopolymer and	Cu^{2+} Ni^{2+}	[23]
Chitosan@Graphene oxide-Hap composite (CS@GO-Hap composite)	Congo red, acid red 1 and RR2 (Reactive Red 2)	[5]
Chemically modified biosorbents	Pharmaceutical waste	[24]

and its properties. The efficiency of the different biopolymers on the removal of different wastewater sources was discussed.

3.2 Quantification of biopolymer

Typically, the quantities and nature of the biopolymer available have begun the important factor determining the ability of waste reduction [28]. The objective of any extraction process is to eliminate quite enough biopolymer as possible while preserving the microbial cell's integrity. Numerous physicochemical processes, such as high-speed centrifugation, boiling in acid or alkali, and the use of cation exchange resins, have been used to remove biopolymer from various types of sludge. In the fact that these approaches have been objectively evaluated, no single approach has been accepted as a regular practice. The use of non-standardized methods makes it impossible to compare outcomes [25]. A new approach for biopolymer extraction based on glutaraldehyde has recently been reported to produce promising results. The addition of glutaraldehyde to activated sludge helps to solubilize the polymeric matrix constituents, causing the biopolymer to be centrifuged away from the bacterial cells [19]. As comparison to three other techniques, the glutaraldehyde process removed more organic matter while causing fewer cell destruction, spatial organization, and intrinsic heterogeneity induced by the formation of diffusion gradients for gases and nutrients. The nature of the microbial community inside the biofilm is determined by this. Any extractive technique destroys the spatial organization of the biofilm itself, resulting in physical damage. The advancement of confocal scanning laser microscopy and its application with fluorescent probes and markers has allowed comprehensive quantitative study of biofilm architecture. Adopting methods including multiple parameters imaging with nucleic acid stains for bacterial cell identification, fluorescent lectin probes for biopolymer staining, and auto fluorescence for imaging algal biomass, the impact of various treatment regimens on mixed-population biofilms could be assessed to overcome the physical damage associated with conventional methods [29].

3.3 Properties of biopolymers

Fundamental and inherent characteristics of a polymer are determined by its configuration and/or chemical characteristics and span a broad range of related properties. Density is a fundamental characteristic of polymers that varies according on their type and components. When compared to conventional polymers derived from petroleum resources, the densities of the majority of biodegradable polymers tend to be greater. One might argue that higher density values equate to increased energy utilization, and as a result, investigation and evaluation on energy conservation are being done and assessed [29]. While crystallinity is not typically considered a self-reflective feature, transition temperatures are reliant on the crystalline structure of biopolymers, which has an influence on a variety of other qualities, including such solubility. In terms of solubility, highly crystalline biopolymers tolerate disintegration better than those with a lower crystallinity. Different degrees of crystallization in a single biopolymer result in a range of melting and glass transition temperatures. Polymer films are classified according to their permeability to water vapor and O_2 into three categories: (i) less penetrable to both water vapor and O_2, (ii) low permeability to water vapor but high permeability to O_2, or (iii) less permeability to O_2 but highly permeable to water vapor. Translucent biopolymeric films have gain significant interest to the point that they are required for constructing a product and it is accomplished by integrating a translucent nucleating additive into the polymers, that also have a tendency to crystallize the polymeric substance into an enormously significant no. of crystals whereas retaining a size smaller than the wavelength of visible light, allowing it visible perceptible range of light to proliferate uniformly along without scattering [24].

The term “synthesis attributes” refers to those that are involved with conferring quality characteristics throughout the manufacturing process. Which include viscosity, heat distortion temperatures, durability, thermal stability index, and a variety of mechanical characteristics that is relevant all across the production stage [19].

Constituent characteristics of polymers are indeed result of a critical combination of relative and synthesizing characteristics that result in specific distinguishing characteristics. For example, the wear endurance of a polymer is dependent on a number of characteristics, including rigidity, friction coefficient, and tenacity. Many polymers, particularly polyesters, are resistant to moisture based on its non-polar and crystalline structure [30].

3.4 Carbon-based biopolymers

Due to the advantages of adsorbents based on carbon, such as thermal properties, extraction behavior, adsorption ability, and specificity, they have attracted extensive attention in the arena of analytical chemistry. Graphene, CNTs, and various biopolymers, CS, and charcoal, make up this type of adsorbent. There are a variety of wastewater treatment methods that have been well researched and commonly utilized, including precipitation chemistry, ion exchange, solvent extraction, nanofiltration, adsorption, and reverse osmosis [31]. The characteristics which are significant when considering wastewater treatment are efficiency, economic effectiveness, and easy handling [21, 22]. Crab and shrimp shell and few fungal species and Insects are the major sources of chitin biopolymer. To increase the mechanical characteristics, thermal properties and pore size of the biopolymer the carbon materials viz., graphene, CNTs, activated carbon, and graphene oxide are incorporated with the chitin and form carbonaceous composites [32]. The most common method of chitosan-activated carbon composite preparation is activated carbon was allowed to treat for 4 h with oxalic acid, filtered, washed with H_2O and then dried for 12 h at 70 °C. At 40–45 °C, agitate chitosan with oxalic acid to create chitosan gel. Activated carbon treated with acid was gradually introduced to the chitosan gel and stirred for 16 h at a temperature of 40–45 °C. The chitosan-activated carbon composite was subsequently prepared by adding this combination dropwise to the NaOH solution [33].

3.5 Microalgae based biopolymers

Microalgae are regarded as potential functional food products owing to its well-balanced constitution, which includes a variety of nutritional and health-promoting substances. Furthermore, its utility in foods isn't really restricted to beneficial effects, because microalgae may also serve as a structural component, such as a texturizing agent. Microalgae that are photoautotrophic are really abundant in fundamental natural polymers including proteins, storage polysaccharides, and polysaccharides associated with the cell wall. Due to several benefits, including better growth and versatility to thrive in a variety of conditions, algal photosynthetic organisms are an ideal resource for biopolymer synthesis [34]. The productivity of algae is significantly larger than that of terrestrial plants, which makes it an attractive choice for polymer synthesis. Algae-based plastic materials have recently emerged in comparison to the conventional feedstock use methods. Natural fibers produced from algae have become incredibly competitive. Photosynthetic organisms, particularly algae, have been investigated as a source of a variety of polysaccharides as well as other naturally occurring bioactive compounds including fatty acids, proteins, vitamins, and minerals. Such chemicals may find use in medicines, industry, agricultural, and foods [35]. Lutzu et al. reported that extracellular polymeric material (EPS) was generated by *Cyanothece* sp. strain, when the cells were exposed to nano and micro plastics [36]. Initially the growth of the algal cells was inhibited by the micro- and nano-plastics. The results indicated that the increase in bioflocculant concentration in reaction medium and the EPS has elevated bioflocculant activity even at small concentrations. Furthermore,

Table 3.2: Comparisons of utilizing microalgal biomass (wet and dry) for heavy metal removal.

	Wet biomass	**Dry biomass**
Benefits	Metabolic activities add favorable conditions to heavy metals treatment by increasing metal ion absorption relative to dead biomass and adsorbing a wider variety of metals.	The biosorption of heavy metals is larger than that of living organisms. Capability of recycling dead biomass. Reliability of simple physicochemical methods for enhancing adsorption capability. There is no requirement for rigorous maintenance. There is no requirement to supplement growth ingredients. Less costly.
Shortcomings	Resistant to physicochemical recycling procedures. pH variations have a substantial influence on the performance of live biomass. The growth media may result in metal deposition and bioremediation hindrance.	Absorption of heavy metals may be preferential with regard to live biomass.
Example	Adsorption capacity of *Spirogyra* sp. and *Nostoc commune* at no pretreatment for selenium (II) is 7.62 and 8.69 mg/g [38]	Dry *Spirulina platensis* could effectively remove Cu(II) up to 817.7 mg/g of algal biomass [39]. Adsorption capacity of *Spirogyra* sp. and *Nostoc commune* at no pretreatment for selenium (II) is 12.1 and 13.5 mg/g [38].

the EPS exhibited very favorable aggregation properties. These findings demonstrate the ability of algal-based biopolymers to substitute toxic conventional flocculants used in water treatment. In addition to that the algal cells aggregate and flocculate nano- and micro-plastics, showing that they are a persuasive, biocompatible alternative to nano- and micro-plastic contamination. This research emphasizes the exciting potential for algae-based natural polymers to substitute toxic substances used for flocculation used in the treatment of wastewater, as well as the possibility to aggregate the micro plastics that treating wastewater systems are still unable to eliminate [18]. The *Cyanothece* sp. was used in industrial wastewater treatment, particularly in bioremediation due to its nitrogen/metal elimination capacities and bioflocculation activity, owing to its capacity to secrete EPS [37]. The benefits and disadvantages of wet and dry algal biomass were discussed in Table 3.2.

3.6 Chitosan

Adsorbents of natural polymer, particularly polysaccharides viz., chitosan and its precursor chitin, have been extensively used. Chitin is one of most ample biopolymer found in nature, subsequently cellulose. Chitin is primarily found in crab and shrimp shells [21]. Moreover, the insoluble nature of chitin precludes its widespread use. Thus, soluble chitosan was synthesized from chitin through a method known as alkaline deacetylation. It is significantly important biosorbent for a wide range of pollutants owing to its enhanced – NH_2 and OH groups. Chitosan, on the other hand, exhibited excellent mechanical properties and thermal resistivity, insufficient structural integrity and acid solubility, and a small surface area. Currently, composites based on chitosan/chitin have been used to adsorb a variety of contaminants from wastewater [40–42]. Cellulose, clay, biomass, silica, resin, synthetic polymers, and variety of carbon materials are used to form chitin and chitosan composites. Numerous changes were done to raw chitosan and chitin to improve the qualities and overcome the existing limits. Among the variety of composites, the composites made using the carbon materials including such graphene oxide, CNTs, biochar, and AC shows a more stable and efficient properties towards the deduction of contaminants present in wastewater [23, 43]. Chitosan derivatives are commonly employed as adsorbents in various studies because of its outstanding performance including dye removal [43], wastewater treatment [1], removal of organic pollutants [5], metal ion sorption [23], and flocculation [44].

Toxic heavy metal ionic pollutant present in the wastewater is positively charged, hence the cationic polymers or polyelectrolytes are important to use as a possible coagulants and flocculants [45]. Chitosan is a cationic biopolymer, and it is hydrophobic, biodegradable, nontoxic and also has a very combative amino and hydroxyl group as well as its coagulative property is highly successful in eliminating various contaminants from the water solution [46].

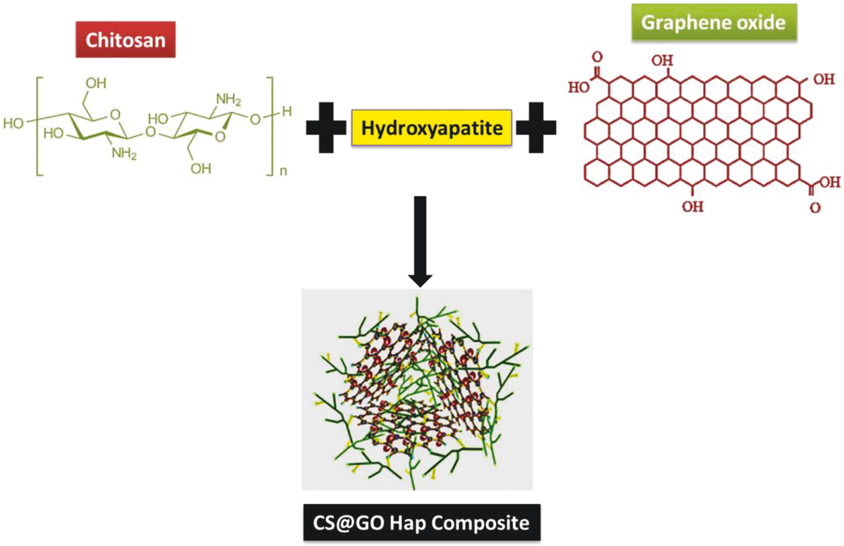

Figure 3.2: Types of biopolymers.

CS and GO (Figure 3.2) composite was prepared and used for the treatment of Reactive Black 5 dye. CS-GO Hap Composite has the maximum *Q* value of 277 mg/g at 25 °C [43]. The removal of phenol on a CS-based adsorbent was investigated by means of a chitosan–carbon nanotubes CS-CNTs composite. Carbon nanotube-grafted chitosan were prepared and used for the removal of phenol present in water and the composite has the Qmax value of 86.96 mg/g of phenol which is significantly high compared to raw chitosan used [10]. This implied monolayer coverage. Chitosan conjugated photo catalysts were prepared by cross-linking with copper and nano-TiO_2. Sequential sorption of As(III) and As(V) has been seen in the existence of phosphate in order to oxidize arsenite with ultraviolet radiation [47].

3.7 Biopolymers derived from bacterial species

(a) Polysaccharides: It is a biopolymer based on sugar and sugar acids. It is being charged or uncharged, homo or hetero polymer, and branched or unbranched. Numerous bacterial species synthesize polysaccharides and either accumulate it within the cells viz., glycogen or release it as extracellular polysaccharides attached to the cell membrane or as unbound external polysaccharides which contributes to the external matrix of bacterial cell wall termed as biofilm (e.g. cellulose and alginate). The pathogens will secrete viral proteins and hazardous compounds (e.g. flagella and exotoxins) while become mobile. Whenever they adopt a sessile habitat, generate a variety of external polysaccharides as surrounding substance, including alginate, cellulose, and hyaluronate. Alginates produce thick polymeric materials with a high water – holding capabilities when they combine with divalent cations. Cellulose production offers comparable benefits to enterobacterial pathogens. *Escherichia coli* generates phosphoethanolamine cellulose, which will be used to stabilize fibers made up of protein by forming mortar-like structures. Such fibers act as a bridge amongst cells in complicated biofilms and offer resilience to adverse environments [25].

(b) Alginate: Alginate is a low-cost biomaterial that is composed of linear polymeric materials of 2 uronic acid (D-mannuronic and L-guluronic acid) residues, connected by 1,4-glycosidic linkages. Numerous uses for alginate-based polymers were described. Recent research has demonstrated that alginate is widely used in treatment of sewage water as an adsorbent for pollutant owing to its benign nature, durability, degradability, and permeability. Radoor et al. [76] used a solvent cast approach for dye adsorption to create novel PVA/SA/ZSM-5 zeolite membrane having a high restoration potential.

3.8 Carbon nanotubes (CNTs)

Nanotechnology advancements combined with membrane filtration have been recognized as realistic and effective techniques for enhancing membrane performance and its synergistic effect on water purification. Adsorption of contaminants occurs primarily at four different types of sites on CNTs, including outer and inner grooves and interstitial channels and the inner area of the nanotubes. CNTs are categorized as single-walled (SW) and multiwalled (MW) CNTs, due to the ability to transfer water pore structure, chemical stability, and mechanical properties. These have piqued investigators' interest in developing composites for treating wastewater. Furthermore, carbon nanotubes have favorable catalytic, adsorbing, and electrochemical properties that are well suited for coupling with membrane processes, therefore improving the performance of polymer composites in water purification. Chemical vapor deposition is the commonly accepted method for the preparation of CNT-composites [32]. MWCNTs–COOH intercalation into GO laminar nanosheets effectively resulted in the fabrication of GO/CNTs composite membranes with outstanding separation capability for the treatment of dyes wastewater [48]. A modified nanofiltration (NF) membranes using GO/MWCNTs were successfully fabricated by interfacial polymerization of piperazine and 1,3,5-benzenetricarbonyl trichloride. This results the water flux of 55.6 L/m^2 h and rate of reduction of Na_2SO_4 to 94% also it has successfully treat the dyeing–printing industry wastewater [49]. The magnetic CNTs were used effectively to remove polyethylene, polyethylene terephthalate, and polyamide present in the wastewater from kitchen treatment plant with the maximum adsorption capacities of 1650, 1400, and 1100 mg with 1 g of M–CNT [50].

3.9 Application of biopolymers in bioremediation

3.9.1 Biopolymers as biosorbents

The adaptability, low cost, high efficiency, effective recovery, and ecologically sustainable operating system all contribute to the increased use of adsorption. Cost-effective adsorbents, often natural and sustainable materials, are used in the adsorption mechanism. It's because there are a lot of them and they are nontoxic [28]. Several polysaccharides, especially chitosan and chitin, have been widely employed in biodegradable polymer biosorbents. The second most prevalent biopolymer spontaneously occurring is chitin. The primary source of chitin is found in crab and shrimp shells [30]. Nevertheless, the fact that chitin cannot dissolve in water makes it inadvisable for widespread use. The alkaline deacetylation of chitin results in the formation of soluble CS. Additionally, CS is one of the significantly important biosorbent for a range of contaminants because of its increased – NH_2 and OH groups [23]. When it came to its mechanical qualities, chitosan did not show positive results, having lower tensile strength, stiffness, and temperature and physical strength and low acid solubility. On top of that, its surface area was too low to be of use [20] in order to address its disadvantages, some modifications have been made to chitosan and chitin characteristics. Biochar made with iron-impregnation is a beneficial treatment approach for the production of more effective and durable adsorbent material for the separation of different xenobiotics from wastewaters [1, 42, 51].

Many peer-reviewed publications have discussed the use of raw chitosan/chitin biopolymer as well as its related adsorbent materials in the treatment of a wide range of pollutants. These reviews were mostly concerned with biopolymer beads, membranes, fibers, and films, along with cross-linked, grafted, impregnated, and magnetic biopolymers. In addition, the incorporation of biomass, cellulose, synthetic polymer, alumina, clay, and iron oxide to manufacture CS composites for treating wastewater are few examples for the composite preparation for various pollutant removals.

3.9.2 Water treatment applications

Combining the properties of carbon nanotubes with those of traditional membrane materials yields membranes with enhanced waste management capabilities. Carbon nanotube-based composites are being used to treatment of wastewater in a number of innovative ways, including removing dyes, removing heavy metals, desalination, oil/water separation, and removing novel pollutants. pH, adsorbent dose, and degree of cross-linking were all demonstrated to be important in lowering turbidity in effluent, with turbidity reduction dependent on these factors and the initial viscosity of the water. Maximum removal efficiency efficacy of up to 92.4% and highest aluminum removal rate of 95 was observed across the turbidity range of applicability [52].

Humic acid induced rice husk has the ability to reduce maximum of 99.52% COD present in real wastewater [11]. Mohammadi et al. [12] reported that the magnetic MW–CNTs improved with CS biopolymer have the highest monolayer adsorption capacity for bisphenol A was 46.2 mg/g at 20 °C. The maximum absorptivity of 86.96 mg/g of phenol was achieved with CNT-grafted chitosan [10]. The maximum oxidative reduction of naphthol blue black in the presence of Hydrogen peroxide was about 86% was achieved using chitosan immobilized by copper oxide nanoparticles synthesized from *Pistacia vera* hull extract [53]. Keratin biopolymer-1 removed around 93% of As and Cd, keratin biopolymer-4 removed around 85% of Cu and V^V(Vanadium), keratin biopolymer-5 removed in the range of 60–90% of Co, Ni, and Zn, whereas keratin biopolymer-6 removed nearly 95% of Cr^{6+} [15].

3.9.3 Desalination

Due to the vast bulk of the Earth's water being saline or brackish, it is impossible to use. Overcoming freshwater incompetence issues could be helped by developing the capacity to use salty and saline water. The study's findings show that functionalized CNTs are used to immobilize the CNTs to form TFC-composite membranes for seawater and brackish water reverse osmosis. Such membranes were shown to have better pore characteristics and a greater hydrophilicity. Brackish water reverse osmosis had a water flow of more than 90% at pressures above 50 bar [54]. CNTs-coated membranes showed higher salt rejection than unmodified polyethersulfone membranes, with an efficiency of 87% for Na_2SO_4. With traditional administration, polyvinylidene fluoride membranes showed improved salt rejection and also opened up an extra route for molecule of water transfer. This technology helps in membrane filtration by allowing only H_2O molecules to reach the vapor phase which exclude salts [55]. EPS produced by the bacterial strains has the maximum flocculation was achieved around 90% for river water and municipal wastewater and 80% for brewery wastewater [3].

3.9.4 Oil–water separation

The drug, petroleum, and food industries all rely on the usage of oil, which needs to be avoided due to the potential for water pollution [56]. Residential sewage, oil refineries, crude oil production and transportation all produce substantial quantities of oil–water emulsions. Causing substantial harm to the atmosphere and posing threat to living beings' health, it is possible to effectively expel an oil-water emulsion into water. Oil elimination in an aqueous environment is contingent on substrate surface, and the latter is primarily governed by surface molecular configuration and microstructure [28]. It is possible to utilize the materials in two different ways to remove oil. The first strategy utilizes hydrophobic materials that are adsorbed directly on for oil in oil/water separation, whereas the subsequent methodology utilizes hydrophobic moieties stacked on a membrane for oil–water separation. Traditionally, ultrafiltration membranes made-up of unprocessed or modified polymers were used to remove oil from water. Adsorbents have been utilized to clean up oil spills in recent years. Adsorbents which separate oil from water employ copolymers, carbon compounds, inexpensive organic matter, and organoclays. In terms of form, a fiber, a film, a powdered structure, or any other porous structure can be a sorbent [21]. There are three primary forms of membrane filtration that've been investigated for oil–water treatment owing to the advantages of lower energy consumption and quality water: nanofiltration, ultrafiltration, and microfiltration. CNT polymer composite membranes were produced in order to extract oil from water. Carbon nanotubes have been included in the blend, allowing for the improvement of mechanical characteristics such as durability, modulus, and rigidity. This demonstrates the membranes' enhanced endurance and their potential for water/oil treatment. The construction of superhydrophobic carbon nanotube-polystyrene composite, superhydrophobic-superoleophilic polytetrafluoroethylene nanofibrous and polyvinylidene fluoride-co-hexafluoropropylene/(polystyrene) composite membranes are few examples for the oil–water separation [57–59]. A wide range of surfactant-stabilized oil-in-water emulsions may be separated using produced membranes with an extraordinary elimination effectiveness (over 99.94 percent) and a favorable flux (5000 $Lm^{-2}h^{-1}bar^{-1}$). Composite membranes revealed a 100 percent rejection rate for oil particulate matter, which was caused by an increase in density gradient mechanisms induced by the integration of carbon nanotubes into filtration membranes, which integrates carbon nanotube adsorption properties with membrane filtration. Underwater superoleophobic membrane formed by crosslinking konjac glucomannan on pristine fabrics divides oil-water blends with maximum rate of 99.9% [21].

3.9.5 Removal of heavy metal ions

Chemical production, mining, metal plating, and battery manufacturing sectors all emit hazardous metal ions into bodies of water. CNTs have recently been utilized as a promising adsorbent for metal ions such as chromium (Cr^{6+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), nickel (Ni^{2+}), cobalt (Co^{2+}), strontium (Sr^{2+}), copper (Cu^{2+}), and lead (Pb^{2+}). CNTs demonstrated a very effective and tunable composite filter for the heavy metals removal from wastewater [9]. The composite membranes were almost 100 percent efficient in removing heavy metal ions. Due to the presence of carbon nanotubes, membranes became adsorptive in nature and reduced the size of holes to between 20 and 30 nm, creating membranes efficient for heavy metal removal during incessant filtering. For example, the composite membranes removed around 94 percent of Cr^{4+} and 78 percent of Cd^{2+}. The removal efficiency of PSF from unmodified membranes was 10.2 percent and 9.9 percent, respectively. Available polymeric composites and its application for various metal ions was discussed in Table 3.3.

Table 3.3: Application of biopolymers on the reduction of metal ions.

Biopolymer	Metal ions	References
CS-BC	Pb(II), Cu(II), Cd(II), Cu(II), Cd(II),Zn(II), Ni(II),Ag(I)	[20]
CS-AC	Cu(II) Cd(II)	[60]
CS-CNTs	Pb(II), Cu(II),Cr(VI), Cr(VI)	[61–63]
CS-GO	Pb(II), Ag(I), Cu(II)	[64]
CS-G	Cd(II)	[65]
AC (Rice husk)-CS composite gel	Cu(II)	[33]
Alginate–CS hybrid adsorbent	Pb^{2+}	[17]
CS/nanoclay composites	Cu (II) and Ni (II) ions	[23]

3.9.5.1 Factors influencing metal ion removal by biopolymers

(a) Temperature: Temperature fluctuation increases/decreases the biosorbent potential of biopolymer; some writers reported an increase in metal adsorption as temperature increased, while others found a reduction in adsorption at elevated temperature. Temperature fluctuations influence the biosorption behavior of diverse biopolymers when exposed to various metal ions [18].

(b) pH: Increased pH values promote metal biosorption, whereas acidophilic pH inhibits it. This could be attributed to the fact that at decreased pH level, the active groups in the polymer are connected to H+ ions and which prohibiting (+)vely charged heavy metals from interacting to the exterior layer. As the pH increases, the active sites become dehydronated, enabling the microalgal cell to attach to metal ions.

(c) Salinity: While the saline environment increases, Na+ competes with the metal active site on the cell membrane, lowering the efficiency of biosorption, similar to low pH levels.

(d) Metal: The concentration of metal dictates the quantity of metal reduced because for some algal cells the increased concentration will inhibit their growth.

(e) Amount of biopolymer: The quantity of biopolymer used for the removal is an important factor influencing the metal ion removal. The higher the quantity, higher the binding site for the metal ions to be adsorbed [66].

(f) Particle size of the biopolymer: The size of the particle is a critical factor determining the rate of adsorption of metal ions. For e.g. for activated carbon, smaller the particle size will lead to high rate of adsorption of pollutants [67].

3.9.6 Removal of evolving contaminants

Arising contaminants such as environmental endocrine disruptors, pharma and personal hygiene products, and organic pollutants [56] are widespread in nature at concentrations ranging from ngL^{-1} to gL^{-1}, but cause significant damage to humans and the environment. Erythromycin, metronidazole, sulfamethoxazole, trimethoprim, ciprofloxacin, amoxicillin, and trimethoprim tetracyclin are few pharmaceutical contaminants present in recent days in domestic wastewaters [24]. Mohammadi et al. stated that magnetic MW-CNTS improved with CS biopolymer was used to eliminate the endocrine disruptive compound-Bisphenol A in wastewater [12]. This study showed that the selected biopolymer composite has the adsorption capacity of bisphenol A is 46.2 mg/g at 20 °C. Wang et al. [68] reported that the novel magnetic chitosan grafted graphene oxide nanocomposite has effectively removed the ciprofloxacin with the removal rate of 72%. Diclofenac was effectively removed by the by adsorption using AC synthesized from potato peels [69].

3.9.7 Removal of dye compounds

Amongst many, degradation of dye applications is significant, as well as the removal of colors from wastewater is critical. Increased dye pollution in aquatic environment is very harmful to plant, animal, and human life. Because wastewater polluted by dye components is toxic to aquatic organisms and reduces aquatic life's photosynthesis process by lowering light penetration, it creates severe ecological consequences. Magnetically active graphene composites seem to be of significant due to their ease of dissociation and low cost. Nanostructures like metal oxides, graphene, and CNTs have revolutionized the field of pollution control. Graphene, a one-atom-thick 2D sheet of *sp*2-hybridized carbon, is the most extensively researched substance on the planet because of its remarkable electrical, mechanical, optical and chemical characteristics [70, 71]. CuI-RGO quasi-shell – core nanocomposites enhanced photocatalytic activity and reliabilities for photocatalytic reduction of RhB with stimulated solar light irradiation. The literature indicated that GO-based composites have been employed for the elimination of cationic and anionic dyes. Such composite materials with metal oxides, carbon derivatives, metal hybrids or polymers are synthesized mostly by solvo-thermal synthesis, hydrothermal procedure, microwave-assisted pathway, one-step sonochemical pathway, co-precipitation and ultrasonication pathway. Retrieval of adsorbent following application has been a concern; to circumvent it, magnetically active graphene-based composites are being produced. Graphene has evolved into an important nanoadsorbent for environmental uses by having high surface area to enhance effective sorption (~2620 m^2g^{-1}). The Qmax for the composite material at pH = 2 and 25 °C temperature was 277 mg/g for the removal of Reactive Black 5 using graphite oxide/chitosan composite [43] (see Table 3.4).

Table 3.4: List of Biopolymers and its application on dye removal.

Dye material	Biopolymer	References
Direct yellow dye	CS crosslinked isovanillin	[72]
Methylene blue	Sodium alginate biopolymer	[73]
Textile wastewater	Polyaniline/dicarboxyl acid cellulose@GO	[74]
Malachite green reactive red - 195	Hexametaphosphate cross-linked chitosan beads	[75]
Naphthol blue black	Immobilization of copper oxide nanoparticles onto CS biopolymer	[53]
Methylene blue Methyl orange	CS/MIL-100 (Fe) composite	[53]
Cross-linked CS-GO	Reactive Black 5 dye	[43]

3.10 Conclusions

Biopolymeric composites are perfectly suited to the oncoming tendency of expeditious and creative materials due to their ability to combine the characteristics of distinct components to create a single hybrid entity with higher performance features and application versatility. Bionanocomposites have aroused interest due to their diverse functional properties, which have piqued the curiosity of several academics and experts. Multiple but distinct synthesis techniques for each biopolymer composite provide up a vast array of possibilities for the creation and usage of bio-based polymer composites. Compared to other carbonaceous materials, AC and GO displays an effective adsorption capability towards variety of pollutants with the greatest surface areas. Copper, chromium, cadmium, and lead metals, as well as methylene blue dye, have been the most treated contaminants. Other pollutants that have been thoroughly investigated include the antibiotics ciprofloxacin and tetracycline, as well as phenols. The combination of chitosan/chitin and carbonaceous materials demonstrated a higher absorption of contaminants than CS/chitin alone. CS/chitin-GO and CS/chitin-AC composites exhibited significantly higher adsorption capabilities for the majority of contaminants than other composites. In comparison to chitin composite, CS composite adsorbents are more efficient. Additionally, by including magnetic elements into composites, the rate of adsorption of the composites was increased due to the growth of the composites structure. Due to its improved pore properties and high adsorption capacities for aquatic contaminants, CS/chitin-carbonaceous polymer composites may be potential material for the adsorption of variety of contaminants present in the wastewater.

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Amare Tiruneh Adugna*

4 Development in nanomembrane-based filtration of emerging contaminants

Abstract: Recently, the concentration of emerging contaminants is increasing in drinking water sources, industrial wastewater, and reclaimed water. It is not possible to remove the emerging contaminants using conventional methods, and the interest to use nanomembrane-based filtration is getting attention. A nanomembrane-based filtration can be manipulated without the use of any special equipment. Different research findings reported better removal of emerging contaminants has been achieved using nanomembrane-based filtration. Moreover, new developments have been examined and implemented at different levels and are expected to continue. Therefore, this chapter provides a brief overview of recent developments on nanomembrane-based filtration processes in the removal of emerging contaminants from drinking water sources, industrial wastewater, and reclaimed water.

Keywords: drinking water; emerging contaminants; filtration; nanomembrane; reclaimed water.

4.1 Introduction to nanomembrane-based filtration

Filtration is a process of separating contaminants from water and wastewater by using natural filter media and membranes. Membranes are used to separate certain components by using a selective layer. The membrane-based filtration technologies are used mainly in water and wastewater treatment which can help in the removal of emerging contaminants. The most common types of membrane-based filters are microfiltration, ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF). Their similarities and differences are clearly presented in Figure 4.1 as shown below. For water and wastewater treatment, NF is the most preferred membrane technology in the last decade [1]. The pressure-driven NF has a 200–1000 Da nominal molecular weight with 0.2–2.0 nm pore size operating at 70–200 psi (5–15 bar) pressures [2]. The emerging contaminants that are dominantly found in water and wastewater, personal care products, antibiotics, pesticides, endocrine disruptors, pharmaceuticals, and other organic pollutants are effectively removed using NF. Multiple mechanisms are used by NF to remove the emerging contaminants such as adsorption which usually occurred at the initial stages. Then, charged solutes are retained using steric and

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electrostatic effects while uncharged solutes are removed by steric effects [3]. But the removal efficiency depends on pH, ionic strength, and organic content of the water [4].

The emerging contaminants were removed in the range of 0–90% and more [2]. It is important to treat extensively before treating using NF, but high energy demand and fouling are the common problems.

4.2 Types and fabrication methods of nanomembrane for filtration

4.2.1 Types of nanomembrane for filtration

Membranes can have symmetric, asymmetric, homogeneous, heterogeneous, charged, or neutral characteristics. The asymmetric membranes are constructed using a minimum of two layers, while symmetric types have similar membrane thickness for most of the time. Separation is mainly done by the active layer which is found on top of the membrane, and this layer is supported by the lower layer which is porous. Its mechanical stability is achieved by the supporting layer as it doesn't have resistance to the permeate flow [6]. Polymeric and ceramic membranes are commonly used by NF. The polymeric membranes deteriorate rapidly than the ceramic because they have

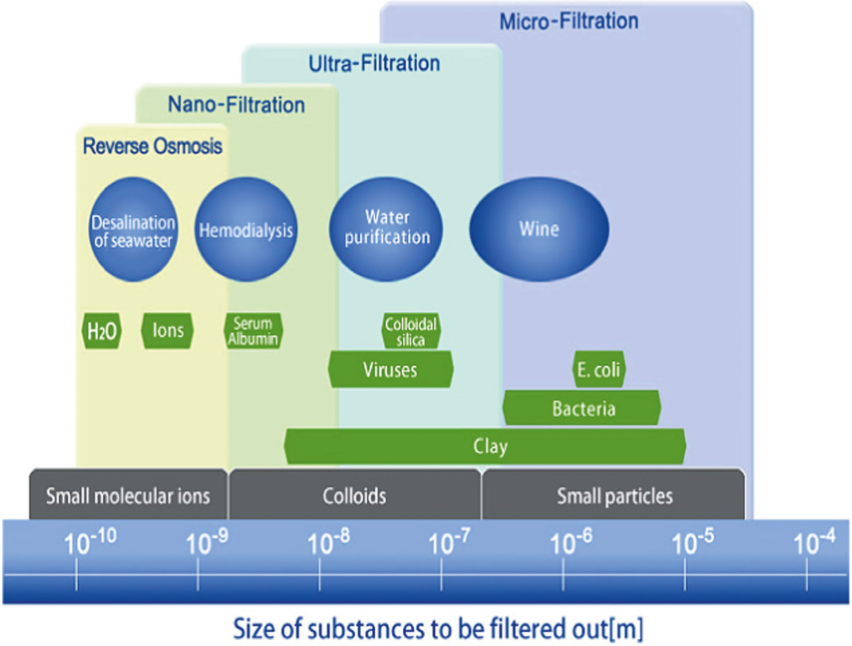

Figure 4.1: Types of membranes [5].

comparatively low fouling and chemical resistance [7], but the ceramic membranes have superior mechanical, chemical, and thermal stabilities [8]. The charge of NF membranes is mostly neutral or negative when they are in an aqueous environment which is related to the properties of material nature. The membranes with a positive charge are highly demanded, and NF membranes quality is affected not only by fiber diameters but also porosity and homogeneity [9].

In addition, their functionality is significantly affected by flux and selectivity: Generally, selectivity is one of the membrane surface properties. It can be defined as the ability to distinguish different types of species that can pass through the membrane which can be modified to ameliorate the effectiveness of filtration. Flux is nothing but the rate of species that are transported across the membrane. The properties of NF membranes are presented in the following Table 4.1.

4.2.2 Fabrication methods of nanomembrane for filtration

Membrane filters are made from synthetic polymers and different natural and inorganic materials. The synthetic polymers that are mostly used in the fabrication are polytetrafluoroethylene (PTFE), polypropylene (PP), polycarbonate cellulose acetate and nitrate, and polyamide (PA). The natural materials used also include cellulose, rubber, and wool. The commonly used inorganic materials include carbons, microporous ceramics, and metals [16]. The membranes may be composed of polymers and ceramics, and the synthetic polymers are getting attention in the research and for commercial purposes. The most commonly used membrane material is polysulfone which has excellent chemical and thermal stability [17]. Additionally, PA, polyvinylidene fluoride (PVDF), PP, polyvinyl chloride (PVC), polyvinyl alcohol, polyethylene (PE), polyethersulfone (PES), polyacrylonitrile (PAN), and chitosan are extensively studied [18]. Figure 4.2 presents the classification of membranes based on construction materials, structural attributes, and configuration.

Table 4.1: The properties of NF membranes.

Membrane type	Pore size (mm)	Contact angle[c] (°)	Zeta potential pH 7 (mV)	Roughness[e] (nm)	Molecular weight cut-off (MWCO)
Dow Filmtec NF 90	0.68	44.7 ± 1.9	−24.9[b]	72.4 ± 5.8	200–400
Dow Filmtec NF 270	0.84	32.6 ± 1.3	−15.0[c]	9.0 ± 4.2	200–400
Koch Membrane MPF 34	0.82	26.9 ± 0.4	+12[d]	[a]	200
GE Osmonics DK	0.76	40.6 ± 5.2	−5.0[c]	16.4 ± 3.1	150–300
GE OsmonicsDuracid	0.47	62.2 ± 4.2[f]	[a]	[a]	150–300

[a]Data not available, [b][10], [c][11], [d][12], [e][13], [f][14] (Source: modified from [15]).

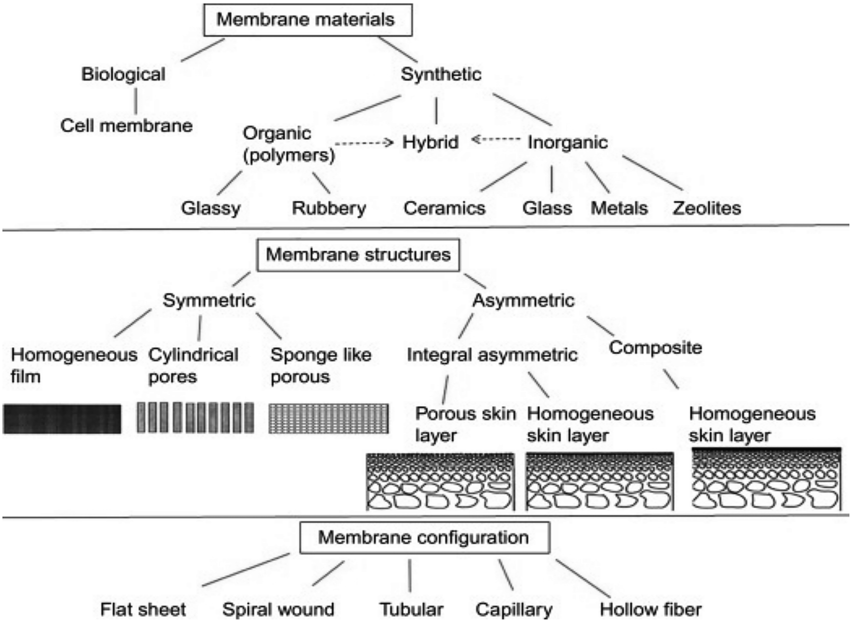

Figure 4.2: The classification of membranes based on the construction materials, structural attributes, and configuration. Reproduced from Gohil et al. [34] by creative commons CC-BY license privilege.

The most common methods to fabricate nanomembranes are electrospinning, phase inversion, sintering, track-etching, interfacial polymerization (IP), and stretching [19]. Moreover, the expectations of NF membranes can be achieved using the miscellaneous techniques using layer-by-layer assembly [20, 21], mussel-inspired co-deposition [22, 23], and using separation process by the thermal-induced method [24, 25]. In the phase inversion method, first, the casting solution should be prepared using the appropriate solvent to dissolve the target polymer to fabricate flat-sheet and tubular membranes. The tubular membranes are preferred as they avoid the use of spacers in module fabrication [26]. The IP method was used to fabricate most of the commercial NF membranes with negatively charged during normal aqueous processes. NF membranes with negative charge exhibited excellent multivalent anions separation but low in the removal of multivalent cations [27, 28].

Using the sintering method, membranes with symmetric structures can be fabricated with a mean pore size of 0.1–10 µm. The PTFE, ceramics, and PE are mostly used to fabricate since the materials have stable chemical properties which make it difficult to achieve pores less than 100 nm and the porosity in the range of 10–20% [24, 29]. The stretching method is used to fabricate symmetric membranes having a pore size from 0.1 to 3 µm and practical to fabricate PTFE membranes. Stretched membranes have porosity from 60 to 80%, but the demand for high operating temperature is the limitation for this technique [30]. The track-etching technique is used to fabricate membranes with pore size from 0.02 to 10 μm, but suitable only for a limited number of suitable polymers [24]. The most common fabrication technique, electrospinning, is used to fabricate electrospun nanofibrous membranes with ease of operation. The other advantages are material selectivity and low cost. The surface-to-volume ratio, high porosity, and variable arrangements affect the fiber characteristics [31].

Particularly, NF membranes are fabricated by direct phase separation and multistep methods. The one-step phase separation is used to prepare NF membranes of integrally skinned asymmetric type by using PES, PAN, and polyetherimide, etc. [32]. The two steps method is used to fabricate NF membranes by deposition nanomaterials (NMs) into the supportive layer or deposition of NMs on the top layer. Thin-film nanocomposite is fabricated particularly using NMs as nanofillers integrated into the IP [33, 34]. Moreover, many inorganic nanofillers finely designed from one-dimensional to two-dimensional (2D) and three-dimensional (3D), such as silver (Ag) [35], zeolite (NaX) [36], zinc (ZnO) [37], titanium (TiO_2) [38], zirconium (ZrO_2) [39], graphene oxide (GO) [40], aluminum (Al_2O_3) [41], carbon nanotubes (CNTs) [42], silicon (SiO_2) [43], iron (Fe_3O_4) [44], cobalt (Co) [45], copper oxide (CuO) [46], and clay nanoparticles [47] in novel nanocomposite membranes development.

Phase immersion precipitation process used to prepare polymer/GO hybrid membranes. Additionally, the following methods are used: vacuum filtration-assisted assembly, dip-coating, and layer-by-layer self-assembly, and pressure-assisted self-assembly [48]. However, the microstructure of interfacial polymeric NF membranes is different from that of GO membranes but it is challenging to add inorganic materials to polymeric materials [49]. Considerable enhancement was achieved by incorporating sulfate groups in chitosan NF membranes particularly on water permeability and selectivity [50]. Additionally, a novel NF membrane was developed by mixing polyelectrolyte complex nanoparticles (PEC NPs) with tunable sulfated groups [51]. Moreover, PVC is gaining more interest since it has appreciable mechanical strength. However, the composite membranes using PVC as support material will be prone to optimization through the suitable reaction. Also, it has a comparatively lower cost than that of the typical support materials [52].

4.3 Separation mechanisms by the NF membrane

The separation mechanisms by NF (steric effect, hydrophobic interactions, electrostatic repulsion, partitioning, and diffusion) are dependent on physicochemical characteristics of solutes, membrane characteristics, and feed water characteristics (ions content, pH, organic matter [OM], etc.). The main separation mechanism of NF membranes is molecular sieving, but the charge effect plays also a significant role in membrane selectivity. The nature of the membrane and electrolytes are responsible for the first effect i.e., charge polarities between the membrane and the solutes. The relative size of ions to the membrane pores determined the second effect, and the differences in dielectric constant between bulk and membrane pores caused the third effect [53].

The mechanism of separation by NF membranes is a complicated phenomenon and is considerably regulated by fluid flow, its characteristics, and interfacial episodes occurring on the outer membrane surface and within porous structures of the membrane as shown in Figure 4.3 below.

NF rejection mechanism is extremely complex and dependent on interfacial and micro-hydrodynamic events that occur on the membrane surface, even within its nanopores (Worou et al. [54]).

The three principles in separating the solutes using NF membranes are:

1) size exclusion (sieving, steric effects),
2) charge exclusion, (electrical, Donnan)
3) physicochemical interactions between solute, solvent, and a membrane.

Generally, exclusion mechanisms mainly depend on membrane pore size, thickness and dielectric constant, solvent viscosity, solute diffusivity, solution temperature, and pH. The most common rejection modeling equation is the Nernst–Planck equation. NF membranes better remove charged and multivalent solutes than uncharged solutes. The removal efficiency is determined by the following formula.

$$R(\%) = (1 - \mathrm{Cp}/\mathrm{Cr}) \times 100,$$

where Cp is the concentration in permeate and Cr is the concentration in concentrate.

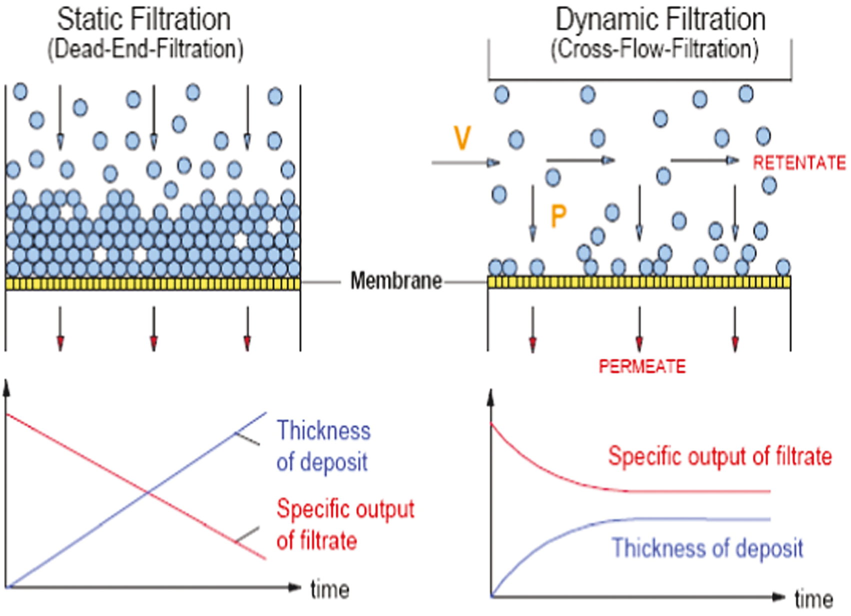

Figure 4.3: Mechanism of separation by NF membranes [5].

4.3.1 Size exclusion

It is the basic mechanism that can be achieved for solutes larger than the pore size of the membrane as they cannot pass through. The solute molecule size is expressed using its molecular mass and diameter, effective molecular size, stokes diameter, or using molecular width or length [55]. The solute transport methods determine membrane molecular weight cut-off (MWCO), and solute rejection is affected frequently by hydrophobic nonspecific interactions of solutes and a membrane [56]. The water contact angle values determine the membrane surface relative hydrophobicity which serves as the means of quantifying method. Usually, low membrane surface hydrophobicity is represented by a low contact angle, and higher membrane hydrophobicity is represented by a higher contact angle. In addition to size exclusion, other separation mechanisms can simultaneously happen. For instance, NF membranes reject bound pharmaceuticals (PhACs) dominantly by size exclusion with or without electrostatic interactions that happened due to the interaction between the complexes and membrane surfaces [57]. Song [58] also found similar rates of natural hormones were retained while different pore sizes of NF membrane, “tight” NF-90 and “loose” NF-270, were used which shows their active layer thickness affects the diffusion behaviors of hormones.

Although fouling is the bottleneck of NF membrane, it has a positive impact on increasing the removal of emerging contaminants as reported by some authors. For instance, Hajibabania et al. [59] reported lower rejection of hydrophilic nonionic and ionic solute when membranes face fouling with humic acids and alginates. Plakas and Karabelas [60], reported a decrease in herbicide rejection due to humic substances (HS) accumulation on NF membranes which created a denser fouling layer, and this enhanced compound adsorption [3] also reported the fouling caused by natural OM improves the removal of most neutral compounds which were considered during the study but there was little impact on ionic PhACs removal. However, Zazouli et al. [61], reported higher rejection for large drugs but a lower rejection was observed for the smallest substance with polarity due to fouling.

4.3.2 Charge exclusion

The other important rejection mechanism used by NF membranes is charge exclusion which is regulated by the Nernst-Planck equation, electrochemical laws, e.g., Donnan effect, and electroneutrality conserved by the general principle across a membrane [62]. The membrane has a composite structure made from porous support and a positively or negatively charged ultra-thin active layer [63]. Deliberately, the electrical charges have been fabricated in the skin layer of an NF membrane. Mostly sulfonic, ammonium, or carboxylic groups are covalently bonded to a membrane matrix [18, 64]. The membrane surface charge sign depends on the pH of the feed water, this will facilitate the dissociation of the sulfonic and carboxylic groups. Hence, neutral aqueous solutions charge became negative for the thinnest layer composite NF membranes [65]. The studies showed that the positive charged NF membranes showed relatively improved removal of multivalent anions such as $Cr_2O_7{}^{2-}$, $AsHO_4{}^{2-}$, $SO_4{}^{2-}$ [27], also, better removal efficiency to multivalent cations as well (e.g., Mg^{2+}, Ca^{2+}) was also reported [66]. Moreover, the electrostatic repulsion is partially weakening due to the adsorption of counter-ions and suspended colloids which accelerate membrane fouling [67, 68].

There are two competing hypotheses related to dielectric exclusion phenomena which are not well understood. The 'image forces' phenomenon Worou et al. [54] is the first hypothesis while the 'solvation energy barrier' mechanism [69] is the second. The basis that occurs during NF membranes separations mechanisms is nano-length scales and extreme spatial confinement [70]. Researches have been conducted to show the excellent removal of multivalent cations and anions. A microporous PES membrane fabricated with two cycles of IP showed outstanding removal of $MgCl_2$ (rejection ≈ 98%) [27]. However, it showed a relatively less removal (rejection ≈ 68%) to Na_2SO_4 due to the Donnan Exclusion effect [71]. Additionally, NF membrane with neutral charge fabricated using a positively charged NF membrane coated with sulfonated poly (ether ketone) [72], with the capacity to reject cations and anions efficiently. Charged NF membranes were also studied to reuse reactive dye effluents [73]. Other studies about a composite membrane that sandwiched a positively charged interlayer with substrate and negatively charged outermost surface and showed better removal [27, 74].

4.3.3 Physicochemical interactions

The physicochemical interactions governed the membrane separation effect which happened at the membrane–solution interface [75], which happened among solute and water molecules and the membrane. Specifically, the solute adsorption on and in the membrane is often connected to hydrogen bonding between membrane and solutes, and to hydrophobic nonspecific interactions [76]. Relatively, mutual interaction values were determined by keeping a system with the same solvent, membrane material, but different pollutant molecules. At the membrane–solution interface, water will be less preferentially sorbed where a lower basicity value of molecules is observed [55]. Moreover, the interaction between solute and membrane is determined by the following parameters: diffusion coefficient, solute characteristics, hydrophobicity, membrane characteristics, solution chemistry, surface morphology and operating conditions, inorganic matrix, and membrane fouling [77]. NF membrane physicochemical parameters can exhibit severe modifications due to the accumulation of foulants through time, which significantly affect solutes removal, as rejection mechanisms are largely regulated by membrane surface characteristics [78]. Other studies also reported that the negative fouling effect on NF membranes performance.

For instance, Effluent Organic Matter (EfOM) fouling significantly affected nonionic PhACs (acetaminophen, carbamazepine, bisphenol-A, etc.) rejections by NF membranes were negatively impacted [79].

There are studies that showed the interaction effect on NF membranes performance to remove emerging contaminants. For instance, better removal of estrogens, PhACs, and pesticides were observed in the presence of OM due to solute–solute interactions [4]. The solutes and type of micro molecules affect the adsorption of PhACs onto organic macromolecules. For instance, authors reported denser fouling due to the presence of calcium which neutralized the carboxylic groups of HS and polysaccharides [80]. However, due to higher calcium concentration, bulk complexation can also occur in the solution, which enhanced the formation of aggregates and lower organic fouling [80]. Furthermore, other findings showed that the thin-film composite (TFC) membranes did not adsorb any hormones which indicated that the affinity of the contaminant depended on the different materials [81]. Much higher concentrations of hormones were adsorbed by PA and the PA active layer of TFC NF membranes compared to the other materials of the membranes which showed the active layer is responsible for the bulk of hormone adsorption [82]. However, there were problems in the rejection of trace contaminants while using polyamide NF membranes in water treatment due to contaminants' interaction with the active layer [83].

4.4 Recent developments in nanomembrane-based filtration for emerging contaminants

The NF technology has gained significant momentum in sectors dominantly in water and wastewater treatment. However, there are concerns such as changes in membrane characteristics, clogging, and adsorbed contaminants leaching. The problems may be defects during membrane production, deterioration both chemically and biologically, scratches, aging, membrane fouling, membrane layers detachment, connectors improper fitting, etc. [84]. Recently, great efforts have been made by scientists to develop nanostructures like nanopores, nanotubes, nanorods, and nanowires applied in different fields due to their excellent physical, chemical, mechanical, and optical properties, i.e., catalytical reactivity, antibiotic resistance, and fouling resistance [85]. For nanostructure fabrication, a wide range of nanoporous oxides like alumina, titania, zirconia, and silica have been developed [86]. NF membrane modified by graft polymerization significantly improved Bisphenol A (BPA) removal 74.1% (raw membrane) to 96.9% (polymerized membrane) [87]. Polymerized NF membrane increased the removal of Ibuprofen (IBP) from 98.1 to 99.7% and salicylic acid from 97.0 to 99.1%. The enhanced removal is achieved due to the membranes' negative surface charge and steric hindrance increment [57]. Additionally, there are the latest developments in polymer–inorganic hybrid membranes. This provides the way to fabricate 2D or 3D pores nanoporous membranes which can control membrane pore size and the area [88].

Membranes can be developed by incorporating NMs applying green chemistry principles is getting attention. For instance, Pervez et al. [89] studied the performance efficiency of PAN electrospun NFs membrane coated with fumarate-alumoxane nanoparticles which improved surface hydrophilicity and reduced the irreversible fouling. Furthermore, a novel polydimethylsiloxane (PDMS) loaded NFs composite membrane demonstrates a superhydrophobic surface that exhibited higher stability during industrial wastewater treatment, and phenol extraction efficiency reached more than 10 times compared to the conventional PDMS membrane [89]. The NMs should be low-cost and nontoxic materials like chitosan and iron-based NMs [90]. However, NF membrane is expensive, requires high energy, membrane properties change due to fouling after fouling or other interactions, and disposal are the major bottlenecks in disseminating at a large scale [91]. Moreover, emerging contaminants such as antibiotics, personal care products, and pharmaceutical compounds are effectively removed by membrane bioreactors combined with nanomembranes [92]. Generally, the ideal NF membrane is not yet developed, as a result mixing different materials to obtain NF membrane with better removal efficiency is a feasible way. Additionally, the following Table 4.2 presents the summary of selected emerging contaminants removal by NF membrane.

4.4.1 Removal of antibiotics and pesticides

NF membranes have been considered as the most appropriate for the removal of pesticides from contaminated water sources [4, 110], and hormones and antibiotics [111]. The hormones were less adsorbed compared to tetracycline which was between 22 and 46%. Approximately 80% of chlortetracycline and 50% polycyclic compounds were observed to be adsorbed on the surface of the membrane [111]. NF membranes are able to remove pesticides, hardness, and nitrates [112], herbicides [113–115], fungicides [116], and insecticides [117]. In detail, NF membrane rejects pesticides from pond water below the limit (0.53 µg L^{-1}) for carbaryl, the limit of detection (0.33 µg L^{-1}) for carbofuran, and less than 3.0 µg L^{-1} for methomyl [118]. The presence of humic acid, sulfates, and chlorides improved the removal of pesticides except for diuron. The removal mechanism was by forming macromolecules or by membrane pore size reduction [110]. In another study, it was observed that the diuron was the least removed pesticide due to the presence of organic substance accentuates its diffusion across the membrane [119].

Regarding the removal of the antibiotic, tighter NF membranes showed more than 90%, whereas the loose membrane exhibited between 52 and 100% [120]. The removal efficiency was strongly influenced by pH, this may be due to concurrent antibiotic speciation changes and membrane charge. Moreover, antibiotics such as norfloxacin (NOR), ofloxacin (OFL), roxithromycin (ROX), and azithromycin (AZI) were studied by different membranes, and results showed that the NFX membrane was efficient

Table 4.2: Summary of selected emerging contaminants removal by NF membranes.

Contaminants of emerging concern (CEC) class	Experimental condition	C_O and water type	Key removal (%)	Key finding	References
Eleven EDCs and PPCPs	Cross-flow TFC or CA MWCOs = 15–300 Da	500 µg L^{-1} SDW/WWE	>70 excluding acetaminophen (<40)	The effect of pH on the retention of negatively charged compounds was slightly positive for NF membranes due to electrostatic repulsion at high pH	[93]
E1, Estrone	Cross-flow MWCO = 490, 560 Da	100 ng L^{-1} SDW	10–40 after 10 h filtration time	The presence of HA in feed solution appeared to improve E1adsorption on membrane significantly as well as E1 retention	[94]
Acetaminophen, amoxicillin, cephalexin, indomethacin, tetracycline	Cross-flow TFC Varying pH and pressure	500 µg L^{-1} SDW	35–>99 w/and w/o alginate	The PhACs retention was influenced by pH, ionic strength, and transmembrane pressure, and those effects were a function of the structure and property of the PhACs and properties of the membrane	[61]
CBM, acetaminophen, atenolol, diatrozate	Cross-flow Polypierazine Pore radius = 0.128–0.258 nm	750 µg L^{-1} WWE	90–95 by 0.128 nm pore radius 20–90 by 0.258 nm pore radius	The study of the retention of neutral compounds by virgin and prefouled membrane demonstrated that the retention was governed by steric hindrance and then was poorly influenced by fouling	[79]
Organic acids including ibuprofen, glutaric acid, acetic acid	Cross-flow TFC polyamide MWCO = 200–300 Da	1.5–13.2 mg L^{-1} SDW	~30–70 (IBP) ~20–<95 (glutaric acid) ~10–80 (acetic acid)	The retention of negatively charged organic acids by NF membranes resulted in a larger retention than expected based on steric/size exclusions due to electrostatic repulsion between solute and membrane as driving factor for retention	[95]

Table 4.2: (continued)

Contaminants of emerging concern (CEC) class	Experimental condition	C_0 and water type	Key removal (%)	Key finding	References
Ten EDCs and PPCPs	Pilot MBR-flat sheet MBR-hollow fiber MBR-NF	0.06–59.5 µg L^{-1} WWE	4.2–>99 (MBR-NF > MBR-flat sheet/hollow fiber)	While using MBR treatment alone cannot completely remove all the contaminants studied. nicotine, caffeine, ibuprofen, and acetaminophen were completely removed from the liquid fraction by this treatment	[96]
Acetaminophen, SMX, TCS	Cross-flow MWCO = 300–550 Da	500 µg L^{-1} SDW NOM/calcium ions	<10 (acetaminophen) 35–80 (SMX) 80–95 (TCS)	For small and neutral-charged target compounds such as acetaminophen, the presence of humic acid and calcium ions increased retention due to an extra hindrance layer provided by the foulants	[97]
Eleven EDCs and PPCPs	MBR-NF Cross-flow MWCO = 210 Da	26.2–433.9 ng L^{-1} WWE	<1–80 (MBR alone) 78–>99 (MBR-NF)	The most important factor influencing fouling formation was the characteristics of the dissolved organic matter in the feed water rather than membrane properties	[98]
Eighteen PPCPs charged (positive, neutral, and negative)	Cross-flow NF270 Polyamide TFC	2000 ng L^{-1} SDW	60–90 (positive) 75–95 (neutral) 85–>99 (negative)	For positively charged or neutral compounds, the NF retention is more variable and lower. The relatively low retention by NF is likely caused by decreased steric hindrance in NF due to larger pore size	[99]
Twelve PhACs	Pilot scale MWCO = 200 Da	<1–58.8 ng L^{-1}	<1–76 (conventional treatment) 24–>99 (NF)	The use of this kind of containerized pilot plant, powered exclusively by a hybrid renewable energy system, allows treating efficiently and sustainably drinking water resources	[100]

Table 4.2: (continued)

Contaminants of emerging concern (CEC) class	Experimental condition	C_O and water type	Key removal (%)	Key finding	References
CBM, diatrizoate	Cross-flow Polyamide TFC	800 µg L^{-1} SDW WWE	53–92 (CBM) 96–98 (diatrizoate)	Both season and water matrix influence the dissolved organic matter composition and consequently retention of low molecular weight compounds with medium hydrophobicity by loose membranes	[101]
BPA, IBP	Cross-flow Surface modified NF	1000 µg L^{-1} SDW	75–95 (BPA) >95 (IBP)	Graft polymerization on the raw NF membrane increased the hydrophilicity and negative surface charge of the membrane in proportion to the amount of carboxylic acid in the grafted polymer chains	[102]
Clofibric acid, DCF, ketoprofen, CBM, primidone	Cross-flow MWCO = 150 Da	100 ng L^{-1} SDW WWE	50–70 (deionized water) 90–95 (MBR effluent) 70–95 (tertiary effluent)	Two mechanisms for the increase in PhAC removal of caused by macromolecules remaining in the WW effluents: modification of the membrane surface due to membrane fouling and association between the macromolecules and the pharmaceuticals	[103]
Eight PhACs	Cross-flow TFC	10 mg L^{-1} SWW	99–99.4	Relating the solute retentions to membranes' porosity has shown that the dominant retention mechanism of the examined unionazable antibiotics by all the membranes was the size exclusion effect	[104]
Ten PCPs	Cross-flow Polyamide TFC MWCO = 150–400 Da	1–150 ng L^{-1} WWE	13–99	Membrane filtration provides sufficient removal of chemical contaminants and a potent hygienic barrier for bacteria	[105]

Table 4.2: (continued)

Contaminants of emerging concern (CEC) class	Experimental condition	C_O and water type	Key removal (%)	Key finding	References
Seventeen PhACs	Dead-end, NF200 MWCO = 200–300 Da	10 µg L^{-1} SDW	35–99 depending on water chemistry conditions	The solution chemistry, organic matter, and salinity affect the retention of tetracycline's and sulfonamides and selected hormones by NF membranes	[106]
ClO4	Cross-flow MWCO = 200, 210, 350 Da	35–99 depending on water chemistry conditions	<5–50 (350 Da) >90 (200, 210 Da)	The results suggest that the solution chemistry condition of feed water affects perchlorate removal efficiency	[107]
ClO4	Cross-flow, ultrathin nanostructured poly-electrolyted-based	<5–50 (350 Da) >90 (200, 210 Da)	70–90	The modified membrane had higher permeability, while the perchlorate retention was not significantly enhanced at the same conditions of feed concentration and pressure.	[108]
Cr, As, ClO4	Cross-flow Polyamide TFC MWCO = 200, 400 Da	70–90	45–75 (ClO4) 75–95 (Cr, As)	The results also show that retention of ions by negatively charged NF membranes is significantly influenced by solution pH	[109]

Source: Reproduced from Kim et al. [57].

[121, 122]. Adsorption amounts of AZI or ROX were better compared to NOR or OFL. In another experiment, alginate was added in feed and over 99% removal of antibiotics was achieved [121]. Some antibiotics including NOR were additionally studied in NF combined with ozone-based advanced oxidation processes which effectively removed the antibiotics [122]. In addition, neutral compounds removal increases in the presence of HS, but above some level, it may not be beneficial to PhAC/EDCs removal due to HS complexation [123]. However, in the NF separation process, the removal efficiency can be improved by combining the NF technique with other processes. Recently, the NF membrane coupled with a column of granular activated carbon (GAC) has shown assured results on the total removal of pesticides and other organic particles and also decrease the regeneration frequency of GAC [124].

4.4.2 Removal of pharmaceuticals

NF membranes can show high rejection efficiencies for a wide range of PhACs [125]. Generally, bigger molecules with a negative charge and higher hydrophilicity are more efficiently rejected. NF membrane has emerged as a preferred technology for surface water treatment while imposing an effective barrier to pharmaceutically active and endocrine disrupting compounds [123]. A few pieces of research were done on the removal of endocrine-disrupting compounds and pharmaceuticals using actual wastewaters, rivers, or drinking water treatment [4] which showed complete removal. During the removal of pharmaceuticals using NF 270, approximately 65 and 83% removal of conductivity and total organic carbon occurred. Whereas, the removal efficiency was 78.9% was for atenolol, 88% for carbamazepine, and 98.0% for sulfamethoxazole, respectively [126]. Furthermore, BPA removal was 74.1% for raw membrane while 96.9% for chemically modified NF using graft polymerization [87]. The membrane polymerized for 60 min showed greater steric hindrance compared to polymerized for 15 min. Yangali-Quintanilla et al. [127], studied some aqueous pharmaceuticals like acetaminophen, naproxen, carbamazepine, sulfamethoxazole, etc., and reported that the tight NF PA membranes, such as the NF 90, may be an effective barrier.

The interactions of OM and PhACs improved in the removal PhACs from aquatic environments [3, 128]. The explicit impact of naturally occurring dissolved OM was investigated which showed higher removal of specific PhAC/EDCs due to HS fraction occurred in natural water while using NF [123]. Moreover, fouling changes membrane properties which affect solute membrane interactions. Bellona et al. [126] reported that acetaminophen, carbamazepine, bisphenol-A, etc. removal by NF was negatively impacted by EfOM fouling. On the contrary, on other hand, Zazouli et al. [61] have observed that the increment in the rejection of large drugs whereas smallest substance with modest polarity (i.e., acetaminophen) presented a lower rejection because of its fouling layer in a polymeric matrix (alginate as model compound). Hajibabania et al. [59]

reported that the rejections of hydrophilic nonionic and ionic solute are found to be lower when membranes are fouled with humic acids and even more with alginates. In yet another study, Yangali-Quintanilla et al. [127] observed that natural OM fouling can ameliorate the rejection of most of the targeted neutral compounds without any significant impact on ionic PhACs rejection.

4.4.3 Personal care products

Among the membrane filtrations, NF performs better in removing personal care products. Yoon et al. [129] found that NF membrane showed better removal efficiency (43–90%) for pharmaceutical and personal care products (PPCPs) compared to UF membrane removal (40%) which might be due to pore size of the membrane and the chemical structure of processed drugs. Radjenovic et al. [130], reported NF membrane removed more than 95% of ketoprofen, diclofenac, and sulfonamoxazole in water. A comparative study conducted for 27 PPCPs removal using an integrated system (Membrane Bioreactor [MBR]-RO/NF and MBR system) showed 41.08 and 95.41% removal for the MBR system while above 95% for MBR-RO/NF [131]. Furthermore, the combination of MBR-NF could remove 13 compounds below detection limits and the MBR-RO combination exhibited better results which were able to remove 20 compounds to below detection limits.

4.4.4 Removal of organics pollutants

The NF treatments are used to remove the majority of organic and inorganic compounds and the NF treatments are used to remove the majority of organic and inorganic compounds and pathogens effectively from raw water [132]. However, low MWCO might be partially removed [133], and the produced water quality may deteriorate in time due to membrane fouling. The NF membrane was extensively examined for the removal of Total Organic Compounds (TOrCs) at laboratory scale and onsite using simulated and real water [134]. All TOrCs are not effectively removed by NF, for instance, the removal of 52 endocrine-disrupting compounds and PPCPs studied using synthetic and real surface water using NF membrane with a nominal MWCO of 200 Da showed 0% to over 90% removal [57]. Radjenovic et al. [130] also reported the excellent removal for nine out of 12 pharmaceuticals from full-scale drinking water treatment plants using the NF membrane with a nominal MWCO of 200 Da. However, less removal efficiency (about 50%) was achieved for gemfibrozil, acetaminophen, and mefenamic acid. Moreover, out of 40 hormones and PPCPs, the NF membrane could effectively remove the majority of the TOrCs (80%), but oxytetracycline, acyclovir, trenbolone, metronidazole, carbamazepine, chloramphenicol, nandrolone, sodium nifurstyrenate, and caffeine were not effectively removed [135].

A commercial NF membrane was also studied to remove nitrate from groundwater, and showed complete removal of phosphate and 55.1–62.2% removal of nitrate which is mainly due to sulfate with nitrate adsorption competition [136]. The fabricated flat-sheet electrospun NFs membrane by using PVDF blended with polymethyl methacrylate showed 48% Chemical Oxygen Demand (COD) removal for secondary effluent from the wastewater treatment plant of the local zoo [89]. In another work, Wu et al. [137], prepared PVP-GO/PVDF membrane using a chemical grafting approach and investigated the performance in treating organic-rich wastewater by applying integrated with algae-membrane photo-bioreactor systems. The performance showed high removal of turbidity (99%), Total suspended solids (99%), COD (94%), and ammonium (93%). The combination of activated carbon (AC) and NF system showed better removal than the reverse combination, i.e., NF-AC system, and dissolved organic carbon was removed > 95% by the combination of AC adsorption and NF membrane separation [138].

4.5 Conclusions

Previous studies showed that the NF membrane can effectively remove emerging contaminants from water and wastewater. There are also advancements to improve the performance efficiency and cost of the membranes. Besides the improvement in quality of the product using NF membranes, there is progress on antifouling and self-cleaning membranes, and preventing leaching of NMs that are incorporated in the NF membrane to improve the performance efficiency. In the future, further research activities should continue to alleviate the existing limitations related to membrane treatment processes, and to develop and propose innovative strategies in order to minimize cost, and to increase the product quality.

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5 Metal nanoparticles and its application on phenolic and heavy metal pollutants

Abstract: The perpetual exposure of several manmade materials and their activities such as urbanization, industrialization, transportation, mining, construction, petroleum refining, manufacturing, preservatives, disinfectants etc., release various pollutants like organic, inorganic, and heavy metals which pollute the air, water, and soil. This poses various environmental issues which are relevant to the ecosystem and human wellbeing that intensify the implementation of new expedient treatment technologies. Likewise, phenolic and heavy metal pollutants find their way into the environment. These phenolic and heavy metals are toxic to the liver, heart and carcinogenic. Therefore, the removal of these kinds of pollutants from the environment is a highly challenging issue. As conventional treatment technologies have consequent drawbacks, new interests have been developed to remediate and remove pollutants from the ecosystem using metal nanoparticles (MPNs). To date, many researchers all over the world have been investigating novel approaches to enhance various remediation application technologies. One such approach that the researchers are constantly showing interest in is the use of nanomaterials with potential applications towards the environment. In this regard, MPNs like Copper (Cu), Nickel (Ni), Palladium (Pd), Gold (Au), Silver (Ag), Platinum (Pt), Titanium (Ti), and other nano metals are serving as a suitable agent to eliminate emerging contaminants in various fields, particularly in the removal of phenolic and heavy metal pollutants. This chapter discusses the mechanism and application of various MPNs in eliminating various phenolic and heavy metal pollutants from the environment.

Keywords: environment; heavy metals; metal nanoparticles; phenolics; pollutants.

5.1 Introduction

Contaminants begin with a substantial cause for various hazardous impacts to the environment and human health. Moreover, annually 80,000 synthetic chemicals are

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being released into the environment from the industrial manufacturing units either as a product or waste by products [1]. One of the reasons for emerging contaminants is due to non-availability of sufficient analytical methods to identify the contaminants. Another reason is the unawareness about the future adverse toxicity of the contaminants on human health and environment and poor knowledge on their permissible limits [2]. Contaminants can be broadly classified into two types based on their source and location as point source and non-point source.

The point source of contaminants means the pollutants which are released from a particular locality and get into the environment. Examples include, contaminants released from industries by activities such as treatment of sewage plants, and extraction of minerals. Non-point source of contamination refers to contaminants from an indefinite, circulated source that usually happens in a large area. For example, in overland, the flow of bio solids, fertilizers, and diffused pollutants are released from various urban and industrial activities [3]. Though diffuse sources have been found in lower concentrations, it is suspected to be more reactive of the natural diminishing process than the point source.

The perceptual exposure of various man-made materials to environments such as urbanization, industrialization, transportation, mining, construction, petroleum refining, manufacturing, etc. are leading to various types of contaminants that pollutes the environmental system. An extensive range of incipient contaminants that have been continuously reported in soil, surface, and groundwater are pesticides, pharmaceuticals, lifestyle and personal care compounds, industrial additives and their by-products, food additives, water treatment by-products, etc. These contaminants can be organic or inorganic, where organics are the detergents, phenolic compounds, processed foods, pesticides, pharmaceuticals, etc., and inorganics are salt and heavy metals. The release of these contaminants pollutes and affects the air, water, and soil quality. This raises a slew of environmental concerns about the ecosystem and human health, all of which hasten the adoption of new conventional treatment technology. These technologies are ineffective and additionally have several drawbacks. So, budding scientists have been involved in the development of novel remediation technologies to remediate and absorb pollutants from the ecosystem.

Various nanoparticles have been attempted by the researchers across the globe to treat contaminants in the environment. Moreover, the characteristic features of nanoparticles are thought to be beneficial in the bioremediation process. To avoid contamination by pollutants, green chemistry focused on the use of safe and environmentally friendly chemicals. The incorporation of green chemistry principles into nanoscience leads to the creation of new green nanoscience research fields [4]. In recent years, many researchers have been working in the field of nanotechnology to generate novel nanomaterials that have been used for developing new applications. The realm of nanoparticles has emerged as metallic nanoparticles or metal nanoparticles (MPNs). Metallic nanoparticles are made from noble metals such as gold, silver, and platinum, which have been used in various fields [5]. Consequently, MPNs are suitable to eliminate emerging contaminants in various sites, particularly in remediation fields and technologies. The advantage of using nanoparticles is that they are good adsorbents because of their larger surface area. Also, their affinity towards targeting compounds is high. Hence, this chapter explores the recent trends and applications of MPNs in the removal of phenolic and heavy metal pollutants.

5.1.1 Metal nanoparticles

Several studies have shown the use of nanomaterials due to their large surface area and surface-free energy, small size, metal atomicity, and reactivity [6]. Metallic nanoparticles are MPNs with dimensions ranging from 1 to 100 nm. In comparison to a bulk compound of the same type, their small size exceptionally provides more contact points [7]. They could also be specially synthesized with the right functional groups to help them bind to the right things. Humans have been using MPNs in the form of colloids or sols for ornamental purposes since the middle ages. One of the examples is the purple of Cassius, a coated gold colloid used as a color in glass enamel and chinaware, was developed by Andreus Cassius in the mid-seventeenth century [8].

Chemical, photochemical, electrochemical, and radiolysis methods have all been used to produce MPNs. Previous research works have shown the use of reducing chemicals in a solution to reduce metallic precursors like Au, Cu, Zn, and Ag to produces metallic nanoparticles. The use of plant extracts in the biosynthesis of metallic nanoparticles has numerous benefits when compared over traditional techniques, the most important of which is that it is ecologically benign and those plant entities are easily available [9]. Metallic nanoparticles can be generated directly in plants by reducing metal ions absorbed as soluble salts, showing that plants are good carriers for nanoparticle creation [10]. Antimicrobial activity has been observed in a variety of metal and metal oxide nanoparticles, including silver, silver oxide, titanium dioxide, zinc oxide, gold, calcium oxide, silica, copper oxide, and magnesium oxide [11]. Metal ions may be reduced by water-soluble active chemicals found in plant extracts, resulting in increased antibacterial capabilities for metallic nanoparticles [12]. Furthermore, dead and dried plant biomass, such as dried leaves, stems, straw, and other materials, can be utilized to make nanoparticles [13]. The synthesis of metallic nanoparticles from plant extracts is gaining momentum, a key area of nanobiotechnological studies. Moreover, antimicrobial, electrical, catalytic, and other biological uses have all made use of metallic nanoparticles [14]. Biosynthesis of plant based nanoparticle is not only simple, sustainable, cost-effective, fast, safe, and ecologically friendly, but it can also be readily scaled up. In recent years, a new nomenclature in the realm of nanoparticles has emerged: metallic nanoparticles or MPNs. Metallic nanoparticles are made from noble metals such as gold, silver, and platinum, which have favorable health benefits [15]. Among these Au and Ag are widely explored MPNs due to its enormous physical and chemical properties. Redox activity, conductivity, surface plasmon resonance, surface enhanced Raman scattering, and fluorescence quenching are the major properties of gold nanoparticles. Other properties like size, shape, light scattering, opto-electronic properties, outstanding biocompatibility, surface functionalization, and also due to its low toxicity attributes basic properties of Au nanoparticles (Au NPs) [16]. Silver nanoparticles properties possess various useful attributes based on its size and shape, surface chemistry, particle morphology, composition and reactivity, efficiency of ion release, agglomeration, dissolution rate, and low toxicity [17]. The micelles of gold and silver nanoparticles in Figure 5.1 show the hydrogen bonds depicted by dashed lines which allows the water molecules to bind with Ag and Au NPs. It's worth noting that negatively charged Ag and Au NPs surrounded by water molecules can form a stable suspension without the addition of stabilizers or surfactants.

The method of preparation of metallic nanoparticles is equally important because processes such as kinetics of metal ions interaction with reducing agents, adsorption process of the stabilizing agent with MPNs, and various experimental techniques have a strong influence on the stability of morphology and physicochemical properties of metallic nanoparticles [8].

5.2 Heavy metals

Currently, we are witnessing an increase in global concerns about their potential detrimental health effects and long-term repercussions of heavy metals on bio-systems. Some of the heavy metals are known to be carcinogenic (hexavalent chromium, arsenic, cobalt, nickel, antimony, vanadium, mercury), whereas others are mutagenic (arsenic, vanadium), teratogenic (arsenic), allergic (nickel), or disrupts endocrine (silver, copper, zinc, selenium). On the other hand, heavy metals like thallium cause neurological and behavioral changes, particularly in children, likewise mercury damages central nervous

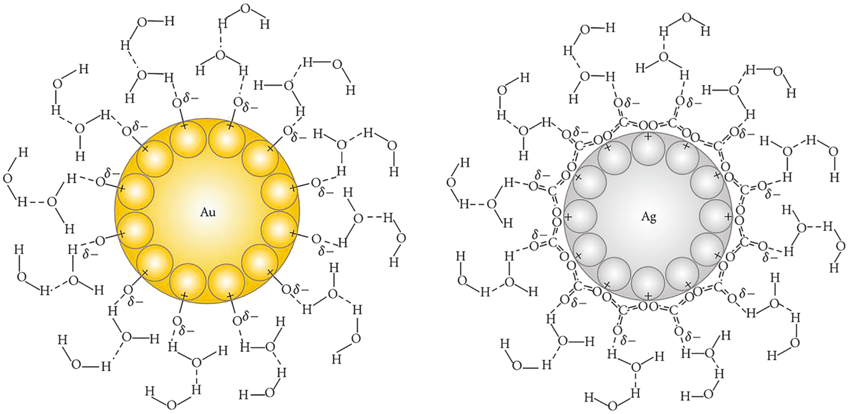

Figure 5.1: Micelles formation in Au and Ag nanoparticles [18].

system, lead, thallium, manganese, and tin damages bone marrow, and metals like cadmium, mercury, heptavalent manganese damages liver and kidney. Among these, some of the metals affect the immune system of an individual [19]. These heavy metals are produced from different activities as mentioned above. The maximum contamination levels (MCLs) have been established by the Environmental Protection Agency (EPA) as a benchmark for drinking water quality and the presence of higher levels of pollutants have negative consequences on health [20]. In the recent past, the development of new and cost-effective 0D, 1D, 2D, and 3D nanomaterials for environmental remediation, pollution monitoring, and other uses has received lot of interest among the researchers and the policy makers. The best choices for heavy metal adsorption and removal are determined to be zero-valent metal and MPNs [21].

5.2.1 Application of metal nanoparticles on heavy metals

Metals with a high melting point and density are known as heavy metals. Although they are generally found in low concentrations, they may be found throughout our planet's crust. Heavy metal is often defined as having a density of at least 5 g cm^3 to distinguish it from other, "light" metals. Heavy metals are often present in the earth's crust in low quantities, ranging from few ppb (noble metals) to up to 5% (iron); heavy metals are chemically bonded in carbonate, sulfate, oxide, or silicate rocks, or they can also be found in their metallic, elemental form. Their leaching and mitigation into soil, rivers, and groundwater were caused by weathering and erosion [22]. Even in low quantities, heavy metals can be hazardous. In the past few decades, there has been a surge in agricultural, industrial, and urban activity, resulting in massive increase in pollution. The major causes of pollution include fossil fuels, municipal garbage, fertilizers, mining and smelting of metals, ferrous ores, pesticides, and sewage sludge [23–25]. Nanomaterials have been scavenging a variety of heavy metals due to their large surface area and strong reactivity. Non-covalent conjugation is a more suitable way for molecules to connect to MPNs because they can do so via a variety of interactions, including specific binding affinity, electrostatic contact, and hydrophobic interaction with heavy metals [26]. Furthermore, popular nano metal oxides such as ferric oxides, aluminium oxides, manganese oxides, magnesium oxides, titanium oxides, and cerium oxides have a large surface area and a clear affinity in clearing heavy metals from aqueous systems [27]. The degradation of heavy metals using MPNs are summarized in Table 5.1.

5.2.1.1 Silver nanoparticles

Among various nanoparticles, silver nanoparticles have been widely used to remediate various heavy metal pollutants. By performing nano adsorbent techniques, silver nanoparticles have been successful in removal of heavy metals. Silver nanoparticles

Table 5.1: Application of metal nanoparticles (MPNs) on heavy metals.

Metal nanoparticles	Application on heavy metal pollutants	Method	Reference(s)
Au nanoparticles	Detoxification of heavy metals	Biomineralization	[24]
Ag nanoparticles	Remediation of Cr and Pb (more efficiently)	Nanoadsorbent	[25]
Ag nanoparticles	To detect heavy metal Cd (II) and Pb (II)	Electrocatalytic method	[26]
Ag nanoparticles	Detection of Cu (II) and Hg (II)	Colorimetric method	[27]
Ag nanoparticles	Change toxicity and bio-accumulation of Cd, As (V), and Cu heavy metals	Surface interaction	[28]
Au nanoparticles	Detect and degrade heavy metals and textile dye	Colorimetric and photocatalyst	[29]
Silver and titanium nanoparticles	Degradation of Copper and mercury	Photocatalytic method	[30]
Ag nanoparticles	Determination of copper, iron, lead, and zinc	Surface methodology	[31]
Gold nanoparticles	Used to detect mercury and lead	Anodic stripping voltammetry	[32]
Ag and Au nanoparticles	Detection of Cd^{2+}, Cu^{2+}, Pb^{2-}, Ni^{2-} and Co^{2-}	Spectrophotometric detection	[33]
Au nanoparticles	Heavy metal detection Hg, Pb, Cd, and As	Colorimetric detection	[34]
Ag nanoparticles	Bioremediation of heavy metals	Ag treated with plant growth-promoting *Rhizobacteria*	[35]
Ti nanoparticles	Increased photocatalysis ability	Photocatalytic activity	[36]
Au and Ag nanoparticles	Bioremediation of copper, zinc, lead, and magnesium	Biosorption	[37]
Au nanoparticles	Detection of Hg^{2+} and Cu^{2+}	Sensitive electrochemical detection	[38]
Au nanoparticles	Detection of Hg (II) in soil, food, and water samples	Optical fiber sensor	[39]
Au nanoparticles	Detection of lead in water and serum	Colorimetric aptasensor method	[40]
Au nanoparticles	Detection of Hg^{2+} and Pb^{2+} ions.	Colorimetric detection	[41]
Ag nanoparticles	Detection of Hg^{2+} and Mn^{2+} ions in an aqueous medium		
Ag nanoparticles	Visual detection of Pb 2+ ion	Visual detection by colorimeter	[42]
Ag nanoparticles	Determination of Hg (II)	Colorimetric detection	[43]
Ag nanoparticles	Detection of Hg^{2+} and Pb^{2+}	Aggregation of aptamer labeled Ag nanoparticles	[44]
Au and Ag nanoparticles	Detection of Hg^{2+}, Mn^{2+}, and Pb^{2+} in aqueous medium	Colorimetric detection	[45]
Ag nanoparticles	Detection and rapid removal of Hg^{2+}	Filter membrane (chemo-sensor and adsorbents)	[46]
Au nanoparticles	Removal of Hg^{2+}	Impregnated zeolites	[47]
Au nanoparticles	Estimation of Cu and Cd (II) from water.	Adsorption	[48]

act as bio-based reductant to remediate heavy metals from pharmaceutical effluents and the maximum removal efficiency against Cr and Pb heavy metals was achieved under optimal conditions [28]. Moreover, various screen-printed carbon nanofiber electrodes are a popular option because of their high performance and low environmental effects. By using silver nanoparticles, silver seed, and silver prism performed an electrocatalytic experiment and detected cadmium (I) and lead (II) [29]. Heavy metals like copper and mercury have been detected using silver nanoparticles by the calorimetric method [30]. Also, silver nanoparticles and citrate-coated silver nanoparticles have been used to detect the toxicity and bioaccumulation of heavy metals. Silver nanoparticles also reduced Arsenate (V) and Copper bioaccumulation and improved Cd acute toxicity and bioaccumulation [31]. Furthermore, silver nanoparticles were involved in the bioremediation process of municipal wastewater treated with *Rhizobacteria* sp., and used for wastewater irrigation. After treatment, the recycled water improved the plant development and removed harmful heavy metals [32]. Mercury (II) was reduced from water using silver nanoparticles doped by synthetic coal fly ash zeolites. Almost 99% of the mercury was removed and complete removal of Hg^{2+} was achieved [33]. The silver nanoparticles with deposited multiwalled carbon nanotubes were used to remove copper (II), cadmium (II), from an aqueous solution, the adsorption rate was confirmed by kinetic studies and thermodynamic studies [34]. Silver nanoparticles are also used in the detection of copper, iron, lead and zinc heavy metals. Glass stir bar coated with silver nanoparticles are used to determine toxic heavy metals by surface methodology [35].

5.2.1.2 Gold nanoparticles

Gold nanoparticles have been used to detect and degrade various heavy metals by photocatalytic method. Moreover, gold nanoparticles have been used to biomineralize heavy metals [36]. Gold nanoparticles detected heavy metal and textile dyes using a beta-cyclodextrin probe [37]. Heavy metal ions are also detected by gold nanoparticles due to their great sensitivity and selectivity; gold-based electrodes are proven to be effective alternatives, particularly in monitoring heavy metals. The simultaneous detection of heavy metal ions has been proposed to determine the concentration of mercury and lead by using gold and mercury electrodes [38]. Heavy metal contaminants like Hg, Pb, Cd, and As has significant impact on environment and human health.

In biological and environment analysis, rapid and simple detection of heavy metals with significant toxicity at low concentration levels is critical. DNA-inspired gold nanoparticles, which use the assembly and disassembly of Au NP for colorimetric signaling of the recognition event between DNA and target heavy metals at the Au NP interface, have become a well-established approach among the many convenient detection methods for heavy metals [39]. Gold nanoparticles are used to detect heavy metal ions like Hg^{2+} and Cu^{2+} by electrochemical method with high sensitivity [40]. Mercury is a bioaccumulative heavy metal contaminant that is hazardous to all living things in the environment. An ultrasonic Hg (II) receptor is explored using chitosan-capped gold nanoparticles on BSA. With a LoD of 0.1 ppb, the sensor can detect Hg (II) in surface soil, water, and food [41]. Gold nanoparticles have been used for the detection of lead, the most dangerous heavy metal that causes severe environmental hazard. Based on the triple-helix molecular switch and peroxide-like action of gold nanoparticles, a calorimetric aptasensor was developed for the selective, sensitive, and quick detection of the lead using all nanoparticles. The aptasensor was successful in detecting Pb^{2+} in both water and serum [42]. Similar detection of lead ions was performed by gold nanoparticles using colorimetry. By simple visual assay of color observed when Ag nanoparticle is added to the lead-containing solution, the color changed suddenly from red to blue in color and detected at rapid fast [43].

The use of gold nanoparticles functionalized by dithioerythritol in a colorimetric absorbance was found to be extremely selective and sensitive in determining Hg (II) ions. Other ions like copper (II), lead (II), and cadmium (II) did not interfere even in the absence of masking agents [44]. Furthermore, studies reported that gold nanoparticles can detect Pb^{2+} and Hg^{2+} via rapid visual detection method using gold nanoparticles coupled with T, G-rich aptamer, a homogenous technique for quick detection of Pb^{2+} and Hg^{2+}. The modified gold nanoparticles gather in the presence of target ions, changing the color of the solutions from a pink color to blue color due to its scattering and aggregation. This method is quick (take 20 min), highly selective for lead, mercury and accurate. It has the potential to be used for water quality control and environmental monitoring in the future [45]. The development of a versatile system for concurrent multiple signal amplification detection and rapid Hg^{2+} elimination is still a key challenge today. For the first time, gold nanoparticles (Au NPs) and the matching filter membrane were employed as chemosensory and adsorbents to detect dual signal amplification and remove Hg^{2+} quickly. Furthermore, the immobilized Au NPs in the filter membrane could enable the rapid removal of mercury ions in Yellow river water and tap water, with a removal efficacy of close to 99% [46].

5.2.1.3 Bimetallic nanoparticles

The presence of heavy metals ions can be detected using bimetallic nanoparticles such as silver and gold colloids. Cadmium, copper, cobalt, lead, and nickel heavy metals were detected by spectrophotometric detection using gold, and silver colloids can be utilized as chemical probes for the presence of heavy metal ions [47]. Bimetallic nanoparticles are also used in bioremediation process. By following biosorption technique, silver-gold nanoparticles remediated copper, zinc, lead, and magnesium heavy metals which are present in the sewage of pharmaceutical industry [48]. Likewise, silver and gold nanoparticles used to perform sensitivity against heavy metals like mercury (Hg^{2+}), manganese (Mn^{2+}), and lead (Pb^{2+}) ion in an aqueous medium. Au NPs detected mercury and magnesium whereas Ag nanoparticles detected mercury and lead [49]. The silica and titanium nanoparticles act as a photocatalyst to degrade heavy metal pollutants from the environment. Heavy metals like chromium (III), cobalt (II), and lead (II) along with tin and also cyanide were completely degraded by photocatalytic activity. Therefore, the photocatalytic activity of silica and titania is significant [50]. As mentioned before, titania acts as good catalyst when vanadium is doped with titania nanoparticles to eliminate heavy metals in water. Under ultraviolet illumination for 24 h, adsorption isotherms for the removal of lead and zinc from aqueous solution were created, and the results demonstrated that titania doped with vanadium increased the photocatalytic activity [51].

5.3 Phenolic pollutants

Phenolic chemicals are frequent industrial wastes that accumulate in the environment and food chain as a result of consumption or uptake. Phenols/phenolic refers to phenol and its derivatives including phenol, cresols, dimethylphenols, resorcinols, and chlorophenols which are key recalcitrant in soil and aquatic environment. These recalcitrant are obtained from petrochemical and oil refineries, commonly employed in the creation of wood preservatives, insecticides, and biocides, as additives in steel mills, refineries, pharmaceuticals, plastic industry, coal-fired power plants, paints, paper, explosives, disinfectants, chemical reagents, and in the production of organic compounds such as dyes, artificial resins, and pulp industries. Phenols interfere in the life cycle of animals/plants, and human through the soil and water contaminated with industrial waste discharged from above mentioned industries. Phenol and its derivatives have sparked widespread alarm around the world. Since 1976, the United States EPA has designated 11 phenolic compounds as a priority water contaminant with potential harmfulness. The content of phenols in a contaminated aquifer groundwater sample was reported to be as high as 25–55 mg/L and in Estonia, oil-shale disposal site soil reported to contain up to 380 mg phenols/L. Under dreadful situations, the phenolic content in wastewater may exceed 200 mg/L. Around 50% of phenol and its derivatives such as p-cresols, 5-methylresorcinol, and resorcinol are effectively removed by microbial degradation process, whereas 2,3- and 2,4- and 3,4-dimethylphenols are resistant to microbial attack and cause serious toxic effect by their metabolites especially in the aquatic environment. Because of their carcinogenic propensity, phenol derivatives such as nitro and chlorophenol are also considered as risk. These study reports emphasize the significance of phenolic pollutants and the importance of developing an efficient treatment solution for remediation of such hazardous wastes [52].

When these pollutants are released into the environment, they contaminate both groundwater and soil. The solubility, stability, bioaccumulation capacity, toxicity, and carcinogenicity of these contaminants cause severe damage to the liver and red blood cells that lead to significant threats to human health. Their presence in the air, water, and food causes serious environmental issues and pose danger to human health. Chlorophenols and nitrophenols have carcinogenic and immunosuppressive qualities;

therefore, the European Union and the US EPA have issued warnings against the use of these chemicals and their deleterious effect on human. As a result of this, phenols were included in their priority pollution lists. The European Community has set a limit of less than one part per million of phenols in wastewater. As a result, developing ways for eliminating such pollutants is critical and has been the subject of extensive research. Common wastewater treatments such as activated carbon adsorption, chemical oxidation, biological digestion, membrane filtering, solvent extraction, and others are deemed as inefficient techniques due to the resistance to biodegradation and the stability of recalcitrant phenolic compounds. Moreover, these traditional treatment methods have drawbacks, such as the development of additional wastes during the process, and extensive time duration which necessitates more steps and increases the expense of the treatment process. Additional disadvantages, such as delayed degradation and incomplete removal, render them unsuitable for industrial use [53].

For the detection of level of phenolic compounds in the environment, standard analytical approaches such as chromatography, laboratory-based spectrophotometry, immunochemical, enzyme-based electrochemical, and biosensing have been established. These traditional methods are inaccurate and have low detection limits, but they are time-intensive and often include complex sample pre-treatment processes. To monitor phenolic compounds in real-world situations and assess the public risk of exposure to these compounds, simple, easy-to-operate, and cost-effective detection technologies must be developed [54].

5.3.1 Effect of metal nanoparticles on phenolic pollutants

In the treatment of phenolic contaminants from environment, several nanoparticles play important role. Because of the large surface area, the nanoparticles boost reactivity, quantum effects that allow for chemical reactions, and surface plasmon resonance aids in toxicity detection [55]. For the breakdown of pollutants, nanobioremediation employs biosynthetic nanoparticles derived from microbes and plants [56]. Several successful nanobioremediation based methods have been reported to eradicate a wide variety of phenolic pollutants (Figure 5.2).

5.3.2 Photocatalytic degradation of phenol using nanoparticles

Photocatalytic degradation of phenol and 2-chlorophenol in wastewater was catalyzed by a semiconductor platinum nanoparticles using TiO_2 as catalyst. This photocatalytic degradation resulted in 87.7% and 100% remediation of phenol and 2-chlorophenol from the contaminated site [53]. A study on photocatalytic degradation of phenol, 2-chlorophenol, and 2-nitrophenol was successfully done by a non-semiconductor particle system using bimetallic alloy Au–Pd nanoparticles which are decorated by

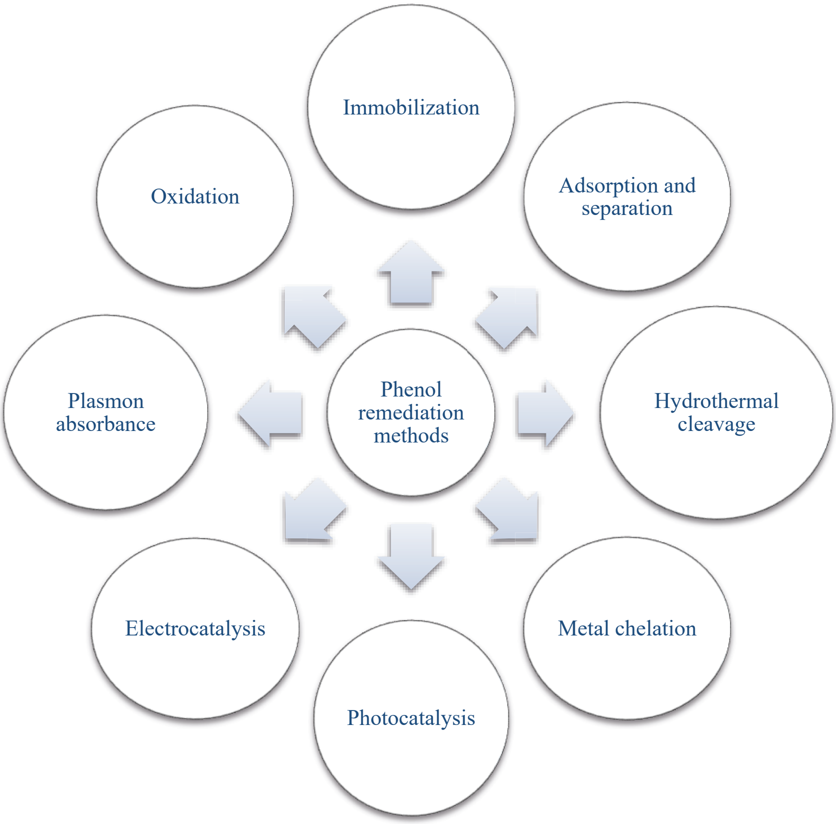

Figure 5.2: Methods of remediation of phenols by nanoparticles.

reduced graphene oxide nanosheets. Recycling ability of the semiconductor nanoparticle were evaluated and the results showed equivalent level of degradation ability of the semiconductor nanoparticle up to five cycles which assured the excellent stability of semiconductor nanoparticles [57]. Previous studies have reported the successful degradation of phenol and methylene blue by photocatalytic process using the prepared hybrid material containing zinc oxide nanoparticles and zinc magnesium–aluminum layered triple hydroxide hybrid. Due to its synergetic effect of metals rendered high charge, carrying ability, and improved visible light absorption activity [58]. Another study demonstrated the degradation efficiency of fabricated platinum to Uio-66-NH_2 against phenol wasover 70% [59]. The degradation of phenolic compounds using MPNs is summarized in Table 5.2.

Copper nanoparticles have been used to eliminate phenolic pollutants. Copper nanoparticles act as copolymer nanoparticles to remove phenol from an aqueous solution. Copper nanoparticles act as chelators that can be used as copolymers to lactose

Table 5.2: Application of metal nanoparticles (MPNs) on phenolic pollutants.

Metal nanoparticles	Method used	Application on pollutant	Reference(s)
Platinum nanoparticles CO_2 catalyst	Photocatalytic degradation	Degrades phenol & 2-chlorophenol	[54]
Au–Pd nanoparticles	Photocatalytic degradation	Degrades phenol, 2-chlorophenol, & 2-nitrophenol	[55]
Copper nanoparticles	Chelation and immobilization activity	Eliminates phenolic pollutants from water	[56]
Ag nanoparticles	Adsorption	Shown 87.65% of efficacy in the adsorption of phenol	[57]
$AgSO_4$ nanoparticles	Photocatalytic degradation	Good catalytic activity to eliminate industrial phenol	[58]
Ni & Co nanoparticles	Hydrothermal catalytic activity	Shows good catalytic activity to eliminate industrial phenols	[59]
Silver nanoparticles	Photocatalytic & electro-catalytic degradation	Phenolic azo dye degradation	[60]
Silver nanoparticles	Plasmon absorbance bands	Visualization & detection of atomic phenols	[61]
Gold nanoparticles	Rapid sensitive detection	Detects and visualize phenols	[62]
Silver & titanium nanoparticles	Photocatalytic activity	Degrades phenol & chemical pollutants	[63]
Ag nanoparticles	Photocatalytic activity	Degradation of 4-nitrophenol and methyl orange dye	[64]
Copper nanoparticles	Catalysis	Degrades 98% of nitrophenol in 100 s	[4]
Zinc sulphide nanoparticles	Separation and ring opening	Degradation of p-nitrophenol in wastewater	[65]
Fe_2O_3 nanoparticles	Photocatalytic activity	Degradation of phenols	[66]
Zinc nanoparticles	Metal chelation process	Degrades phenol & methylene blue	[67]
Platinum nanoparticles	Photocatalytic activity	Degrades 70% of phenol	[68]
CO, Ni & Cu nanoparticles	Catalytic activity by MPNs and cationic microgel polymerization	Exhibits catalytic activity to eliminate 2-nitrophenol, 4-nitrophenol, and also dyes	[69]
Pd nanoparticles (a hybrid of iron oxide and palladium NPS)	Oxidative degradation	Eliminates chlorophenols and phenols	[70]
Gold – Pd/TiO_2 nanoparticles	Photocatalytic degradation	Quickly degrades phenols and improves the efficacy	[71]
Ag, Ni, & Co nanoparticles	Catalytic activity	Catalyzes nitro-phenolic compounds (ortho-meta, para-nitro phenol)	[72]
Silver nanoparticle	Catalytic activity	Diparticle and triparticle composite removal by sorption and filtration	[73]

by an immobilization system. Furthermore, a study reported that the laccase immobilized metal chelated nanoparticles eliminated more than 96% of phenol. White metals like lanthanum, $LaCO_3OH$ were fabricated with silver phosphate nanoparticles to enhance photocatalytic degradation for the removal of toxic phenolic pollutants [60]. The hydrothermal catalytic activity of nickel and cobalt MPNs was found to exhibit the best photodegradation performance. Nickel and cobalt decorated with carbon/ZrO_2 were highly stable. Under 200 °C for 240 min, the "Ni_3CO @C/ZrO_2" showed good catalytic activity. These research reports are being useful for developing non-noble metal catalysts to eliminate industrial phenol in near future [61].

5.3.3 Electrocatalytic degradation of phenol using nanoparticles

Both photocatalytic and electrocatalytic mediated degradation of phenolic azo dyes in wastewater was reported. Especially, the electrochemical method of degradation of phenolic dyes was accelerated by the use of silver nanoparticles. This phenolic water-soluble dye degradation showed good efficiency [62]. Ortho-trihydroxy aromatic phenols like gallic acid, pyrogallol, tannic acid, etc., were detected and visualized by chitosan-capped silver nanoparticles. Change in the color of the aqueous medium from yellow to orange due to the plasmon absorbance bands formation while degradation of phenolic by the catalytic reactivity of silver nanoparticles was detected by the inexpensive and highly sensitive colorimetric probe or else can be visualized through naked eyes. Phenols could not induce the color change even in very high concentrations. Therefore, chitosan-capped silver nanoparticles are used as a highly sensitive colorimetric probe for the visualization and detection of aromatic phenols [63].

5.3.4 Biocatalytic degradation of phenol using nanoparticles

Rapid and sensitive detection of phenols was reported by the ssDNA regulated system using unmodified gold nanoparticles in water samples [64]. Also, the degradation of phenolics was done by colorimetric probe of ssDNA – Au NPs. This can be visualized either by the naked eye or by visible absorption spectroscopy. Various MPNs can be used for photocatalytic activity and biocatalytic activity. Toxic petrochemical pollutants like phenol, benzene, and toluene have been degraded by photocatalytic activity. By using silver and titania nanoparticle hybrid nanocomposite degraded phenolic pollutants from an aqueous solution of methylene blue dye [4]. The degradation of 4-nitrophenol and methyl orange dye was effectively done by photocatalytic activity of gold nanoparticles green synthesized by *Myristica fragrans* leaves. The kinetic reaction and efficiency of catalytic dosage were examined on the degradation of pollutant [65]. The existing methods for synthesizing cuprous catalysts are difficult and time-consuming and making them unsuitable as substitutes for the catalyst of the noble metal catalyst in the removal of organic contaminants. A study reported a one-pot method developed to synthesize the cuprous or copper nanoparticles which showed ultra-quick degradation of 4-nitrophenol (98%), methyl orange (97%), and congo dye (96%) in 100 s [66]. The degradation of phenol is effectively estimated by photocatalytic activity by Fe_2O_3 nanoparticles produced from *Phylanthus nururi* and *Moringa stenopetala* leaves. Separation of 2-, 4-chlorophenols, 2,3-dichlorophenols and their mixture from wastewater by magnetic field and degradation was accelerated by *Rhodococcus rhodochrous* DSM 6263 immobilized on Fe_3O_4 nanoparticles [67]. The p-nitrophenol degradation mediated by separation, formation of reactive hydroxyl radicals, and double bond breakage and ring opening, accelerated by the ZnS nanocrystals. Also, experimented trapping of reactive species confirmed quick production of radicals like $O_2^{\cdot}$ and $^{\cdot}OH$. After 240 min, the degradation efficacy against phenol was significant and found to be 90–92% [68].

The metal-chelated chitosan-based nanoparticles are available to support laccase immobilization in elimination of phenolic pollutant [69]. By following the anaerobic, mixed consortium mediated synthesis of silver nanoparticles examined for the removal of phenolic pollutants. The surface morpho-changes were observed due to the adsorption of phenol. These silver nanoparticles have shown 87.65% efficacy in the removal of phenols. Furthermore, studies need to prove the phenolic compound adsorption of silver nanoparticles [70]. Other MPNs like cobalt, nickel, palladium, and titanium are also used to detect and catalyze phenolic pollutants from the environment.

5.3.5 Microgel – nanoparticles based remediation

Investigating the microgel and MPN composites synthesized by polymerization technique to reduce the different aromatic phenolic pollutants was reported previously. Nanoparticles like Cobalt, Nickle, and Copper polymerized with cationic microgel, for example, p(3-acryamidopropyl)-trimethylammonium chloride made as composites to exhibit catalytic activity to eliminate 2-nitrophenol, and 4-nitrophenol. Similarly, dyes can also be degraded by this method [71]. Chlorophenols and phenols are eliminated by the oxidative degradation method using palladium nanoparticles. The hybrids of iron oxide nanoparticles and palladium nanoparticles showed an excellent catalytic activity. To evidence this, a study reported by performing this method thereby reduced and mineralized phenolic pollutants very efficiently and quickly [72]. The photocatalytic degradation of phenol carried out by gold–palladium nanoparticles catalyzed by TiO_2 which was synthesized by the sol-immobilization method under Taylor flow regime operation demonstrated the comparison study between Au–Pd and with TiO_2. Under visible light, 1% Pd/TiO_2Au degraded phenol quicker and efficiently than Au–Pd/TiO_2, 1% Au/TiO_2 and 0.5% Au/TiO_2 [73]. Nitro-phenolic compounds like ortho-meta-para-nitro phenol and amino acids were catalyzed by silver, nickel, and cobalt nanoparticles prepared by the impregnation method which is separated by γ-Al_2O_3. The catalytic activity of silver is higher than nickel and cobalt nanoparticles [74]. Maximum removal of toxic phenol mediated by mixtures of 10 nm & 70 nm and 40 nm & 70 nm diparticle mixtures of silver nanoparticles at 180 ppm showed complete phenol removal on all the membranes by the adsorption and nanofiltration process. The triparticle and diparticle studies reveal that the particle mixtures result in more phenol removal than the individual particles [75].

5.4 Conclusions

Much research has been conducted to date to enhance the quality of water, soil, and air, which is directly related to human health and safety as well as to the environment. Pollutants can be effectively removed using nanomaterials with specific physical and chemical characteristics. MPNs are preferred for removing heavy metals and organic contaminants because they have demonstrated good outcomes in a variety of applications. This chapter looked into the recent trend of employing MPNs to detect and determine the phenolic and heavy metal pollutants. Various MPNs like gold, silver, platinum, titanium, zinc, copper, cobalt, nickel, and palladium used to detect and eliminate the phenolic pollutants and heavy metals (Hg, Mn, Mg, Cr, Zn, Cd^{2-},Cu^{2-}, Pb, Ni, Co) from the environment by photochemical process, adsorption, oxidation, metal framework, electrochemical, phytocatalytic, and photocatalytic process. These MNPs are widely used as a good catalyst and also it has oxidizing and substantial adsorption property. MPNs are broadly used to detect phenolic and heavy metals due to their sensitivity and selectivity against them. Similarly, detection of this kind of pollutants is mostly carried out by colorimetric detection using its absorbance within a short period of time and this can be one of the ultra-rapid response methods to detect heavy metal pollutants. Gold and silver nanoparticles are widely used in the remediation of phenolic and heavy metal pollutants. Furthermore, studies should be focused on other MPN which is going to be cost-effective and fills the research gap.

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6 Nanobiocatalysts and photocatalyst in dye degradation

Abstract: In the modern era, the world today is in a mission for a new method of environmental bioremediation in faltering the damage, especially in polluted water. Recently, the global direction is regulated toward an alteration from the usual chemical-based methods to a supplementary ecofriendly green alternative. In this perspective, biocatalysts are appreciated as an economical and clean substitute which was meant to catalyze degradation of unmanageable chemicals in a rapid, green and ecologically stable manner. Among the various sources of water pollution, the textile manufacturing industries were thought to be a major dispute due to release of effluents in natural water bodies such as rivers. Other industries like paper, pulp and tannery pharmaceutical industries were also responsible in contaminating the water bodies. Photocatalysis was considered as an auspicious method for the removal of dyes from the natural bodies, specifically those with hard organic compounds; using enzymes. The present chapter briefly emphasizes on the effective methods used for degradation of dye effluents; their importance of photocatalytic and biocatalytic solution to the current environmental difficulties and future opportunities are discussed.

Keywords: biodegradation; nanomaterial; oxidoreductases; photocatalysis; synthetic dye; toxicity.

6.1 Introduction

Water is the most important natural resource and also part as one of the basic needs of all living organisms. Among 75% of surface water in the earth only 5% of fresh water can be utilized by humans as well as all living things [1]. Application of synthetic dyes is unavoidable in the modern era. Water pollution is the major problem and threatening to the living community due to the discharging of untreated effluents from industries like textile, leather, paper, paint, ink, food, photographic, pharmaceutical, cosmetics

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and pulp industry which releases organic and inorganic toxic pollutants that mix up in the water bodies of living community leading to serious effects [2, 3]. These dyes found to be highly useful but on the other hand, it creates negative impacts when its toxic effluents accumulate in water resources. It was reported that about 10% of the dyes from the industrial effluent could persist in the released wastewater [4]. The WHO reports that around 844 million people lack the access of pure drinking water worldwide [5]. Improper management of polluted water leads to various diseases including cholera, typhoid, hepatitis, giardia, Alzheimer's and COVID-19 [6]. Hence regulation of contaminated water by wastewater treatment and recirculation are the key research focus in the recent era [7–9]. Dyes have different structural forms such as acidic, basic, azo, diazo, reactive, disperse, anthraquinone based and metal-complex dyes. Textile industries play a vital role in discharging toxic dye effluents. Unless an appropriate handling, the effluents will create lots of toxicological impacts in the environment [10]. The toxicity of dyes is interrelated to their complex arrangements with numerous functional groups including, $-NHR$, $-NH_2$, $-COOH$, $-OH$, $-NO$, $-NO_2$ and, the occurrence of phenolic rings as well [11]. The presence of these compounds is the reason for coloration of water, that prevents the diffusion of sunlight, leads to disturbance in the ecosystem. Due to the xenobiotic nature of these dyes, they can easily resist to the conventional degradation process. Hence there are several strategies available for the removal of dyes from water [12] such as UV-source, flocculation, electro coagulation and activated carbon sorption were found to be very expensive also with low degradation rate. Apart from that lots of toxic chemicals and substances were used during the process [13]. On the other hand, semiconductor nanoparticles are considered to be the smart way to degrade the dye effluents as they are efficient and cost-effective compared to conventional methods.

Abundant techniques have been developed for eliminating a synthetic dye from aqueous effluents to condense their effects on the environment such as adsorption, Fenton-like reactions, activated sludge, membranes, reductive degradations using zero-valent iron and photo-catalysis. Most of the methods exhibited better removal efficiency yet faces several disadvantages since they can only trap impurities but not destroy them [14]. The dye effluents which are released into the environmental water bodies shows increased color, pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), increased metal and salt contaminants. On the other hand, synthetic dyes retain complex aromatic structures which are hardly biodegradable and hence finds difficult to degrade [15].

In the recent era nanoparticles play a vital role in interdisciplinary research in all aspects in discovering an innovative platform in biological sciences, specifically as degrading agents of various hazardous dyes that contaminate the environment [16–18]. Nanoparticles differ in terms of chemical, electrical and physical properties. Universal current research was focused on synthesizing nanoparticles in fabricating catalyst and their diverse application [19]. In general nanoparticles such as zero valent iron (ZVI) was an important and essential particle to degrade the organic dye rapidly [20–22] when compared to the microbial degradation and showed a higher degradation rate. Nanobiocatalysts such as titanium, zeolite etc. have been reported to possess the capability to enhance the rate of degradation and recycling. Specifically, for the degradation of azo dye compounds, titanium dioxide nanotubes exhibited a significant result and have been used as a solid substrate. Biomass conversion to biofuels could be done by immobilizing the enzymes in nanoparticles, hence developing a nanocatalysts. Nanocatalysts would enhance fast and explicit responses easily on recycling procedure [23], such as metal oxide nanocatalysts which could be further renowned into alkaline earth metal oxides (CaO, MgO), nano sulphated titanium oxide, iron cadmium and metal oxide nanocatalyst. Nanocatalytic properties are influenced by factors such as porous nature, modifiable surface area, composition, shape and size [24].

Photocatalysis is the clean and safe method in the current period of dye degradation or bleaching technique [25]. It is necessary to have a strict control on temperature and pH during biological treatment process. Degrading the synthetic drug is an elaborate process and disposes a large amount of sludge. Moreover, disposal of dyes from industries into water bodies hinders sunlight penetration into water and reduces the photosynthetic action. Predominantly, photocatalyst is a promising method in degrading the synthetic dyes effectively by coupling with light energy to excite photo persuaded electrons. During dye degradation process complex form of dye molecules get oxidized and convert into smaller molecules such as CO_2, H_2O and other byproducts. For the past few decades researchers focused on photocatalytic degradation of dyes due to its nontoxic and cost effective. Photocatalytic process mainly involves electron transfer from the valance band to the band conduction of the particular semiconductor surface on illumination with a suitable wavelength of light. Here in this chapter, we focused on photocatalytic dye degradation and its mechanism of action with special emphasis on recent progresses, nanomaterials and its applications.

6.2 Nanoparticles in dye degradation

Degradation of dyes and treatment of wastewater using nanomaterials or the enzymes of microorganism (biocatalyst) are promising and so effective in the few past decades [26–28]. Therefore, utilization of biocatalyst or photocatalyst in removal of dyes had pursued a great attention. The size of nanoparticles and nanomaterials was <100 nm and possess high surface area ratio. Moreover, it has an excellent photocatalyst properties both visible and UV radiation due to the semiconducting properties of nanoparticles. Owing to its outstanding physical, chemical and mechanical properties development of nanotechnology empowered a great application on the usage of advanced materials such as nanotubes and carbon-based materials was highly competent on the existing graphene two-dimensional carbon sheet with 59 atoms organized in a hexagonal linkage [29, 30]. Zinc oxide (ZnO) nanoparticle is one among the supreme resourceful nanomaterial for dye degradation due to its semi conductive property, wide band gap which helps them to be active in the presence of UV light. Globally, ZnO nanoparticle seeks attention by the researchers for their elite optical and chemical behaviors [31]. It has the ability to mineralize the organic chemicals to carbon dioxide and mineral acids to produce hydrogen peroxide [32].

Dye degradation reaction in wastewater system is significantly persuaded by the visible or UV light. It is important to notice that the many semiconductors could powerfully correlate with the photons since their band gap exist in the similar range. Due to their large band gap the metals results in the absorption of UV light. Moreover, apart from the band gap, the possible absorbents should be that it produces easily; they also should be cost effective, photo stable and non-toxic [33, 34]. Utilization of metallic oxide on dye degradation may enhance the capacity of adsorption at the catalytic surface, regulating the photosensitive band gap, ability to absorb light of the photocatalyst and inhibits the combination of charged molecule coupled with charge transfer. Similarly, same as ZnO, titanium dioxide (TiO_2) was also characterized by their chemical and physical stability. These nanoparticles exhibited good environmental remediation and an active photoelectrode which was widely used in variety of environment and energy devices subsequently from the discovery of Fujishima et al. [35]. In the presence of photocatalyst, dyes can be degraded upon irradiation with visible light also due to their absorption property [36]. The mechanism of action behind photocatalysis of titanium oxide comprises of the metal oxides with light energy wherein they generate electron hole pairs in which the band gap was greater than UV light. They get excited under UV light due to their band gap and the electrons from the valence band hop to the conduction band by leaving back the positive holes (h^+) (Figure 6.1). These photos promoted electrons and h^+ diffuses to the surface of TiO_2 which can be misused for the progression of numerous redox processes. Reaction of holes with water, generate the utmost critical and strong oxidizing free radicals, $^{\bullet}OH$. Therefore, when an organic compounds captivated on the surface of the photocatalyst is oxidized by $^{\bullet}OH$. Theses unstable electrons react with oxygen molecule to produce superoxide ion $O_2^{-\bullet}$ thereby attacking an organic compound as well. $O_2^{-\bullet}$ react with the dyes to produce CO_2 and H_2O finally [37].

However, in spite of an expanded absorption wavelength range, many of these procedures also undergo a series of problem from a greater recombination rate of generated electron–hole pairs by an augmented number of defect sites inside the TiO_2. With this note a novel technique plasmonic photocatalysis was investigated recently, based on the grouping of noble metal nanoparticles for the improvement of visible light-active photocatalysation [38, 39]. Metals such as gold (Au) nanoparticle have the ability to absorb visible light strongly by localized surface plasmon resonance (LSPR). It is able to persuade highly energetic electrons through light absorption that could be injected into an adjacent TiO_2 matrix enhancing the photocatalytic activity in visible light significantly [40, 41].

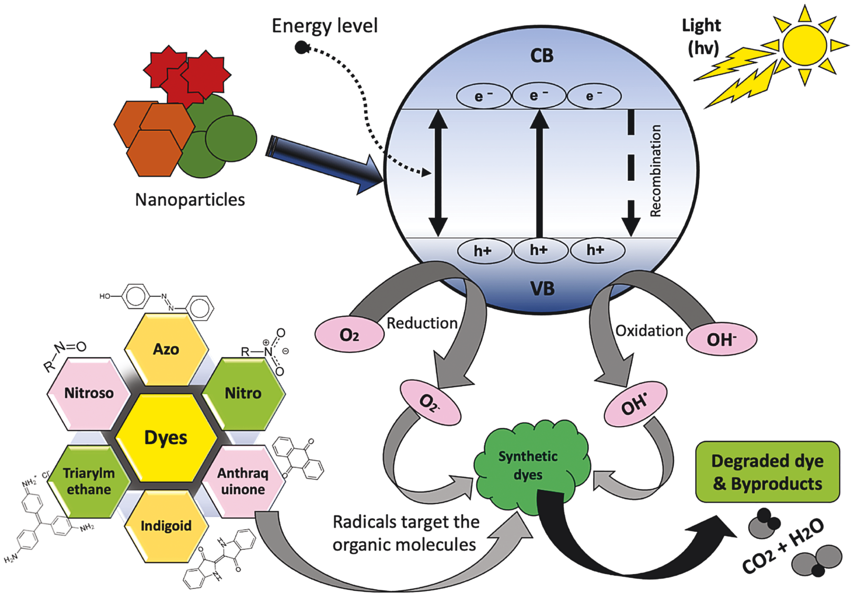

Figure 6.1: General mechanism of photocatalytic degradation of different dyes.

Fe_2O_3 nanoparticle was evaluated with various green synthesis methods for degrading the reactive dye by irradiation of UV light due to its greater ability in oxidation of organic dyes. This efficiency could be based on the presence of two stable oxidation state of iron that stimulates the competence of iron nanoparticle as photocatalyst [42]. Research reports of Bibi et al. [43] reported that textile dye was successfully degraded due to the photocatalytic potential of the synthesized Fe_2O_3 nanoparticle. The photocatalytic activity of iron nanoparticles is due to the Fenton's reaction. Usually, in an acidic environment Fentons reaction exhibit an efficient degradation process generating hydroxyl radicals [44], which contains hydrogen peroxide and Fe_2^+, Fe_3^+, Fe_2+/Fe_3+ or Cu_2+. FeO, Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite) are the agents used in Fenton and Fenton-like reactions [45–47]. The mechanism behind the action of UV light irradiation with Fe_2O_3 nanoparticle was, once it got irradiated by UV light, it generates an e^- and hole (h^+) pair. Reduction of ferric cation to ferrous happens via reaction with the electrons produced from photoreactions. The electron may have excited from valance band to the conduction band, thereby separating the (h^+), which was the one accountable for the conversation of H_2O into $^\bullet OH$ radical leading to degradation of dye by oxidative method. Moreover, the electrons from the active compounds react with molecular oxygen and convert to superoxide ions, whereas the $^\bullet OH$ radical degrades the organic species into harmless end product since it is a strong oxidizing agent [48]. Correspondingly, manganese oxide is the other metal which could remove the harmful contaminants, heavy metals and dyes in effluent and industrial wastewaters. Moreover, the adsorption ability of manganese oxide (MnOs) was based on their BET surface area and polymorphic structures. Modified manganese oxide like hydrous manganese oxide (HMO) was prepared by adding $MnSO_4.H_2O$ into NaClO solution which was proved to adsorb various heavy metals from industrial effluents. The mechanism behind adsorption involves metal ion adsorption on the external surface followed by diffusion of intra particles [49].

6.3 Hybrid and heterogeneous photocatalyst

Development of hybrid catalyst provides significant greater quantum profit than conventional photocatalysis system. Under visible light irradiation, surface plasmon resonance or graphene like carbon nitride as a polymeric photocatalyst have a great attraction towards degradation of environmental pollutants due to their stable visible-light-driven photocatalyst by means of suitable band energy, their nontoxic properties, chemical stability and easy availability [50]. Graphene like carbon nitride is one among such good catalytic source due to their exclusive physicochemical properties. Hybrid photocatalyst based on Ag/AgCl/AgBr.AgI, have enhanced stability and catalytic performance of single photocatalyst such as tremendous visible light absorption. This is because of their symbiotic effect by Ag or AgCl and the surface plasmon resonance activity of silver nanoparticles. In this same ways other particles such as TiO_2 nanotubes or Al_2O_3 presented an extraordinary degradation capacity against organic pollutants under visible light. The high photocatalytic activity showed by the combinational or hybrid catalyst was due to their attribution towards enhanced separation effectiveness by easy transfer of e^- and h^+ on heterojunction boundaries thereby improving the absorption of light via plasmon effect of silver nanoparticle. Similarly, Ag and AgBr also revealed a synergistic interaction between semiconductors and plasmonic metals leading to a great photocatalytic activity against pentachlorophenol degradation [51]. The mechanism behind degradation process was that electrons change from CB with high Fermi level transfer to the CB of second material with low Fermi level, whereas positive holes from VB move from low fermi composed material to high fermi composed material [40]. Moreover, heterogeneous junction flanked by g-C_3N_4 and BiOClBr was produced and examined for its prospective degradation of photooxidation, specifically rhodamine B, which exhibited an extreme degradation capacity at least irradiation of visible light. This heterogeneous pairing of by g-C_3N_4 and BiOClBr splits charge carriers from the intersections in effectively degrading rhodamine B [52].

Adsorption of dyes is an easy and effective technique in treating wastewater effluent that persists with a high amount of dye. Among many dye removal adsorbents such as SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3 and carbon was evidenced to act as a better catalyst. Yet the activated carbon is at high cost and low selectivity for either ionic or non-ionic dyes [37, 38] Upon considering all these factors many recent works implicates degradation and mineralization of industrial effluent with dye contaminants by heterogeneous photocatalyst. Refinement of water effluents containing dye was performed by heterogeneous photocatalyst. Heterogeneous photocatalyst includes oxidation of bio recalcitrant organic compounds that depends on generation of highly reactive species leading to degradation of recalcitrant molecules into biodegradable compounds. They either undergo, homogenous or heterogeneous photocatalytic oxidation resulting in the production of hydroxyl radical species, H_2O, O_3, Fenton reagent, NaOCl, and many others either alone or in combination with light [53] that oxidizes the dyes or pollutants. Nano degradation of pollutants and dye by advance oxidation process is a promising and effective method in degrading highly toxic by producing reactive species such as hydroxyl radicals. In heterogenic catalysis degradation, process involves synthesis of catalyst by absorbing photons of ultra-band gap energy in visible light by the help of VB and CB of semiconductors leading to the production of electrons and positive holes instantaneously. Generation of electrons and positive hole pair associate to release heat and stimulate the reduction and oxidation process by adsorption on the photocatalyst. In the process of dye degradation, the synthesized electrons combine with the adsorbed oxygen to produce superoxide radical ($O_2^{-}\cdot$). On the other hand, positive holes of VB react with water molecule that was absorbed on photocatalytic surface leading to the production of hydroxyl free radical ($OH\cdot$) [54]. Among various photocatalytic materials silver and TiO_2 are one of the specific interest due to its effective photocatalysis process because of its better absorption of visible light with the band gap lower than 3 eV.

6.4 Photocatalysts and nano photocatalyst in dye degradation

The photocatalytic management completely transforms the pollutants in to harmless by-products such as carbon dioxide and water. When compared to catalytic dye degradation, photocatalyst is a cost effective and eco-friendly process. Prominently the time duration taken for photocatalytic dye degradation was very short. During photocatalysis photons involved in the reaction enables the catalysis at the time of reaction Bahal et al. [55]. Affinity of nanomaterials towards electron is the key factor for photocatalytic degradation of dyes in wastewater due to the ionic nature or presence of unpaired electron acts as a chelating agent which alleviate the nanoparticles produced [56, 57]. Additionally, metal oxide nanomaterials integrated with gallic acid also exhibited good photocatalytic degradation of dyes [58]. The oxidation process during photocatalytic reaction involves in splitting the pollutants into their equivalent simpler form. Oxygen act as an electron acceptor in the existence of protons finally electrons are generated and degrade the complex form of dye into simple [59, 60].

The contaminants from the environment were first transferred to the surface of the photocatalyst and the dyes to be degraded are absorbed onto the surface where oxidation and reduction reaction happens. The photo generated electrons in the conduction band (CB) and holes in valence band (VB) enforce the reduction process producing reactive oxygen species such as hydroxyl and superoxide was produced (Figure 6.2). These radicals react with the pollutant/dyes turning out to H_2O and CO_2 [60, 61]. Numerous semiconductors like titanium oxide (TiO_2) and others are disposed to light radiation (UV and visible) and then being utilized as photocatalyst in industrial effluent dye degradation process. Correspondingly, green synthesized nanoparticles widely use organic dye degradation based on photocatalytic mechanism [62]. Elsewhere, metal-incorporated nanomaterials were familiarly used for the degradation of azo dyes since they have high efficacy for the photocatalytic degradation of organic dyes. Bioactive compounds like polyphenolics (gallic acid) incorporated metal oxide had also been reported to degrade reactive azo dyes [58]. Biopolymer like chitosan-acrylic imbedded with nano-TiO_2 has the efficacy of photocatalytic degradation of malachite green upto 90% under neutral pH [55]. In the same way, nano-iron oxide (Fe_3O_4) incorporated with chitosan has been reported to be used for dye contaminated wastewater treatment [63].

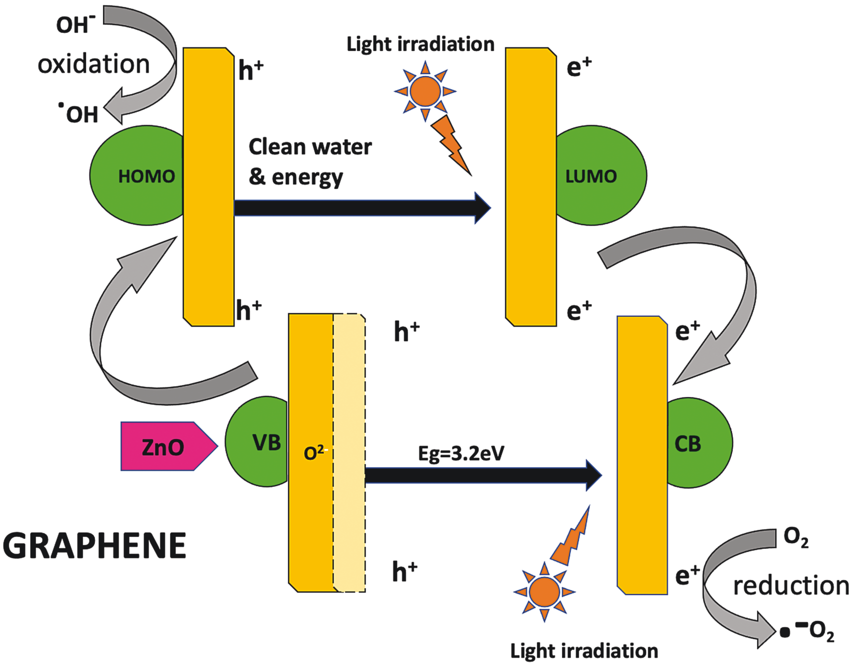

Figure 6.2: Mechanism behind photo catalysis reaction under light irradiation.

From the earlier reports it was evident that thiazine dye was the most investigated group of colorants including methylene blue and xanthene which are the second most studied group of dyes that controls rhodamine B as well [64]. Methylene blue could be removed significantly by ZnS and chitosan incorporated quantum dots acting as semiconductor that improves the dye removal process via nano-photocatalytic reaction [65]. Almost 90% of the photodegradation method of methylene blue was success using chitosan/ZnS based nanomaterials. Other nanomaterial like Ag–TiO_2 incorporated with resin biopolymer also increased the photocatalytic degradation activity against rhodamine B [66]. Similarly, chitosan/ZnO/AgCl nanocomposite otherwise called biopolymer-metal oxide nanocomposite used to degrade ethylene blue [67]. Green synthesized chitosan-coated $CuSO_4$ nanocomposite from *Psidium guajava* extract potentially showed effective degradation rate of Congo red and methylene blue [68]. In addition, duel metal oxide biopolymeric nanocomposites synthesized cellulose and reacted with ZnO/CuO can successfully degrade rose Bengal dye [69].

6.5 Nanocatalyst in industrial effluents

To degrade dyes, present in industrial effluent a diversity of photocatalysts such as metals, metal oxides, semiconductors, carbon-based nanostructures, quantum dots, metal–organic frameworks, magnetic cored dendrimer, and other materials have been comprehensively studied. Numerous nanocatalysts are actively engaged in treating the industrial effluents including, photocatalysts, electro catalysts and Fenton based catalysts to develop chemical oxidation of organic pollutants. Free radicals/reactive species possess a redox potential and plays a vital role in photocatalysation. Semiconductor photocatalysts can directly degrade the dyes by instant generation of reactive species based on their band position. Direct degradation process and sensitization-mediated degradation process are the two major methods of photocatalytic degradation. The direct photodegradation method implicates the excitation of semiconductor photocatalysts in light irradiation which leads to a shift of photo excited electrons by means of dissolved oxygen in the solution. This might be due to the conduction band of photocatalyst which is more negative when compared to the reduction potential E ($O_2/{\cdot}O_2^-$), thus forming $\cdot O_2^-$ anion and H_2O_2. The formation of H_2O_2 further converts into ^-OH radical. In the intervening time, the absorbed water molecule during excitation oxidizes to produce hydroxyl radical since the VB is more positive thereby producing highly reactive species of $\cdot O^{2-}$ and $\cdot OH$ that ultimately leads to the degradation of dye molecules with the blended support of photo excited electrons.

To further confirm the contribution of $\cdot O_2^-$ anion and H_2O_2 in photodegradation of dyes many recent research had been focused towards the action of free radical during dye degradation methods. Among which, the result of Cao et al. and Che et al. is a noticeable one [50, 51]. The results of Pu et al. revealed a photodegradation of methyl orange with TBA as the $\cdot OH$ scavenger. At the same time results of Cao et al. suggested that the combination of $AgSiO/Ag_2CO_3$ photocatalysts elicited the photodegradation of dye effectively into $\cdot O_2^-$ and photo excited holes. According to his results the rate of photodegradation declined marginally which recommends that the main active species would not be hydroxyl radical species. Degree of photodegradation in the presence of $AgNO_3$ is due to the reduction in the production of $\cdot O_2^-$ reactive species from photo excited electrons. Sensitization-mediated degradation process is another way of degradation process. If there was a limited photon energy to excite the catalytic reaction to generate reactive free radicals, degradation of dyes could be possible by the process of photosensitization. In the visible light the dyes could be able to excite to its excited state producing electrons at LUMO level which is more negative than the CB of photocatalyst. To initiate the process of degradation the excited electrons transfer towards the photocatalyst through the production of reactive oxygen species [70].

Moreover the detailed study of Atta et al. [71], on quaternized diethylethanolamine cation in combination with 2-acrylamido-2-methylpropane sulfonate-co-vinylpyrrolidone (QAMPSA/VP) with silver and magnetic nanoparticle complex has proved to degrade methylene blue dye by reduction reaction. Furthermore, capping agent was also bound to it to defend the produced NPs from oxidation or thermal degradation. Application of ionic liquids and their polymers are a promising source because of its non-toxicity, thermal stability and melting temperature that are extensively used to formulate inorganic and metal oxide nanoparticles (NPs). Among various nanomaterials used magnetite and silver nanoparticles was the best to oxidize and degrade the industrial contaminants since they possess catalytic activity. Additionally, magnetic polymer composites existed as an adsorbent that aids in decontaminating the organic and inorganic impurities due to elevated biocompatibility, large surface area, good dispersibility in fluids, extraordinary adsorption and catalytic activity, and their easy departure by relating a peripheral electric or magnetic field [72]. Due to the presence of sulfonate group in 2-acrylamido-2-methylpropane sulfonate-co-vinylpyrrolid it is predicted that Fe_3O_4 and Ag nanoparticle possess a negative surface charges on their surface which would enable the electrostatic attraction of methylene blue there by enhancing the catalytic potential to improve the activity of AgNPs or magnetite in degradation process.

6.6 Biocatalyst and nanobiocatalyst as dye degrading agent

Modern biotechnology has perceived a budding attentiveness towards the development of green and sustainable biodegradation process using biocatalyzation. Enzyme based biocatalyst was a promising method that promote ecofriendly green processes due little chemical consumption and less or no toxic by-products. The drawback of using enzyme biocatalyst was due its high operative cost and low stability. Immobilization of enzyme on coupling with supporting materials had increased their stability against physical or chemical attack; in addition it can also be recycled in a continuous industrial procedure [73]. Immobilization of enzyme and nanocarriers increase the biocatalyst biocycle thereby reducing the cost. Up to date, nanomaterials have been used for the expansion of nanobiocatalyst carrier such as nanofiber, nanotubes, nanoparticles, nanocomposites and nanosheets. Nanocarriers with exclusive characteristics are adding functional groups at the surface to immobilize several enzymes thereby reacting to exterior stimuli, surface area could be increased enabling diffusion of substrate, improving the mechanical and thermal stability of nanocarriers [74]. Coupling of nanomaterials and enzymes employs physical adsorption through various methods such as physical adsorption via electrostatic interactions, hydrophobic interactions, hydrogen bonding or van der Waals forces, covalent binding, cross-linking of enzymes or physical entrapment or encapsulation.

As previously mentioned, oxidoreductases enzymes such as lignin peroxidase (1,2-bis(3,4-dimethoxyphenyl) propane-1,3-diolhydrogen peroxide oxidoreductase) (LiPs), Manganese peroxidase (Mn(II)): hydrogen-peroxide oxidoreductase (MnPs), horse radish peroxidase (HRPs), laccases and tyrosinases are the frequently engaged enzymes in green biocatalyst. These oxidoreductases demonstrated a massive possibility in the biodegradation or mineralization of collection of toxic compounds such as phenols, bisphenols, and derivatives natural or synthetic dyes [75]. Lignin peroxidase undergoes the process of oxidative cleavage or depolymerization of lignin in the occurance of $H_2O_{2.}$ At the beginning LiP was discovered from ligninolytic fungi called, *Phanerochaete chrysosporium*, which was now identified in various microorganisms. Since it possess less specificity and redox potential, lips coupled with carrier molecules (like Ca-alginate beads, Na alginate, lignocellulosic residue and enzyme immobilized with nanotubes) hold a discrete potential to oxidize a widespread of aromatic phenolics and non-phenolic compounds or organic compounds like xenobiotic. The carbon nanotube associated – LiPs displayed an augmented explicit activity. Further, it also proved to be a best degrading agent of the tested dye, Remazol Brilliant blue R (RBBR) with a boundless catalytic efficiency and stability [76].

Laccase, an oxidoreductase enzyme which was secreted by some white rot fungi which has received considerable attention for the reason that it only requires oxygen as a co-substrate and catalyze the oxidation process of phenolic and non-phenolic compounds [77]. During synthetic dye degradation, it helps in catalyzing elimination of hydrogen atom from the hydroxyl group by electron oxidation method, generating non-toxic products [78]. In addition, it is grouped into phenol oxidases since it catalyzes one electron oxidation of the substrate accompanied with the reduction of oxygen in water. It is a monomeric, dimeric or tetrameric glycoproteins positioned at the catalytic site. It occupies two separate metal active sites, the T1 single site ligand binding with two histidines and one cysteine and T2 trinuclear active site cluster are eight histidines [79]. The T1 active site is close to the exterior surface wherever organic substrates (mainly phenols or arylamines) are oxidized discharging one electron to the T1 copper ion. Laccases is recognized as a beneficial biocatalyst in the modern biotechnological applications for their nonspecific oxidative capacity that adds benefit to pulp bleaching in paper industry, textile dye decolourization and bioremediation of environmental pollutants [80].

Laccase has the potential to oxidize various organic compounds like diphenolic compounds or their by-products such as hydroxy-, carboxy-, methoxy-, amino- or sulpho groups by radical scavenging ability. Phenols are considered to be the primary substrate since they have less redox ability allowing them to generate electrons via Cu T1. Apart from fungi, bacteria and plants also possess laccases which has a low redox potential [81]. The reaction starts with deprotonation of hydroxyl groups resulting in the construction of unstable phenoxy radical which leads to the formation of quinone. This associates the development of oxidation without the combination of forming byproducts wherein as the oxidative consequence oxidative decarboxylation of diverse products are reduced. Among various synthetic and organic dye degradation process, degradation of azo dye using laccases are well studied. They appropriately fit into the group of aromatic compounds comprising of one or more azo bonds (–N=N–) in it. Nevertheless, these bonds could be replaced with benzene or naphthalene consisting of various functional groups including –Cl, $-CH_3$, $-NO_2$, $-NH_2$, –OH and –CO. Degradation process of azo dye continues symmetrically or asymmetrically by an extreme non-specific redox mechanism resulting in phenolic products.

The first step in dye degradation, was the formation of electron deficient reaction center results in high reactive intermediates leading to neutrophilic attack by $-SO_3$, –OH or halogen nucleophiles forming asymmetric cleavage of azo bond as a result. The degradation process of azo dye using laccases results in the formation amine or toxic byproduct is a disadvantage, yet research of Du et al. [82] concluded that these products in water solution by *Aeromonas* sp. strain DH-6 have lesser phytotoxicity when examined on Chinese cabbage. On the other hand, bis azo dye degradation undergo in a complicated process wherein the cleavage takes places asymmetrically requiring electron for reduction process. The enzyme laccases have the ability to transfer electron to azo dye since it is rich in four histidine copper binding domain in the catalytic site. On the other hand, biodegradation of Congo red degradation complete the byproduct mechanism yet continue forming other nontoxic degradation products in an ecofriendly manner.

6.7 Green synthesis of biopolymer nanobiocatalyst

Green synthesis of nanoparticle is very productive, ecofriendly and cost effective process. Natural biopolymers play a vital role in multiple applications in the recent era. Biopolymers are a collection of monomers and are carbon neutral for the climate. It enables the nanomaterial synthesis since the morphology of biomass is usually designed at the nano sized material. These polymeric nanomaterials which are solid colloidal particles ranging from the size of 10 nm–1 µm. These polymerases could be identified in many organisms including plants, animals and microorganisms. Polysaccharides derived from plants or microbial source are a rich source of chitosan, starch, chitin which are commonly used for the synthesis of nanoparticles that had proved to be a good source of dye degradation. Among which chitosan had been reported to remove dye from wastewater treatment [83, 84]. It also permits rapid and simple rescue of the photocatalyst that can be reprocessed with or without any regeneration [78]. Biopolymeric nanomaterials could be developed by attaching metals to it and by intramolecular hydrogen bonding these biopolymers form capsules. Natural biopolymers like starch have the ability to integrate with metal oxide and hence developing polymeric nanocomposites as complex (Figure 6.3). Among the biopolymer's chitosan has been used for dye and other organic compounds degradation (Table 6.1) [85].

Chitosan biopolymer has high surface area and during the photocatalyst process it reduces the other intermediates. Also it permits fast and uncomplicated retrieval of photocatalyst and reprocessed with or without any regeneration. Due to this property chitosan act as a strong support material of metallic nanoparticles. In the process of photocatalyst, photons are able to prompt catalysis reaction with oxygen that accepts electron which was generated by damaging the complex dyes. Whereas in case of materials exposed to visible light, degradation of dye in wastewater takes place with the polymeric nanomaterial photocatalytically. Recent research reports of Adnan et al. [78] showed that chitosan permits rapid and uncomplicated retrieval of the photocatalyst, which could be recycled with or without any regeneration. Owing to the unique nature of biopolymers it can be easily coupled with nanomaterials possessing various physiological properties that support dye degradation. In this order, silver [62], titanium oxide and zinc oxide also play an important role as nanomaterials with interdisciplinary applications. Chitosan and silver (Ag) are the frequently used combination of biopolymer-based nanomaterial dye treatments due to its extensive range of applications [128]. Biopolymers can be combined with nanomaterials and the incorporated solid colloidal particles of biopolymer are within the size range of 10 nm–1 μm [129].

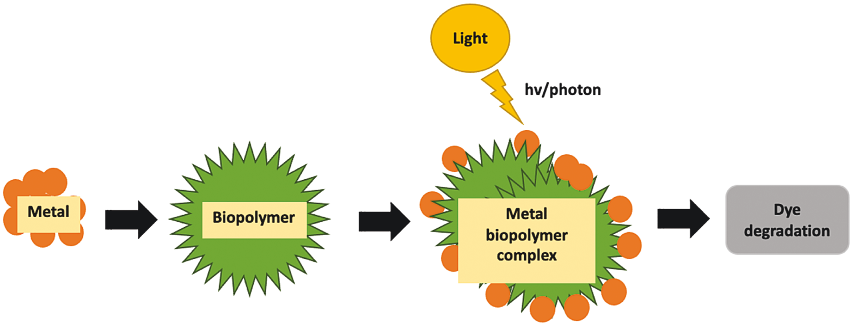

Figure 6.3: Metal-incorporated bio polymeric nanoparticles for dye degradation.

Table 6.1: Biopolymeric and green synthesized nanomaterial used for the degradation of dyes.

Sl. No.	Type of Nano-material/Catalyst	Biopolymer	Degradation of dyes	Refs.
1	Palladium (Pd)	Chitosan c-nanotube supported	Congo red, methylene blue, methyl orange and methyl red	[86]
2	Chitosan/Fe	Chitosan	Basic dye	[87]
3	Lanthanum (La)	Chitosan	Methylene blue	[88]
4	Cupper (Cu)	Chitosan	Congo red	[89]
5	Silver (Ag)	Chitosan	Ponceau BS dye	[90]
6	Cupper (Cu)	Chitosan-coated cellulosic microfibres	Methyl orange and Congo red	[91]
7	Silver (Ag)	κ-Carrageenan gum	Methylene blue and rhodamine B	[92]
8	Gold (Au)	Alginate beads	Azo dye acidic orange 7 and reactive orange 5	[93]
9	Gold (Au)	Bacterial cellulosic fibre	Azo dye	[94, 95]
10	Palladium (Pd)	Carboxymethyl cellulose	Azo dye	[96]
11	ZnO	Quince seed mucilage	Methylene blue	[97]
12	ZnO	Chitosan in the form of hydrogel beads	Methylene blue	[67]
13	ZnO	Chitosan	Chromium complex dye, direct blue 78, acid black 26	[87]
14	Fe_3O_4	Chitosan	Hazardous dye X-3B	[78]
15	MnO_2	Cellulose	Indigo carmine dye	[98]
16	TiO_2	Chitosan–acrylic acid biopolymer	Malachite green	[99]
17	ZnO	Cellulose	Dye-containing wastewater remediation	[99]
18	TiO_2	Chitosan	Acid orange 7, acid red 18, acid blue 113, reactive yellow 17, reactive black 5 and direct blue 78	[100]
19	ZnO	Cellulose acetate polymeric sheet	Congo red, methyl orange and methylene blue	[101]
20	TiO_2	Bacterial cellulose	Basic dye	[95]
21	TiO_2	Oak gall tannin	Direct yellow 86	[102]
22	ZnO	Conducting polyalanine polymer	Methylene blue and malachite green	[103]
23	ZnS	Chitosan	Methyl orange	[104]
	ZnS	Chitosan	Methylene blue	[65]
24	AgCl	Chitosan in the form of hydrogel beads	Methylene blue	[67]
25	Fe_3O_4	Immobilized laccase from Bacillus sp. MSK-01 conjugated with thiolated chitosan	Reactive blue 171 and acid blue 74	[105]
26	TiO_2	Chitosan–epichlorohydrin	Reactive red 120	[106]

Table 6.1: (continued)

Sl. No.	Type of Nano-material/Catalyst	Biopolymer	Degradation of dyes	Refs.
27	$CuSO_4$	Chitosan-coated nanocomposite from *Psidium guajava* aqueous leaf extract	Congo red and methylene blue	[68]
28	SiO_2	Chitosan/carbon nanotubes	Direct blue 71 and reactive blue 19	[87]
29	$AgNO_3$	Chitosan and guar gum	Binary dye	[107]
30	ZnS	Chitosan	Organic dye	[104]
31	TiO_2	Chitosan–epichlorohydrin	Reactive red 120	[106]
32	ZnO	Arabic gum-grafted polyacrylamide hydrogel	Malachite green	[108]
33	Ag/TiO_2	Carboxymethyl cellulase and gelatine	Organic dye	[109]
34	$AgNO_3$	Tangerine peel containing carbohydrate polymers	Methyl orange	[110]

Green synthesized nanoparticles photocatalytic activity against dye

Sl. No.	Type of Nano-material/Catalyst	Green plants and parts used	Name of degraded dye	Refs.
35	CuO-NPs	*Diospyros montana* leaf	Methylene blue	[111]
36	AgNPs	*Brassica oleracea* flower	Methylene blue	[112]
37	SeNPs	*Mucuna pruriens* seed	Methylene orange, Coomassie brilliant blue and bromophenol blue	[113]
38	AgNPs	*Andean mortino* berry	Methylene blue	[114]
39	AgNPs	*Allium cepa* (onion)	Methylene blue, MR, eosin yellowish, safranin, direct and reactive dye	[115]
40	AgNPs	*Plukenetia volubilis* oil	Methylene blue	[116]
41	AgNPs	*Capparis petiolaris* fruit	Methylene blue	[117]
42	$AgTiO_2$	Rambutan Peel	Methylene blue	[118]
43	Fe_3O_4NPs	Andean blackberry leaf	Methylene blue, Congo red and methylene orange	[119]
44	AgNPs	*Sacha inchi* Shell biomass	Methylene orange	[120]
45	AgNPs	*Morinda tinctoria* leaf	Methylene blue	[121]
46	FeO-NPs	*Amaranthus spinosus* leaf	Methylene orange and methylene blue	[122]
47	AgNPs	*Psidium guajava* leaf	Methylene orange and Coomassie brilliant blue G-250	[123]
48	FeO-NPs	*Wedelia urticifolia* leaf	Methylene blue	[124]
49	AgNPs	*Lantana camara* flower	Methylene blue	[125]
50	FeO-NPs	*Ruellia tuberose* leaf	Crystal violet	[126]
51	AgNPs	*Mussaenda glabrata* leaf	Rhodamine B, methylene orange and 4-nitrophenol	[127]

To summarize, discharge of toxic industrial dyes in the environment leads to various harm to other living organisms. It is said that few aromatic amines could be degraded by a category of microorganism slowly, yet sometime the process may not be completed as well. Hence removal of toxic metals, contaminants and dye is the need of the hour in the present era before reaching the residual water bodies. Modern biotechnology had now come up with many promising technologies in the removal of dye and other toxic from wastewater such as enzyme based degradation, nanomaterials, green technology etc. in the present chapter we had discussed on the techniques involving both photocatalysis accompanied by nanotechnology. Photocatalysis is one of the effective methods to effectively mineralize toxic organic compounds, hazardous inorganic materials by generating hydroxyl ions acting as an effective oxidizing agent. During photocatalysis reaction, photo-generated pairs (h^+ and e^-) due to oxidation and reduction reaction persuade the production of powerful reactive species such as hydroxyl and superoxide radicals with the moistness and atmospheric oxygen. From various studies it is proved that, the electrons from light, holes, hydroxyl radicals and superoxide reactive radicals encounter with the industrial pollutants via redox reaction. Hence the target pollutants/effluents are degraded into H_2O and CO_2, whereas the other part of the electron–hole which ultimately leads to recombining themselves or with supplementary photo generated electrons or holes inside or external, which was reduced to photocatalytic proficiency of the photocatalyst [130, 131]. The free radical species are highly active to oxidize and destroy the organic matter, gas or microbial organism. Usually during light irradiation at the suitable wavelength electrons excite from VB to CB yielding an e^-/h^+ pair. Yet, during reduction process in water and oxygen, oxygen was picked up from CB to produce superoxide anion and hydroxyl radical. These two radicals are highly reactive which helps in reacting with pollutants are industrial effluents to complete mineralization process. From the results of Lee et al. [132], it is concluded that, the prepared TiO_2 and Au nanoparticles immobilized on the surface of PDMS sponge pores were studied for photocatalytic potential under UV & visible irradiation by analyzing the decomposition rate of RB under specified condition. The results were proved to be effective against degrading the dyes and exhibited significant photocatalytic potential under UV & light irradiation. The results also claim that the PDMS-nanoparticle complex is stable to be recycled many times.

6.8 Conclusions

Textile industries utilize and release a massive amount of harmful dyes leading to release of pollutants in the water bodies if untreated. Apart from many conventional and traditional methods used to remove toxicants, implementation of nanoparticles could be used in dye degradation in a better way. The present chapter was discussed briefly on the photocatalytic and nanobiocatalytic activity of nanoparticles. Evaluation of nanoparticles such as gold, silver, iron and titanium has drawn considerably attention due to large surface area, large band gap, easy production, characterization including biomolecules and phytochemicals. Photocatalysis reaction enhances biodegradation of industrial dyes in wastewater. Green photocatalytic dye degradations method of removing water pollutants especially dyes were also proved to be better and less toxic than the other methods, also it shows uniform deposition of the particle. Nevertheless, nanoparticles are produced by means of natural sources such as plants. Accumulation of these nanoparticles and degradation or reusability is a big task. Moreover, the mechanism of the product interfering with the nano-carrier to be understood clearly for further development. Even though, nanobiocatalyst had showed noble results in dye degradation, investigation of multistep enzyme-based methods for large-scale operations, specifically those comprise immobilized enzyme should be researched more that would be an advantage in future. However, when compared with other methods, nanocatalyst exhibited better catalytic activity in degradation of toxic dyes. On the other hand, composition, preparation method of biocatalyst should be concentrated more in order to reduce the cost as well as the stability.

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7 Trends in microbial degradation and bioremediation of emerging contaminants

Abstract: Modernization and modern ways of living demands more improved products from pharmaceuticals, cosmetics, and food processing industries. Moreover, industries like pesticides, fertilizers, dyeing, paints, detergent etc., also needs improvised products as per demand. As the new product emerges, the pollutants from these industries also constitute new type of danger to the environment and serious health risks to the living organisms. These emerging contaminants (ECs) are from different category of sources such as personal care products (PCPs), pharmaceuticals (Phcs), endocrine disrupting chemicals (EDCs), etc. These ECs can easily escape from the conventional water treatment and eventually get discharged in to the surface water and thus enters in to the ground water, soil, sediments, and also into the oceans. When these contaminants emerge we also require progress in tremendous process for preventing these hazardous chemicals by effective removal and treatment. For the past 50 years, both developed and developing countries are working on this treatment process and found that Microbial degradation and bioremediation are very useful for effective treatment to prevent their emissions. This treatment can be designed for any sort of ECs since the microbial members are so versatile to redesign their metabolic pathways when subject to exposure. However, implementing bioremediation is not alone efficient to degrade ECs and hence, combination of bioremediation, nanotechnology and physical treatment method will also provide sustainable, potent and fast degradation process. In this Book Chapter, we discuss in detail about the ECs, sources of microbial degradation process and its usefulness in the bioremediation of these ECs.

Keywords: bioremediation; degradation; emerging contaminants; microbial; treatment.

7.1 Introduction

Nowadays, modern lifestyle of people is possible through successful story of chemical and pharmaceutical industrial sector in the last century. But they contribute huge environmental pollution causing disturbances in the ecological

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balance as well as it causes serious health effects to living organisms. During the last two decades, tremendous effort was made to prevent pollution caused by the industrial sector. Nowadays, effective proper treatment methods were available to prevent the emission of such pollutant into air, water and soil. However, products from pharmaceutical (Phc) and chemical industries like disinfectants, pesticides, Phc, personal care products (PCPs), herbicide, dyes, detergents, paints, preservatives chemicals, food additives etc., also contribute new source of pollution to environment and its cause health hazard for the product consumers. Exponential population growth and change in the climate will pose water pollution threat to the natural water resources. Even today, we are facing lot of struggle to get sufficient water to meet agricultural, personal care, industrial, recreational, laundry, and drinking purposes. Existence of some organic pollutants in the water sources especially medicines, disinfectants, PCPs, detergents, and their resultant chemical transformations are gaining more attention in the recent years [1]. Nowadays, Government must pay attention to these xenobiotic organic compounds degradation in urban waste management. Thus, there is a need to understand, in an integrated assessment, management, and hazardous effects of chemicals to both people and ecosystem. The current chapter, we gave outline about our current knowledge and awareness about emerging pollutants in the environment and its bioremediation aspects. Huge amount of literature are available about emerging contaminants (ECs), we are discussing the various sources of emerging contaminants, types of ECs and their hazardous nature, conventional, and recent bioremediation methods available for treating emerging contaminants [2–5].

The treatment of emerging contaminants is a major issue since their potential risks in causing ecosystem damage which directly affects the human health. Biodegradation is the process of converting large molecular weight compounds in to low molecular weight compounds. If these pollutants are organic, it will be converted to carbon dioxide and water which are simpler compounds. If the pollutants are inorganic, they are converted in to least toxic substances. Thus, biodegradation is one of the most useful and natural method to overcome these ECs. Moreover, this technology is cost effective and complete degradation of pollutants makes it as a promising technology which are investigated by many research group worldwide [6, 7].

The main challenge with the above mentioned ECs is their removal from the sources due to their ready solubility, reactivity, and mobility. Even large water bodies are affected by the release of treated effluents containing very low concentrations of ECs. The normal removal techniques involving physical and chemical methods are very costly and less efficient when compared to the biological removal methods. The use of biological treatment methods to remove different organic and inorganic wastes from water and soil are previously investigated in detail [8–12]. The biological methods mainly rely on microbial process of degradation that includes many additional approaches to accomplish efficient degradation such as use of biofilms, rhizosphere, consortia, nanoparticles, etc [2]. In addition, exploring combinatorial approach with engineering and scientific approaches like, nanotechnology, electrokinetic process, etc., are essential to enhance the removal and degradation of ECs [2, 3]. This review is intended to explain the failure of the conventional treatment which is a risk for the environment while discharging the treated sources and to explain the new technologies available for the possible removal of ECs using microorganisms.

7.2 Persistence of emerging contaminant in the environment

The majority of chemicals that ingested by the consumers are released in sewage, causing contamination in the environment. Chemicals having similar structures can be utilized to make products with comparable functions. However, for the same application and usage, chemical compounds with various structures and characteristics are commonly used. Phc substances are frequently categorized based on their intended use and biological activity.

Huge development of industrial sector for mass production of various improved products generates various types of emerging contaminants. Environmentally, ECs are poorly degraded, and they infiltrate soil and water resources, having negative environmental and health effects on all living creatures. PCPs, Phcs Phcs, pesticides, flame retardants, endocrine disrupting chemicals (EDCs), textile dye pollution and antibiotic resistance genes (ARGs) are only a few examples of ECs. These ECs can easily escape from the conventional water treatment and eventually get discharged in to the surface water and thus enters in to the ground water, soil, sediments, and also into the oceans. These ECs are frequently discovered in most of the water resources and sludge wastes from treatment plants of sewage. Antibiotics from contaminated water sources allow microorganisms to produce antibiotic resistance genes, which then spread throughout the ecosystem, posing a hazard to human health and safety aspects of water [13]. Most of the ECs are stable, nonreactive, and more challenging to destroy naturally in less duration. ECs are increasingly water soluble causing to accumulate in aquatic environment [14]. ECs are classified into two types (i) based on its structure; (ii) based on products.

Hormonal chemicals can also have an impact on human health due to bioaccumulation [15]. In recent years, dangers and effects of these ECs to the environment and human health have gained much attention [16]. Various physicochemical approaches on the removal of developing pollutants have been recently developed. To stimulate the oxidation of developing contaminants, researchers used hydrogen peroxide, ozone, TiO_2, peroxy monosulfate, activated carbon adsorption, UV light and the photoassisted Fenton method [17–19]. These approaches, however, are expensive and may result in secondary contamination. Furthermore, these procedures are ineffective at removing ECs. Most organic matter in sewage may be removed using the Conventional Activated Sludge (CAS) method. The typical activated sludge technique, on the other hand, has a low EC removal effectiveness and is closely associated with the production of a large amount of waste obtained from activated sludge process. The majority of ECs is not eliminated from treated wastewater and is eventually disposed into surface water, ground water, sediments, and oceans [20]. As a result, an effective bioremediation approach for eliminating ECs from the environment is required.

Mostly, ECs are rarely properly monitored in our environment, and because they are not handled and monitored, they pollute our drinking water [21]. There is a knowledge gap in monitoring and controlling environmental pollution caused by ECs. Despite the fact that large volumes of human Phcs are released into the environment, there are few severe requirements for environmental evaluation. Efficient treatment and degradation of ECs pollutant in wastewaters is necessary prior to their release into the environment. As a result, the existence of emerging pollutants at trace levels in wastewaters, as well as their physico–chemical behavior during drinking water production and wastewater treatment, is a major topic which is to be investigated further.

7.3 Conventional methods of treatment and its disadvantages

Generally, the wastewater treatment process aims to remove solids, soft sediments, organic, and inorganic materials and also aims to remove the pathogenic microbes. Many methods are used to remove the pollutants such as

i. Physical Methods
ii. Chemical Methods
iii. Biological Methods

Various studies, all over the world, have shown us there are more and more emerging contaminants which are often present in the discharged wastewater even after their treatment. The incomplete removal of many ECs often leads to a threat to the environment [22–24]. Even the advanced treatment of municipality and sewage treatment plants failed to remove these ECs. Complete removal of ECs is always a problem because of more and more varieties of compounds, diversity in each molecule, unique characters, and presence in very low concentration; all these makes it tough to remove EC’s by conventional methods [25–27]. The types of advanced process like oxidation process, Filtration, usage of activated charcoal and constructed wet lands etc., are also seems to be inefficient when treated independently [28–34]. The various disadvantages of these processes are

- ECs are found to be more resistant and so it is not reacting under physical and chemical methods of removal.
- Effluents from particular industries have many types of ECs and so all the compounds are not removed.
- Even though some compounds are removed, they are not completely removed; traces are present in the treated samples, which are enough to cause serious issues.

- For complete removal, if the effluents are retained in the treatment plants, for long time, the cost increases.
- ECs are readily dissolving in water so, if there is any leakage it easily gets in to the ground water.
- Even some advanced techniques require light energy and latest modeling of treatment tanks, which also increases the cost.
- Chemical processes can adversely convert the ECs in to more toxic, more resistant and more complex structure which worsens the effect.
- High energy demands and high emissions of CO_2 make these technologies unaffordable.
- Developing countries and poor countries, which needs a cost effective system founds these methods as not up to their reach.
- Thus advanced treatment method used for effluent and exhausts is expensive. The world needs a sustainable technology which is the future to remove these ECs.

7.4 Microbial sources for degradation of ECs

Persistence of xenobiotic compounds used in pharmaceuticals, plastics, and industrial effluents, etc., is mainly occurred due to poor degradation efficiency with conventional degradation processes. Efficient degradation of emerging contaminants is achieved by microbial cultures and their consortia in terms of development of synthetic microbial consortium, recombinant DNA technology and *in silico* strategies to keep away from conventional burning and land filling methods. Microorganisms can generally use up any of the chemical composition so which it can metabolize them for their cell growth and energy production as they can live as an autotrophs, auxotrophs, and heterotrophs. The designing of microbial degradation process of treating contaminants requires frequent analysis of microbial process. The process of degradation results in an absolute deprivation of contaminants is called mineralization. This biodegradation of pollutants can be done aerobically (in the presence of O_2) or anaerobically (in the absence of O_2). The microbial sources that is involved and considered for differential degradation in multiple environments varies as biofilms, extremophiles, microbial fuel cells, and bioreactors, genetically modified microbes (GMOs), microbial-nanomolecules, etc.

7.4.1 Microbial biofilms

A mass of bacterial cells that are surface intact within an extracellular polysaccharide matrix is known as biofilms. Matrix formation in biofilms possesses many noncellular materials based on their colonization at environment. The mechanism of microbial biofilm formation is mainly utilized in wastewater treatment as they are very active, resistance to harsh environment and they are close to natural biofilm systems with widespread microbial diversity [35]. Hence, exploring these biological processes will be lucrative, user-friendly and free of other contaminating microbes. In fact, biofilm mediated wastewater treatment strategies are adapted to buildup efficient biofilters in order to remove ECs [36]. Because ECs can easily get trapped by microbial communities or biofilms in many possible ways and thereby, convert into non-toxic substances or reduces the accessibility of the ECs in that environment. Biofilms can be widely and effectively grown on solid media as it renders large surface to expand their films which in turn, trap large quantity of ECs from the environment as represented in Figure 7.1. Owing to their exotic microbial degradation rate, biofilms are considered to develop as an advanced technology i.e., biofiltration for the wastewater treatment (Figure 7.2). They are also reported to be involved in biodegradation, bioaccumulation, biosorption, and

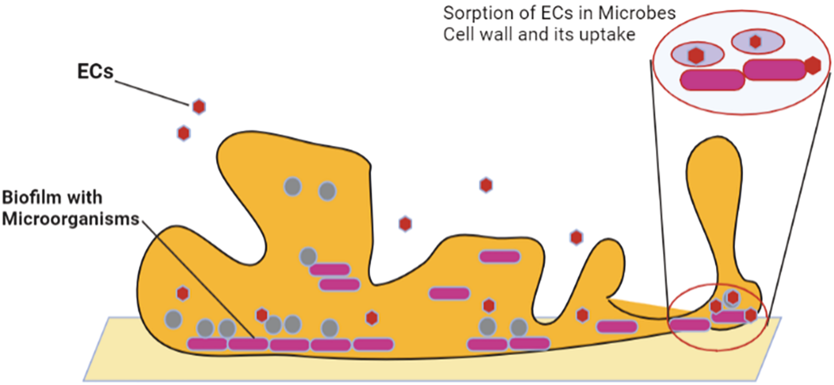

Figure 7.1: Course of interaction between ECs and biofilm.

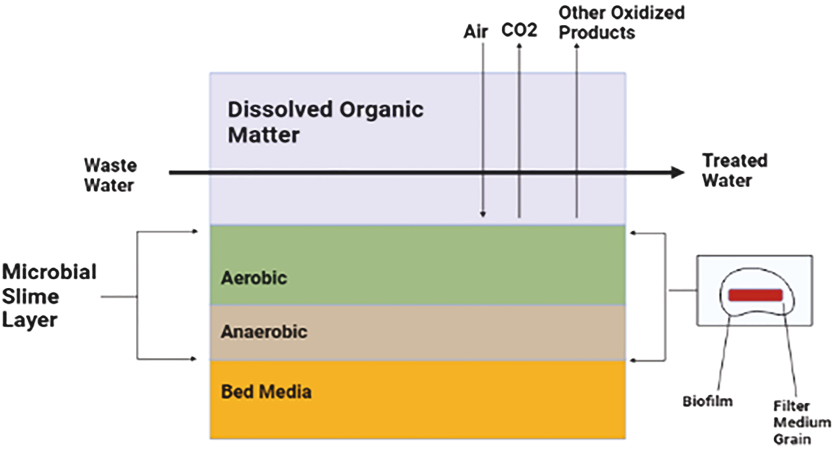

Figure 7.2: Role of microbial biofilms in pollutant removal.

biomineralization [37, 38]. However, the interactions between microbial biofilm and ECs are affected by different environment factors such as pH, temperature, mass of cells in a film, their nutrients, etc.

7.4.2 Microbial consortia

Natural biodegradation process is usually possible and stable by the combined effects of several microorganisms as microbial mixtures (Bacteria, fungi, and algae). Each organism acts upon the products of each conversion process to attain complete mineralization. The same concept of combining the communities of microorganisms called as microbial consortia can be used to construct a bioreactor for pollutant removal. When incorporated with these microbial consortia the process of biodegradation or bioremediation will be very efficient in removing ECs present in a particular effluent due to their exotic metabolic activities. Periphyton is one of the previously reported microbial consortia which comprises of bacteria, fungi, algae, diatoms, and protozoa. Another consortium comprising algal and bacterial members was found to be very effective against antiinflammatory drug – salicylates [39, 40].

7.4.3 Extremophiles

Very ancient microbial communities that live under extreme environment such as hot, ice, acid, and salty niches are known as extremophiles (mostly belongs to Archea group). They have specialized proteins that make them sustained in extreme environmental conditions. Understanding the uniqueness of these, extremophiles, it is demonstrated in many reports that extremophiles can be used for microbial degradation to remediate emerging contaminants where normal microbe cannot survive [41, 42]. Extremozymes of such bacterial groups do similar enzymatic functions as like the normal enzyme performance. In addition, they are potential enough to stimulate biochemical reaction that occurs within the cell at extreme environments. Hence, proteins from extremophiles are of bioremediation importance in industries for low cost waste management systems. However, genetic manipulation strategies have to be adapted to enhance or to develop a strain which remediate multiple sources of ECs. The role of extremophiles on the degradation of different pollutants is summarized in Table 7.1.

7.4.4 Microbes as energy source

Bacteria as catalysts to oxidize organic and inorganic matter (pollutant) and produce electricity are known as microbial fuel cells (MFCs). Bacterial cells utilize the contaminant to oxidize and yield electron and protons. Microbes decay the

Table 7.1: Extremophilic bacteria in degradation of ECs.

Extremophile	ECs	References
Thermus scotoductus and *Thermoanaerobacter* sp.	Enzymatic uranium and technetium	[41]
Anoxybacillus sp.	Polyaromatic hydrocarbons dyes, antibiotic residues, phosphates and heavy metals	[42]
Talaromyces emersonii, *Mucor* sp., *Rhizopus* sp., and *Thermomucorindicae seudaticae*	Water pollutants and decolorization of dyes	[43]
Arthrobacter psychrolactophilus	Organic compounds in wastewater	[44]
Colwellia and *Cycloclasticus*	Propane, ethane, and butane and BTEX	[45]
Halophiles	High salt sludge	[46]
Acidithiobacillus ferrooxidans	Mineral bioleaching	[47]
Stenotrophomonas chelatiphaga	TBT	[48]

contaminant i.e. organic matter on the anode and produced free H^+ ions and electrons. Such flow of electrons that is generated produces electricity. Wastewater treatment technology nowadays prefers single compartment, continuous flow, and membraneless MFCs [49].

7.4.5 Bioreactors

This process is a conventional method in which microbial aggregates are used to degrade the available pollutants to some extent. But when the process of adsorption is combined with the activated sludge, together they can overcome each other's weakness so that it will be advantageous for the removal of ECs [50, 51]. EC's are immobilized in a biomatrix and then, they are treated via biodegradation. Designing the bioreactor is a very convenient process according to the volume of the wastes and maximizes biodegradation so that risks during the treatment process and optimization can easily be screened and controllable. Many antibiotics, fluroquinones, EDCs, herbicides, and insecticides are efficiently removed by this process [52, 53]. The advantages of the bioreactor based treatment process are low cost, large volume of ECs removal in a feasible way. Microorganisms that cultivate in front of oxygen are considered for aerobic treatment processes. Tannery soak liquor is degraded by utilizing many species of halotolerant bacteria such as *Pseudomonas aeruginosa*, *B. flexus*, *Exiguobacterium homiense,* and *Staphylococcus aureus* [54]. However, anaerobic process provides medium to high organic impurities (Chemical Oxygen Demand (COD) > 1000 ppm) upon the treatment of wastewater. This treatment is carried out by anaerobic microorganisms along with anaerobic filters (up-flow and down-flow), and up-flow anaerobic sludge blanket reactors [55, 56].

7.4.6 Microbial immobilization with nanoparticles and nanobiomolecules

A process of using microorganisms or plants to synthesize nanoparticles from their precursors is known as green synthesis. To aid microbial assisted degradation of ECs, heavy metal based contaminants are utilized to synthesize nanoparticles using microorganism as metal chelating agents and thereby confer nanobioremediation. Certain contaminants are converted into either nontoxic or passivated to the sediments by the treatment of microorganisms and nanoparticles due to the high surface area properties. In addition, biogenic nanoparticles synthesized via microorganisms possess potential catalytic action on contaminants which are summarized in Table 7.2. As an alternative attempt, nanoparticles are presently considered for immobilization with microbes as a carrier. Long term stabilization of microorganisms that are involved in bioremediation essentially requires immobilized cell technology in a bioreactor or in an environment. Due to the flaws in the use of conventional materials (alginate and Polyvinyl alcohol), nanoparticles are currently used as immobilization carrier for enhanced cell adhesion upon bioremediation process [57].

7.4.7 Genetically modified microbes (GMOs)

Manipulating the gene that involves in pollutant degradation is engineered into microbes and hence, one can produce and release as GMOs. Hence, they are prospective

Table 7.2: The role of nanobiomolecules in pollutant removal.

S. No.	Nanoparticles	Microbial source	Pollutant treatment	References
1	Silver and gold nanoparticles	*Cylindrocladium floridanum*	4-nitrophenol	[58]
2	Silver nanoparticles Nitrogen-doped TiO_2 nanoparticles	*Phanerochaete chrysosporium*	Cd^{2+}, 2,4-DCP	[59] [60]
3	Fe_3O_4 nanoparticles	*Phanerochaete chrysosporium*	Phenols in wastewater	[61]
4	Magnetic nanoparticles immobilization	Fungi	Wastewater	[62]
5	Fe NPs immobilization	*Phanerochaete chrysosporium*	Pb(II)	[63]
6	α-Fe_2O_3 MNPs immobilization	*Bacillus badius* and *Bacillus ensimensis*	Atrazine	[64]
7	Carbon Nanotube immobilization	*Pleurotus ostreatus*	Remazol brilliant blue R	[65]

Table 7.3: The specific genes used in GMOs for the treatment of ECs.

GMOs	Pollutant treatment	Plasmids	References
Pseudomonas putida	Crude oil, camphor, octane, salicylate, and naphthalene	CAM and OCT, XYL, and NAH plasmid	[67]
Alcaligenes eutrophus AE104	Chromium	pEBZ141	[68]
Rhodopseudomonas palustris	Hg^{2+} removal	–	[69]
Mesorhizobium huakuii subsp. *rengei*	Phytochelatins and accumulate Cd^{2+}	PCS; PCSAt	[70]

in bioremediation under different environments with higher level of potential for chemical contaminants in a broad range. The summary of the reports that investigated in these approaches are tabulated (Table 7.3). By considering the issues with the release of GMOs into the environment, the strategies such as suicidal gene systems antisense technology are currently being followed and hence, horizontal gene transfer will be prevented [66].

7.5 Microbial process of degrading the emerging pollutants

7.5.1 Bioremediation of ECs

Biodegradation and bioremediation are mostly misconsidered as similar words as well as representing similar process too. But Bioremediation is a process which includes biodegradation as one of the technique and it is defined as biological treatment of polluted backgrounds [71]. The surroundings may be either soil or water. Bioremediation as a process uses living organisms like microbes and plants with their built in capability to degrade or convert pollutant or toxic organic or inorganic contaminants. Hence, to convert the contaminants into nontoxic stuff, the assorted metabolic routes of microorganisms are followed via mineralization by bioaccumulation, biodegradation, bioremoval, bioreduction, bioprecipitation, and immobilization.

The above mentioned processes of bioremediation are eco-friendly and very specific in terms of the pollutants. When plants such as poplar tree (*Populus nigra*), vettiver grass (*Vettiveria zizanoides*), common reed (*Phragmites australis*), and *Eleocharis acicularis* are efficient in bioremediation their prolonged time for efficient removal makes the microbial remediation as a prime most preferred process than using plants [72]. The process of bioremediation is an age old technology useful for the removal of the pollutants in the environment. But these ECs are very viable in toxicity, new in variety and resisting and escaping the normal ways of treatment. Thus here we concentrate about the major types and methods which may be useful for the removal of the pollutants [73].

7.5.2 Biodegradation using various types of microbes

The biodegradation of ECs in water, soil is also a recent methodology involving lignolytic fungi such as *Trametes versicolor*, *Stereum hirsutum*, and *Pleurotus ostratus* are effective against many Phc ECs such as sulfonamide, barbiturate etc., Designing of a bioreactor with *Trametes versicolar* seems to be a promising approach recently. Other fungal members of *Aspergillus* (Brown rot fungi) and members of *Phanerochyte* (White rot fungi) show a great biodegradation capability [74–79]. Bacteria's such as *Bacillus cereus*, *Micrococcus*, *Enterbacter ludwigii*, *Aeromonas hydrophillia*, *Psuedomonas monteilii*, and *Comamonas testosteroni* are also very much efficient against ECs as listed in the following Table 7.4 [80, 81].

Complexion biological, chemical, and physical procedures are adapted for the bioremediation of radioactive contaminants. Different types of mechanisms including oxidation, reduction, precipitation, sorption, etc. can influence the toxicity and transfer of radioisotopes in biogeochemical systems [82]. The following mechanisms are used for microbial bioremediation:

(1) Sequestration of ECs by cell wall components or by intracellular metal binding proteins and peptides
(2) Modification of biochemical pathways
(3) Enzymatic conversion

Table 7.4: Microorganisms and their target ECs.

S. No.	Name of the bacteria	Target ECs	Category
1.	*Bacillus cereus*	Decabromo diphenyl ether	Flame retardants
2.	*Micrococcus* sp.	Polycyclic naphthalene	Polyaromatic hydrocarbons
3.	*Enterobacter ludwigii*	Synthetic progesterone	Endocrine disrupting chemicals
4.	*Aeromonas hydrophila*	Synthetic progesterone	Endocrine disrupting chemicals
5.	*Psuedomonas monteilii*	Synthetic progesterone	Endocrine disrupting chemicals
6.	*Comamonas testosteroni*	Synthetic progesterone	Endocrine disrupting chemicals
7.	*Exiguobacterium acetylicum*	Synthetic progesterone	Endocrine disrupting chemicals
8.	*Chryseobacterium indologenes*	Synthetic progesterone	Endocrine disrupting chemicals
9.	*Pantoea* sp.	Uranium	Radionuclides
10.	*Psuedomonas* sp.	Uranium	Radionuclides
11.	*Enterobacter* sp.	Uranium	Radionuclides
12.	*Klebsiella* sp.	Uranium	Radionuclides

(4) Inhibit in the toxic metal invasion with precise efflux systems

Microorganism-assisted biotransformation resulted in removal of radionuclides by any of the above mechanisms. Such approaches for radioactive materials rely on the active metabolizing efficiencies of different types of microbial cells. Heavy metals such as Pb, Hg, Cd, etc., are effectively absorbed by several microorganisms that are also listed in Table 7.5. It is inferred that individual strains and group of microbial cells are involved in remediation of heavy metal and radioactive contaminants that may absorb or detoxify the pollutants into microbial cells via active or passive transport processes. The mechanism of absorption and conversion into nontoxic metal ions/compounds are schematically represented in Figure 7.3.

7.5.3 Biosorption

The involvement of biomass or the living organisms which are used for the absorption of the ECs is known as biosorption. These living organisms are called as biosorbents which includes plants, algae, fungi, and bacteria. The rate and efficacy of the biosorption depend on the optimization of environmental parameters such as pH and temperature. Apart from the living organisms, the polymers secreted by the microorganisms can also be used for the biosorption of pollutants [93]. A cork plant can absorb fluroquinone antibiotic effectively. Marine bioresources such as *Posidonia oceanic*,

Table 7.5: Microbial bioremediation of heavy metals.

S. No.	Contaminant	Microbes employed	Type of microbe	References
1	Hg, Cr(VI)/Zn (II)	*Pseudomonas aeruginosa* and *Staphylococcus epidermidis*	Bacteria	[83, 84]
2	Cr (VI)	*Termitomyces clypeatus*	Fungi	[85]
3	Cu, Zn, and Cd	*Saccharomyces cerevisiae*	Fungi	[86]
4	Cu (II)/Ni (II) and Pb (II)	*Desmodesmus* sp. and *Fucus vesiculosus*	Microalgae	[87, 88]
5	Radionuclides	*Deinococcus*, *Geobacter*, *Serratia*, *Kineococcus radiotolerans* and *Hymenobacter metalli*	Bacteria	[89]
6	Heavy metals, pesticides, polycyclic aromatic hydrocarbons	Plant growth promoting rhizobacteria Vesicular arbuscular mycorrhiza	Bacteria Fungi	[90, 91]
7	Pb, Cr, and Cd	*Bacillus subtilis*, *B. megaterium*, *Aspergillus niger*, and *Penicillium* sp. *B. megaterium*	Bacteria and fungi	[92]

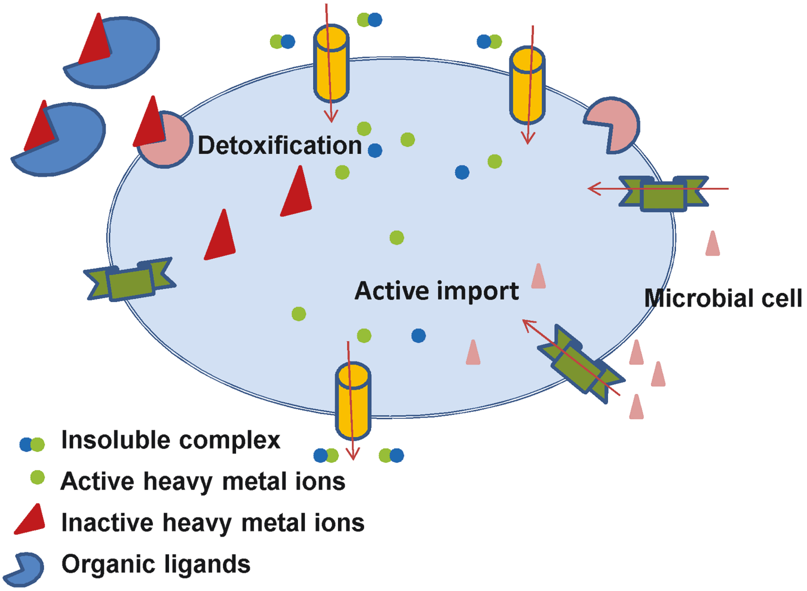

Figure 7.3: Detoxification/invasion of heavy metal contaminants by microbial cells.

Turbinaria conoides (Brown Algae), marine brown, andmacro alga *Padina pavonia* removes uranium [94]. Recently, microorganisms such as *Rhizopus arrhizus* is efficient against EDCs whereas *Citrobacter freudii* and *Fusarium* sp. can absorb radionuclides [95]. Some of the microorganisms such as *Pseudomonas fluorescens* excrete an exopolymer which can absorb the ECs as shown in Figure 7.4. Even the best known polymers

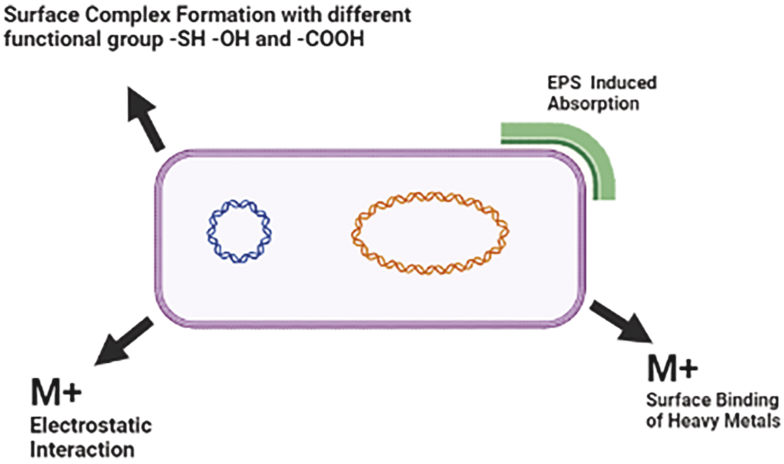

Figure 7.4: Biosorption of heavy metals by bacterial cell.

Alginate and chitosan are also good biosorbents of the recent ECs [96]. In fact, carcinogenic heavy metals are biosorbed the dead bacterial cells either via exopolysaccharides (EPS) or cell wall-mediated adsorption. However, the rate of biosorption by the heavy metal alleviating microbes is limited due to the inadequate supply of nutrients and pollutant, pH, and temperature of the environment.

7.5.4 Biostimulation, biopiling, and bioaugmentation

Volatile low molecular weight pollutants in bulking agents can also treated by the process called biopiling in which heat or air supply is given to enhance the microbial activity and hence, the rate of bioremediation time will be reduced [97]. Biostimulation is the process of additionally including nutrients, electron transferring substrates like oxidizers/reducers, etc. to enhance the bioremediation. Figure 7.5 explains the mechanism of biosorption and the influence of external factors like heat and nutrients that enhances bioremediation process.

For example, removal of pentachlorophenol by indigenous microbes using lactate and anthraquinone-2,6-disulfonate in soil [98] and for phenol toxicity using glycerol in *Ralstonia taiwanensis* [99] Bioaugmentation refers to inclusion of peripheral degradation competency among microbial strains or consortia of microorganisms. For example, inoculation of endogenous microorganism with external microbes causes remediation of PCB at the contaminated sites [100]. Higher absorption of ECs in microbial cells stable enough to resist contaminants is known as bioaccumulators. In fact, the process of bioaccumulation is toxicokinetic in nature which influences the response of microorganisms to emerging contaminants [101–103].

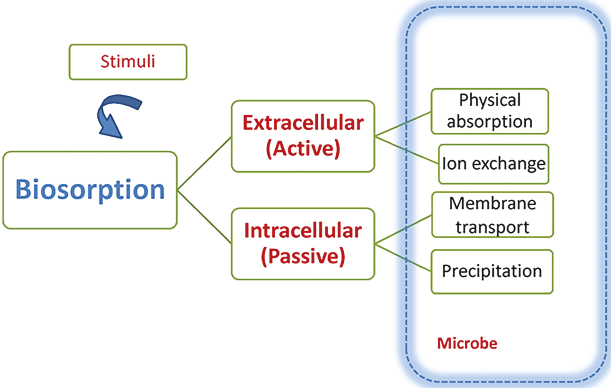

Figure 7.5: Mechanism of biosorption based on microbial uptake of contaminants.

7.5.5 Rhizoremediation

Rhizoremediation is one of the remediation approaches that mutually performed under rhizosphere in which plant roots and soil microbiota aids in supplementing necessary nutrients for N_2 fixation and also aids in developing defense mechanism from phytopathogens. As root exudates contain essential nutrients such as simple carbohydrates, organic substances, hormones, and amino acids, it allows the microbes for better growth as well as in degradation of pollutants [104]. Plant rhizosphere naturally possesses sufficient vicinity as it has larger root systems and facilitates effective bioremediation of ECs in soil [91]. Plant growth promoting rhizobacteria (PGPR) and Vesicular Arbescular Mycorrhiza (VAM) fungi in the rhizosphere commonly accomplish the process of rhizoremediation. In fact, the response of microbes in rhizosphere region are varying by the physiological conditions such as pH, stimuli/chelating agents, and electron/proton donor according to the nature of contaminants [105]. Thus, rhizoremediation resolves the issues related to the use of individual treatment methods adapted in soil environment because it is a fusion process of bioaugmentation with plant-assisted remediation. In mycoremediation, mycorrhizal fungi (VAM) are involved in the degradation of perilous waste products. Competitive absorption of ECs between mycorrhiza and plant roots increases the possibility of potential remediation process in soil [91]. Rhizosphere colonizing plant growth promoting bacterial genre like *Azotobacter*, *Bacillus* sp., *Pseudomonas* sp., etc. are considered to be an active candidates in degradation of ECs. Nevertheless, rhizoremediation gets slow down upon the interruption of certain physiological factors like soil organic matter, mass of microbes, energy sources and soil chemical properties, etc. Large quantity of contaminants also hinders the tolerance level of plants to accumulate them without causing undesirable reactions in plant metabolism. Hence, exploitation of manipulation techniques such as bioaugmentation, biostimulation, and rhizosphere engineering process enable improved performance in rhizoremediation [90].

7.6 Necessity of microbial degradation

A lack of appropriate elucidation of the plastic management strategies is being observed especially during the degradation stages of biodeterioration, biofragmentation, assimilation, and mineralization [106]. Physical and chemical properties of plastics are altered by chemoorganotrophic microbial consortia that are exploited on plastic waste. There are few case studies on plastic degrading microbial groups that are highlighted by Buragohain et al. [106]. Though complete Genomic sequencing of potent microbial strains such as *Shewanella oneidensis* MR-1, *Pseudomonas aeruginosa* KT2440, *Deinococcus indicus* R1, and *Dehalococcoides mccartyi* WBC-2 gives insights on the genes involved in degradation [107], the appropriate genetic manipulation and exploitation of engineered strains to the field requires massive trials. Meta-genomic, -trans-criptomic and -proteomic, and analysis of strains at contaminated sites will be very useful for understanding the mechanism of action on pollutants. According to the report by Misra et al. [107] and Withers et al. [108], metabolomic study and complete genomic sequences of microorganisms in the standard database cites provide detailed insights to elucidate their capability in biodegradation of environmental contaminants.

7.7 Challenges in microbial degradation

Despite of tremendous advantages in the use of microbes on the degradation of ECs, there are following challenges in the successful adaptation in the efficient removal of emerging contaminants [109, 110]:

a) Chemical nature and size of the contaminating sites.
b) Biological factors such as nutritional requirements of microorganisms, concentration of microbial biomass, substrate based enzyme inhibitions, occurrence of predators at the contaminated sites, and chemical induced mutation.
c) Microbial growth inhibiting environmental factors temperature, pH, oxygen level, and osmotic pressure.
d) Use of normal microbes at the contaminated sites at extreme conditions.
e) Difficulty in degradation employing microbes for plastics due to their high molecular weight, complicated chemical structures and functional groups, thermal stability, solubility, prolonged fragmentation, etc.
f) Sustainability of GMOs with good gene stability, and human and environmental safety in natural state.

7.8 Scope of microbial degradation of emerging contaminants

Presence of ECs even at lower concentration causes high risks to living organisms in marine as well as environment. A strategy of microbial degradation based on detoxification process via bioremediation is considered as one of the best methods for efficient removal of contaminants [2]. Bioremediation prevents the adverse effect of ECs from causing disease to humans, animals, and plant. Though it is a time-taking process, one has to choose the strategy which is effective and lucrative in treatment at contaminated sites. In fact, this single approach alone will not result to complete removal or detoxification of ECs. Among several reported research investigations, microbial degradation places vital role in treating broad spectrum of ECs at higher degradation volume [4]. Future perspectives of microbial degradation also relies hybrid systems that include allied as well as advanced technologies such as nanotechnology and bioprocess chemistry. Advanced oxidation and electrokinetic process induced bioremediation in soil environment effectively mobilizes the organic and heavy metal pollutants in soil, enhances the microbial action [3, 5] and more importantly, reduces the time of treatment. Similarly, immobilization of microorganisms and microbial enzymes with nanoparticles promotes high reactivity and absorption rate on pollutants. This strategy can also applied in fusion with photocatalytic action of nanoparticles to convert the bio-recalcitrant pollutants into readily degradable products. Owing to an increase in the intake of pharmaceutical compounds and consumer products by the humans, necessity and demand for microbial degradation of ECs are enormous to protect the food chain in terrestrial and aquatic environment.

7.9 Conclusions

The removal of emerging contaminants is a great challenge before conservation of our environment just because the ECS in its low concentration are capable of causing heavy damage. Moreover, our day to day life and lifestyle produces number of different novel variants of EC’s to the environment. Their ready solubility, stability and resistance need an efficient treatment method for their complete removal. Thus this review highlighted the normal conventional methods are very disadvantageous over the microbial remediation process. The process of microbial degradation proves that the depollution strategy of ECs is very sustainable, environmentally safe, potent, and lucrative process. The strategy of using single efficient microbe or using microbial consortia has proven its efficiency in removal of ECs. When these methods are clubbed together with the conventional bio-treatment process, shows increased potential in the removal of these ECs. Thus, the microbial bioremediation and biodegradation process which is proven as efficient treatment process is still in its optimization stage and needs intense research and conversion into practicable method. Moreover, it is essential to further understand the response of microbial sources to the diverse physico–chemical nature of pollutants and their degradation performance in view of their genetic pool and degradation rate for better solution to contaminant free environment.

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8 Recent endeavors in microbial remediation of micro- and nanoplastics

Abstract: Petrochemical plastics are frequently utilized in our daily lives for various purposes such as packaging and transportation, but their burden on the environment is considered one of the most man-made pollution crises. These pollutants are slowly fragmented in the environment into microplastics and nanoplastics by consolidated actions of abiotic and biotic factors. Microplastics and nanoplastics can easily be dispersed in the atmosphere and be harmful to all kinds of life. As a result, the remediation of micro- and nanoplastics has recently received a tremendous research impetus in the realm of an ecologically benign approach, notably microbial-based remediation. Thus, the current article looks at the formation, properties, analysis, and biological effects of micro- and nanoplastics. The content is then streamlined towards a comprehensive discussion on microbial-mediated degradation of microplastics and nanoplastics, with an emphasis on front-line bacteria and enzymes, as well as remediation mechanisms. Further, technologies for the removal of microplastics and nanoplastics from the environment are presented for possible remedial considerations. An attempt is also made to highlight the practical snags of microbial plastic degradation while aiming to alleviate the environmental burden of plastic waste.

Keywords: biodegradation; enzymes; microbial remediation; microplastics; nanoplastics.

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8.1 Introduction

The desire to make our lives easier and more comfortable has resulted in countless scientific innovations across many disciplines, resulting in a variety of products that are indispensable in our day-to-day activities. Products that need inexpensive technology are currently extensively produced in various nations. Plastics are such products derived from petrochemicals that are manufactured on a large scale for a range of applications, with an estimated production of 360 million tons in 2018 and predicted to rise by four-fold by 2050 [1]. Despite their apparent use, plastics are recalcitrant in nature, and as a result, they remain undegraded in the landfills or the natural environment, be it polar, ocean, land, and freshwater [2]. Although incineration and mechanical and chemical recycling have been used to manage just 21% of plastic waste, the processes generate toxic byproducts, are costly, require more energy, and are incapable of handling the volume of plastic waste released into the environment. Properties that render plastic to remain undegraded for up to thousands of years include lack of functional groups for microbes, high-molecular-weight, crystallinity, long-chain polymer structure, and hydrophobicity [3]. Thereby, the plastic waste decomposes gradually in the environment as a consequence of the actions of chemical, physical, and biological factors, resulting in the formation of microplastics (MPs) and nanoplastics (NPs) [4].

Microplastics and nanoplastics are mainly formed from their parent plastics such as polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PUR), and polyethylene terephthalate (PET) in terrestrial and freshwater environments, mainly in the photo-decomposition process [1, 5]. These types of plastic particles are easily dispersed in the atmosphere, are more toxic, and have therefore recently attracted the attention of the scientific community as to their origins, fate, and pollution [4, 6]. A commendable share of research has also proved the toxicity of microplastics and nanoplastics to marine, freshwater, and terrestrial life [3, 6]. Further, nanoplastic demonstrated a nanoscale effect due to size, shape, altered chemical changes, and density, with its impact on the environment requiring sufficient consideration in terms of determination and pollution consequences [7]. Moreover, biodegradable plastic has been put forward as a strategy to remediate the environment from the deleterious impact of microplastics and nanoplastics, but its market share is still no more than 2% when compared to fossil-based plastics [8]. Plastic-degrading microbes and their enzymes, on the other hand, provide a facile and promising approach to depolymerize microplastics and nanoplastics into monomers for recycling or mineralize them into carbon dioxide, water, and new biomass [3, 4, 9]. Over 300 microbes, mainly bacteria and fungi, have reported acting on plastics [10], albeit not directly on microplastics and nanoplastics, but the microbial actions on microplastics and nanoplastics will likely be easier and faster. Thus, this article focuses on the consequence of microplastics and nanoplastic pollutants on the environment. Also, the microbial-mediated degradation mechanisms of microplastics and nanoplastics, performed microbes, and enzymes are summarized. Finally, recent attempts in the microbial remediation of microplastics and nanoplastics waste are discussed for further removal aspects.

8.2 Synthetic plastics and types

Plastics are synthesized from petroleum-based chemicals or natural substrates. Petrochemical plastics such as PE, PS, PP, PVC, PUR, and PET are nonbiodegradable and account for more than 80% of global plastic usage [1, 11]. Certain nonbiodegradable plastics such as PE and PET can be entirely or partially biobased. Further, synthetic plastics are divided into two groups: those with only a C–C backbone and those including heteroatoms in the main chain. Among the most widely used plastics, PET and PU contain heteroatoms in the main chain, whereas PP, PE, PS, and PVC have a sole C–C backbone. The polymer's molecular bonds are thought to be a key component in plastic enzymatic degradability. Thereby, PET and PUR are composed of polymers with hydrolyzable chemical linkages in their backbone, hence they are more prone to biological attack than PS, PE, PVC, and PP. Polymers containing heteroatoms in the main chain, on the other hand, have better thermal stability than polymers with simply a C–C backbone. Prior to further depolymerization, the very stable C–C bonds must be oxidized in PS, PE, PVC, and PP.

Biodegradable plastics, on the other hand, such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), or poly(butylene succinate-co-butylene adipate) (PBSA), are made from either renewable-based materials like starch or cellulose or petrochemical-based (e.g. PCL and PBS). The well-known advantage of utilizing biodegradable plastics is that they may be broken down by microorganisms in an ecologically benign manner, thus reducing greenhouse gas emissions. However, characteristics such as poor mechanical or surface properties, as well as high cost, have hampered the use of biodegradable plastics in some applications.

8.3 Formation, properties, and analysis of microplastics and nanoplastics

In this section, readers are introduced to the formation, properties, and analysis of microplastics and nanoplastics. To begin, the sources of microplastics and nanoplastics are mostly single-use plastics and fishing gear, but also clothes and cosmetics, agricultural textiles and runoff, paints, tires, and urban dust [11]. These plastics can break down into micro- and nanoplastics via the biodegradation or non-biodegradation processes (Figure 8.1) [4, 12]. Nonbiodegradation processes include physical deterioration, thermal degradation, oxidative-thermal degradation, photodegradation, and hydrolysis, whereas biodegradation processes include microbial breakdown of plastics. Now, the formation of microplastics and nanoplastics alters their mechanical properties, and thereby increasing their specific surface area, resulting in enhanced physical–chemical reactions and interactions with organisms [2].

Microplastics are typically categorized as plastic in the 1 µm to 5 mm size range that comes from primary and secondary sources [11]. The primary sources are premade plastic pellets, also known as microbeads, which are often used in health and personal care items (toothpaste, scrubs, cleaning materials, and cosmetics). Secondary microplastics are formed mostly as a product of the breakdown of larger plastic materials in the environment, and they are also a major source of plastic pollution [4]. Macroplastics (>5 mm) and microplastics are further broken down into nanometer-sized particles, resulting in nanoplastics (Figure 8.1). Thus, nanoplastics are defined as plastic particles with sizes ranging from 1 to 100 nm that exhibit colloidal behavior. These kinds of plastic nanoparticles are also deliberately synthesized as plastic nanoparticles, for example, for use in personal care items and other consumer products [7]. Nanoplastics have received special attention due to their distinct physiochemical nanoscale properties, which include high surface area, hydrodynamic size, purity, chemical composition, doping, morphology, redox parameters, and so on. Thereby, the behavior and interaction of nanoplastics with living organisms distinctly differ

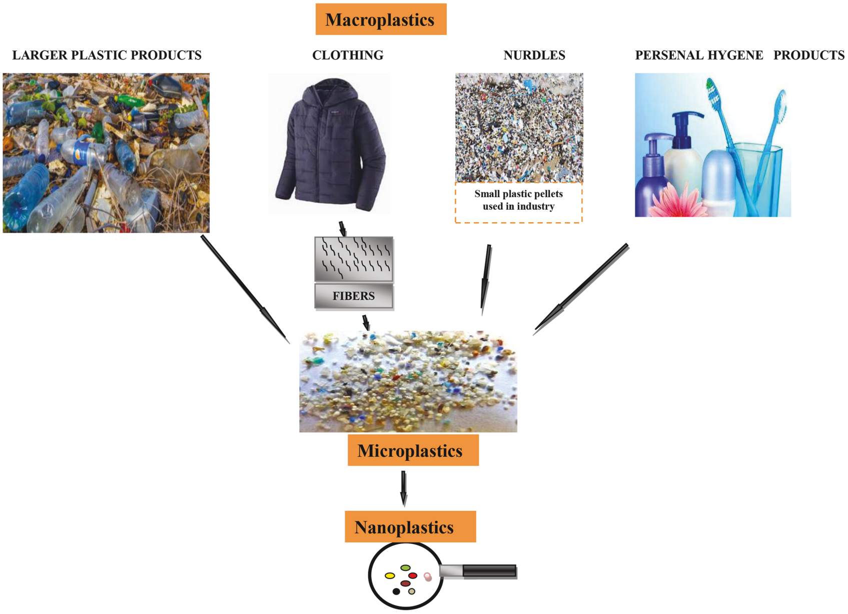

Figure 8.1: Micro- and nanoplastic formation from their parent substrate.

from larger pieces of bulk materials but are not adequately researched and are thus difficult to characterize [13]. However, the shape, diversity, small size, lightweight, and low density of microplastics and nanoplastics contribute to their widespread transport and facile dispersal across large distances on land and within aquatic systems, impacting global biodiversity [14, 15].

Nanoplastics made from bulk plastic materials are characterized in terms of chemical composition, shape, size, and surface, and so on. Various techniques, such as scanning electron microscope, transmission electron microscope, Fourier transform infrared spectroscopy (FTIR), stereo- (or dissecting) microscopy, atomic force microscopy (AFM), and Raman spectroscopy can be used to achieve this [11, 16–19]. The reader may find excellent review papers that provide an in-depth look at techniques of detection and characterization of nanoplastics [20, 21].

8.4 Environmental and health implications of micro- and nanoplastics

Pollution from micro- and nanoplastics is a worldwide exemplar that raises animal, environmental, and human health concerns. Recently the potential of these wastes has received increasing attention of particular concern on the aquatic, marine, and land environment [4]. Besides, micro- and nanoplastics can absorb long-lasting organic pollutants and pathogenic bacteria from the surrounding media, potentially causing toxicity throughout the food chain [6], and eventually reaching people through bioaccumulation. The surfaces of micro- and nanoplastics provide essential substrates for the development of microbial biofilms, facilitating opportunistic bacteria and persistent species to transfer [22].

MPs and NPs have been reported to harm fish and other marine organisms in marine environments, notably the oceans, by reducing reproduction, growth, and fitness, as well as affecting the biodiversity of microbial communities [6, 23, 24]. Ingestion of nanoplastics in fish resulted in neurotoxic effects on locomotor activity, and microplastics can also increase cellular oxidative stress on cell structures [23]. In addition, the presence of microplastics in the stomachs of commercially edible fish species poses a hidden risk to human health due to ingesting exposure. MPs residues in the deep sea also have an impact on marine benthic organisms such as oysters and mussels [24]. In mussels, it causes inflammation in the long run and reduces the stability of lysosome membranes, whereas in oysters, it increases mortality, slows growth, influences energy absorption, and interferes with reproductive ability and offspring progression. Furthermore, micro- and nanoplastics have been reported to be harmful to microorganisms such as yeast cells, marine bacterium *Halomonas alkaliphila*, microalgae, and others [4].

Research on MPs pollution has concentrated on aquatic environments since these are the largest sink. In recent years, however, scientists have been interested in the impact of micro- and nano-plastics (MNPs) on terrestrial ecosystems and organisms [14, 15]. The extensive use of agricultural plastic films and particles in industrial production applications is seen as exacerbating MP pollution, with the soil acting as an important long-term sink for microplastics, leading MPs to gradually impact soil geochemistry and microorganisms [15]. Polystyrene MPs demonstrate this by inhibiting the proliferation and even death of earthworms and collembolans (hexapods) in the soil [25]. Other species have been reported to be impacted by MP contamination, including birds (affected by digestive enzyme blockage, reduced steroid hormone levels, and impaired reproductive function), turtles (due to nutritional deficiencies), and whales (by starvation) [6].

Furthermore, micro plastic-driven modifications in soil hydrological characteristics could affect soil microbial growth, with prospective effects on important symbiotic connections in terrestrial ecosystems such as mycorrhizal groups and N-fixing organizations [26]. The potential biophysical effects on the soil surface are particular attention to the soil microbiome as the mechanistic knowledge in the failure of biodiversity is not well known [14]. Agricultural farmland soil may be particularly vulnerable to the accumulation of MPs and NPs. Biodegradable plastics are a step in the right direction to alleviate concerns about MPs and NPs in soil. According to Chinaglia et al. [27] under standardized laboratory tests (e.g., ASTM D5988 21), MPs of size 50–75 µm (the diameter of a human hair) are readily biodegradable. However, it is unclear when qualification these results translate NPs in soil and there is no report on the impact of NPs on soils; and need for further investigation. A study indicated the harmful impacts of NPs on several aquatic species including toxicological effects, biological effects, return on investment (ROI) manufacturing, and dysfunction of reproduction [13]. There is also a lack of understanding about how NPs are transported to the food supply chain and how they accumulate and communicate with the environment, especially with organisms.

Therefore, humans are ubiquitously exposed in their daily environment to MPs and NPs, and these can rise through inhalation, ingestion, and dermal contact; and causes health treats in the digestive tract and inflammation in the mucosa [4, 6, 11]. Inhaled airborne microplastics derive from dust including rubber tires and synthetic textiles [4, 11], ingested as they are prevalent in the food source, beverage, and water supplies [6]. This is not known whether ingested microplastics can be degraded to nanoplastics in the human GI tract. While the skin membrane was too fine for microplastics or nanoplastics to pass through, they can enter through wounds, sweat glands, or hair follicles [2]. This is due to the long-term weathering of these polymers, leaching of polymer chemical additives, residual monomers, exposure to pollutants, and pathogenic microorganisms all being active in the environments [4, 12]

8.5 Microbial mediated-degradation mechanisms of microplastics and nanoplastics pollutants

Microbial degradation is an ecofriendly method to reduce microplastics and nanoplastics pollutants [4]. These processes are governed by various factors, including biotic (the action of release enzymes/free-radicals), nonliving chemical or physical factors (temperature, pH, salinity, oxygen level, moisture, and UV radiation), and polymer properties (chemical structure and molecular weight), all play significant roles in their degradation [4, 12]. The mechanisms associated with MNPs degradation are not well understood [3], and the relevant degradation pathways have not been clear, this is due to chemical structure, and higher molecular weight plastic polymers hinder microbial degradation processes. In general, microorganisms degrade polymers into monomers or mixtures of monomers via two major mechanisms: extracellular or intracellular degradation [3]. Microbes accumulate on the surface of MNPs during intracellular degradation, causing the polymers to break down into short chains. Extracellular degradation, on the other hand, includes microorganisms secreting extracellular enzymes that degrade complex MNPs into short chains or smaller molecules that can pass through the semi-permeable membrane [12]. These short-chains are then mineralized by microorganisms and the final products into CO_2, H_2O, or CH through aerobic or anaerobic metabolism. The aerobic process may take place in sediments or landfills, partially aerobic in compost or soil. During aerobic biodegradation, carbon dioxide, and water are produced while carbon dioxide, water, methane, and hydrogen sulfide are produced by anaerobic biodegradation, and products can then utilized as carbon and energy sources for microorganisms [9].

Therefore, the role of microorganisms in plastic degradation can be implied by the following steps: biodeterioration (polymer physical, chemical, and mechanical properties are modified by abiotic and biotic factors), biofragmentation (catalytic cleavage of polymeric plastics into oligomers, dimers or monomers by microbial enzymes, or free-radicals), assimilation (the integration of molecules inside microbial cells), and mineralization of MNPs (complete degradation molecules into oxidized metabolites, i.e. CO_2, CH_4, and HO) (Figure 8.2). Numerous microorganisms in terrestrial, marine, and freshwater habitats might easily develop biofilms on the plastic surface [22]. By producing extracellular polymeric substances (EPS), microorganisms may be able to protect themselves from harsh or severe environments, harmful chemicals, and acquire nutrients. Harrison et al. reported that seawater bacteria were observed on the surfaces of low-density polyethylene plastic establishing biofilms [28]. The microbial assemblages on the LDPE surface produced EPS and other metabolites that can break down detritus such as microplastic-related chemicals and perhaps increase the adsorption of other polymers/microbes. The mechanisms of microbial adhesion to the polymer surface, on the other hand, are unknown.

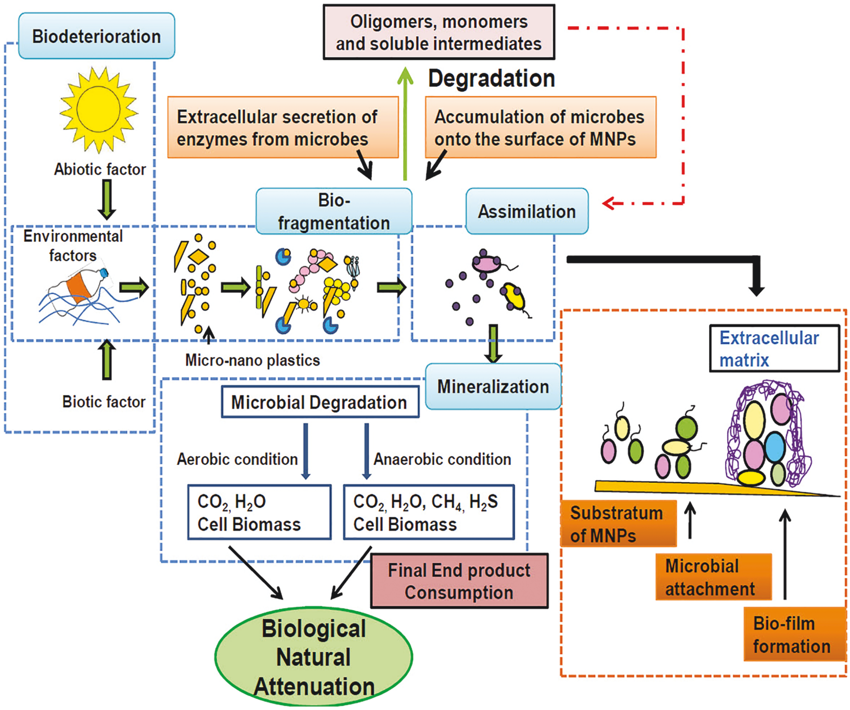

Figure 8.2: Microbial remediation mechanisms of micro-nanoplastics pollutants (Adapted from Tiwari et al. (Copyright© 2020 Published by Elsevier Ltd.) [4]).

Microbes involved in the degradation/size reduction of plastic wastes can also accumulate MNPs; these can be analyzed through changes in physicochemical properties, identify the degraded products, and associated cellular responses [16, 17, 29]. Studies indicate that the role of plastic degrading microbes and their enzymes are important in the MNPs degradation process; these remain toxic products in the environment waiting to be degraded. Moreover, the microbial enzymes involved in plastics degradation are not completely understood because different microorganisms encode different enzymes, and different types of plastics require different enzymes for degradation. Therefore, a collaborative recent research approach with various technologies is required to get a concrete solution in the remediation of micro-nanoplastics.

8.6 Recent endeavors in micro- and nanoplastic microbial remediation

8.6.1 Exemplary microbes and enzymatic degradation of micro- and nanoplastics

Plastics degradation by microbe and/or enzyme is a promising approach to mineralize them into carbon dioxide, water, and new biomass, with concomitant production of higher-value biproducts [3, 4, 9]. Generally, hydrolyzable functional group is found to be lack in the C–C backbone of the plastic polymeric matrix [11]. Hence, the biological degradation of plastics using enzymes is observed to be typically a tricky process [12]. However, to begin with, the degradation of plastics encompasses collaborative action of abiotic and biotic parameters by reducing the molecular weight [4, 12]. Leja and Lewandowicz have observed that the carbonyl group present in the plastic polymers is attaining additionally vulnerable to enzymatic degradation when it is exposed to UV radiation [30]. Several investigations have been carried out using different microbial enzymes for the degradation of different plastics [31–34]. Remarkably, hydrolyase (lipase, urease, and protease), and lignin-degrading enzymes (manganese-dependent peroxidase, and laccase) are widely used enzymes by researchers (Table 8.1). However, it should be also noted that a number of bacterial strains isolated from diverse habitats have also been reported to metabolize a component [such as bis (2-Ethylhexyl) phthalate, DEHP] of plasticized PVC rather than the backbone of PVC [34, 35]. The main enzymes involved in the microbial breakdown of PVC are yet unclear.

Several researchers, in fact, simply report the isolation of plastic-degrading microorganisms without identifying the enzyme involved in the process. Azeko et al. reported a strain *Serratia marcescens* isolated from ground soil capable to degrade PE and reached 36% weight loss in an incubation period of 70 days [42]. The bacterial strains *Enterobacter asburiae* YT1 and *Bacillus* sp. YP1 were also isolated from the gut of the waxworm *Plodia interpunctella* and their capacity to degrade PE was tested after a 60-day incubation period. Over a 28-day incubation period, viable biofilms were produced, and pits and cavities on the surfaces of the PE films were detected using scanning electron microscopy (SEM) and AFM [31]. Several other studies were also indicated the degradation of PE by diverse microbes (Table 8.1).

Thermostable laccase has shown reasonable degradation on the polyethylene (PE) while incubating at 310 K for 48 h. Interestingly, during the degradation of PE, the activity of laccase has been improved by 13-fold when the reaction is carried out with copper treatment. Santo et al. have observed from their study the percentage of PE biodegradation was improved by 75% when copper was supplemented to *Rhodococcus ruber* C208 cultures [47]. In the same way, a partially purified cocktail of enzymes, manganese-dependent peroxidases which were isolated from *Phanerochaete chrysosporium* has been examined by Yee et al. under the limiting circumstances of carbon and nitrogen for PE degradation [33]. Despite its widespread use, only four microbial enzymes have been identified as being involved in PE breakdown. These are manganese peroxidase (MnP) (which could reduce the tensile strength and average molecular weight of PE film), the combined soybean peroxidase (SBP) and hydrogen peroxide (could oxidize the surface of the PE film and reduce the surface hydrophobicity), extracellular laccase (could oxidize the PE films to generate carbonyl groups and decrease the molecular weight), and three alkane hydroxylase genes, *alkB*, *alkB1*, and *alkB2*, (that have been reported to degrade low molecular weight PE) [33, 38].

Table 8.1: Microbes and enzymes associated with (micro-nano) plastic degradation.

Strain/Enzyme	**Isolated source**	**Tested plastic (Micro-nanoplastics)**	***In vitro***	**Degradation efficiency**			**References**
			Incubation time, dates	**Weight loss%**	**Molecular weight**	**Degradation product**	
Comamonas acidovorans	Soil samples of Tsukuba City in Japan	Polyester PUR film	7	48%	–	Detected	[36]
Bacillus subtilis	Soil sample from a mesocosm study	Polyurethane	24 h	–	–	Zone of clearance was observed	[37]
Stenotrophomonas panacihumi	Soil of waste storage yard	PP film	90	–	Increased	–	[38]
Bacillus sp. strain 27; *Rhodococcus* sp. strain 36	Mangrove environments	PP microplastic (Mineral salt medium)	40	4–6.4	–	–	[39]
Xanthomonas sp.; *Sphingobacterium* sp.; *Bacillus* sp. STR-YO	Field soil	PS film	8	40–56	–	–	[40]
Rhizopus oryzae NA1; *Aspergillus terreus* NA2; *Phanerochaete chrysosporium* NA3	Soil buried expanded PS film	PS film	56	–	Increased	Detected	[41]
Bacillus sp. AIIW2	Marine	Unplasticized PVC film	90	0.26	–	Detected	[35]
Pseudomonas citronellolis *Bacillus flexus*	Soil	Plasticized PVC film	45	19	Decreased	–	[34]
Serratia marcescens	Ground soil	LLDPE film	70	36	–	–	[42]
Enterobacter asburiae YT1; *Bacillus* sp. YP1	Gut of waxworm	LDPE film	60	6–11	Decreased	Detected	[31]
Thermobifida fusca	Compost	PET bottle and pellets crystallinity 9%	180	50	–	–	[43]

Table 8.1: (continued)

Strain/Enzyme	Isolated source	Tested plastic (Micro-nanoplastics)	*In vitro* Incubation time, dates	Degradation efficiency			References
				Weight loss%	Molecular weight	Degradation product	
Ideonella sakaiensis	PET recycling factory	Low-crystallinity PET film	42	–	–	Almost complete degradation achieved	[32]
Bacillus subtilis; *Pseudomonas aeruginosa*	Soil	Polyester PUR pellets	20	–	–	Detected	[44]
alkB1, *alkB2* gene	*Pseudomonas aeruginosa* E7	LMWPE fil	50	19.6–27.6	–	–	[38]
Catalase, Peroxidase, Laccases	*Klebsiella*, *Staphylococcus*, *Micrococcus*, *Chaetomium*, *Pseudomonas putida* AJ.	Polyvinyl chloride (PVC)/Vinyl chloride monomer					[34, 35]
Lipase	*Bacillus* sp. strain 27 and *Rhodococcus* sp. strain 36, *Stenotrophomonas panacihumi* PA3-2	Polypropylene (PP)/ Propylene monomer					[38, 39]
MHETase, PETase, Lipase, α- or β-hydrolases	*Ideonella sakaiensis* 201-F6	Polyethylene terephthalate (PET)/ Polyethylene monomer					[32]
Lipase, Cutinase	*Arthrobacter* sp., *Bacillus* sp. BCBT21, *Klebsiella pneumonia* CH001, *Comamonas acidovorans*, *Pseudomonas putida* S3A, *Aspergillus flavus, Rhodococcus*, *Penicillium oxalicum*	High-density polyethylene (HDPE)/ Polyethylene monomer					[45]
Nylon hydrolase	*Pseudomonas* sp.	Mixture of plastics with nylon/Ethylene monomers with nylon					[46]

Aside from PE, a variety of fungi and bacteria have been found to be capable of degrading polyurethane (PUR) [36, 37]. PUR esterase, an enzyme which is used to degrade a solid-polyester–PUR, which was acquired from *Comamonas acidovorans* (strain TB-3) has shown an appreciable degradation on PUR in hydrophobic PUR-surface-binding domain and a catalytic domain. Nakajima et al. used GC–MS to investigate the metabolites produced by the hydrolytic breakage of ester linkages in PUR [36]. Howard recognized that the enzymes, papain and urease can degrade medical polyester polyurethane through hydrolyzation of the urea linkages and urethane. The degradation reaction resulted in hydroxyl groups and free amine [37].

PET is another commonly used plastic, and researchers are actively searching for microorganisms and enzymes that act on it. In this regard, Müller et al. observed that the hydrolase enzymes obtained from the actinomycete bacteria, *Thermobifida fusca*, can also degrade the aromatic polyester, polyethylene terephthalate (PET) [43]. They reported that the rate of erosion of PET was found to be 8–17 mm/week at a moderate temperature of 55 °C. Another study from Yoshida et al. showed that the PETase extracted from the bacteria, *Ideonella sakaiensis* 201-F6, can break the PET significantly. They observed that *I. sakaiensis* utilized only PET as energy and carbon source during the degradation process [32].

Eisaku et al. attempted to isolate PS-degrading microorganisms from several environmental samples and showed that *Bacillus* sp. STR-YO, *Xanthomonas* sp., and *Sphingobacterium* sp. could break down PS [40]. According to Atiq et al., three fungi and bacteria recovered from extended PS films buried in the soil were able to adhere to and utilize PS, as indicated by SEM, FTIR spectroscopy, and high-pressure liquid chromatography (HPLC) [41]. However, the observed PS biodegradation rates by these strains were relatively low. Moreover, with respect to the PS-degrading enzymes, alkene monooxygenase and esterase, secreted by a bacterium *Pseudomonas* sp., and actinomycetes were able to depolymerize PS into low molecular products [48].

Raghul et al. investigated biodegradation studies on polyvinyl alcohol (PVA) using the enzymes secreted from an aquatic microorganism, vibrios. They isolated *V. alginolyticus* and *V. haemolyticus* from the benthic zone that had capable of secretion of exoenzymes such as proteinases, lipases, and polysaccharases [49]. From this study, PVA-LLDPE plastic films were observed to lower down their tensile strength up to 25% by these species.

Certain microbes, such as *Pseudomonas stutzeri*, *Acinetobacter* sp. 351, *Pseudomonas* sp. E4 *Brevibacillus*, *Pseudomonas* sp. AKS2, *Aspergillus terreus*, *Aspergillus japonicas*, *Streptomyces setnii*, *Streptomyces badius*, and *Streptomyces viridosporus* play a key role in the degradation of low-density polyethylene (LDPE) [44, 50, 51]. Various competent microorganisms were also reported elsewhere that can produce plastic degradation enzymes. For example, proteases from *Brevibacillus* spp. and *Bacillus* spp. were reported to have the ability in breaking the PE [12, 52]. *Pseudomonas* spp. produces polyhydroxyalkanoate (PHA) depolymerases (serine hydrolases) that can attack the cyclic components and branching chains of the polymers [12]. A study also reported that *Candida rugosa*, *C. acidovorans*, and *Pseudomonas chlororaphis* were also showed the active degradation of plastic and its derivatives [44].

Finally, few studies have tested microplastic degradation instead of using the bulk plastic substrate. In this regard, the two marine bacteria, *Bacillus* spp. strain 27 and *Rhodococcus* spp. strain 36, isolated from mangrove environments, were also able to grow in aqueous synthetic media containing PP microplastics [39]. A variety of techniques, including SEM and FTIR studies, were used to validate the biodegradation of PP microplastics. Additionally, a microplastic derived from PET was reported to be degraded by the engineered strain, which can grow with PET as the only carbon source [53]. The strain is employed as a bacterial whole-cell biocatalyst, removing feedback inhibition, and the biodegradation of the PET particles is revealed via a layer-by-layer degradation process.

8.6.2 Merits, demerits, and biodegradation assessment

Plastic biodegradation is simple, less extensive, and straightforward. However, this approach has certain drawbacks, notably in detection techniques involving weight loss. Additionally, the leaching of additives results in considerable weight loss. Furthermore, the Sturm test revealed that the false production of carbon dioxide was detected during the biodegradation of plastics. This may result from the loss of additives and decomposition of low molecular weight constituents. This kind of microscopic alteration in chemical change may distress the strength of polymers [29]. In this regard, some techniques can be used to overcome this issue. FTIR can be used for detecting and identification of structural changes in the surface due to weight loss during degradation progression. This technique makes available a clear understanding of N–H stretching of aldehyde group, C=O stretching of aldehyde group, C–C=C symmetric of aromatic ring, and C–O stretching of ether group [54]. A well-known method, SEM can be used to examine the morphology of the polymer's surface before and after degradation. SEM analysis, at the right magnification, provides valuable information without the need for surface metallization [16]. In recent studies, FTIR and SEM techniques were carried out to assess the loss of weight during degradation of plastics by the strains, *Aspergillus sydowii* PNPF15/TS and *A. terreus* MANGF1/WL [17]. The SEM image analysis showed that the formation of scions and holes were observed on the surfaces of polythene film strips during fungal degradation. During polythene degradation, significant changes were noticed in carbonyl index using FTIR analysis. The difference in the carbonyl index for the strips of untreated and pretreated PE was observed to be maximum with the fungi degradation. Other sophisticated approaches also used by different researchers to evaluate the biodegradability of plastic polymers such as differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), contact angle measurements, X-ray diffraction (XRD), and nuclear magnetic resonance spectroscopy (NMR) [18, 19].

Esmaeili et al. carried out a study on LDPE biodegradation by mixed culture of *Aspergillus niger* and *Lysinibacillus xylanilyticus*. They analyzed UV exposed LDPE and non-UV exposed LDPE films for biodegradation. The degree of crystallinity was measured using XRD in both cases, before and after incubation with and without the presence of the selected microorganisms. The results revealed that there were no discernible variations in the degree of crystallinity between the films incubated without microorganisms and the control. Furthermore, both non UV-irradiated and UV-irradiated films showed decreased crystal sizes and crystallinity following biodegradation [51].

8.6.3 The insights into the composition of Epiplastic Organisms: Omics approach

There are abundant microbial species on the earth. They are carrying out various functions at different levels. For the biodegradation of plastics, microorganisms are not only indispensable. It is also imperative to concern about reservoirs of various nutrients that can be causes of certain enzymes and catalysts. They play a vital role in recycling dead organic matter [9, 12]. In this context, it is imperative on knowledge of insights into the microbe community. The genome-level study of the particular species could provide the prevailing characteristics of the microbe that can help to identify the source of a specific case. Commonly, microbial species inhabit the plastisphere via colonizing solid surfaces, with a sedentary lifestyle being preferred [50]. Moreover, different molecular tools could help to uncover the community assemblage [55]. The biodegradation of specific contaminations using the microbe residing in unusual environments can be an important feature of pollution decrement. Use of the molecular level facts and details from microbial species can help to identify the microbial degraders and the corresponding genes responsible for the degradation of a specific contaminant. The application of next-generation sequencing tools, such as metagenomic approaches, can be a valuable tool for governing the interaction between various microorganisms. It also aids in obtaining facts and statistical data regarding microbial communities. Genetic information on diverse ecological microorganisms may be useful in finding responsible enzymes capable of digesting certain contaminants [56].

8.6.3.1 Metagenomics

A facile technique, metagenomics, can offer a large-scale inspection of the complex microbiome [56]. Metagenomics encompasses sampling the genome sequences of organisms that inhabiting a normal environment. Using metagenomics, a large quantity of information on microorganisms can be conquered that were not even known. The main approaches of metagenomics are depicted in Figure 8.3. Metagenomics is a popular tool for exploring uncultured species in the field of microbial diversity.

As explained, metagenomics can be a proven technique to investigate the hidden genetic structures. A notable example which studied by Sulaiman et al. for LC cutinase activity. In this study, the functional screening metagenome was used by tributyrin agar plates for LC cutinase activity. The study utilized the fosmid library of a leaf branch compost metagenome. Then, the protein engineering was applied to modify and termed as LC cutinase. LC cutinase serves as a potential model for mechanistic study. It has a better role in surface modification and the degradation of PET fibers [57]. Wei et al. have taken better metabolically active catalysts by high-throughput screening methods. In this method, polyester hydrolase activities were investigated for hydrolysis of PET [58]. However, the detection of new microbial polyester hydrolases and the construction and assembly of metabolically active enzymes are still challenging to eradicate polyethylene waste [59]. Different communities of archaea, bacteria, and eukaryotes (single-celled) may occupy the plastisphere. They play a vital role in plastic degradation and also in human health [60]. In this view, this cultivation inhibition can be altered in the view of the microbial diversity and limited our appreciation of the microbial world through screening throughput and computational techniques [61]. So, it is indispensable to identify the genetic diversity, ecological roles, and population structure using a culture-independent approach. Recently, the shotgun metagenomic sequencing technique was applied by Pinnell and Turner for bioplastic microcosms and biofilms fouling plastic. The study explained that plastic biofilms are significantly affected by sulfate-reducing microbes [56]. In such a way, the studies on bio-plastic exposed

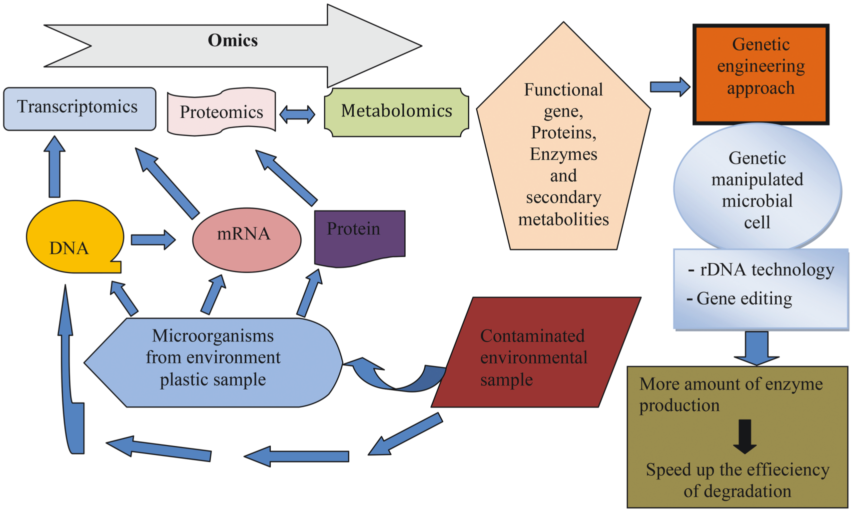

Figure 8.3: Application of omics-based technologies to generate efficient engineered bacteria and microbial enzymes for robust removal of micro-nano-plastic.

enhancement of the activity of depolymerases, esterases, dissimilatory sulfite reductases, and adenylyl sulfate reductases were also carried out [62]. Yet another study, for new species, *Desulfobacteraceae*, *Desulfovibrio*, and *Desulfobulbaceae* among the sulfate-reducing microbes, the metagenomic reconstruction of genomes was recognized. These genomes carry genes that are fundamental to both bioplastic degradation and sulfate reduction [56]. From the outcomes, it can be understood that the bioplastic can promote a rapid and remarkable shift in benthic microbial diversity and genomes, selecting for microbes that highly participate in the degradation of bioplastic and sulfate reduction. Metagenomics, or the culture-independent genomic analysis of assemblage microorganisms, has enabled large-scale investigations of complex microbiomes and answered some metabolic pathways of polymer degradation (Figure 8.3).

8.6.3.2 Metatranscriptomics

In the metatranscriptomics approach, DNA is transcribed into mRNA. The study of the metatranscriptomics profile of microbial diversity may be performed in a sample of a specific environment. Identification of mRNA transcripts for a certain microorganism can aid in the regulation of gene expression in a model based on specific atmospheric conditions [63]. Some complications are found to extract the mRNA from various environmental samples because of its short life which creates hindrance to separate mRNA from other RNA species [55]. Hence, this kind of mRNA sequencing approach becomes limited. This issue can be overcome by using an expression profile of the whole genome of microbial diversity. Shokralla et al. reported that the use of pyrosequencing can resolve and detect active genes [64]. Moreover, researchers are still investigating the presence of short RNAs and micro RNAs in various environmental strains to explain their roles in metabolic progressions. Still, they attempt to compare the generated metatranscriptomics datasets to other references of the same origin.

8.6.3.3 Metaproteomics

Only gene expression cannot indicate the function of microorganisms in a certain environment, therefore protein expression, which determines the proteomic profile of the organism of interest under the conditions examined, adds to the picture. Metaproteomics provides an effective alternative for recognizing the function, composition, and structure of different proteins present in genetic material. Henceforth, we can elucidate precisely about the limitation of molecular genomics for characterizing the function of the gene [63, 65]. So that, the environmental dynamics and fluctuations in the ecological system of a specific area can be understood precisely because the proteins can reflect the same. In addition, different genes functionality can be revealed by metaproteomics, thereby we can synthesis new proteins for specific benefits to the environment and microbial community. Protein characterization can also support acquiring more data of the phenotypic structures and folding patterns of proteins for a particular microbial community.

8.6.3.4 Metabolomics

The gene expression and characterization of protein alone may not express the various metabolites and whole-genome structure present in a sample. Hence, the study of metabolites, that is, the molecules or fragments that are percolated out into the surrounding environment, is required. This approach is called metabolomics [63]. The host environment can be affected by microbial diversity. Therefore, the use of the microbiome is gaining significant importance for understanding the roles of different pollutants and contaminants present in an environmental surrounding. The information attained from metabolomics differs from the datasets of metaproteomics and metatranscriptomics since the latter methods are elucidated in the sequencing of the genome, but the former identifies the significant metabolites. The quantification and recognition of metabolites in a specified environmental sample can be assessed using different techniques such as nuclear magnetic resonance spectroscopy, mass spectroscopy, and chromatography (liquid chromatography, gas chromatography, and ion-exchange chromatography).

8.6.4 Technologies for the remediation of micro-nanoplastics waste

8.6.4.1 Biotechnology

Biotechnological approaches such as enzyme engineering [65], strain engineering [66], *in silico* genome mining [55], and metagenomics [56] have been developed to address the remediation of microplastics and nanoplastics. Through improved enzyme activity, protein-engineered bacterial strains can improve microplastic biodegradation [65]. For example, PET films/fibers were hydrolyzed more effectively by engineered bacterial strains than by wild-type enzymes. Engineered cutinases from *Thermomonospora curvata* also improved MP enzyme kinetics and biodegradation rates. Microbes can benefit from strain engineering since it can speed up their enzymatic activity. In this context, one modified strain of *Bacillus subtilis* showed increased PETase activity (ca 4-fold) [66]. The *B. subtilis* strain was generated by inactivating twin-arginine translocation complexes, which enhanced the degradation of microplastics and nanoplastics. The biotechnological potential of in silico genome mining could hasten the decomposition of microplastics [55]. Genome mining can also be combined with genomic, transcriptomic, and metabolomic data. In order to establish the active expression of a PETase-like enzyme/SM14est protein from a native Streptomyces signal peptide sequence, heterologous gene expression in *E.coli* was used. To efficiently degrade PS, a combination of physicochemical and biological treatments, such as ozonization, can be used in conjunction with biological material (*Penicillium variabile*) [67]. Another aspect of biotechnology is metagenomic analysis, which is crucial for identifying new enzymes for biodegrading microplastics. Shotgun metagenomic sequencing of biofilms revealed the distinct enzymes responsible for plastic degradation in this setting [56]. For example, new species of *Desulfovibrio, Desulfobacteraceae*, and *Desulfobulbaceae* have been identified among the vast SRM, and their genomes contain genes essential for bioplastic degradation and sulfate reduction [4].

8.6.4.2 A synthetic biology approach: microbial consortium

A microbial consortium is a symbiosis system that existing with the function-based microbial species. Recently, researchers are showing huge interest in finding a potential synthetic microbial consortium for the degradation of plastics polymers [52]. There is more intention has been given to organize and optimize the members of the microbial consortium for a specific application, especially, the degradation of plastics [68]. Different enzymes and their reaction mechanisms are involved in the complete mineralization of biodegradation of plastics, typically, that does not occur in a single microbe. That can be comfortably performed by a microbial consortium. Recently, some of the potential microbial consortia have been explored for the degradation of plastics, the same has been presented in Table 8.2.

Syranidou et al. documented tailored indigenous microbial consortia that have prominent pertinency for the degradation of polyethylene, polystyrene, and other

Table 8.2: A representative study on microbial consortia approach for the biodegradation of plastics.

S. No	Microbial consortium	Plastic polymers	References
1	*Pseudomonas aeruginosa* MZA-85 and *Bacillus subtilis* MZA-75	Polyurethane	[69]
2	*Pseudomonas aeruginosa* and *Microbacterium paraoxydans*	Low-density polyethylene	[70]
3	*Pseudomonas and Bacillus* species	Polyethylene terephthalate	[71]
4	*Stenotrophomonas* sp. and *Achromobacter* sp.	Unpretreated low-density polyethylene	[72]
5	*Pantoea* sp., *Enterobacter* sp., and *Enterobacter* sp.	Low-density polyethylene	[73]
6	*Pseudomonas geniculata* WS3 and *Actinomadura* (isolated from dairy waste sludge)	Polylactic acid beverage cups	[74]
7	*Rhodotorula mucilaginosa*, *Cladosporium sphaerospermum*, *Penicillium chrysogenum*, and *Serratia marcescens*	Polylactide	[75]

plastic derivatives [44]. Moreover, a combination of cultures of *A. niger* and *L. xylanilyticus* which were isolated from landfill province showed a substantial degradation on LDPE. In this case, the biodegradation of LDPE was observed to be more effective in the presence of microorganisms. biodegradation of UV-irradiated and non UV-irradiated LDPE were found to be 15.8 and 29.5%, respectively at the end of 126 days [51]. In such a way, biodegradation studies on polyester polyurethane (PU) were reported by Shah et al. They investigated the mixed culture of *Pseudomonas aeruginosa* MZA-85 and *Bacillus subtilis* MZA-75. It was observed that the films of polyester PU attained the maximum weight reduction in 20 days. In addition, a Sturm test was performed to measure the carbon dioxide evolution during biodegradation which confirmed that the much higher CO_2 production compared to control [69]. Generally, there are two important aspects are responsible for developing the stable and efficient synthetic microbial consortium. Firstly, the organization of microbial consortia and the design principle applied for the goal. The regulatory mechanisms and fitness is considered as the second important factor [76]. The interaction among the microbes such as energy exchange, cell-to-cell communications, metabolites are mainly considered for the design, organization, and development of synthetic microbial consortium. Yet another important thing is understanding the above factors. This can provide clear guidance on the development of a synthetic consortium of microorganisms for effective polymer dissimilation [10].

8.6.4.3 Enzyme technology

Many microbe-derived enzymes may be utilized to efficiently break down plastics, particularly micro- and nanoplastics. For example, immobilization technology enables selective depolymerization, catalyst recovery, and enhanced enzyme performance [77]. The technique can also be coupled with nanotechnology to generate nanobiocatalysts. Schwaminger et al. recently immobilized PETase enzymes to magnetic iron oxide nanoparticles for the breakdown of microplastic PET [78]. The approach allows for high enzyme loading of up to 0.47 $g\ g^{-1}$, strong affinity, and magnetic separation. Lipase and cutinase were covalently immobilized on carrier nanoparticles (SiO_2 and $Fe_3O_4@SiO_2$) for enzymatic decomposition (hydrolysis/oxidation) of electrospun polycaprolactone fiber mats [77]. The authors further verified the degradation of the synthetic polymers through morphological (SEM) and weight loss studies.

8.6.4.4 Membrane technology

Microplastics and nanoplastics discharged into the environment from wastewater treatment plants can be removed using a number of techniques, including granulated activated carbon and sand filtration, coagulation–flocculation, precipitation, and sedimentation [79, 80]. However, these approaches have drawbacks in terms of the generation of a high volume of chemical sludge, which is linked with numerous difficulties such as an increase in turbidity and a loss in disposal potential. Membrane technology has been demonstrated to be more effective than older techniques in removing microplastic pollution from wastewater treatment plants [4]. It has a number of advantages over traditional approaches, including a high rate of contamination removal, simplicity to operate, and low sludge creation. Mostly, membranes-driven separation processes are made through ultrafiltration, nanofiltration, and reverse osmosis [79, 81]. Membrane ultrafiltration is well-established for removing pollutants from wastewater treatment, such as microorganisms, tiny organic acids, and soluble microbial metabolites. Nanofiltration can also be used to remove nanosized pollutants [81]. Membrane technology is thus an excellent way for removing microplastics and nanoplastics from water bodies, and further degradation and utilization of these harmful contaminants is necessary for a pollution-free world [4, 79, 81].

8.6.4.5 Nanotechnology

Nanotechnology has the potential to be a promising technology for investigating appropriate strategies for cleaning up microplastics and nanoplastics in the environment [4]. The addition of nanoparticles to microbial cultures improves plastic biodegradation [78]. The presence of SiO nanoparticles has been shown to affect the growth of bacteria that degrade plastic [77]. This nanoparticle improves bacterial growth by drastically increasing the rate of plastic breakdown. However, when bacteria are given a small amount of nanoparticles, they work well and degrade plastics by weakening the hydrocarbon chain and forming different byproducts. According to Kapri et al., adding nanoparticles such as superparamagnetic iron oxide (SPION) and nano barium titanate (NBT) to LDPE improves degradation [82]. The presence of nanoparticles in bacterial culture media not only boosts their development by accelerating the exponential phase, but it also improves the biodegradation efficiency.

8.7 Practical snags and the future direction of research

Plastic production and consumption will continue to rise in the future, posing a further threat to the environment. Although multiple microorganisms have been reported to degrade plastic, its slow biodegradation is still limiting the large-scale bioremediation process. Moreover, it remains difficult to identify and isolate potentially active and functional enzymes for MNPs breakdown. Metagenomics approach may help to uncover uncultured microbes that could offer to set up function-based assays. In this regard, wide researches should be undertaken on this area. Moreover, synthetic biology technology may be used to produce engineered bacteria with enhanced metabolic abilities and greater potential to break down MNPs pollutants. Also, debates still remain regarding the mechanism and how the microbes and enzymes work on the degradation of MNPs. Therefore, it is important to identify appropriate microbes that can act on a wide spectrum of polymers, in specific, high molecular weight polymers. Besides, still there is a notable research gap on the reusability to build new materials using the monomers, dimers, and oligomers formed after the degradation of plastics. Finally, the use of enzymes and microbial actions which helps for restructuring and degradation of MNPs to ameliorate the biodegradation is a future challenge.

8.8 Concluding remarks

An accretion of micro and nanoplastics (MNPs) is looked as a serious issue among the environmental pollutants while they persist for a long time. While the cytotoxicity, neurotoxicity, and genotoxicity impacts of these pollutants on marine and terrestrial fauna and flora are well-known, efficient removal of these pollutants necessitates a wide range of research on environmentally friendly approaches, notably biodegradation processes. Several studies have proven that the remediation of MNPs through biotechnological approaches, notably with the use of microbes and their enzymes. This methodology can provide a virtuous platform for the effective remediation of MNPs via an ecofriendly style. Even though a collaborative action of nanoparticle technology, enzyme technology, and metagenomics is effective in the remediation of MNPs, it needs to acquire the insights of “micro-nanoplastics activeness” and its alleyway. Alternatively, biodegradable plastics are more sustainable compared to petrochemical plastics, and therefore it is critical to address the challenges that have limited the use of biodegradable plastics in some applications. Consequently, worldwide micro-nano-sized plastic pollutants can be considerably reduced for healthy future generations.

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9 Phytoremediation as an effective tool to handle emerging contaminants

Abstract: Phytoremediation is a process which effectively uses plants as a tool to remove, detoxify or immobilize contaminants. It has been an eco-friendly and cost-effective technique to clean contaminated environments. The contaminants from various sources have caused an irreversible damage to all the biotic factors in the biosphere. Bioremediation has become an indispensable strategy in reclaiming or rehabilitating the environment that was damaged by the contaminants. The process of bioremediation has been extensively used for the past few decades to neutralize toxic contaminants, but the results have not been satisfactory due to the lack of cost-effectiveness, production of byproducts that are toxic and requirement of large landscape. Phytoremediation helps in treating chemical pollutants on two broad categories namely, emerging organic pollutants (EOPs) and emerging inorganic pollutants (EIOPs) under *in situ* conditions. The EOPs are produced from pharmaceutical, chemical and synthetic polymer industries, which have potential to pollute water and soil environments. Similarly, EIOPs are generated during mining operations, transportations and industries involved in urban development. Among the EIOPs, it has been noticed that there is pollution due to heavy metals, radioactive waste production and electronic waste in urban centers. Moreover, in recent times phytoremediation has been recognized as a feasible method to treat biological contaminants. Since remediation of soil and water is very important to preserve natural habitats and ecosystems, it is necessary to devise new strategies in using plants as a tool for remediation. In this review, we focus on recent advancements in phytoremediation strategies that could be utilized to mitigate the adverse effects of emerging contaminants without affecting the environment.

Keywords: biomagnification; detoxification; emerging contaminants; environment; phytoremediation.

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9.1 Introduction

Environmental pollution has been one of the major outcomes in the post-industrialization era. The industries that have been a source of pollutants has ranged from normal mining process to the highly advanced products such as electronics, solar cells, lithium-ion batteries and even the most recent nanomaterial-based products. Though these industries have contributed a lot in terms of improving the life style and ease of living, they on the flipside have been availed at the cost of the environment. These pollutants from natural and anthropogenic activities have slowly found their way into the food chain of the humans either through biomagnification or through direct consumption, thus causing various health hazards to the human health. In this scenario, these emerging new age pollutants present in the environment have to be removed using sustainable and cost-effective methods in the bioremediation process [1].

Phytoremediation is one of the various remediation techniques wherein, plants and algal based remediation of the pollutants is performed in a more sustainable and cost-effective manner. There has been a concerted effort by the researchers in identifying an efficient phytoremediation approach for degrading both organic and inorganic contaminants. Initially, phytoremediation was one of the most sought techniques in cleaning the wastewater consisting of both types of contaminants. In this effort, water hyacinth had played a major role in remediating the contaminants. Further, the plants used for phytoremediation can be processed for other potential uses as in case of water hyacinth [2].

It has been observed by the previous researchers that many persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) produced by both natural and anthropogenic sources have been a cause of concern in terms of increased incidence of mutation and hormone related cancers [3, 4]. In addition, another class of emerging organic pollutants have been the polybrominated diphenyl ethers (PBDEs) that is predominantly used in textiles, paints and electronic circuit boards (ECBs) has been the root cause of reproductive disorders, disruption in thyroxine homeostasis [5]. These POPs that have been recognized as the emerging contaminants have started to occupy natural resources such as marine ecosystem [6] and as well as in soil [7], where their binding with other biomolecules such as lipids and carbohydrates make them a stable feature in the nature.

In addition to the organic contaminants, inorganic contaminants have been a persistent enemy in polluting the environment to a greater extent; with their half-lives being greater than the organic contaminants it becomes even more important for addressing the issues. Inorganic pollutants are artificial substances that arise from cosmetics, pesticides, pharmaceuticals, agricultural runoff, aquaculture and health care products, which have become one of the major causes of concern as an emerging contaminant in the past decade only [8]. With the increase in utilization of new artificial substances there is a definite fear of increase in the concentration of these inorganic pollutants in various walks of life. The issue of inorganic pollutants has been addressed through the various other remediation processes, but phytoremediation has been identified to be the most effective way of restoring the native environment in the polluted sites [9, 10].

The metal contaminants released from motor transportation are one of the major emerging contaminants in addition to air pollution [11]. Besides, the transportation industry also contributes heavily to pollution in the form of synthetic and natural polymers used in tire manufacturing [12]. Similarly, other emerging contaminants like perfluorinated compounds, flame retardants, disinfectant by-products, hormones, steroids, nanomaterials, benzotriazoles, detergents and sulfamethoxazole has also contributed in polluting the environment [13, 14]. Other than these contaminants, antimicrobials like rifaximin, linezolid, and penilloic acid are also reported in wastewater effluents coming from hospitals and pharmaceutical industries. The treatment processes of wastewater effluents also serve as a source of new contaminants which is a threat to human health [14, 15]. For instance, microbial degradation of drug allopurinol in wastewater bioremediation results in the discovery of oxypurinol as emerging pollutant [16].

It was reported by Yang and Zhang [17] that many bromides and iodides disinfection agents were found in the chlorinated saline sewage effluent. Due to the recent advancements in analyzing techniques we are able to identify and detect this emerging contaminant which is having a great impact on aquatic life, environment and as well on human health [14]. In this review, we have tried to bring insights into the recent trends that have emerged in the phytoremediation of the EOPs and EIOPs that can pose a persistent damage to the environment in the future. The over dependency on technology will constantly pave way for novel and more persistent pollutants, that has an effect on the environment and thereby, different strategies of phytoremediation could play an important role in the removal of these pollutants (Figure 9.1). Thus, concerted strategies to develop novel phytoremediation techniques as well as to identify new potential plant and algal varieties have to be initiated to counter the problem of pollution in future.

9.2 Transportation and manufacturing by-products

In older days, Butyl rubber (IIR) has been used for tire manufacturing because it has great properties such as low permeability, damping and high chemical stability to liquids and gases to enhance the tire property. However, it has some limitations like poor adhesion, low cure rate and compatibility with unsaturated rubber. In recent days, bromine is added with butyl rubber to form brominated butyl rubber (BIIRs) tire. As a result, the brominated butyl rubber overcomes the limitations of IIR by reveal greater cure rate, blending, and better compatibility with other rubbers. But this

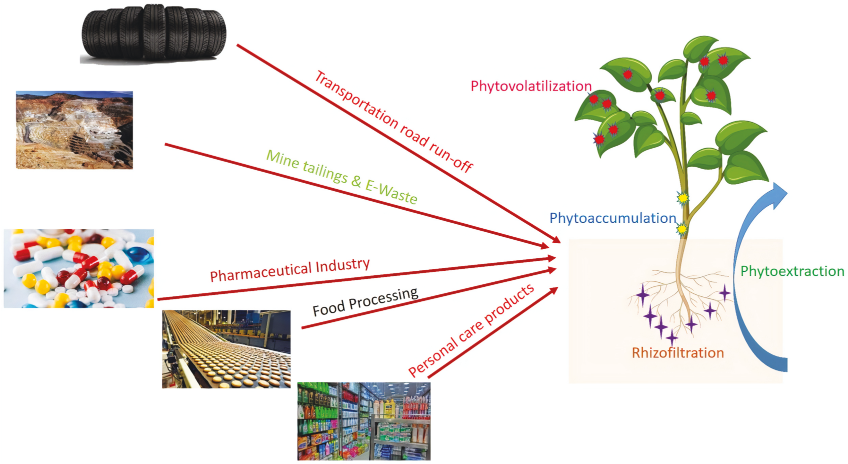

Figure 9.1: Sources of emerging environmental contaminants and its remediation through plants.

advancement is recognized as major emerging environmental contaminants, which is formed from tires undergoing friction on the road. It is anticipated that this surface runoff transport tire wear particle from the road towards the water bodies [18] and or to its surrounding environment. Along with bromide, titanium, copper, chromium, lead and zinc are other notable contaminants that have similar effects to both life and environment [19]. Studies on these emerging contaminants are very important because of the adverse effects on human health which is not completely understood. These emerging metals could bind on fatty tissue of human beings leading to damage of specific organs and nervous system as well as it affects the roadside vegetation and wildlife. Moreover, the aquatic organisms are more sensitive to these emerging contaminants which interfere with normal function of the endocrine system [20]. There is not much of research that has been conducted especially on the remediation aspect of the transport vehicle released contaminants that contaminate soil and water. Even though numerous methods are being used in removal of such heavy metals, there are certain limitations. Despite many remediation techniques, phytoremediation is becoming a convincing tool to detoxify the hyper-accumulation of these emerging toxic metals in soil and water. The plants can reduce the toxic substances to less toxic chemicals/metals by phytostabilization, phytoextraction, phytovolatilization, and rhizo/phyto filtration (Figure 9.2) [21]. The emerging metal Br was accumulated by wheat (*Triticum aestivum* L.) and pea (*Pisum sativum*) plant successfully through phytoextraction method [22]. The heavy metal Mg, Zn contaminated soil was restored through the process of phytoextraction by three forest spp. Scot's pine, Norway spruce and oak aided with application of sewage sludge [23]. In addition to the above said plants species that are involved in phytoextraction of heavy metals and halogenic substances, there are few more plant species that have shown the ability to produce the

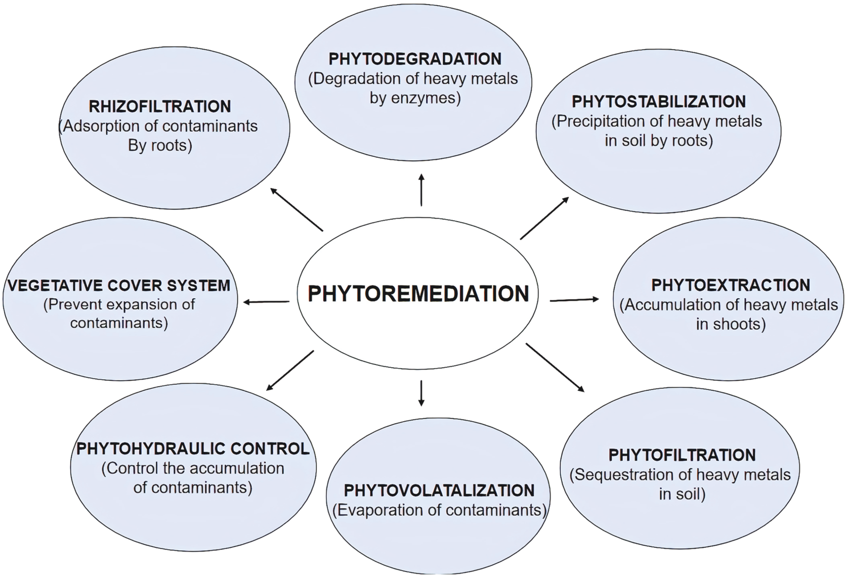

Figure 9.2: Various phytoremediation mechanisms involved in the restoration of environment.

phytoremediation effect in the environment (Table 9.1). Hanafiah et al. [24] reported that the aluminum (Al) was effectively removed by a method of phytoremediation using *Ipomoea aquatica* and *Centella asiatica*. These studies have shown that the surface runoff transport tire wear particle from the road could be accumulated and remediated by planting the above said plants on road sides. Moreover, the polybrominated diphenyl ethers (PBDEs) have been ubiquitously found in different environment [42]. Notably, the PBDEs are high in cars and other finish products that cause serious damage to both living organisms and the environment. Over the years, numerous remediation methods have been used for effective removal of PBDEs including physical, chemical, biological and combined techniques. Since, the recent studies reported that phytoremediation have been used for successful removal of PBDEs. Farzana et al. [43] investigated the PBDEs removal ability of three mangrove plants viz. *Aegiceras corniculatum*, *Kandelia obovate* and *Avicennia marina*, effective accumulation was observed in all the three plants. Yang et al. [44] investigated the removal of BDE-3 by white radish (*Raphanus sativus* L.) wherein accumulation was observed in different parts of the plant. The common aquatic plants such as *Scirpus validus*, *Phragmites australis*, *Alternanthera philoxeroides*, *Oryza sativa*, *Cyperus papyrus*, *Acorus calamus* and *Colocasia esculenta* have potential to remove PBDEs from contaminated soil [45]. Among all test plants, the *Oryza sativa* has more potent to uptake and accumulation the PBDEs in root. In addition, phytoremediation with special microbes is the most effective and successful method to remove BDE. This

Table 9.1: Selected plants used for phytoremediation of metal contaminants.

Name of the contaminants	Method of remediation	Plant type used	Plant parts involved in remediation	Reference
Cd, Zn and Pb	Phytoaccumulation	*Scots pine* (*Pinussilvestris* L.) and *Norway spruce* (*Piceaabies* L.)	Hole plant absorption	[23]
Al and Fe	Phytoaccumulation	*Ipomoea aquatica* and *Centellaasiatica*	Hole plant absorption	[24]
Pb, Cd, Cu, Zn and Ni	Phytoextraction	*Amaranthus* spp.	Young plants	[25]
Cd, Cr, Pb, Zn, Ni and Cu	Phytoaccumulation	*Jatrophacurcas*	Hole plant absorption	[26]
Cr, Cu and Pb	Phytoaccumulation	Macrophytes (*Hydrillaverticillata* and *Marsileaminuta*)	Hole plant absorption	[27]
Al, Cu, Zn, Pb and Cd	Phytostabilization	*Jatrophacurcas*	Roots	[28]
Cr	Phytostabilization	Weed plant (*FIpomeacarnea* and *Jatrophagossypiifolia)*	Root and shoot	[29]
		Juncusacutus	Hole plant absorption	[30]
		Mauritius hemp (*Furcraeagigantea* Vent.)	Biomass of root and leaf	[31]
		Crown of thorns (*Euphorbia milli*)	Hole plant absorption	[32]
		Rose	Root and shoot	[33]
		Tubersoe (*Polianthestuberosa*)	Hole plant absorption	[34]
		Pterocarpusindicus and *Jatrophacurcas* L.	Root and shoot	[35]
		Fenugreek (*Trigonellafoenumgraecum* L.) Spinach (*Spinaciaoleracea* L.) and Raya (*Brassica campestris* L.)	Hole plant absorption	[36]
Bromine	Phytoextraction	*A. thaliana* and *S. grandiflora*	Hole plant	[37]
		Wheat (*Triticumaestivum* L.) and pea (*Pisumsativum*)	Leaves	[22, 38]
Polybrominated diphenyl ethers	Phytoextraction	Couch grass and wheat	Leaves, upper part of plant	[39]
Bromide		Kandeliaobovata	Root	[40]
		S. grandiflora Salicorniabrachiata, *Suaedanudiflora*, and *Salvadorapersica*	Root, stem and leaves	[41]

combined remediation method actually helps to increase the rate of phytoremediation [46]. For instance, the plant *Laccaria amethystine* and *Cenococcum geophilum* were inoculated with Japanese black pine seedlings had reduced the concentrations of BDE [47].

9.3 Pharmaceutical products

In the past, the benefits of these pharmaceutical products outweighed their effect on the environment, but in recent times these products are considered as one of the emerging pollutants that has adverse effects on living organisms [48]. Pharmaceutical products enter the soil and aquatic ecosystem as sewage sludge residues, human and animal excretion [49, 50]. The pharmaceutical products that are classified as emerging contaminants include analgesics, antibiotics, anticoagulants, anticonvulsants, antihistamines, antipyretics and beta blockers [51]. The emergence of steroid hormones (estrogen, progesterone, testosterone, phytosterols, glucocorticoids) and veterinary growth hormones commonly used to treat human and animal diseases as contaminants is a real concern as they have long-term and short-term effects on human health [52, 53].

Recently phytoremediation has been successfully employed to remove emerging pharmaceutical contaminants from aquatic systems. The contaminants are either degraded by rhizospheric activity of microbes or chemically altered by plant roots [54]. Kotzya et al. [55] have reported that the analgesics such as acetaminophen, ibuprofen and diclofenac which at higher concentrations cause hepatotoxicity in humans can be removed using *Armoracia rusticana* hairy root cultures and *Linum usitatissimum* suspension cultures. Also, the hydroponic set up of *Lupinus albus* and *P. australis* plants showed the effective removal of acetaminophen and ibuprofen, respectively. Studies *in vitro* using the plant *Cicer arietinum* (black chick pea) which has previously exhibited ability to remove heavy metal contaminants has showed promising results in remediating the antibiotic tetracycline as well [56]. This result has paved the way to explore more about the phytoremediation ability of *C. arietinum* on other pharmaceutical products. Shikha et al. [57] have extended the focus to look for the phytoremediation ability of *C. arietinum* on ciprofloxacin (antibiotics), progesterone and estrogen (hormones). The overall percentage of remediation of the plant was found to be 60% for ciprofloxacin 63.3% for estrogen and 64.66% for progesterone, respectively [57]. Pharmaceutical compounds such as acetaminophen, carbamazepine, clofibric acid, diclofenac, ibuprofen and propranolol were shown to be effectively removed by two aquatic plants – *Spirogyra* sp. and *Lemna* sp. [58]. Similarly, Martins et al. [59] have demonstrated that the plant *Solanum nigrum* L has tolerance mechanism against paracetamol suggesting that they can be used for the phytoremediation of paracetamol.

Brassica juncea was another plant that was used for the phytoremediation of aspirin and tetracycline. The study found out that the average remediation rate was approximately 90% for aspirin (analgesic) and 71% for tetracycline (antibiotic), respectively [60]. Similarly, Hoang et al. [61] have found that wetland plants *Rhizophora apiculate Blume Fl. Javae* and *Acrostichum aureum* L. could be used for the phytoremediation of antibiotics such as ciprofloxacin and norfloxacin detected in shrimp farm sediments [61]. Experiments carried out using the hairy root cultures of *Helianthus annuus* (sunflower) has shown that the plant could be used to degrade tetracycline and oxytetracycline from aqueous media. The mechanism of degradation involves the rhizospheric activity of the root system and involvement of reactive oxygen species (ROS) [62]. Aquatic plants, *Pistia stratiotes* (water lettuce) and *Myriophyllum aquaticum* (parrot feather), were demonstrated to show high modification rates for both tetracycline and oxytetracycline, used in veterinary medicine in aqueous media [63]. Also, macrophytes such as *Ceratophyllum demersum*, *Egeria densa* and *M. aquaticum* were shown to effectively remove diclofenac and microcystin-LR from contaminated reservoir, thereby suggesting that aquatic macrophytes could play a significant role in the removal of pharmaceutical contaminants [64]. Turcios et al. [65] have shown that the haplophyte, *Tripolium pannonicum* could be used effectively to remove several emerging pharmaceutical contaminants, thereby suggesting the role of *T. pannonicum* in up taking and degrading xenobiotic compounds. Thus, phytoremediation seems to be a better option for the removal of pharmaceutical contaminants but requires the proper selection of plants based on the type of contaminants and the mechanism of remediation. Further research is needed to look into identifying several other pharmaceutical contaminants and the means of remediating them.

9.4 Personal care products

The use of personal care products has seen a rise in the last few decades among the growing population. It includes a diverse group of products ranging from beauty, personal products to cleaning products that are used on a daily basis [66]. The cosmetic products that are intended for external use on humans also contains several toxic and nonbiodegradable compounds like organic and inorganic filters, parabens, triclosan and microplastics [67]. Aryal et al. [68] have demonstrated that the roots of zucchini (*Cucurbita pepo* cultivar Gold Rush) and pumpkin (*C. pepo* cultivar Howden) hydroponically grown were able to accumulate triclocarbon and triclosan. Experiments were also conducted on food crops to evaluate whether they can uptake and accumulate contaminants. The crops were grown on hydroponic media and were exposed to contaminants like triclocarban and triclosan. The results indicated that food crops such as asparagus, celery and pepper showed high levels of accumulation and translocation of triclocarban while broccoli, cabbage, and asparagus showed accumulation of triclosan [69].

Similarly, the aquatic plant duckweed was investigated for its ability to remove emerging pharmaceutical and personal care contaminants. The results showed that DEET (N, N-diethyl-m-toluamide) was removed in negligible levels but there was an increase in the removal of ibuprofen and triclosan. Specifically, triclosan was removed by the passive sorption process while the degradation products of triclosan were removed by the enhancement of microbial degradation. This suggests that the aquatic plants utilize both the active and passive process for the efficient degradation of emerging pollutants [70]. Couto et al. [71] have demonstrated that the salt marsh plants *Spartina maritima* and *Halimione portulacoides* also have the ability to remediate caffeine, oxybenzone and triclosan through plant uptake and adsorption. Apart from aquatic plants, free floating macrophytes, *Landoltia punctata* and *Lemna minor* have also been shown to remove methyl and propyl parabens from domestic sewage [72]. More studies are warranted in the field to ascertain the role of plants in remediating emerging contaminants especially chemical compounds from personal care products.

9.5 Nanomaterials

Nanomaterials are widely used in industrial and domestic sectors especially in manufacturing pharmaceutical, cosmetic and medical products thereby increasing their presence in the environment. The toxicity of these nanomaterials, their adverse effects on living forms and the nonavailability of standard detection methods is a major concern [73]. Zainab et al. [74] have reported the occurrence, risks and toxicological effects of silver nanoparticles on humans and environment. They have shown that *P. stratiotes* (water lettuce) and *Eichornia crassipes* (water hyacinth) could be used for the efficient removal of silver nanoparticles from water. Similarly, Hanks et al. have demonstrated that *P. stratiotes* acts as a good phytoaccumulators and could reduce even higher concentrations of silver nanoparticles present in contaminated waters [75]. The salt marsh plant, *P. australis* has also been shown to possess the ability of up taking silver nanoparticles and thereby, could be used for the phytoremediation process [76]. A study conducted on to investigate the phytoremediation potential of aquatic plants (*Elodea canadensis*, *Limnobium laevigatum*, *Najas guadelupensis*, *P. stratiotes* L., *Salvinia natans* L., *Riccia fluitans* L. and *Vallisneria spiralis* L.) showed that there were changes in the levels of metal nanoparticles (Ag^+, Ag_2O, Cu, Mn, Zn) after the exposure to plants suggesting the phytoremediation role played by these plants [77]. Similarly, Bernas et al. [78] has shown that silver ions and silver nanoparticles in aqueous medium can be removed using the common water weed *E. densa*. They found that the plant showed better bioaccumulation of silver at low concentrations and thereby could be used as a potential plant for the phytoremediation of silver nanoparticles [78]. These studies indicate that more research is required to identify plants that have the potential to remediate these nanomaterials.

9.6 Food processing and packaging materials

Food additives which are added intentionally or unintentionally for commercial purposes should not contaminate the food [79]. Among the many methods that are available for treating the contaminants, bioremediation is the more effective method. In bioremediation phytoremediation is getting more importance because of its advantages and more effective treatment [80]. Emerging contaminants in the food processing and packaging industry especially include acrylamide, 1,4, dioxane and Bisphenol A (BPA).

Acrylamide intake was mainly through the food which has undergone heat treatment at high temperatures of more than 120 °C [81]. It is a neurotoxic, mutagenic and carcinogenic chemical that can be released into the soil through water run-off [82]. Annie Melinda et al. [83] studied the ability of the tropical plants for the accumulation of the acrylamide in the root, shoot and the whole plant. Study shows that among the six plants, mustard (*Brassica* sp.) shows the highest accumulation in root, shoot and the whole plant at levels of 2372.9, 4081, 6512.8 mg/kg, respectively. In another study, *Arabidopsis* sp. the model plant from Brassicaceae family was used for the remediation of acrylamide contamination and the results showed the accumulation and degradation of the contaminant by the same plant [84].

1,4-Dioxane is a chemical in chlorinated solvents which can be used as a stabilizer in the production of deodorants, paints, dyes, antifreeze, shampoos and cosmetics, food products as an adhesive material, pesticides and food additives. This compound is a potential carcinogen and it can cause serious liver toxicity and degeneration of hepatic cells [85]. It has been reported that the remediation of the compound is challenging because of its physical and chemical properties, and other methods like adsorption by activated carbon, reverse osmosis, membrane filtration proves to be ineffective because of its neutrality and smaller size [86, 87]. Phytovolatilization can be used for the treatment of dioxane, the hybrid poplar trees can readily take up the pollutant from the dissolved soil water and which can be transferred to the environment in the nontoxic form through stomata; this method can remove up to 80% of the dioxane contamination [88]. Bioaugmentation of the poplar tree in the rhizosphere region with *Mycobacterium dioxanotrophicus* and *Pseudonocardia dioxanivorans* can increase the potential of the degradation of 1,4 dioxane. Combining the phytoremediation and the bioaugmentation is also a potential method for the treatment of the dioxane contamination [89].

Bisphenol A (BPA) is used in several industries for the production of construction pipes, drinking water pipes, recyclable water bottle, food cans, toys and car tires, as paper coatings, electrical and electronic equipments. BPA is an endocrine disruptor, can mimic the hormones which may act as an antagonist of androgen and estrogen, can affect fetal development, carcinogenic, liver damage, cause cardiovascular diseases and diabetes [90]. Zaho et al. [91] studied about the *in vitro* removal of BPA contaminated water by using two submerged macrophytes *C. demersum* and *Myriophyllum* *spicatum* from Donghu lake. Among the two plants *C. demersum* proved to have the potential in removing the contaminant from water. In another study *Panicum virgatum* was tested for the removal of the BPA from landfills and this switch grass proved to be effective in the remediation of the pollutant [92]. *In vitro* study of *P. stratiotes* also showed the removal of BPA from the water [93]. The mangrove plant *Bruguiera gymnorhiza* is also very effective in the removal of the contaminant and almost 99% of the BPA was removed from the wastewater along with the reduction in the TDS [94]. The tropical plants *Dracaena sanderiana* in association with bacteria *Bacillus cereus* strain BPW4 and *Enterobacter* sp. strain BPW5 was able to remove the BPA from the industrial contaminated water [95].

9.7 Mining by-products

Mining for organic and inorganic elements have been an age-old tradition with the requirement of the tools for human life became a necessary evolution thousands of years ago. Mining plays an important role in the development of various civilizations of the world. The pace of mining amplified post-industrialization, with requirement for metals, fuel and other elements necessary for energy generation [96, 97]. The mining industry has served to be a boon to the human kind for bringing in development, but the pollution that is generated due to the mining tailings was not addressed efficiently in the early years.

In the recent years, many researchers have focused on addressing the contamination in the mining sites using the phytoaccumulation and phytoextraction techniques. A study by Marrugo-Negrete et al. [98] had showcased the ability of herbs such as *Stecherus bifidus*, *P. marginatum* and sub shrubs such as *C. annum* and *Jatropha curcas* to accumulate Mercury (Hg) in the roots and shoots of the plants. An earlier study by the same group in 2015, had suggested that *J. curcas* (Euphorbiaceae family) showed the highest accumulation of Hg in the second and third month of exposure [99]. Similar studies in the mining sites of heavy metals using the assisted phytoremediation techniques with plants such as *Chrysopogon zizanioides* and *Typha latifolia* in the presence of Aluminum sulfate and EDTA showed significant increase in the accumulation of Hg, Zn and As from the mining sites [100].

Studies on remediating chromium contamination in mining sites using the herbs such as *Vetiveria zizanioides* assisted by microorganisms such as *B. cereus* have shown a promising efficiency in removal [101]. In addition there have been studies on other plants such as *Sesbania sesban* and *Prosopis laevigata* associated with *Bacillus* sp. has promoted the accumulation of Cr from the soils by increasing the available form of Cr in the soil [102]. Another study by Zhang et al. 2020 [103], showed that *Paspalum conjugatum* expressed abilities to hyperaccumulate Cd and Pb from the mining sites [103]. The remediated sites showed a significant decrease in the rare earth metals (Table 9.2).

Table 9.2: Important rare earth metals produced as mine tailings that are phytoremediated using plant species associated with microorganisms.

Mining sites	Plant species	Type of phytoremediation	References
Mercury (Hg)	*J. curcas*, *P. marginathum*, *C. annuum and S. bifidus*	Phytoaccumulation	[98, 99]
Chromium	*Suaeda vera*, *Vetiveria zizanioides* *Tagetes erecta*	Phytoaccumulation associated with microbes	[101], [102]
Arsenic (Ar)	*P. vitatta*, *P. cretica*, *B. nivea*	Phytoaccumulation	[100]
Cadmium (Cd)	*Paspalum conjugatum*, *Pseudotsuga menziesii*	Phytoaccumulation	[103, 104]

9.8 Batteries and E-waste

9.8.1 Lithium

Lithium is one such alkali metal that has gained importance since the advent of the lithium-ion batteries. This has contributed to a greater extent to the expansion of the electric or hybrid vehicles in this decade [105, 106]. Since the world has started to move towards a cleaner fuel, there should be little apprehension about the increase in sales in lithium-ion powered vehicles. Lithium is an element that is extracted from various sources such as sea water, geothermal brines and hard rocks [107]. Since lithium is present in combination of other elements such as Na, Ca and Mg in the environment, there is high possibility of these metals being released in to the environment. Besides, the lithium-ion batteries (LIBs) are manufactured by using other electrode materials such as Nickel, cobalt and Manganese, which form the part of the cell housing materials [108]. Also, the purification of the Li involves utilization of soda ash for conversion of naturally occurring lithium chlorides to lithium carbonates. Thus, the whole process of both extraction and purification of the lithium ions, along with the manufacturing the LIBs is a process that involves large scale contamination of the environment. This has made the remediation of these metals, SO_4^-, chlorides and Li itself from the environment becomes more necessary, either through bacterial remediation or with phytoremediation techniques. Phytoremediation of Ni, Co and Mn has been conducted with plants such as *Alyssum murale*, as the plant has been found to serve as a good hyperaccumulator and thus also help in the process of phytomining. The plant *A. murale* belonging to Brassicaceae has been considered a model organism for phytoremediation, in case of Ni and Co remediation [109]. Further, it has been identified by Tappero et al. [110] that *A. murale* can be used for hyperaccumulation of metals used in LIBs. Also, in a study by Henschel et al. [108] it has been observed that Li hyperaccumulation by *A. murale* was satisfactory enough to be considered a very good plant for phytoremediation in LIBs associated contamination sites.

Besides, silica has been one of the most sought-after materials for manufacturing solar panel wafers currently, but it has been in use for many years in industries involving metal manufacturing, structural clay products and furnaces. Despite being a very dangerous pollutant, silica dust has been observed to be one of the components in the soil that has the ability to reduce the accumulation of toxic of heavy metals like As and Cd in rice plants [111, 112]. This ability of silica to reduce accumulation of heavy metals can also be used for improving the efficiency of growing plants in heavy metal contaminated sites.

9.9 Radioactive elements

Radioactive minerals have been mined from the environment since the early part of the 20th century for various purposes, but its usage has been vastly advanced with the introduction of radioactive elements like uranium and thorium for energy production purposes in the last century. The mining of the radioactive elements has also enhanced the challenge of dealing with the contamination in the local areas of mining and as well in the extended regions around it. The radiation that emanates from the radioactive elements can cause mutations in the human system leading to birth defects and cancer [113]. To deal with these ill effects of the radioactive elements various strategies have been followed, of which phytoremediation was used for removal of the contaminants with moderate efficiency [96].

It has been identified in a study by Dushenkov et al. [96] on the phytoremediation of the contaminated Chernobyl site that, *Amaranth cultivars*, peas and sunflower had accumulated radioactive ^{137}Cs with moderate ability. Of these plants, *Amaranthus retroflexus* sp. had shown a high accumulative capacity in a combined manner [96]. Studies have revealed that *Juncus effuses* had the highest ability to uptake the ^{226}Ra from the soil with compared accumulation ability being 35 times the control site [114]. It was also observed that *Acacia albida* and *Acacia nilotica* had also recorded an ability to absorb the uranium present in the soil [115]. The most recent study was on the ability of *Eichhornia crassipes or water hyacinth in uptake of the radionuclides* ^{37}Cs and ^{60}Co from water. It was observed that the uptake of either of these elements from water by the plant was complementary in nature [116]. Besides the above represented work on the phytoremediation of the radionuclides, there has been dearth of the research in the recent times. Hence, with nuclear energy being the cleanest form of energy to the environment, the attention on even mitigating this problem will help the energy become the most advantageous form of power production.

9.10 Conclusion and future prospects

This review has been focused on countering the various emerging contaminants that have been or will be a threat to the environment in the future. The observations by various researchers have shown that there have been efforts to mitigate the effects of pollutants in the environment through bioremediation procedures. But the fundamental understanding of the remediation process has been that phytoremediation with slight modifications in its implementation has potent application in restoring the contaminated land and water resources to its native state. The new and emerging pollutants have posed challenges in this regard; thus, it has become a necessity to identify and analyze the plant species that can be employed in the remediation process. Further research is warranted specifically to identify emerging contaminants and also to mitigate the health hazards of these contaminants through novel phytoremediation strategies.

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10 Recent advances and prospects for industrial waste management and product recovery for environmental appliances: a review

Abstract: Any material when utilized for a required period of time and segment, the leftover residues of those materials are known as waste. Enormous waste is generated during such wear and tear process of materials depending on the usage and functions in a routine lifestyle. Those generated waste when overloaded beyond the capacity of natural recycling processes, would influence the environment and human health. Hence, the waste generated from used materials should be managed according to the environmental impact. Even though wastes are also sometimes rich in organic compounds, nutrients, and energy resources, they are not experimented and managed appropriately. Recently, different feasible techniques are invented and followed to recover and reuse the efficient resources that can create and support sustainable livelihood by creating green economy effects by reducing waste. In this chapter, the emphasis has been given to providing an overview of recent advancements on bio-based waste management and product recoveries such as microbes mediated approaches, biorefineries for waste valorization, and bioenergy from industrial waste.

Keywords: bioenergy; industrial effluents; microorganisms; product recovery; waste management.

10.1 Introduction

The rapid growth in urbanization significantly contributes to a notable increase in numerous wastes such as municipal, industrial, agricultural, and food debris materials. Due to anthropogenic proceedings, millions of tons of wastes are produced every

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day [1]. Commonly, waste is defined as a material supposed to be disposed of by assuming that no longer it can be used. The waste can be defined as the leftover products yielded when the raw materials are utilized to harvest any useful product for regular day-to-day use and functionalities. Due to large manufacturing processes, industries produce a huge amount of waste material which in some way or other are not disposed of on a routine basis and hence accumulates on a larger scale leading to a greater version of threat to the environment [2]. Presently, developing countries are facing several issues of concern for managing these overloaded wastes. Innovative efforts and ideas are posed by the researchers and scientists to manage the waste of all sectors to reduce the negative impacts on humans and the environment. Several studies reported that the wastes contain voluminous organic compounds, nutrients, and energy. But they are not managed and exploited properly for the reuse and recovery of values. The incorporation of an integrated approach that employs wastes and by-products can reduce the need for feed-raw materials and can induce a high production ratio. Furthermore, effective recovery of resources from wastes can create a sustainable livelihood by minimizing the wastes that impose a green economy [3]. Hence, there is an imperative need for reusing and recovery of industrial wastes. Based on this perception, different advanced techniques and novel approach used to remediate industrial wastes are mainly emphasized in this chapter.

10.2 Classification and characteristics of wastes

Waste can be produced in the form of gas, solid, liquid, and heat. Generally, the four main sources of wastes are municipal, industrial, biomedical, and electronics [4]. Prior to employing the most suitable management measures, the wastes should be identified and characterized based on their source. Further, they are classified with respect to their diverse varieties based on materials, a pattern of degradation, and environmental impact [5]. Based on materials, the wastes are classified as solid waste, liquid wastes, and air emissions. Waste such as plastics, scrap iron, bottles, electronic waste, medical waste is classified as day-to-day routine solid waste, wherein Styrofoam containers from industrial processing, commercial, and municipal outlets are far more unmanageable solid wastes. Liquid wastes are known to be unwanted residues discharged from small-scale to large-scale producers in the form of fluid into the water environments [6].

Principally, the liquids wastes are generated from domestic wastes, textile, oils refineries, distilleries, manufacturing industries, pulp and paper, tanneries, chemicals, etc. The release of harmful waste gases into the atmosphere usually happens from different industrial sources such as power plants, factories, and combustion gases from vehicles. Also, certain toxic volatile gases are released from various industrial processes and are known to be the foremost wastes of air emissions [7]. The wastes materials of fruits, paper, wood, and other biodegradable substances are considered to be a biodegradable factor. Those wide ranges of wastes like ceramics, plastic bottles, cans, bags, styrofoam, containers are not easily degraded and are categorized as nonbiodegradable wastes. Based on their environmental impacts, some wastes, which are hazardous to handle industrially, commercially, economically, and agriculturally are safely transported from the production site to the appropriate dumping areas. Apart from these, a few wastes which are not having any negative impact on the environment are usually dumped near a free soil area or water ecosystems.

10.3 Industrial waste

Generally, wastes from industries are a mixture of by-products in the form of liquid and solids released by different process units. Recently, the growth of industrialization had increased rapidly. Consequently, huge volumes of waste either in the form of liquid or solids as well as air emissions are generated from different industries. Specifically, from tanneries, slaughterhouses, distilleries, and poultries. There is no doubt that the Industrial sectors are constantly releasing various types of untreated effluents, hazardous substances, toxic materials, flavoring agents, heavy metals, and colored ingredients [8]. Therefore, industrial wastes management should be considered seriously for human health and environmental safety. Some of the major sources of waste pollutants from Industrial sources and their impacts on the environment are highlighted in Table 10.1.

Table 10.1: Some major sources of industrial wastes.

Industrial sources	Major pollutant from waste	Environmental impacts
Chemical industries, smelting, and painting	Heavy metals	They lead to activity inhibition of bodily enzymes. Mercury transforms into soluble methyl mercury by action of bacteria which contaminates aquatic life
Paper and textile industries	Alkali compounds	Alkali compounds affect aquatic life
Petroleum plants	Petrochemical and its derivatives	Affects marine life by toxic environment
Mine drainage	Acids	Metal corrosion and concrete corrosion
Oil refineries	Oil	Creates harmful for fish, marine, and birds

10.4 Waste management practices

Rapid urbanization and the growing population are the most reasonable factors for the increasing volume of large-scale disposable wastes [9]. In developing countries, lack of infrastructure amenities such as management for the sewage system and solid waste is a serious cause for the accumulation of the wastes. However, such kind of waste management issues has been found due to the paucity of knowledge and appropriate education [10]. The need for proper management of these wastes becomes more important on the way to their disposal or storage that should not affect the environment. Nowadays, there are various types of waste generated by industries and the clearance issue has evolved as a major massive task to handle. Generally, waste management practices deal with the collection, storage, and proper disposal. The controlling of waste generation and its appropriate maintenances are also crucial for a hygienic environment. Using the recent scientific advancements, scientists and researchers are looking for different techniques to recover and reuse the wastes by imposing novel treatment technologies [11].

10.4.1 Recycling

The process of recycling is nothing but to convert the waste into useful products. In practice, this process faces hard to practice since it needs to collect valuable substances like metals and other values from the wastes. It is well-known that collecting valuable materials substances from the waste is cheaper than extracting and purifying them from its raw materials. Recently, Bing et al. [12] have found that the use of glass fiber-reinforced polymer (GFRP) waste to reinforce the construction concrete was observed to be a novel mechanical recycling method. They pointed out the toughness and flexural strength and the concrete were significantly improved by the addition of waste GFRP. Elena et al. have studied that the use of wastes collected from construction and mining industries clay bricks. From their studies, it was found that the incorporation of waste from construction/mining was notably improved the plasticity properties of clay brick without technological properties modification [13]. In another study, the production of liquid fertilizer was investigated via recycling to meet commercial feed solution for the hydroponic system by Zuhaib et al. In addition, they showed the production of feed for chicken with better quality compared with the one available in the market from the recycling of the food wastes [14]. Yet another recent study, Yonghui et al. [15] has shown that the better efficient adsorbent in terms of electrostatic attraction which can dominate in the removal of Pb^{2+} and Cd^{2+} can be prepared from multiple recycling of food waste.

10.4.2 Techniques for solid waste management

Different methods are in practice for waste management that can refurbish the wastes into the more suitable form in order to minimize their toxicity and volume. Consequently, the processing of waste disposal should cause the least or nil effect on human health and the environment. Keeping this view, the management techniques for solid

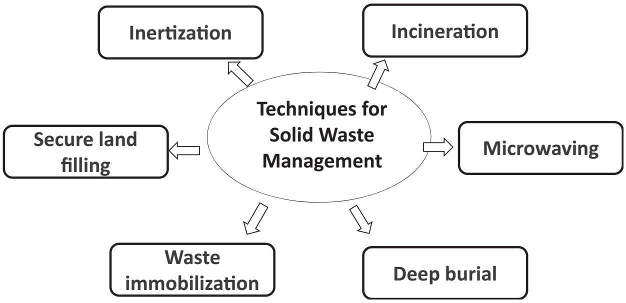

Figure 10.1: Common techniques for solid waste management.

wastes are employed mainly to emphasize reducing the rate of solid waste materials by recovering energy and resources [16]. Generally, three methods are employed for solid waste management, namely, reduce, reuse, and recycle. However, the construction and debris wastes do not fall under these categories that can be disposed of by landfill method. Figure 10.1 presents the most commonly used solid waste management methods.

Most countries are following land discarding methods for handling solid waste. The two simple ways for land discarding are namely, dumping and landfilling. Dumping is a technique, where the wastes are tipped, releasing a foul odor [17]. In general, garbage is dumped in the rural areas of developing countries. In the landfilling process, wastes are deposited on the top of land surfaces by a carefully planned procedure. The land area should be isolated from the groundwater location by the double bottom layer of soil. Yet another general method for treating solid wastes is a thermal treatment which includes incineration, plasma arc, pyrolysis, and gasification.

During incineration, the wastes are disposed of by ignition to release heat energy, steam, and ash. This method is mainly based on the principle that focusing on waste-to-energy. Traditionally, boilers and furnaces are used for burning the wastes to generate steam, heat, or electricity. Plasma arc technology is used to liquefy the inorganic portions of solid wastes [18]. For this purpose, the heat obtained from a plasma arc is employed. The wastes which are tested with the help of the plasma arc method include medical incinerator ash, open burning ground soil, waste paint, longhorn sludge and surrogate absorbent materials, agricultural and plastic/glass blast media. In the pyrolysis process, organic materials are decomposed at raised up temperature in absence of oxygen. During this process, a mixture of ignitable gases such as hydrogen, methane, carbon monoxide, a complex of hydrocarbons, and solid and liquid residues are produced [19]. Gasification is a special type of pyrolysis technique, which is carried out in the presence of a small amount of air or oxygen. The ignitable gases that evolved during gasification are further burned in industrial boilers and used to generate electric power. Solid waste such as wood, paper, textiles, plastics, rubber, oils waste, and other debris can be burnt in the open air. This process is called open burning. This process releases harmful gases and smoke into the atmosphere.

Open burning disposal is cheap, convenient, and comparatively easy [20]. Accordingly, it is adopted in most developing and underdeveloped countries. However, the burning of wastes significantly reduces the dumping volume of waste, so that, the life span of the dumpsite can be increased.

Recently, an alternative decomposes method, supercritical water decomposition, is gaining interest among environmentalists. This method is called hydrothermal monophasic oxidation [21]. In this process, hazardous wastes are oxidized by the use of supercritical water. During this oxidation process, waste materials are dissolved into supercritical water along with molecular oxygen. Biological composting, one of the common traditional methods, is normally used for decomposing organic wastes such as plants, papers, food scraps, etc. that can be digested easily. Further, digested materials can be used as agricultural manure or landscaping. In addition, methane gas can be generated during digestion which is used for electricity generation [22].

10.4.3 Techniques for liquid waste management

Effluents from sewage, different industries, and agricultural areas are the major sources for liquid waste generation which release an untreated significant volume of liquid waste [23]. Liquid waste causes harmful effects to the environment when they reach the ecosystem without adequate treatment. Accordingly, liquid waste effluents, colloquially, wastewaters, should be properly treated before discharging [24]. Wastewater treatment needs a sequence of different steps (Figure 10.2). In every step, one or various appropriate technical processes or equipment are required. Generally, physicochemical and biological treatment methods are conventionally adopted to treat liquid waste. However, treatments based on biological techniques are used extensively since these methods are efficient in nature, cost-effective, harmless, and easy to

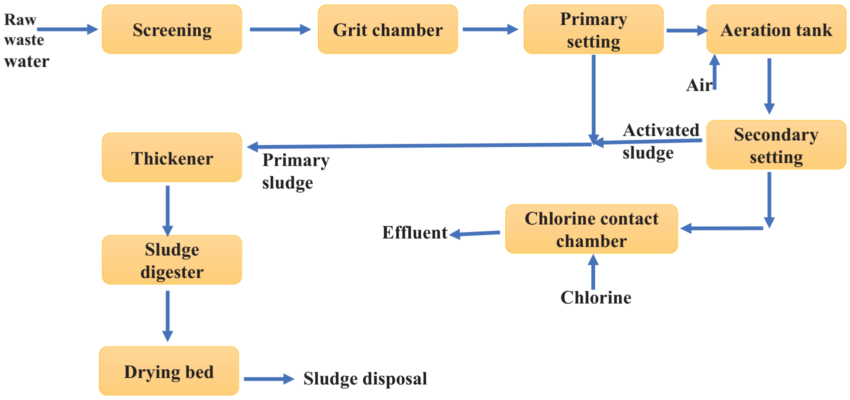

Figure 10.2: The techniques for liquid waste management.

manage conditions. Based on the degree of elimination of pollutants, the treatment system has been categorized into a different sequence of steps, namely, pretreatment, primary, secondary, and tertiary treatment [25].

The pretreatment or preliminary process is the first step which includes a collection of effluent and pumping into for further treatments. The raw wastewater may consist of various kinds of trash such as jam or clog, hence the purpose of the preliminary treatment is to remove these trashes for protecting the treatment equipment [26]. Different processes such as screening, shredding, grit removal, pre-aeration, and addition of chemicals are the common techniques involved in the preliminary treatment. In the primary treatment, suspended and floatable solids are reduced or eliminated by physical separation [27]. The settleable organic materials are also minimized using a settling tank for lowering the BOD. During this process, it is expected to remove, 40–60% of total suspended solids, 90–95% of settleable solids, and 25–30% of BOD of the wastewater. Further, the sludge is taken into the middle of the tank to a hopper. Followed by, the surface skimmers are used to remove the floating materials [28]. The liquid waste effluents are further subjected to secondary treatment for removing the residual organic constituents and suspended solids. During this process, colloidal organic and biodegradable dissolved contents are removed by aerobic biological treatment. This can be achieved using O_2-producing microbes with inorganic end-products such as NH_3, CO_2, and water. As a result, the BOD can be removed successfully by a secondary treatment which was not achieved by primary treatment. Tertiary treatment is aimed to remove color, BOD, phosphates, suspended solids, nitrates, and other pollutants which are not sufficiently removed from secondary treatment. Advanced treatment such as membrane filtration, ion exchange, coagulation, adsorption, chlorination, and other treatments are included in this step. Besides, affordable-cost methods such as lagoons or oxidation ponds are also practiced as the best option.

10.5 Exploitation of microorganisms for waste management

So far, approximately 5000 bacterial species have been explored which are found in water, plants, the human body, soil, air, animals, food products, and on other surfaces. Microorganisms taxonomically include fungi, bacteria, protozoa, nematodes, and algae. They form major biomass on the biosphere, and they are balancing different living forms. The microorganisms that exist on the subsurface show astonishing biological adaptability [29]. They perform different processes in the ecosystem and support the production of valuable nutrients such as nitrogen, oxygen, carbon, and other indispensable elements required for the survival of animals and plants through biogeochemical cycles [30]. Microorganisms have potential degradation capability under anaerobic and/or aerobic circumstances with high metabolic rates. Unsurprisingly, almost all-natural products are degraded by different microorganisms, particularly, fungi and bacteria. They degrade dead animals, plants, and other organic matters with the release of different nutrients. Based on the metabolism, microorganisms can be potentially exploited for generating biofuels, preservation, production of food, monitoring pollutants, waste treatment and cleaning up, and medicinal products development. Microorganisms are surviving for millions of years; therefore, they are well-known for their greatest adaptation capabilities. Some of them have the naturally occurring capability to transform or degrade a various range of compounds such as polychlorinated biphenyls, polyaromatic hydrocarbons, radionuclides, and metals present in the waste effluents from different domestic and industrial sources. In such a way, microorganisms are potentially used for waste management through three major processes, namely, bioremediation, bioaugmentation, and decomposition.

Bioremediation can be defined as the diminution, elimination, or transformation of contaminated compounds using biological agents [31]. Undoubtedly, an aquatic ecosystem is most affected through any point or nonpoint source of contaminants. Water pollution seriously impacts the aquatic ecosystem, terrestrial animals, and also human beings. Consequently, it is important to treat such effluents before they are discharged into the aquatic ecosystem. The use of microorganisms can be effectively utilized for bioremediation to treat these effluents via environment-friendly with cost-effective approach. The bioremediation process can be ameliorated with the addition of appropriate microbes that are skilled with degrading hazardous materials. For the treatment of hazardous waste, the microorganisms are either prepared in the laboratory or may be isolated from the appropriate natural environment and inoculated in the treatment plants. At present, different researches are ongoing for developing specialized microorganisms by genetically engineered techniques to achieve the optimized bioremediation process. However, bioremediation depends on hydrogeological conditions, whereas, different factors such as contaminants, microbial ecology, and chronological parameters could widely influence the process.

Microorganisms are more familiar with the degradation of pollutants with nutrition and energy as end products [32]. However, the activity of microorganisms can be ameliorated by providing some nutrients as external supplements, such as nitrogen and carbon sources, oxygen, substrates such as methane, toluene, and phenol. To date, *Arthrobacter, Alcaligens, Corneybacterium, Acromobacter, Flavobacterium, Pseudomonas, Mycobacterium, Rhodococcus, Nocardia, Vibrio* species, and *Sphingomonas* are the microorganisms that are extensively employed for the bioremediation process. In specific, for liquid waste treatment, *Lactobacillus plantarum*, *Streotococcus lacti*, *L. casei*, *Rhodopseudomonas palustrus*, and *Rhodobacter spaeroide* are widely used. Recently, some particular species of cyanobacteria such as *Synechococcous* sp., *Nodularia* sp., *Cyanothece* sp., and *Oscillatoria* sp. are found to be high potential for the biosorption and degradation of industrial wastes [33]. As a result of bioremediation, detoxification of effluents can be achieved with different useful end products such as biofertilizers, harmless chemicals, feed, and biofuels.

There are numerous methods and trends implemented to reap the fullest benefit of bioremediation and industrial waste management process. In that way, certain techniques involved in industrial wastewater management like fixed bed biofilm reactor along with membrane bioreactor is the latest substitute to conventional technologies. This technology is far advanced than the usual paper recycling method. Bacterial cultures are also used as a crucial element in industrial wastewater management, bacterial sources possess a large range of potential for bioremediation and they are economically beneficial too. Several microorganisms, such as *Desulfovibrio vulgaris*, *Arthrobacter*, *Pseudomonas* sp., *Serratia marcescens*, *Ochrobactrum* sp., *Bacillus* sp., *Cellulomonas* spp., *Acinetobacter*, and *Ochrobactrum*, have been known to reduce highly soluble and toxic Cr (VI) to less soluble and less toxic Cr III [34]. Application of Oxygenic Photosynthetic Bacteria (Cyanobacteria) in bioremediation is posed to be a successful mechanism as nitrate removal by these organisms is generally very effective [35]. Also, numerous studies have reported that the use of microalgae to extract nutrients from various wastes is an economically beneficial bioremediation method to avoid further degradation of the water quality in wastewater. Textile wastewater (TWW) contains the nutrients required for algae cultivation (phosphate, nitrates, micronutrients, etc.) [36].

Biological methods for waste treatment are critically dependent on microbes that can develop in the effluents and activated sludge. However, many pollutants with the complex structure are more resistant to effectual degradation; hence they can persist in the environment for a longer period. This limitation can be overcome by the bioaugmentation process. In bioaugmentation, microorganisms that can degrade recalcitrant molecules are added to the polluted ecosystem [37]. This method is proven to be cost-effective and eco-friendly compared to the physicochemical method. several studies have been reported that this approach is effective in removing the toxic pollutants from the contaminated soils [38].

10.6 Decomposition

In the decomposition process, complex organic substances are broken down into lower fragments as compost by both biological and chemical processes [39]. Decomposition is a biological action that has been happening in nature since the first life originated on this earth. In recent times, humans have endeavored to control and exploit organic wastes, such as vegetable and animal manures, and make them into valuable products as a soil amendment by “composting”. Generally, decaying organic substances are decomposed by bacteria, fungi, actinomycetes, and other saprophytic organisms by two processes, namely, aerobic decomposition, and anaerobic decomposition [40].

In the aerobic process, decomposing takes place in the presence of oxygen. It commonly occurs in nature on ground surfaces where the dead plants and animals get converted into stable humus. During this process, oxygen is utilized by the organisms and organic substances are get fed upon. Additionally, microbes use carbon, phosphorus, nitrogen from their source for nutrition requirements. Since carbon is a major element of cell protoplasm, it requires more than nitrogen [41]. Generally, two-thirds of the carbon is needed for respiration in terms of CO_2, and one-third is combined with N_2 in all the living cells. In an anaerobic process, oxygen accession will not require, for the instance, the decomposition occurs at the bottom of marshes. In this case, degradation is carried out by putrefaction that takes place with a foul smell of H_2S. In putrefactive action for breaking down the organic substance, the air is not required to conduct the decomposition process. The microbes utilize nitrogen, phosphorus, and other essential nutrients for their survival. During this process, by utilizing organic nitrogen, ammonia and organic acids are produced as end products. Additionally, the carbon which is not used for metabolism is liberated as the methane gas.

10.7 Valorization of food processing waste by biorefinery technology

10.7.1 Biorefinery from brewer’s spent grain (BSG)

A considerable volume of brewer’s spent grain (BSG) is generated as a by-product from the beer-brewing process. BSG can be obtained throughout the year and it has been found with various attractive compounds [42]. Hence, it can be a potential feedstock for the biorefinery process to accomplish different value-added compounds. Generally, it is produced during the step of mashing the barley; further, it is separated by a mesh filter. Approximately, 20 kg of BGS (wet mass) can be obtained from the production of 100 L of beer. BSG is categorized as lignocellulosic material [43]. Chemical composition studies on BSG showed that it contains starch (2–12%), cellulose (12–33%), hemicellulose (19–42%), lignin (12–28%), lipids (6–10%), proteins (15–31%), phenolic compounds (0.7–2%), and ash (1–4%). However, these values depend on different aspects such as harvesting period, variety of cereal, malting configuration, type of added hops, and mashing methods, etc. It has 70–80% of moisture content with high protein and carbohydrates that can provide a susceptible and favorable condition for microbial development [44]. Figure 10.3 presents a simplified block diagram of the biorefinery process applied to BSG.

10.7.2 Biorefinery from olive waste

The recognition and consumption of olive oil have spread from Mediterranean provinces to all over the world because of its significant health benefits. The world market for olive is led by Spain. Mainly, the processing of olives is processed by mill

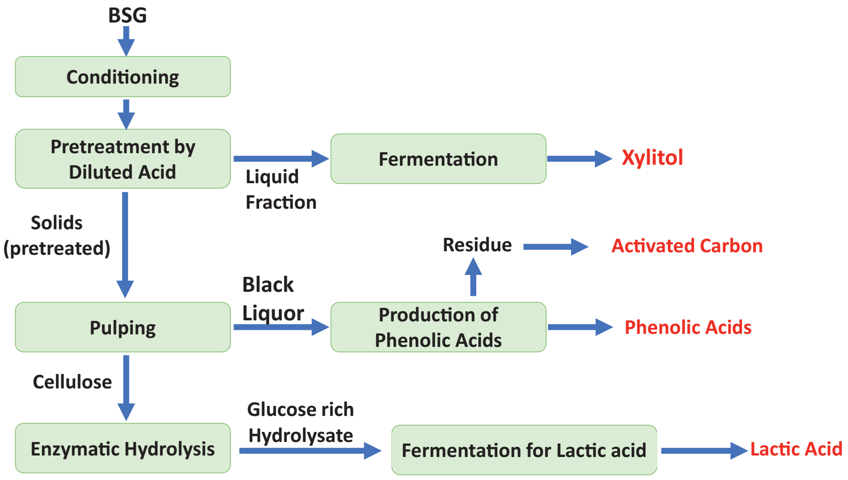

Figure 10.3: Schematic representation of biorefinery for the production of lactic acid, xylitol, phenolic acids, and activated carbon on BSG.

technology which consists two-phase centrifugation scheme [45]. During the processing of olive, olive stones, olive pomace, olive leaves, olive tree pruning, and wastewater are found to be major wastes. Different studies have proven that various value-added compounds can be acquired from olive wastes through biorefinery context; the same has been summarized in Figure 10.4.

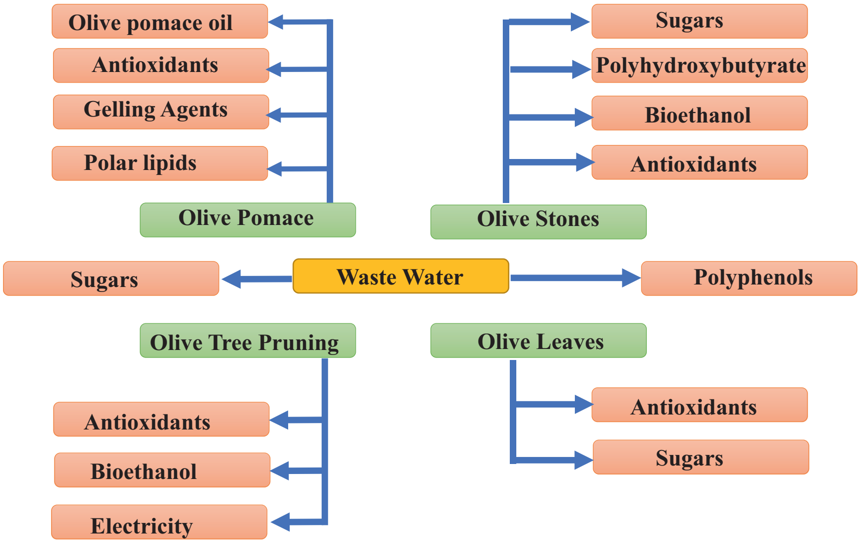

Figure 10.4: Value-added compounds obtained from olive wastes.

10.7.3 Biorefinery from potato peels

Potato is one of the most consumed vegetables worldwide. It has a carbohydrate content, mainly starch. Also, it contains, minerals, phytochemicals (phenolic compounds and carotenoids), proteins, and vitamins. Food processing industries, such as chips, puree, French fries are producing huge volumes of peels as a waste by-product. The peeling methods such as mechanized knife peelers, lye peeling, and abrasion determine the value of potato peel. Peels produced from the potato food processing industry can be used as a substrate for different microbes for the production of enzymes, feed for animals, fertilizer [46]. Also, the peels of potato can be a potential feedstock for extracting different valuable compounds such as steroidal alkaloids, polysaccharides, antioxidants, and biopolymer films. The proposed steps and schematic representation for the value-added compounds that can be derived from potato peels are summarized in Figure 10.5.

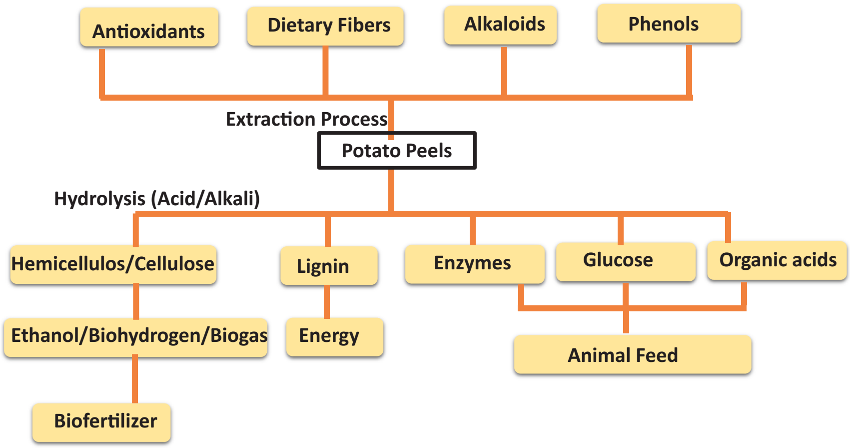

Figure 10.5: Summary of processes for the production of value-added compounds from potato peels.

10.8 Nutrients recovery from dairy product industries waste

The dairy industry contributes a significant part to the food industry. It greatly contributes to the generation of a huge volume of liquid wastes. The major waste from this industry is cheese whey. Records documented that 9 kg of cheese whey can be produced per kg of cheese produced [47]. Generally, cheese whey can be used directly in the liquid form. However, it is treated to further transformation into various food products, including lactose, protein concentrates, powdered whey from cheese, and lactose-free by-products [48]. Dairy residue can represent the biggest reservoirs of sugars (mainly lactose) and proteins and has been widely examined for recovery purposes [49]. Paola et al. [50] pointed out that nanofiltration, ultrafiltration, and ultrasound-assisted ultrafiltration are efficient methods for the recovery of valuable products from whey. Abhishek et al. [51] documented that the potential use of milk permeates as feedstock for the production of lactulose, using $CaCO_3$-based catalysts. In another study, it has been proven that the retentate can be used to produce whey protein concentrate powder, while the permeate is used as a lactose source [52].

10.9 Energy production from the waste

Recently, waste to energy gains potential interest to treat waste with the simultaneous conversion of waste into chemical and thermal energies. Different wastes such as sludge effluent treatment plants, sludge, sewage outlet, and gaseous can be applied for this technique [53]. The most successful technique is energy production by incinerating

Table 10.2: Energy densification technique and gasification type for MSW.

Particulars	Remarks
Energy densification technique for MSW	
Refuse derived fuel (RDF)	Magnetic separation, shredding, or extrusion techniques are used for RDF systems. It needs to separate combustible and non-carbonaceous matter from MSW for producing higher calorific combustion.
Pelletization	Generally, pellets resulted from biomass waste, waste from food, and agricultural sectors. The pellet's durability and quality depend on temperature, applied pressure, and the size of the particle of the feed. The pellets from waste are used for combustion instead of their raw materials.
Torrefaction	Torrefaction is one of the efficient techniques for energy-dense biomass with improved hydrophobicity and grindability. It is considered a mild pyrolytic conversion of biomass into energy-dense storable product.
Hydrothermal carbonization (HTC)	This process converts wet biomass into hydrochar of higher heating value without pre-drying. Hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) are upgraded forms of HTC.
Gasification type	
Modular gasification	Can be done with biomass and MSW. HelioStorm ionic gasification is used for small-scale energy production.
Updraft gasification	Can be done with waste biomass such as switchgrass, rice husk, rice straw, bagasse, paper mill sludge, and poultry litter.
Bubbling fluidized bed gasification and combustion	Can be done with biomass, MSW, and RDF. It is operated at 800–850 °C.
Downdraft moving-bed gasification	Works with common biomass waste which operates at 982 °C.

MSW [54]. The positive results and easy initiative toward the MSW handling management, the candidature of waste to energy makes a sustainable and reliable technique [55]. Some of the recent techniques adopted for MSW to energy densification and gasification are summarized in Table 10.2.

10.10 Recovery of resources from waste

These days, due to urbanization and human activities, waste is unavoidable. It is produced by the different activities of agricultural, residential, commercial, and industrial processes. One of the effective handling methods for managing waste is the recovery of resources. Phosphorus is one of the most essential elements. At the present time, reserves of phosphorus are being depleted in most of the countries [56]. Therefore, phosphorous recovery from phosphorous-containing wastes is gaining huge interest. However, still there are different issues that remain in the successes for the recovery of phosphorous from industrial waste at a large-scale level. Hence, the exploration of large-scale phosphorous recovery is required and would help economically to process the solid waste. Usually, after dewatering the sewage sludge is taken into the incineration process [57]. As a result, ash enriched with phosphorous is generated as a by-product [58]. From this ash, phosphorous can be recovered environmentally and economically, which would provide a sustainable management technique for handling sewage sludge processing. In such a way, different extraction and precipitation methods are employed for the recovery of phosphorus during waste handling of metal(loid)s. The recovered phosphorus shows a great significance in the production of fertilizers [59]. E-waste, wastes generated from abandoned electronic and electrical equipment [60]. It has significant contents of valued metals, including, gold. So far, several critical assessments are carried out by different researchers to recover the metal(s) from e-waste to develop an environmentally friendly method with an economically viable technique. However, different chemical processing methods are available to recover metals from e-waste [61].

10.11 Legislation on waste management

Legislation for waste management is more important because it regulates and directs the transport, handling, storage, and disposal of waste. The use of proper legislation can minimize environmental and health risks. Food waste can be considered was nonhazardous whenever it does not manifest any evidence to be considered as “hazardous” [62]. However, these approaches should not apply to animal-derived wastes. Such kinds of issues can be by regulated Legislation concerning avoiding the dissemination of serious diseases such as Bovine spongiform encephalopathy [63]. In this context, according to directive 2008/98/EC (2008), the rules say in Europe for the handling of waste and its management hierarchically according to the following priority order: prevention of waste generation, reuse, recycling, energy recovery, and disposal (e.g., landfilling). But in the case of food waste, the directives should be framed for collecting biowaste with respect to maximum environmental protection. It aims to promote anaerobic digestion of residues and composting. However, this legislation for treatments should be carefully taken care of for their valorization within the bioeconomy concept. Concerning this, government bodies should publish a set of rules for amending these directives which targeting at the separate collection of biowaste from the household.

10.12 Future prospects

Countries (developed and developing), regions (urban and rural areas), and the residential and industrial sectors all have varied approaches to waste management. Trash management, on the other hand, aims to limit the negative consequences of waste on human health, the environment, and aesthetics. Industrial waste is any material rendered unusable during a manufacturing process, such as that of factories, industries, mills, and mining operations. Hence, waste generation can be drastically controlled by implementing the legislation policy on waste management as a key component in business or industry as mandatory to get accreditation at national and international standards. The guideline pushes businesses to increase their environmental efficiencies year after year by reducing waste and implementing resource recovery strategies. By lowering the cost of analyzing, dismantling, or identifying valuable components in goods end of life (EOL), various types of support and technology can boost EOL product recovery productivity. If technology progresses the productivity of retrieving only one type of product, its value may plummet if it is no longer used to recover that type of product. The elimination of waste material creation, also known as waste reduction, is an important strategy of waste management. Historically, the waste management business has been a late adoption of technology such as GPS, RFID (Radio Frequency Identification) tags, and coherent software packages that allow for improved data collection without estimation or manual data entry. Waste management concepts take into account things like waste hierarchy, product life cycles, resource efficiency, and the polluter-pays principle. Incineration, recycling, landfill, pyrolysis, resource recovery, reuse, composting, and biological remediation are some of the most common waste disposal and management methods that need to be improved with continuous research and development to increase their potential to manage the waste as well as the utilization of generated by-product by enhancing product recovery practices.

10.13 Conclusions

Waste substances are may be considered to be of no further use to the consumers or the manufacturers. Anyways, human activities are responsible for waste production and accumulation. Mainly, wastes are generated from industrial sources, agricultural and domestic sources. Depending on their sources, the main components of the wastes are inorganic, organic, and various harmful chemical compounds. In order to concern the environmental impacts, the management of these wastes' disposal is most important, which includes conventional and biological methods. The biological methods are mostly recommended since the processes are eco-friendly in nature. In biological methods usually, microorganisms, such as algae, bacteria, fungi are involved in different processes such as composting, activated sludge, trickling filters, oxidation ponds, etc. In another way, the recovery of resources such as energy, nutrients, and essential chemicals could be a sustainable solution for waste management. Industrial wastes which contain valuable resources can be processed for the recovery of various value-added products including gaseous biofuels, nutrients, liquid biofuels, and metals, etc. Even though there different technologically developed systems are currently employed, it is required to study the recovery of value-added products from wastes either by separate or process integration. With respect to characteristics of wastes, the sustainable process development for the recovery of bio-based and nontoxic by-products should be considered in a future study. Also, the optimization of exploitation of waste is a needs huge concern to develop better sustainable techniques. To achieve effective utilization of resources, the research focus can be given to the concept of biorefinery which can be applied to bio-based industries.

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Index

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