Emerging Contaminants and Associated Treatment Technologies

M. Vasanthy
V. Sivasankar
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Organic Pollutants

Toxicity and Solutions

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Emerging Contaminants and Associated Treatment Technologies

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Dedicated to my beloved mother Late Padmavathi Venkataraman

Foreword

The stability and the toxicity of persistent organic pollutants (POPs) represent a global threat for health and environment. Indeed, POPs can be found far from the place of their first emissions, in countries where they have never been used. POPs are still hazardous even for a long time after they have been banned. POPs are carcinogenic, mutagenic, reprotoxic or endocrine disruptors for humans and living species. Since POPs are persistent in soils, surface waters and underground waters, they lead to the contamination of the fauna and flora, and then to the contamination of humans by the way of the food chain. Therefore, it is important and vital to develop several remediation methods. Chemical, physical, biological and physicochemical methods must be implemented in order to restrict the dissemination of new POPs and to decrease the exposure of humans to their contaminated environment with old POPs. Because POPs are stable, their destruction needs the development of the more recent methods such as biotechnology and nanotechnology.

The editors of *Organic Pollutants: Toxicity and Solutions*, Muthunarayanan Vasanthy, Venkataraman Sivasankar and Thangaiya Ganesan Sunitha, are well-known experts in drinking water and wastewater treatment, in the synthesis of various kinds of pollutant adsorbents and in the characterization of solid wastes including the role of marine microplastics particles. We have been working together for some time now and have already co-authored quite a few papers. I have also read several of their research papers and book chapters. They constitute an efficient team. Together, they are editors or co-editors of six books. Once again, their writing skills are clearly apparent in the present book where the toxicity and possible treatments of main pollutant families are presented. Detailed chapters can be found within the book; however, it is interesting to give a different perspective of the present book.

Obviously, the old and new POPs are presented with their sources and adverse effects, and particular attention is given to old POPs like chlordecone in the Caribbean, triclosan and lindane. The toxicity of large classes of chemicals is exposed for aldehydes, phthalate esters in Indian rivers, disinfectants and their by-products, pharmaceuticals, personal care products, textile dyes, pesticides, nanocatalysts and various solid wastes including the role of interactions between microplastics and pollutants. General treatment methods like adsorption, absorption, bioremediation technologies, eco-friendly remediation, uses of algae in removal methods (phyco-remediation) and effluent mineralization are presented. Specific pollutant treatments are detailed for pharmaceutical containing wastewaters, lindane and chlordecone remediation, phenol removal, and remediation of textile dyes.

Environmental pollution is certainly too large a subject to be treated in just one book. The treatment remediation of old and new POPs is expected to be a long battle, but very likely to be won, especially in the removal of pollutants from soils and waters. The present book will be very useful and enlightening for many industrial and academic scientists and research students.

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Persistent Organic Pollutants (Part I): The “Dirty Dozen” – Sources and Adverse Effects

Rupesh Narayana Prabhu and Jagadeesan Lakshmipraba

Abstract Persistent organic pollutants (POPs) are carbon-based pollutants existing in our environment for extended periods of time. POPs are of global concern due to their far-reaching presence in the environment. They are present in the lithosphere (soil), hydrosphere (water), biosphere (living beings), and atmosphere (air). Both natural and anthropogenic forms of POPs are known. POPs can be considered as “forever chemicals” as they are resistant to degradation in the ecosystem via biologically, chemically, and photolytically to varying degrees and as such are persistent in our environment. They have the ability to biomagnify via the food chain and can bioaccumulate in the various organisms in the ecosystem due to their high lipid solubility. They can be transported over long distances by water and wind and are found in many regions where there are no major sources of POPs. The comprehensive pollution of the environment and living organisms by POPs has resulted in acute as well as chronic toxic effects in many living species. Under the leadership of United Nations Environment Programme (UNEP), the Stockholm Convention of Persistent Organic Pollutants was held in 2001. In this treaty, 12 classes of organic chemicals (also referred as the “dirty dozen”) were identified as POPs. In this chapter, the source, structure, general characteristics, and uses of the intentionally produced and unintentionally formed “dirty dozen” will be disclosed. The major adverse effects caused by the “dirty dozen” on human health and the environment will be also summarized.

Keywords Persistent organic pollutants · The “dirty dozen” · Sources, properties, and adverse effects

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1 Introduction

Persistent organic pollutants (POPs) are chemicals containing carbon existing in our environment for extended periods of time. POPs are of global concern due to their widespread existence in the environment and are perceived in the biosphere (living beings), hydrosphere (water), lithosphere (soil), and atmosphere (air). Both natural and anthropogenic forms of POPs are known. POPs can be obtained naturally as a result of volcanic activities, vegetation fires, and other numerous biosynthetic pathways. However, most of them are man-made and enter the atmosphere through various industrial sources (e.g., heating stations, power stations, incinerating plants), household furnaces, agricultural sprays, etc. Various activities such as the rectifying and maintenance of equipment, combustion of coal, incineration of wastes (municipal, medical, or hazardous wastes), landfills (hazardous waste or plastic waste), cement manufacturing plants, organochlorine pesticide plants and storage, fly ash storage, utility of obsolete oil, sewage sludge, etc., can also lead to the accumulation of POPs (Halsall, 2007; El-Shahawi et al., 2010). They have the ability to biomagnify via the food chain and have a tendency to bioaccumulate in the various organisms in the ecosystem. Many POPs are semi-volatile. They can be present either as vapors or can be adsorbed on small particles in the atmosphere, and they can be transported over long-range prior to deposition. Many POPs are found thousands of kilometers from any major sources of POPs as in open oceans, deserts, and even the Arctic. POPs can be considered as “forever chemicals” as they are resistant to degradation in the ecosystem via biologically, chemically, and photolytically to varying degrees and as such are persistent in our environment (Harrison & Harrad, 2001; Abdallah, 2015; Alharbi et al., 2018). POPs have low solubility in water but have high lipid solubility due to which they easily bioaccumulate in fatty tissues. Due to bioamplification of POPs, the life forms at the top of the food chain (humans and other carnivores) have the highest amount of POPs in them when compared to the vegetarians at the bottom. POPs can enter the human body through (i) eating food or drinking water contaminated with POPs, (ii) breathing air that is contaminated with POPs, (iii) vehicle exhaust, and (iv) dermal method by coming in contact with products made with POPs. Many POPs are polyhalogenated (especially chloro or bromo) derivatives of organic compounds. POPs are/were used as solvents, pharmaceuticals, insecticides, pesticides, and industrial chemicals. The industrial wastewaters contain a large amount of POPs. POPs generally exhibit potential adverse effects on the health of living beings (humans and wildlife) as well as the environment.

2 Compounds Listed as Persistent Organic Pollutants

As a consequence of their properties, both physical and chemical, as well as the widespread use, there has been appreciable contamination globally due to POPs in recent decades. The far-reaching pollution of the environment and living organisms by POPs has resulted in acute as well as chronic toxic effects in many living species (Carpenter, 2013). The delegates from various countries signed a treaty in May 2001 as a part of the Stockholm Convention on Persistent Organic Pollutants which was mediated under the leadership of the United Nations Environment Programme (UNEP). The treaty came into effect 3 years later in May 2004 with 179 countries in compliance with the treaty. The prime features of the Stockholm Convention covered the necessity of the developed countries to provide fresh and supplementary monetary resources, to take steps to eradicate the generation and use of deliberately produced POPs, to remove unintentionally generated POPs, as well as to regulate and dispose POPs wastes in an environmentally safe approach (Lallas, 2001).

Many pesticides, chemicals of industrial use, and industrial by-products were classified into three different Annexes (A, B, and C) in the Stockholm Convention, based on the extent of toxic effects on human beings and the environment. The manufacture and utility of chemicals under Annex A have to be completely stopped, the chemicals under Annex B have restricted utility whereas any inadvertent production of pollutant will fall under Annex C (Porta & Zumeta, 2002; Haffner & Schecter, 2014; Paraitamby & Kee, 2016; Tang, 2013). In the beginning, 12 types of organic chemicals (also referred as the "dirty dozen") were identified as POPs (Table 1), with a ban on these harmful chemicals.

In subsequent years, additional chemicals were added biennially to the list of POPs based on the amendments in the years 2009, 2011, 2013, 2015, 2017, and 2019. The new POPs incorporated to the list in the Stockholm Convention held in

Table 1 Chemicals listed as POPs in annexes of Stockholm Convention, 2001

Sl. no	Chemical name	Annex
1	Aldrin	A
2	Chlordane	A
3	DDT	B
4	Dieldrin	A
5	Endrin	A
6	Heptachlor	A
7	Hexachlorobenzene (HCB)	A, C
8	Mirex	A
9	Toxaphene	A
10	Polychlorinated biphenyls (PCBs)	A, C
11	Polychlorinated dibenzodioxins (PCDDs)	C
12	Polychlorinated dibenzofurans (PCDFs)	C

2009 were pentachlorobenzene (or PeCB), α-hexachlorocyclohexane (or α-HCH), hexabromobiphenyls (or HBBs), perfluorooctanesulphonic acid (or PFOS), β-hexachlorocyclohexane (or β-HCH), pentabromodiphenylether (or penta-BDE), lindane (or γ-hexachlorocyclohexane or γ-HCH), tetrabromodiphenylether (or tetra-BDE), chlordecone (or Kepone), hexabromodiphenylether (or hexa-BDE), heptabromodiphenylether (or hepta-BDE), and perfluorooctanesulphonyl fluoride (or POSF). In the subsequent Conventions, endosulfan and related isomers were incorporated in 2011 as POPs, whereas hexabromocyclododecanes (or HBCDs) were listed in 2013. In the Stockholm Convention held in 2015, additional chemicals, namely, hexachlorobutadiene (or HCBD), polychlorinated naphthalenes (or PCNs) as well as pentachlorophenol (or PCP) and its salts and esters, were included to the list of POPs. Decabromodiphenyl ether (or deca-BDE) and short chain chlorinated paraffins (or SCCPs) were added in 2017, whereas Dicofol and perfluorooctanoic acid (or PFOA) and its salts and related compounds were added in 2019. In addition to these chemicals, a few chemicals such as Dechlorane Plus, Methoxychlor as well as Perfluorohexanesulphonic acid (PFHxS), its salts, and related compounds are proposed for listing under the Convention to be held in future.

3 The Dirty Dozen

In the Stockholm Convention of 2001, 12 classes of organic chemicals (or the “dirty dozen”) were included in the list of POPs, with a ban on the production and/or the use of these toxic chemicals. The initial set of 12 POPs that caused adverse effects on the ecosystem were further classified into three (industrial chemicals, pesticides, and by-products). In this section, the structure, sources, physical properties, uses, and adverse effects of the “dirty dozen” (Fig. 1) will be discussed.

3.1 Aldrin and Dieldrin

Both these POPs are anthropogenic organochlorine compounds which were manufactured on a commercial scale until 1990s. They were widely used as insecticide to treat soil and plant seeds. Both belong to the group of chlorine cyclodiene insecticides or diene-organochlorine insecticides. They were used to treat soil to kill corn rootworm, wireworms, cutworms, grasshoppers, locusts, termites, and other insect pests. Aldrin can be prepared by the Diels-Alder reaction of nonbornadiene and hexachlorocyclopentadiene (Jubb, 1975). Dieldrin is the epoxide derivative on aldrin and can be prepared by the action of peroxyacid (e.g., peracetic acid) on aldrin (Fig. 2). Plants and bacteria can also metabolize aldrin to dieldrin, which has the similar toxic effects and slow rate of decomposition as that of aldrin.

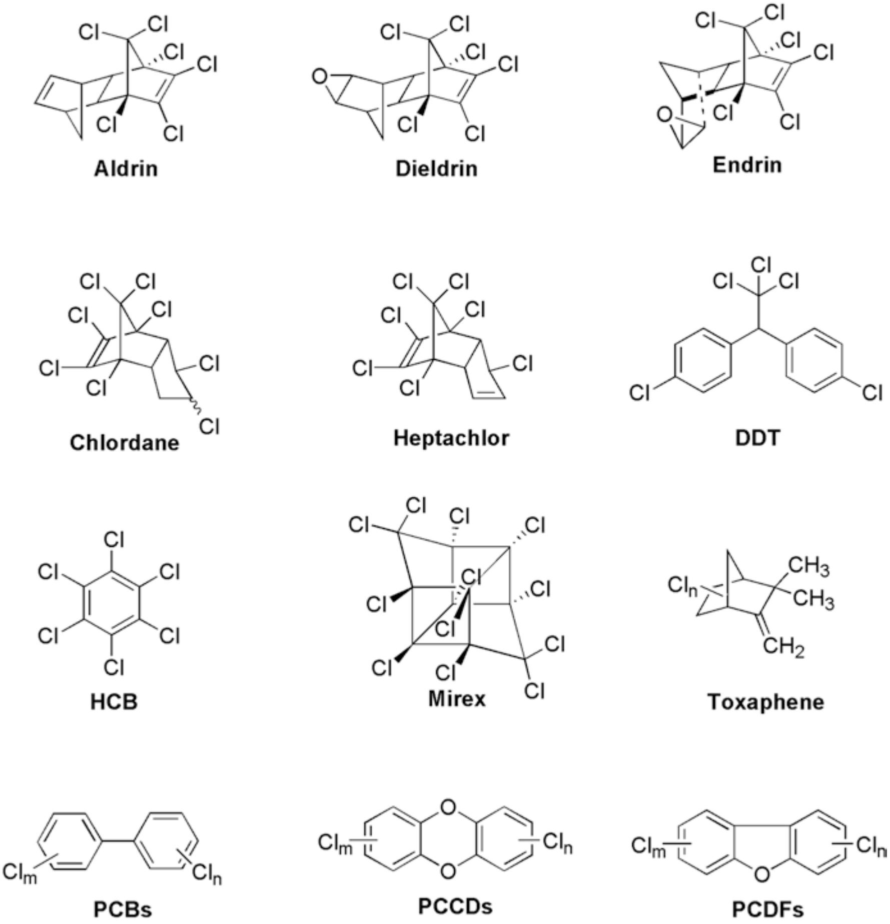


Fig. 1 POPs listed in the Stockholm amendment, 2001 (the "dirty dozen")

Aldrin and dieldrin are poorly soluble in water. However, they dissolve in oils, waxes, fats, and many organic solvents. Once released to the environment, they have very slow rate of decomposition (Yang et al., 2012). The residues of these two POPs can be present in the soil for lengthy duration of time and can contaminate the animal and plant materials that are added to the topsoil. Aldrin is estimated to possess a half-life of around 1.5–5.2 years, whereas the half-life of dieldrin can be around 4–10 years. The photo-oxidation half-life of aldrin and dieldrin in the atmosphere is estimated to be around 1–9 hours and 4–40 hours, respectively (Jorgenson, 2011). In air, aldrin and dieldrin can be easily transported by dust particles. A variety of dairy products (e.g., butter and milk) and animal meat are the best predictors of the presence of aldrin and dieldrin concentrations.

Both aldrin and dieldrin have good solubility in lipids, and hence they accumulate in human and animal body fat, intestines, liver, and breast milk. Signs and

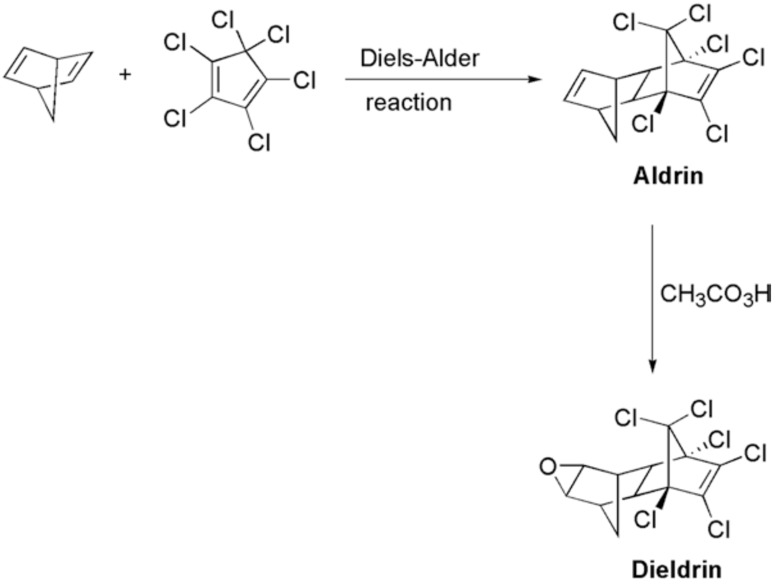


Fig. 2 Synthesis of aldrin and dieldrin

indications of aldrin and dieldrin accumulation may encompass depression, dizziness, severe headache, nausea, incoordination, gastrointestinal disturbances, muscle twitching or jerks, and seizures. The muscle seizures may even last for a few hours. It also affects the proper growth of teeth in children. Both are associated with various health issues such as breast cancer; Parkinson's disease; giddiness; muscle twitching; loss of consciousness; damage to the nervous, endocrine, and reproductive systems; and birth defects (Salama et al., 1993; Lui et al., 1997; Hooker et al., 2013; Wrobel et al., 2015). An oral dosage of about 5 grams of aldrin and dieldrin is estimated to be lethal in the case of an adult male. In addition, aldrin and dieldrin also affects the growth of many birds, land animals, and marine living species (Villaescusa, 1992; Tate & Heiny, 1996).

3.2 Endrin

Endrin, an organochloro compound, was mainly employed as an insecticide on grains, cereal, rice, apple trees, sugarcane, tobacco, and cotton. It was also used to control voles, corn borers, mice, cut worms, cotton bollworms, and grasshoppers (Smith, 1991). It was commercially available as granules, powdered form, pastes, and emulsion. Similar to other POPs, endrin has better solubility in organic solvents such as acetone, benzene, or xylene than in water. Endrin synthesis starts with the condensation of chloroethene with hexachlorocyclopentadiene. The resulting compound obtained then undergoes dehydrochlorination, followed by reaction with cyclopentadiene to result in the formation of an intermediate, isodrin. Epoxidation of isodrin with peracetic acid results in the formation of endrin. Dieldrin and endrin are stereoisomers with comparable properties. Endrin can be metabolized at a faster rate by animals. It does not accumulate significantly in fat to the same extent as other POPs with similar structure. It is volatile and enters the atmosphere. It can also contaminate surface water due to soil run-off. Endrin can be retained in soil of high amounts of organic matter, transported or degraded in the soil. Endrin can have a half-life of up to 12 years in soil, which in turn depends on the nature of the soil (Nash et al., 1972). Food intake, inhalation, and dermal contact are the fundamental sources of exposure of endrin to humans. Endrin can also reach developing fetuses through the placenta. Infants are susceptible to the exposure of endrin by drinking breast milk of exposed woman (Al-Saleh et al., 1998). Anti-12-hydroxyendrin, 12-ketoendrin, and other metabolites are formed by the metabolism of endrin, which are responsible for endrin toxicity. The health issues related to endrin accumulation include seizures, headache, vomiting, diarrhea, dizziness, confusion, teratogenic effects, and birth defects in infants (Ottolenghi et al., 1974; Rowley et al., 1987; Honeycutt & Jones, 2014). It can also affect the central nervous system, and in case of high dosage may even result in death if appropriate treatment is not given immediately. An increase in fetal mortality and other issues has been reported in some mice, ducks, and rats due to exposure to endrin. It is also highly toxic to many organisms in water such as aquatic invertebrates, other fishes, and phytoplankton (Fulton et al., 2013).

3.3 Chlordane

Treatment of cyclopentadiene with hexachlorocyclopentadiene resulted in the formation of the Diels Alder adduct, chlordene. Chlordane can be obtained by the chlorination of chlordene intermediate (Dearth & Hites, 1991). Two isomers, α-chlordane (or cis-chlordane) and β-chlordane (or trans-chlordane), were obtained (Fig. 3). β-chlordane was found to be more bioactive when compared to the α-isomer. Chlordane, an organic compound containing multiple chlorine atoms, was earlier used as pesticide for the treatment of corn, citrus crops, fruits, nuts, sugarcane, potatoes, jute, cotton, oilseeds, and also for the control of termites.

Chlordane is exceedingly soluble in water with appreciably good solubility in various organic solvents. It has high binding ability with aquatic deposits. Its half-life in the environment is 10–20 years. Its high partition coefficient and persistence provides the required conditions for bioaccumulation in various organisms (Olisah et al., 2020). Chlordane has been detected even in the Arctic due to ability to be hauled over long range, which, in turn, is favored by its semi-volatility, high stability, and low water solubility (Bidleman et al., 2002). The exposure of chlordane results in various health issues in small fishes, shrimp, and birds such as quail and ducks (Huang et al., 2004, 2006). Exposure of chlordane occurs predominantly

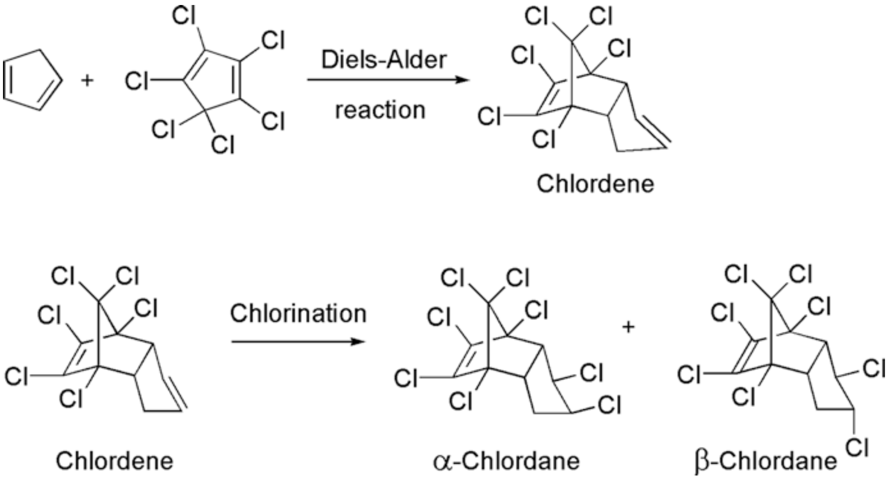


Fig. 3 Synthesis of chlordane

through air. It can also enter human body by inhalation of air in homes treated with chlordane, eating of high-fat content food (e.g., fish, meat, dairy products) and by consumption of crops grown in soil contaminated with chlordane. In pregnant women, chlordane can migrate across the placental membrane and absorb in the fetuses. Presence of chlordane in humans can result in seizures, type-2 diabetes, blurry vision, diarrhea, insulin resistance, bronchitis, immune dysfunction, sinusitis, vomiting, migraines, weakness, and anemia. It is considered as a carcinogen to mankind. It is also known to cause non-Hodgkin lymphoma as well as cancer in other parts (breast, prostate, testicles) of the body (Suwalsky et al., 2005; Khanjani et al., 2007; Cook et al., 2011; Lim et al., 2015; Evangelou et al., 2016).

3.4 Heptachlor

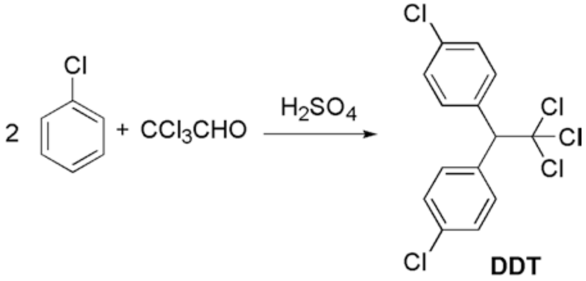
Heptachlor is another polychlorine containing organic compound which was used by farmers to kill insects on crops and in seeds. It used to control wireworms, cutworms, thrips, ants, maggots, weevils, termites, and other insect pets. It was applied to both uncultivated and cultivated soils. Exterminators and home owners used it to eliminate termites (Plimmer, 2003). Heptachlor was available as wettable powders, dusts, oil solutions, and emulsifiable concentrations. It has very high stability and can hence persist in the environment for decades. Heptachlor is metabolized to form mainly heptachlor epoxide (Bidleman et al., 1998; Kania-Korwel & Lehmler, 2013), which is more toxic than heptachlor. The intravenous lethal dose for heptachlor epoxide is 10 mg kg^{-1}, whereas that for heptachlor is 40 mg kg^{-1}. Diels-Alder reaction of cyclopentadiene and hexachlorocyclopentadiene, followed by the chlorination of the resultant adduct yields heptachlor. As an insecticide, heptachlor is about three to five times more active than chlordane, but it is more resistant to caustic alkalis and water (Hayes, 2010).

Heptachlor has a soil half-life of about 0.5–3.5 years, whereas heptachlor epoxide last for about 5–15 years in soil. Heptachlor strongly adsorbs on soil and hence resist leaching to groundwater. Similar to other organochlorine pesticides, heptachlor is also potential groundwater pollutant. To humans, heptachlor is highly deadly compound. It can be absorbed through gastrointestinal tract, lungs, eyes, and skin and stored in fatty tissues. It can damage the liver and also cause overstimulation of the central nervous system. Other symptoms include liver dysfunction, muscle tremors, oxidative stress, convulsions, dizziness, salivation, reproductive dysfunction, labored respiration, lethargy, and irritability (Rodgers, 2001; Prado et al., 2009; Luderer et al., 2013; Singh et al., 2019). Deaths due to respiratory failures were also reported in several cases. People with liver damage are at more risk in being affected by heptachlor. Both heptachlor and its epoxide can cause infertility and also improper maturing of the offspring. Heptachlor can easily make way across the placental membrane and has also been detected in human milk. Both are considered to be potential human carcinogens. In addition, heptachlor is also toxic to many birds, rats, and aquatic species, and decline in the population of several species were observed (Campagna et al., 2007; Fenoglio et al., 2009; Martínez-Ibarra et al., 2016).

3.5 DDT

DDT or dichlorodiphenyltrichloroethane, presumably the most:infamous POP, is another organochlorine compound (Mansouri et al., 2017). During the Second World War, it was developed as an insecticide to protect against typhus, malaria, dengue fever, and treatment of lice in many countries (Dunlap, 2014). Over the years, DDT has been marketed under different trade names in various countries. Paul Hermann Müller, a Swiss chemist, discovered the insecticidal action of DDT for which in 1948 he received the prestigious Nobel Prize in Physiology or Medicine. However, in tropical regions, DDT was found to be less effective to control malaria and treat mosquitoes because of the poor infrastructure and continuous life cycle of mosquitoes. To kill or keep away mosquitoes, DDT is generally coated on the interior walls of lodgings in these areas. This technique reduces the prevalence of DDT resistance by mosquitoes and also decreases environmental damage. DDT can be prepared (Darling, 1945) as the major product by the action of chlorobenzene on trichloroacetaldehyde (or chloral) using catalytic amount of sulphuric acid (Fig. 4). Commercially available DDT may also have the presence of impurities such as dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE). DDT is highly insoluble in aqueous medium, but it has appreciably better solubility in copious organic solvents, oils, and fats. DDT has been available in many forms, such as aerosols, water-wettable powders, solution in xylene or other petroleum products, smoke candles, and emulsions. In 1962, in his book *Silent Spring,* Rachel Carson, an American biologist, described the adverse effects on

Fig. 4 Synthesis of DDT



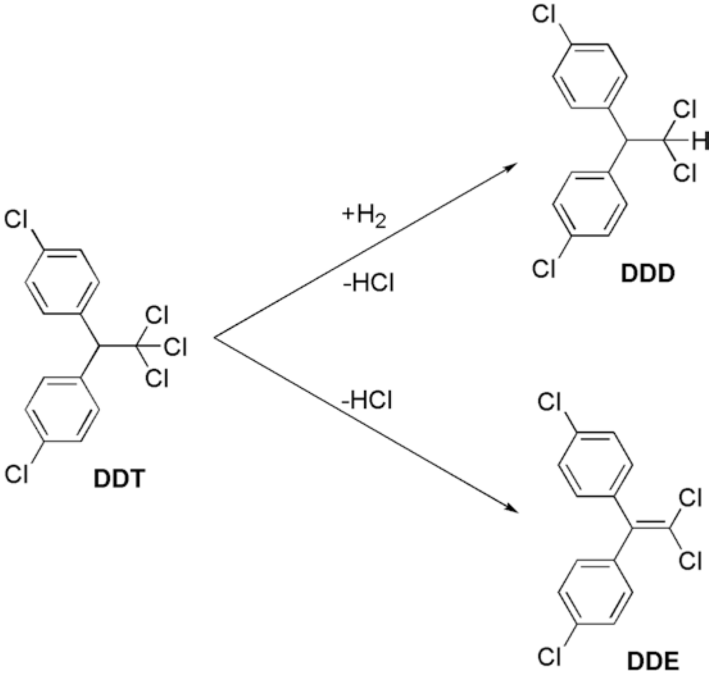


Fig. 5 Degradation of DDT to DDD and DDE

human health and environment for using DDT and other pesticides. In this book, DDT was used to tell a wider story of the devastating outcome of the overuse of insecticides (Carson, 1962).

Volatilization, biodegradation (aerobic and anaerobic), photolysis, and runoff are the primary pathways of loss and degradation of DDT. The chief degradation products as well as the major metabolites of DDT are DDD and DDE (Beasley et al., 1998; Guo et al., 2009; Purnomo et al., 2011). DDT is degraded to DDD by reductive dechlorination and to DDE by dehydrochlorination (Fig. 5). Both these breakdown products are also persistent, and their harmful properties are similar to that of DDT. As a result of their persistent nature and longer half-life, the presence of DDT and its metabolic products were noted even in the Arctic (Geisz et al., 2008). These

POPs are conveyed from warmer region to colder region of the Earth by a phenomenon called the grasshopper effect or the global distillation. DDT can be readily adsorbed on soils and sediments (Morrison et al., 2000). It can result in long-term exposure affecting various organisms. In soil, a half-life of 22 days to 30 years has been reported for DDT. However, in aquatic medium, a half-life of up to 150 years has been reported.

In insects, DDT is known to cause mutations, spasms, and even death. DDT is also lethal to a large range of aquatic species such as sea shrimp, daphnids, and crayfish. DDD, DDE, and DDT can magnify through the food chain. They are stored in the body fat. In many birds of prey species (e.g., osprey, peregrine falcon, brown pelican, bald eagle, and waterfowl) found in European countries and Northern America, DDD, DDE, and DDT have resulted in decline of population as well as thinning of eggshells (Lundholm, 1997). In addition, DDT and its metabolites affect the female fertility by varying the development and function of ovaries as well as reproductive organs in farm animals and laboratory animals and even humans (Tiemann, 2008). Intake of foods (e.g., dairy products, fish, meat) is the prime source of exposure of DDT as well as its metabolite products in humans. In addition, breathing and touching products that are contaminated with these can also cause in their absorption. In humans, exposure of DDT and its metabolites can cause seizures, apprehension, endocrine disruption, vomiting, fatigue, vertigo, hypersensitivity to stimuli, diabetes, non-Hodgkin's lymphoma, and cancer (breast, liver, colorectal, biliary tract, testicular, pancreatic, endometrial, prostate). There are also a few reports on reduced probability of pregnancy, premature labor, improper thyroid functioning during pregnancy and childhood, development of autism in newborns, impaired lactation, androgen receptor antagonism, hormonal imbalance, and improper liver functioning (Longnecker et al., 1997; Rogan & Chen, 2005; Cohn et al., 2003, 2007; Coster & van Larebeke, 2012; Brown et al., 2018; Leung et al., 2020).

3.6 Hexachlorobenzene (HCB)

Hexachlorobenzene (HCB) was to keep safe the seeds of sunflower, onion, wheat, and sorghum against fungus. HCB was also utilized as an industrial chemical to prepare synthetic rubber, pentachlorophenol, dyes, and pyrotechnic compositions. It was also used as a wood preservative before being banned (Bailey, 2001; Barber et al., 2005; Wang et al., 2010). HCB is prepared by the exhaustive chlorination of benzene (Fig. 6). It is also obtained as a by-product during the manufacture of various industrial chemicals such as pentachlorobenzene, trichloroethylene, perchloroethylene, and tetrachloro methane. It is also produced by the incineration of many chlorinated materials. It is almost insoluble in water but is sparingly soluble in many organic solvents. It has a better solubility in ether, benzene, and chloroform. It is highly volatile and can easily accumulate in the atmosphere. HCB can bioaccumulate and biomagnify in the lipid-rich tissues of the living organisms. It can be found

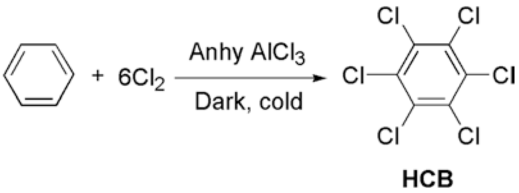


Fig. 6 Synthesis of HCB

in oceans, sediments, and treated and background soil (Egeler et al., 2001). HCB is also highly resistant to breakdown. It can also be transported to a long range in air. The half-life of HCB in soil can range from 3 to 6 years. It is highly combustible, generating toxic chlorine fumes.

HCB can enter the human body through skin, food intake, and breathing. Children playing in HCB-contaminated soil can be exposed to HCB through breathing and skin. It is considered to be probable carcinogen (liver, thyroid, kidney) to humans. In addition, HCB can cause liver dysfunction, excitation of central nervous system, hyperpigmentation, porphyria turcica (a disorder of haem biosynthesis), respiratory depression, pneumonitis, reproductive toxicity causing malformation of the embryo, birth defects, skin lesions, hirsutism, and impaired functions of various organs. Pregnant women can transfer HCB to fetus via placental transfer and through breast milk (To-Figueras et al., 1995; Sala et al., 1997; Pohl et al., 2001; Ribas-Fitó et al., 2002; Reed et al., 2007; Weldon et al., 2011; Starek-Świechowicz et al., 2017). HCB causes longstanding detrimental effects in marine environment as it is persistent and is very toxic to marine organisms. Hence, release of HCB in to drinking water, ground water, and surface water should be avoided.

3.7 Mirex

Mirex is a polychlorinated organic compound. It was sold as an insecticide against termites, native ants, harvester ants, and fire ants (Alley, 1973) and also as a fire retardant for rubber, plastics, electrical goods, paint, and paper. The use of mirex is banned due to its adverse effects on living species and environment (Kaiser, 1978). Mirex can be prepared by the dimerization of hexachlorocyclopentadiene using a Lewis acid such as aluminum chloride as catalyst (Prins, 1946). The combustion products of mirex are the toxic gases such as chlorine, phosgene, carbon monoxide, carbon dioxide, hydrogen chloride along with other chlorine-containing hydrocarbons. Slow oxidation of mirex results in the formation of chlordecone. In presence of sunlight, mirex is degraded by dechlorination to toxic products such as 8-monohydromirex (or photomirex), 10-monohydromirex, or 2,8-dihydromirex (Burns et al., 1997; Lambrych & Hassett, 2006).

Mirex is an example of a stomach insecticide. It means that it must be consumed through mouth and ingested by an organism to be toxic. It is highly stable and chemically robust bioaccumulative pollutant (Huckins et al., 1982; Polese et al., 1996). It does not leach into groundwater. It has been detected even in the Arctic, indicating its persistent nature and ability to be transported over long distances. It is water insoluble, but has good lipophilicity. It is highly resistant to photolytic, microbial, chemical, metabolic, and thermal degradation. It can bioaccumulate in sediments and biomagnify through food chain. Mirex has a half-life up to 10 years, depending on the conditions of the soil. It is highly toxic to aquatic life as it can accumulate in the adipose tissue. Mirex can enter body through skin, inhalation, and ingestion. It can result in gill damage, kidney lesions, disruption of metabolism, numerous birth defects, and delayed mortality in mammals, fishes, and other living organisms. Fish and meat contaminated with mired are the major food sources. Mirex has been detected in milk. Exposure to mirex affects lungs and central nervous system. It also results in headache, vomiting, reproductive toxicity, liver dysfunction, skin irritation, eye irritation, renal dysfunction and impairs neurodevelopment. It is supposed to be carcinogen for humans as well as an endocrine disruptor. Mirex interferes with various estrogen-related functions such as ovulation, pregnancy, and growth of endometrium (Chu et al., 1981; Faroon et al., 1995; El-Bayomy et al., 2002; Puertas et al., 2010).

3.8 Toxaphene

Toxaphene (alternative name, camphechlor) is an immensely complicated mixture of several components. It is produced by the reaction of camphene (a bicyclic monoterpene with the formula $C_{10}H_{16}$) with chlorine gas. It generally constitutes a mixture of a large number of polychlorinated compounds. $C_{10}H_{10}Cl_8$ is considered to be the average elemental composition of toxaphene with about 67–69% by weight of chlorine content (Holmstead et al., 1974; Shields et al., 2015). Similar to other organochloro compounds, toxaphene is water insoluble. It is readily soluble in different aliphatic organic solvents. Toxaphene is an example of nonsystemic and contact insecticide. It was used for pest control on vegetables, nuts, fruits, soybeans, small grains, cereal, cotton as well as to control flies, scam mites, lice, and ticks. In the early 1970s, it was used as a replacement of DDT. It is an example of POP and can be present in air, water, and soil (Pearson et al., 1997). Its rate of break down is very slow with half-life up to 12 years in soil (Tsai, 2010).

Toxaphene is volatile and can be transported in air over a long range (Rice et al., 1986; Datta et al., 1999). It can bioaccumulate is sea birds, fishes, and other aquatic species. Toxaphene is highly toxic to fishes, algae, and some other marine mammals in which it results in reduced egg viability and dramatic weight loss (Oetien & Karl, 1998; Perez-Rodriguez et al., 2020). In animals, toxaphene induces morphological changes in kidneys, liver, and thyroid and also energizes the central nervous system leading to increased neuronal activity and hyperpolarization of neurons. It can also affect the spleen, thyroid gland, adrenal gland, and immune system; cause cancer; interfere with various estrogen-related functions; induce weight gain; damage genetic information within a cell; and elevate serum cholesterol (Chu et al., 1988; Goodman et al., 2000; Bartoš et al., 2005; Wrobel & Mlynarczuk, 2018).

There are three major paths of exposure to toxaphene, namely, absorption through skin from direct contact with the contaminated soil, ingestion of food, and inhalation of contaminated air. It is accumulated in lipid-rich tissues and is also detected in breast milk, urine, and blood (de Boer & Wester, 1993; Gill et al., 1996). The compound is carcinogenic to mankind. It can also result in damage to kidneys, lungs, and liver. Exposure to very high levels may cause respiratory failure and sometimes even cause death. It causes convulsive seizures and bronchial carcinoma, affects the nervous system, and generates deleterious reproductive effects in humans (Saleh, 1991; Soto et al., 1994; Bonefeld-Jørgensen et al., 1997; Gauthier et al., 2001; Leonards et al., 2012).

3.9 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are very stable mixtures formed by the multiple chlorination of biphenyl ring (Fig. 7). They have the general formula $C_{12}H_{10-x}Cl_x$. They were once used in electrical apparatus as dielectric and coolant fluids for capacitors and transformers, in paint additive and in carbonless (or non-carbon) copy paper, lubricating oils, in heat transfer fluids, etc. Other applications included casting agents, stabilizing additives in flexible PVC-coated materials, flame retardants, de-dusting agents, pesticide extenders, waterproofing compounds, as well in cements and paints as plasticizers (Godish, 2001). PCBs have high viscosity, are hydrophobic, and are poorly soluble in water. They dissolve to varying extent in fats, oils, and organic solvents. PCBs can easily penetrate through skin. Even latex (natural rubber) and polyvinyl chloride (PVC) can absorb PCBs. Neoprene, polytetrafluoroethylene (PTFE), polyvinyl acetate (PVA), butyl rubber, polyethylene, and nitrile rubber are some of the materials that resist the action of PCBs. In spite of their hydrophobic nature, PCBs accumulate to a vast extent in the ecosystem. PCBs tend to sink to the bottom of ocean trenches where they accumulate. They are also found in the atmosphere (Wethington & Hornbuckle, 2005; Jamshidi et al., 2007). PCBs up to four chlorine atoms can be hauled over long distances in air. Concentration of PCBs in atmosphere is the minimum in rural areas and the maximum in cities with suburban and urban areas having intermediate concentrations. In the biosphere, certain eukaryotes and bacteria have the potential to degrade PCBs. They are also degraded by the action of the sun. Lesser the number of chlorine atoms, faster is the degradation. Meta and para substituted PCBs degrade at a faster rate than the ortho counterpart. PCPs have the tendency to biomagnify and bioaccumulate in various organisms. Plastics are the chief source of PCB pollution in the ecosystem (Schmidt et al., 2017; Ferreira et al., 2019). PCBs can have life time of over 10 to 15 years.

The toxic effect varies among congeners and depends on the structure and number of chlorines on the PCB. PCBs can be classified into coplanar (or non-ortho) PCB and noncoplanar PCB (Winneke et al., 1998; Chauhan et al., 2000; Simon

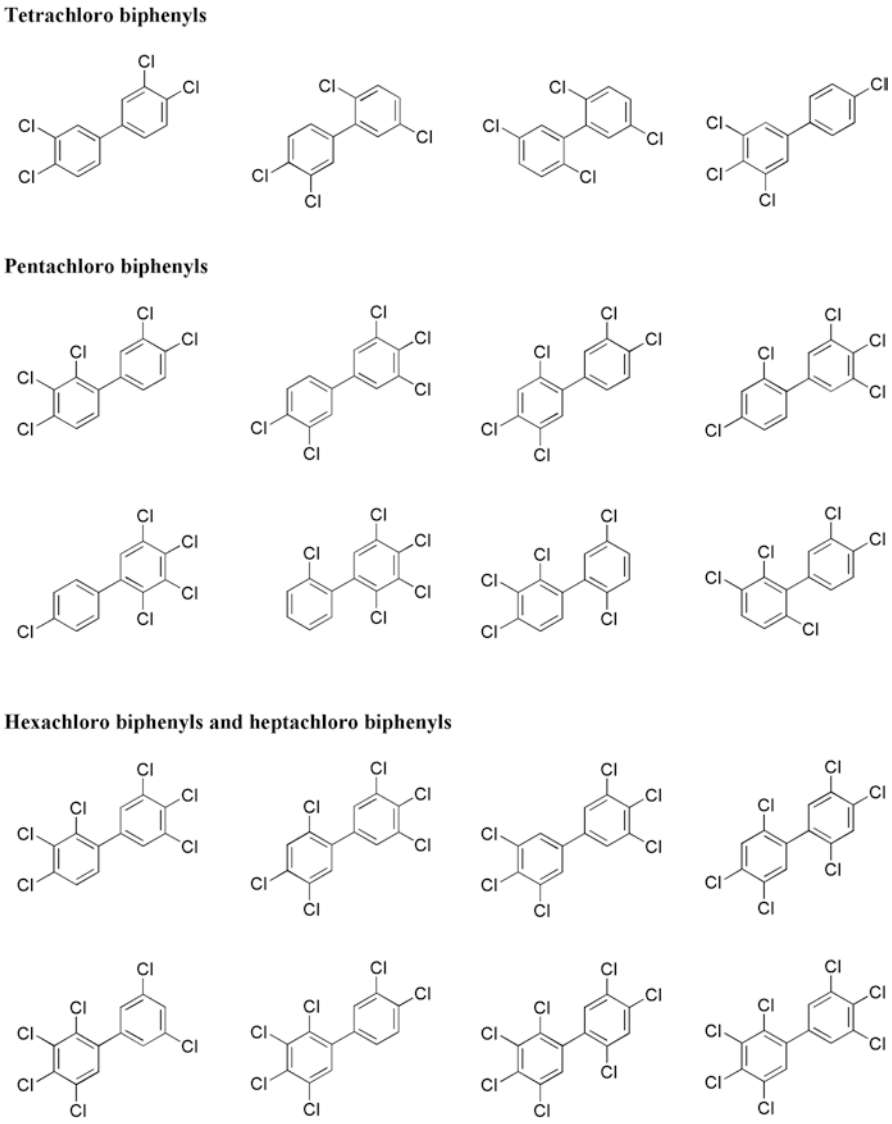


Fig. 7 Structures of some PCBs

et al., 2007; Totland et al., 2016). In coplanar PCBs, the two phenyl moieties are present in the same plane giving rise to a rigid structure. They are characterized by the absence of chlorine on the ortho position (C2-carbon) of the biphenyl ring system. In noncoplanar, chlorine atoms are present at the ortho position (C2-carbon) of the biphenyl system and at high concentrations. The coplanar PCBs generally are more toxic congeners than the noncoplanar derivatives.

The chief sources of exposure to PCBs are polluted air and food. Dairy products, fishes, chicken eggs, and meat have a large amount of PCBs. PCBs are identified as contaminants in breast milk and human blood (DeKoning & Karmaus, 2000). Exposure to PCBs can result in neurotoxicity, obesity, fatigue, liver cancer, skin conditions (e.g., rashes or chloracne), diabetes, anemia, pigmentation of nails, ocular lesions, blocking of functioning of thyroid system, depression, dermal lesions, headache, swelling of the eyelids, cardiovascular disease, breast cancer, coughs, prostate cancer, and even death in humans and mammals. They can induce apoptosis of thymocytes and monocytes. In females, PCBs can induce problems related to estrogenic activity, irregular menstrual cycles, and reproductive dysfunction. Effects due to PCBs are found to be transgenerational, and the chemicals can be detected in the mother's body for up to 7 years. It can induce poor cognitive development, motor control problems, and immune compromise in children as well as decrease in testosterone levels in adolescent boys (Safe & Hutzinger, 1984; Shin et al., 2000; Stewart et al., 2000; Aoki, 2001; Tan et al., 2003; Pocar et al., 2006; Katarzyńska et al., 2015; Putschögl et al., 2015; Fiandanese et al., 2016; Leng et al., 2016; Lim et al., 2017; Gupta et al., 2018).

3.10 Polychlorinated Dibenzodioxins (PCDDs)

Polychlorinated dibenzodioxins (PCDDs) are another category of very poisonous group of polychlorinated organic compounds (Fig. 8). More than 70 different PCDD congeners are known. They are examples of aromatic diether with dibenzo-1,4-dioxin skeleton. PCDDs are formed from natural sources. Artificially they are obtained during the incineration of chlorine containing organic materials, combustion of waste materials (sewage sludge, municipal solid waste, hazardous waste, medical waste), as by-products in the chemical industries dealing with the preparation of chlorine containing hydrocarbons, in the manufacture of chlorinated phenols, photochemical degradation of triclosan (an antimicrobial compound), and in the chlorine bleaching of textiles or wood pulp and automobile emissions (Yasuhara et al., 2003; Kulkarni et al., 2008). They are frequently (but incorrectly) mentioned as dioxins for the sake of simplicity, due to the presence of 1,4-dioxin as the central ring. They are regarded to be environmental pollutants (Hester et al., 1995; Marquès et al., 2018). PCDDs are lipophilic in nature and easily bioaccumulate in wildlife and humans. Even small exposures of PCDDs may reach harmful levels over time. They are stored in fatty tissues (Moon et al., 2011). They are not easily metabolized. They cannot be easily excreted also. The half-life varies from 4 to 13 years in humans for PCDDs containing 4 to 8 chlorine atoms (Milbrath et al., 2009). The toxic effect varies among PCDD congeners and in turn depends on the number and position of chlorines. Derivatives in which chlorine is present in the 2,3,7, and 8 positions are found to have more toxicity. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is the most toxic of the lot (van den Berg et al., 2006).

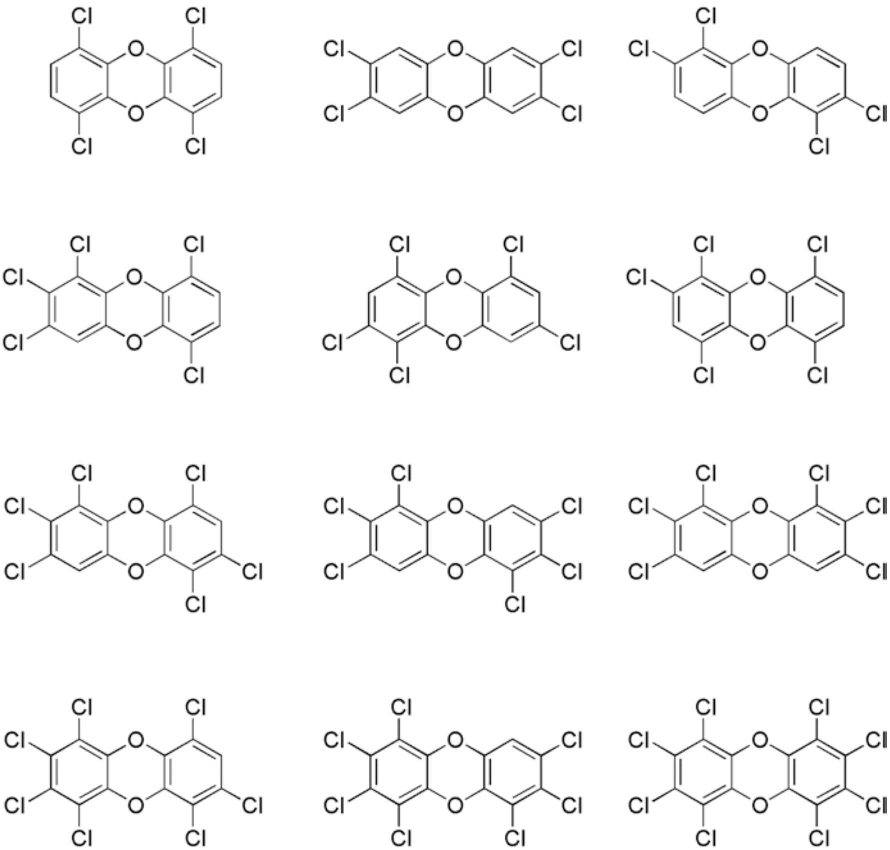


Fig. 8 Structures of some PCDDs

Humans and animals can be exposed to PCDDs through breathing, coming in contact with soil or other materials containing this pollutant, eating food (e.g., meat, fishes, and dairy products), or drinking water containing dioxins. In the case of people living in industrialized countries, the concentrations of PCDDs are generally higher. Breast milk may also contain PCDDs and are harmful for infants. They are also present in cigarette smoke (Liem et al., 2000; Schecter et al., 2001, 2006; Weber et al., 2008).

Exposure to PCDDs is known to cause chloracne, tumors, cleft palate, enzyme disorders, thyroid disorders, diabetes, thymus involution, and damage to immune systems. They are also considered to be potential carcinogen. Other effects such as abnormality in the development of enamel in children, endometriosis, and reproductive toxicity are also observed. It is also shown to be hepatotoxic (liver toxicity), mutagenic, and teratogenic (birth defects), endocrine disruptor and immunosuppressor. Birth defects and stillbirths were also observed in lethal exposure of some

PCDDs (Peterson et al., 1993; Mukerjee, 1998; Geusau et al., 2001, 2002; Eskenazi et al., 2002; Alaluusua et al., 2004; Arisawa et al., 2005; Bock & Köhle, 2006; Kransler et al., 2007; Warner et al., 2020).

3.11 Polychlorinated Dibenzofurans (PCDFs)

Polychlorinated dibenzofurans (PCDFs) are derived from dibenzofuran, where several of the eight hydrogens are replaced by chlorine atoms. PCDFs are also produced by the burning of chlorine containing materials at high temperatures or of non-chlorine containing organic compounds in presence of chlorine donors. Other sources of PCDFs include volcanic eruptions, accidental fires, PCB spills (containing PCDF contamination), and chlorine bleaching in paper mills. The properties as well as the toxicity of PCDFs are comparable to that of the PCDDs. They are highly stable and persistent. They have strong affinity for sediments. They also have a high probability to accumulate in lipid tissues. They are present throughout the ecosystem, including water, air, soil, vegetations, and animals. The toxic effect varies among PCDF congeners and in turn depends on the number of chlorine atoms and their position on the ring. Derivatives in which chlorine is present in the 2,3,7, and 8 positions are found to have more toxicity. 2,3,4,7,8-pentachlorodibenzofuran is the most toxic when compared to other PCDFs.

Similar to that of PCDDs, there exists much concern about the potential health risks of PCDFs also. Exposure to PCDFs generally takes place through contact of the contaminated soil or materials with the skin and by breathing the contaminated air. Eating of food materials of animal origin is another source of exposure of PCDFs (Kumagai et al., 2002; Fernández-González et al., 2015). Human exposure to PCDFs primarily results from food, particularly animal products. Exposure to PCDFs results in neurobehavioral developmental toxicity in children and infants, reproductive toxicity, damage to central nervous system, elevated cholesterol in the blood, retardation of placental-related functions, estrogen-related issues, cancer, endocrine disorders (mainly affecting steroid hormones and thyroid functioning), lower birth weight, diabetes, teratogenic problems, and damage to immune systems (Safe, 1990; Tanabe et al., 2004; Chao et al., 2007; Huang et al., 2007; Wilhelm et al., 2008; Konishi et al., 2009; Everett & Thompson, 2016).

4 Summary

Persistent organic pollutants (POPs) are considered as “forever chemicals” due to their resistance to degradation, semi-volatility, lipophilicity, ability to be transported over long range, and high persistence in the ecosystem. Their ability to biomagnify and bioaccumulate in lipids has made them “silent killers.” Twelve classes of organic compounds (also termed as the “dirty dozen”) were classified as POPs in

2001 by the Stockholm Convention. POPs have various adverse on health of the living beings (plants, animals, and humans) and the environment. The world is under great threat due to the extensive use of POPs in the agricultural and industrial sector. Endocrine disruption, cardiovascular issues, reproductive dysfunction, carcinogenic effects, teratogenic effects, obesity, diabetes, and sometimes even death are some of the major health issues on humans and other living beings associated with the "dirty dozen."

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Persistent Organic Pollutants (Part II): The New POPs – Sources and Adverse Effects

Rupesh Narayana Prabhu and Jagadeesan Lakshmipraba

Abstract Persistent organic pollutants (POPs) are organic pollutants that exist for extended periods of time in our environment. Due to their ubiquitous presence in the environment (water, air, soil, and living beings), both natural and man-made forms of POPs are of global concern. They can be considered as “forever chemicals” due to their resistance to degradation in the ecosystem via photolytically, biologically, or chemically to diversified degrees. They have the potential to biomagnify via the food chain, and due to their high lipid solubility they can bioaccumulate in the various organisms in the ecosystem. They are transported beyond international borders by water and wind and are detected in places far from their sources. The comprehensive contamination of the living organisms and environment by POPs has resulted in acute as well as chronic toxic effects in many living species. Under the leadership of United Nations Environment Programme (UNEP), 12 classes of organic compounds (or the “dirty dozen”) were initially identified as persistent organic pollutants in the Stockholm Convention of Persistent Organic Pollutants held in 2001. In the subsequent Stockholm Conventions held biennially from 2009 to 2019, additional chemicals were considered as new POPs. In this chapter, the source, structure, general characteristics, and uses of the intentionally produced and unintentionally generated new persistent organic pollutants introduced from 2009 will be described. The major adverse effects caused by these new persistent organic pollutants on human health and the environment will be also summarized.

Keywords New POPs · Sources, properties, and adverse effects

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1 Introduction

Persistent organic pollutants (POPs) are natural and anthropogenic forms of organic pollutants that exist in our environment (soil, air, living being, and water) for longer duration of time. POPs are of great concern worldwide due to their ubiquitous existence in the environment (El-Shahawi et al., 2010). They have the ability to biomagnify via the food chain and because of their appreciable lipid solubility, they can bioaccumulate in the fatty layers in the various organisms in the ecosystem. POPs are transported beyond international borders by wind and water and are found in places far from its sources. POPs can be considered as "forever chemicals" due to their ability to persist in the environment for longer durations without any significant chemical, photolytic, or biological degradation (Harrison & Harrad, 2001; Alharbi et al., 2018).

2 Compounds Indexed as Persistent Organic Pollutants

The overarching pollution of the environment and living organisms by POPs has resulted in acute as well as chronic toxic effects in many living species. Under the leadership of United Nations Environment Programme (UNEP), 12 classes of organic compounds (or the "dirty dozen") were identified as persistent organic pollutants in the Stockholm Convention of Persistent Organic Pollutants held in 2001 (Lallas, 2001), with a worldwide ban on these chemicals. These initial persistent organic pollutants identified as the "dirty dozen" included Aldrin, Dieldrin, Mirex, DDT (or Dichlorodiphenyltrichloroethane), Endrin, Chlordane (or Kepone), Heptachlor, Toxaphene, Hexachlorobenzene (or HCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (or PCDFs), and polychlorinated dibenzodioxins (or PCDDs). Based on the extent of toxic effects on human beings and the environment, many pesticides, chemicals of industrial use, and industrial by-products were classified into three different Annexes (A, B, and C) in the Stockholm Convention. The production and use of chemicals under Annex A should be completely eliminated, the chemicals under Annex B have restricted use, whereas any inadvertent production of pollutant will fall under Annex C (Porta & Zumeta, 2002; Tang, 2013). In subsequent years, additional organic pollutants were included in the list of POPs (Table 1) based on the amendments held biennially from 2009 to 2019. In addition to these chemicals, a few chemicals such as Dechlorane Plus, Methoxychlor as well as Perfluorohexanesulphonic acid (PFHxS), its salts, and related compounds are proposed for listing under the Convention to be held next.

Table 1 New POPs listed in Stockholm Convention amendments 2009–2019

S. no.	Chemical name	Annex	Year of listing decision	Main uses
1	α-Hexachlorocyclohexane (α-HCH)	A	2009	Pesticide
2	β-Hexachlorocyclohexane (β-HCH)	A	2009	Pesticide
3	Chlordecone (Kepone)	A	2009	Pesticide
4	Hexabromobiphenyls	A	2009	Flame retardant
5	Hexabromodiphenyl ether and heptabromodiphenyl ether (hexa-BDE, hepta-BDE)	A	2009	Industrial chemical
6	Lindane (γ-HCH)	A	2009	Insecticide; used to treat lice and scabies in humans
7	Pentachlorobenzene	A, C	2009	Pesticide, industrial chemical, and by-product
8	Perfluorooctanesulphonic acid (PFOS), its salts, and perfluorooctanesulphonyl fluoride (PFOSF)	B	2009	Industrial chemical
9	Tetrabromodiphenyl ether and pentabromodiphenyl ether (tetra-BDE, penta-BDE)	A	2009	By-product
10	Endosulfan and related isomers	A	2011	Pesticide
11	Hexabromocyclododecane (HBCD)	A	2013	Flame retardant
12	Hexachlorobutadiene (HCBD)	A, C	2015	By-product in manufacture of chlorinated aliphatic compounds
13	Pentachlorophenol (PCP) and its salts and esters	A	2015	Pesticide, industrial chemical
14	Polychlorinated naphthalenes (PCNs)	A, C	2015	Industrial chemical
15	Decabromodiphenyl ether (deca-BDE)	A	2017	Industrial chemical, flame retardant
16	Short chain chlorinated paraffins (SCCPs)	A	2017	Industrial chemical
17	Dicofol	A	2019	Pesticide
18	Perfluorooctanoic acid (PFOA) and related compounds	B	2019	Industrial chemical

3 New POPs Listed in Stockholm Convention Amendments – Post the "Dirty Dozen"

Depending on the toxicity and adverse effects on the environment, after 2001 many other compounds were added to the existing list of persistent organic pollutants, with a ban on the production and/or the use of these toxic chemicals. The new POPs that cause unpropitious consequences on humans and the environment were placed in three categories, namely, pesticides, industrial chemicals, and by-products. In this section, the adverse effects of the new POPs added in the Stockholm Conventions which were held biennially from 2009 to 2019 will be described.

3.1 Hexachlorocyclohexanes (HCHs)

Hexachlorocyclohexanes (HCHs) are derivatives of cyclohexane with one hydrogen atom and one chlorine atoms attached each of the six carbon atoms. HCHs can be prepared by the chlorination of benzene at around 500 K in presence of ultraviolet light. The aromatic nature of the benzene ring is lost, and the net effect is the addition of six chlorine atoms across the three double bonds. Since HCHs are prepared from benzene, they are also erroneously known as benzene hexachlorides or BHCs. Of the isomers known, this chapter will focus only on three stereoisomers, namely, α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), and lindane (γ-hexachlorocyclohexane or γ-HCH or gammallin), that were indexed as POPs in the Stockholm Convention (Fig. 1).

Lindane was used in agricultural field as an insecticide for the seed treatment of barley, rye, corn, sorghum, canola, oat, and wheat. It was also used as a veterinary drug for the treatment of scabies and pediculosis in pets and livestock, but not without serious side effects (Mallinckrodt & Machbert, 1997; McCarthy et al., 2004; Thomas et al., 2006). α- and β-HCHs can also be obtained as by-products during the commercial manufacture of lindane. α- and β-HCHs lack the insecticidal properties but are present in commercially available lindane as impurities. HCHs have varying extent of solubility in organic solvents such as ethanol, ether, and benzene. They have poor solubility in water. They are highly stable and persistent in the ecosystem. HCHs can be conveyed over long distances by natural processes such as grasshopper effect or global distillation. The transport potential of HCHs is higher when compared to many other contaminants and HCHs are detected even in the Arctic (Su et al., 2006). In soil, they can leach to surface water and ground water and have the potential to bioaccumulate in food chains and biomagnify (Bidleman et al., 2007; Niu et al., 2013).

HCHs are considered to be extremely hazardous. α-HCH and β-HCH are considered to be more toxic than lindane. HCHs can enter the body by eye contact,

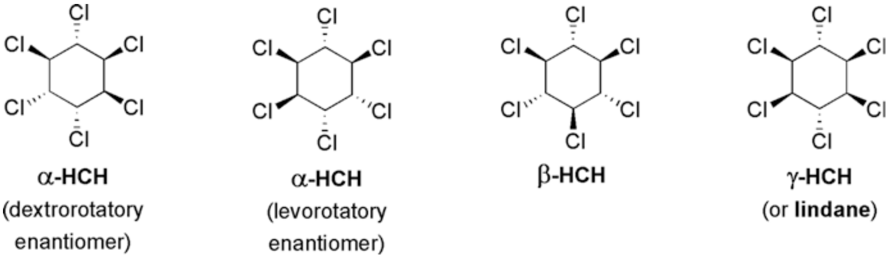


Fig. 1 Structures of α-, β-, and γ-hexachlorocyclohexanes

swallowing them, absorbing them through the skin, and inhaling air contaminated with HCHs. Intake of foods, such as milk, meat, and produce, is another source of human exposure of HCHs (Yu et al., 2009). They possess a great threat to seed-treatment workers. HCHs can accumulate in the brain and the placenta. It is also detected in human milk. HCHs can cause variable thyroid hormone levels, burning sensations, chemical homeostasis, aplastic anemia, oxidative stress, seizures (in rare cases), renal dysfunction, itching, rashes, dryness, testosterone- and estrogen-related issues, reproductive effects, and skin irritations. They have neurotoxicity and can also damage the dopaminergic system of the brain, resulting in improper development of the brain. Exposures to HCHs were also linked to Alzheimer and Parkinson's diseases. They are also potential human carcinogens (Willett et al., 1998; Hall & Hall, 1999; Sujatha et al., 2001; Álvarez-Pedrerol et al., 2008; Nolan et al., 2012; Loomis et al., 2015; Zhang et al., 2017).

3.2 Chlordecone

Chlordecone or Kepone is an example of organochlorine compound and is obtained when Mirex undergoes degradation (Fig. 2). It was used as an insecticide and fungicide on ornamental shrubs, tobacco, and non-bearing citrus trees. It was used to control banana root borers, ants, and roaches. It was mainly used in the French West Indies between 1972 and 1993. It can easily bioaccumulate in marine species and animals living in areas where chlordecone is used for pest control. In the environment, chlordecone does not undergo any significant abiotic or biotic breakdown. It is fairly immobile and highly persistent in water or soil for years. It is distributed in large amounts in crops, ground water, spring water, rivers, soils, and aquatic biota (Cabidoche et al., 2009).

The toxic nature of chlordecone toward humans was found out only in 1975, after a poisoning incident at Virginia, USA. The contamination of chlordecone was also found in the James River, Virginia. The fishes in the James River were observed to have a high content of chlordecone present in them (Luellen et al., 2006). Human exposure to chlordecone may arise from devouring food contaminated with this pesticide such as bananas, root vegetables, cucurbitaceous food, and seafood (Dubuisson et al., 2007). Chlordecone is highly lipophilic with a high content seen

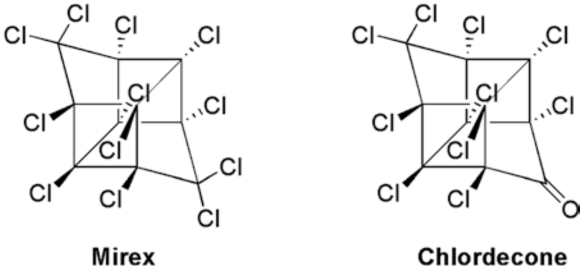


Fig. 2 Structures of Mirex and chlordecone

in the liver and blood plasma. It can cut across the placental barrier and is also transferred to newborn through maternal milk thereby exposing the developing species during the early stages of growth (Boucher et al., 2013). Developmental disorders, neurotoxicity, diabetes, prostate cancer, endocrine disruption, oligospermia, lowered sperm motility, cerebral anomalies, estrogenic effects, and reproductive toxicity and other toxic effects include oculomotor dysfunctions, hepatomegaly (enlarged liver), incoordination, irritability, slurred speech, ataxia, mood disorders, appendicular intentional tremors, and recent memory loss were also reported (Faroon et al., 1995; Laessig et al., 2007; Dallaire et al., 2012; Kadhel et al., 2014; Multigner et al., 2010, 2016).

3.3 Hexabromobiphenyls

Hexabromobiphenyls are derivatives of biphenyls containing six bromine atoms (Fig. 3). They belong to the broader group of pollutants, polybrominated biphenyls (or PBBs). They are the bromo analogs of the corresponding hexachloro derivatives of PCBs. They were utilized as flame retardants in a diversified range of plastic

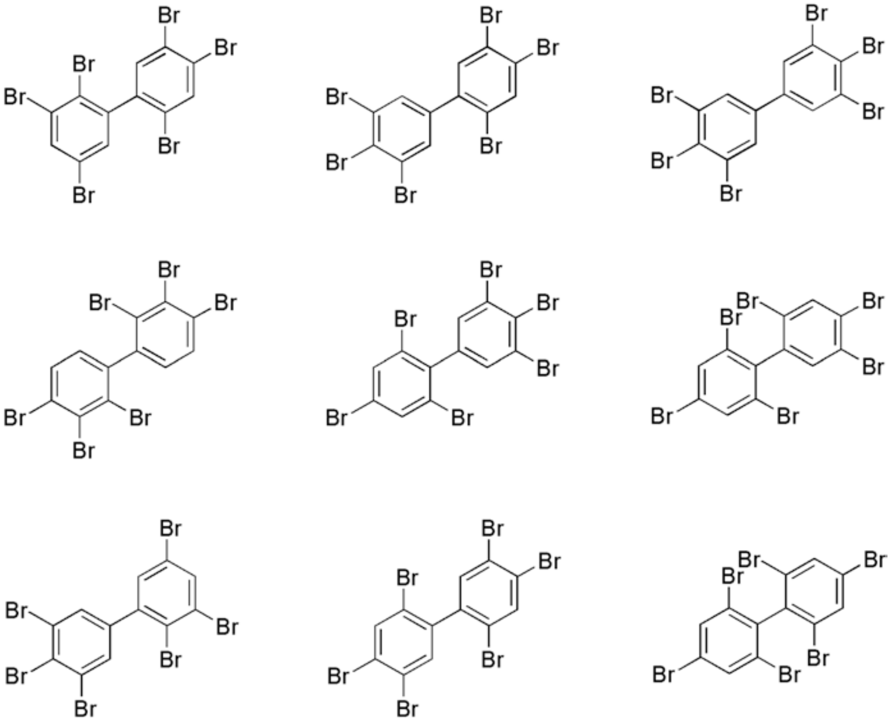


Fig. 3 Structures of some hexabromobiphenyls

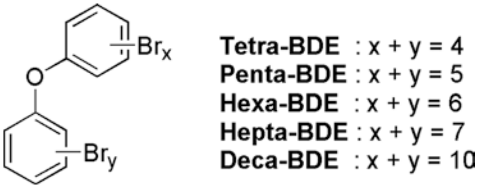
products (laptop cabinets), home electrical appliances (TV and radio parts), polyurethane foams (for automobile upholstery), textiles, etc. 2,4,5,2′,4′,5′-Hexabromobiphenyl was the chief ingredient of FireMaster BP-6, a flame retardant, consisting of about 18 different congeners of PBBs (Safe et al., 1978). In 1973, contamination of livestock feed with FireMaster BP-6 led to the death of several thousands of cattle, sheep, chickens, and pigs in Michigan, USA (Carter, 1976).

Similar to PCBs, hexabromobiphenyls are insoluble in water and are soluble in organic solvents, for instance, benzene or toluene. They bioaccumulate in food chain, which is supported by monitoring the results from many wildlife studies. Exposure of the coplanar stereoisomer of 3,3′,4,4′,5,5′-hexabromobiphenyl can cause cellular oxidative stress, disorders related to central nervous system, skin acne, immune system abnormalities, and neonatal fatalities even at low doses. Hexabromobiphenyls are classified as possible human carcinogens. The other symptoms of exposure of hexabromobiphenyls included joint pain, hypothyroidism, loss of appetite, nausea, lethargy, and abdominal pain (Bekesi et al., 1978; Bahn et al., 1980; Curran et al., 2006). Girls who were exposed to hexabromobiphenyls in utero had an earlier age of menarche when compared to those who were not exposed to this pollutant (Blanck et al., 2000).

3.4 Bromodiphenyl Ethers (BDEs)

Polybromodiphenyl ethers (or PBDEs) are derivatives of diphenyl ether containing multiple bromine atoms. They have the general formula $C_{12}H_{10-x}Br_xO$ (where $x = 1$ to 10) and depending on the number and location of the bromine atoms a total of 209 congeners are possible. Lower brominated PBDEs have 1–4 bromine atoms, whereas higher brominated have 5–10 bromine atoms. This section discusses only the five types of PBDEs (Fig. 4) that were classified as POPs. The total number of isomers for tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, and deca-BDE are 42, 46, 42, 24, and 1, respectively. PBDEs were primarily used as flame retardants in upholstery, textiles, electronic devices (e.g., computers, TV sets, and radio), carpets, and electrical equipment (e.g., printed circuit boards or insulation board) (Rahman et al., 2001). PBDEs can be prepared by the bromination of diphenyl ether in presence of suitable catalyst. Deca-BDE is the completely brominated PBDE congener (Om et al., 1996).

Fig. 4 Structures of PBDEs



The presence of PBDEs is a global issue with pollutants found even in remote areas. They are lipophilic compounds. They are structurally similar to PCBs and PBBs and hence with regard to the chemical properties, distribution in the ecosystem, long-distance transport, and persistence, the trends of PBDEs are similar to that of PCBs and PBBs. Concentrations of PBDEs in the environment are higher than that of the PCBs. PBDEs are known to biomagnify even in the Arctic food web. They were also detected in dust, indoor air, and electronics recycling sites. PBDEs are observed in umbilical cord blood and breast milk. Other primary sources of PBDEs include diet (especially seafoods), eggs, meat products, oils, vegetables, and dairy products (Guo et al., 2007; Frederiksen et al., 2009; Toms et al., 2009; Möller et al., 2011; Rosenberg et al., 2011). Exposure to PBDEs affects the thyroid hormone, brain, hepatic enzyme activity in offspring, reproductive system, liver, and thyroid hormone. They also cause developmental neurotoxicity, teratogenic effects, homeostasis, endocrine disruption, and nervous system toxicity (Zhou et al., 2002; Schecter et al., 2006; Costa & Giordano, 2007; Tseng et al., 2006, 2008; Vilberg et al., 2007; Koren et al., 2019; Li et al., 2020).

3.5 *Pentachlorobenzene*

Pentachlorobenzene (PeCB or PCBz) is a chlorinated hydrocarbon and the derivative of benzene with five chlorine atoms. A large number of industrial process involving carbon and chlorine, especially those involving high temperatures, are known to produce pentachlorobenzene as the undesired by-product. Other intentional and unintentional sources of PeCB formation in the ecosystem include incomplete and uncontrolled combustion of industrial, household, or medical wastes containing chlorinated compounds, combustion of biomass containing chlorine and carbon, degradation of pentachloronitrobenzene, anaerobic dechlorination of HCBs, and forest fires (Pavlostathis & Prytula, 2000; Bailey et al., 2009). PeCB has been detected in the atmosphere, soil, water, lake sediments, and biota.

PeCB does not have any known commercial uses at present. It was used initially along with PCBs in electrical equipment. Earlier, it was also mixed with other PCBs and used as flame retardant, dyestuff carriers, wood preservatives, and fungicide. It was also used as an intermediate in the production of quintozene (or pentachloronitrobenzene). It is persistent and bioaccumulative. A very long residence time and ability for long-distance transport in the atmosphere was observed for PeCB. PeCB is very toxic to insects, rats, mice, and aquatic species, but it is moderately toxic to humans. It accumulates more in placenta than in breast milk. PeCB is accountable for the depletion of thymic lymphocytes, hampering of placental function, stimulation of estradiol and testosterone secretion as well as inducing histopathological changes in the liver and histopathological effects in the kidney (Giddings et al., 1994; Landrum et al., 2004; Gregoraszczuk et al., 2011, 2014; Sun et al., 2019).

3.6 *Perfluorooctanesulphonic Acid (PFOS), Its Salts, and Perfluorooctanesulphonyl Fluoride (PFOSF)*

Perfluorooctanesulphonic acid (PFOS), its salts, and perfluorooctanesulphonyl fluoride (PFOSF) constitute a class of organofluoro compounds with consumer and industrial applications. The base catalyzed hydrolysis of PFOSF results in the formation of salts of PFOS; acidification of these salts (van Dyke, 1963; Hebert et al., 2002; Zhang et al., 2002) with concentrated sulphuric yield the free PFOS which can be separated by fractional distillation (Fig. 5). These fluorochemicals are used in various stain repellents for carpets, wax, varnishes, paints, fire-fighting foams as fluorosurfactants, polishes, fat and oil repellents in food packaging, hydraulic fluids for airplanes, insect baits in controlling leaf-cutting ants, and impregnation agents for leather, paper, upholstery, and textile. They were also used in semiconductor industry, metal plating (hard metal and decorative plating), and water repellents for clothing (Lehmler, 2005; Paul et al., 2009).

These organofluoro pollutants have been detected in air, soil, surface water, tap water, ground water, industrial effluents, and marine organisms. They may result in long-term adverse effects in marine environment and are toxic to aquatic organisms. Non-selective toxicity has been reported in rabbits, rats, and monkeys. Adverse effects due to exposure of these fluorochemicals include inhibition of gap junctional intercellular communication hindering the cell growth, increase in liver weight, developmental toxicity, increase in free cholesterol and triglyceride levels, aphagia, neuroendocrine issues, mitochondrial uncoupling as well as cause peroxisome proliferation in rats and mice (Berthiaume & Wallace, 2002; Hu et al., 2002; Starkov & Wallace, 2002; Alexander et al., 2003; Austin et al., 2003; Grasty et al., 2003; Lau et al., 2004). Ingestion and inhalation of dust contaminated with these polyfluoro compounds are the main source of human exposure. The toxicology data on humans are limited. Available human data suggest that these organofluoro compounds can also bind to human serum proteins. These chemicals can also cross placental barrier and are primarily retained in liver and blood. A lower birth weight was observed due to exposure to PFOS, with female infants being more vulnerable to PFOS when

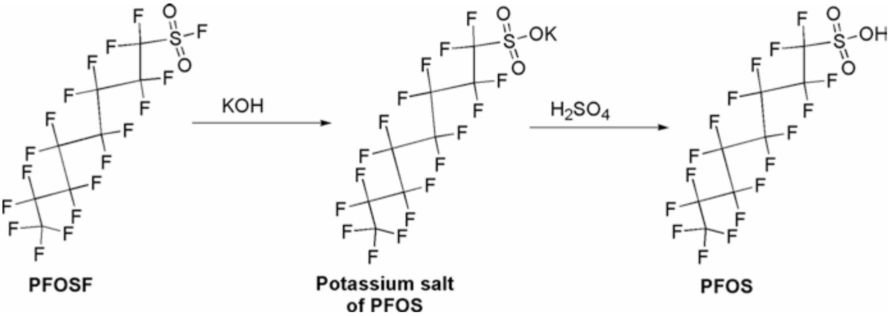


Fig. 5 Synthesis of PFOS from PFOSF

compared with male infants. An impaired sperm quality with lowered sperm concentration and count as well as altered pituitary gonadal hormones was observed in men due to the presence of these organofluoro compounds. Bladder cancer and mortality were also reported among the employees in the manufacturing facility of these chemicals (Luebker et al., 2002; Olsen et al., 2003; Shipley et al., 2004; Alexander & Olsen, 2007; Fei et al., 2007; Joensen et al., 2009; Washino et al., 2009).

3.7 Endosulfan and Related Isomers

Endosulfan is a chlorine containing organic compound used globally in agriculture. It was used as a wood preservative and also to control insect pests such as cabbage worms, leafhoppers, aphids, potato beetles, and whiteflies before being phased out worldwide. It can be prepared by the Diels-Alder reaction of cis-butene-1,4-diol to form the Diels-Alder adduct, followed by the reaction of thionyl chloride with the resulting adduct. Endosulfan can exist as the endo and the exo stereoisomers (Fig. 6) which are also known as α-Endosulfan and β-Endosulfan, respectively. The β-isomer is known to convert irreversibly to the α-isomer due to more thermodynamic stability of the latter (Schmidt et al., 1997, 2001).

In air samples, the α-isomer is predominant, whereas in rain samples the β-isomer is more (Chan & Perkins, 1989; Burgoyne & Hites, 1993). If there is additional oxygen attached to sulfur, then the compound is called endofan sulfate and is formed by the oxidation of endosulfan. Additional breakdown products of Endosulfan are Endosulfan furan and Endosulfan diol. The oxidation and the breakdown products of Endosulfan are also of toxicological concern. Endosulfan is a ubiquitous contaminant in the environment. It is subject to long range transport in the atmosphere and is a persistent pollutant. It can bioaccumulate in fishes. Endosulfan is toxic to many birds and aquatic organisms (Tumburu et al., 2011). It shows moderate toxicity toward honey bees and also can result in reduced population of beneficial insects. Absorption of Endosulfan may take place through skin contact, inhalation, ingestion, or through transfer across the placental membrane. In humans and animals, it causes endocrine disruption, DNA damage, developmental dysfunction, permanent brain damage, teratogenic effects, elevation of testosterone biotransformation and

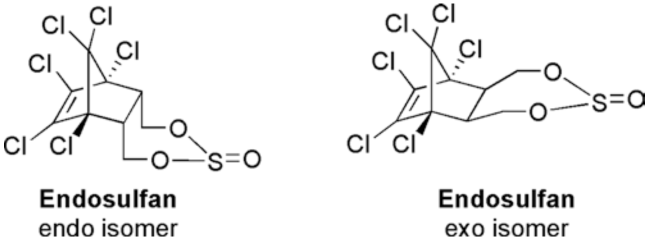


Fig. 6 Stereoisomers of endosulfan

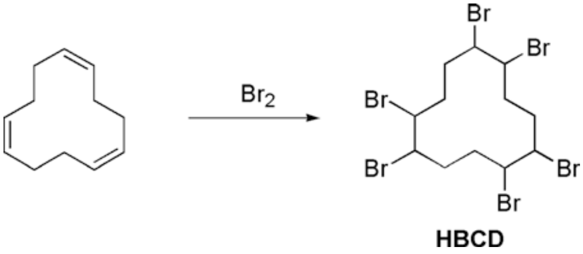
elimination, modulation of estrogen dependent genes, delay in sexual maturity among boys as well as reproductive dysfunction. It also shows convulsions, estrogenic effects, skin irritation, staggering, rashes, hyperactivity, neurotoxic effects, diarrhea, lack of coordination, nausea, vomiting, tremors, difficulty in breathing, temporary blindness, and unconsciousness. A low dose of 35 mg kg^{-1} has been documented to be fatal for humans resulting in death (Soto et al., 1994; Wilson & LeBlanc, 1998; Saiyed et al., 2003; Singh et al., 2007; Varayoud et al., 2008; Silva & Gammon, 2009; Sebastian & Raghavan, 2016; Menezes et al., 2017).

3.8 *Hexabromocyclododecane*

Hexabromocyclododecanes (HBCDs or HBCDDs) are a class of organobromine compounds which consists of six bromine atoms attached to cyclododecane ring. HBCDs can be produced by the bromination of cyclododeca-1,5,9-triene (Fig. 7). A mixture of 16 possible isomers in the case of 1,2,5,6,9,10-hexabromocyclododecane (HBCD) comprising of four meso-forms and six pairs of enantiomers, making it a concern for the manufacture in the pure form (Law et al., 2005). Technical HBCD, however, consists of a mixture of isomers. It was used as a brominated flame-retardant additive in textile, polystyrene foams, unsaturated polyesters, polyvinyl chloride materials, etc. It was also used as thermal insulations of construction materials, wall coverings, roller blinds, electronic and electric equipment, and back coating of upholstery (Zhan et al., 2019).

The presence of HBCDs has been detected in a wide range of biotic and abiotic environment (e.g., sediment, soil, air, freshwater, terrestrial water, marine organisms, sewage sludge), human breast milk, birds, food, and in remote area such as the Arctic (Jo et al., 2017; Cao et al., 2018). HBCDs are highly persistent, resistant to degradation through photolytic, biological, or chemical processes as well as bioaccumulate in aquatic and air-breathing organisms (Harrad et al., 2009). Dust, air, food, and consumer products are the main sources of exposures of HBCDs to humans. Exposure may be via oral or dermal. Many in vivo and in vitro studies in human and animal cell lines have showed immunotoxicity, damage to nervous system, thyroid toxicity, reproductive effects, oxidative stress, neurotoxicity, and

Fig. 7 Synthesis of HBCD



altered lipid metabolism (Covaci et al., 2006; Szabo et al., 2010; Marvin et al., 2011; Du et al., 2012; Gannon et al., 2019; Moreau & Nong, 2019; Shi et al., 2019).

3.9 Hexachlorobutadiene (HCBD)

Hexachlorobutadiene (HCBD) is completely chlorinated derivative of butadiene. HCBD is generally obtained as a by-product in the manufacture of tetrachloromethane (CCl_4) and tetrachloroethene ($CCl_2 = CCl_2$). It can also be synthesized by the direct chlorination of butadiene or butane. Its most common use is as solvent, mainly for chlorine and other chlorine containing compounds. It is also used as a scrubber for the removal of chlorine bearing contaminants (Rossberg et al., 2006; Marshall & Pottenger, 2016). In IR spectroscopy, HCBD is used instead of Nujol as mulling agent to analyze C-H stretching frequencies, though precaution is needed as some organometallic compounds react with HBCD (Girolami et al., 1999). The applications of HCBDs as algicide and herbicide were known, but they are now prohibited due to their high toxicity. Other uses of HCBD are as protective coatings, chemical intermediates in the manufacture of chlorofluorocarbons, rubber and lubricants, plastic additives as well as in the manufacture of carbon hollow spheres, organosilicon polymers, and photopolymerized films. HCBDs are highly persistent in the environment, can travel long distances without decomposition, and can bioconcentrate in fishes and other aquatic species.

HCBDs have been detected in human liver samples. Cereals, fish, poultry, eggs, milk, bread, fruits, vegetables, meat, and meat products are the main sources of HCBD intake (Fernandes et al., 2019). The exposure of HCBDs is generally though dermal, oral, and inhalation routes. HCBDs are also labelled as confirmed animal carcinogen and genotoxic compounds. In mice and rats, the damage of cortical renal tubules, lipid peroxidation in renal cells, downregulation of regucalcin, and abnormal sperm morphology were observed. The other effects of exposure of HCBDs include depression of central nervous system, fatty liver degeneration, cyanosis, nephrotoxicity, and epithelial necrotizing nephritis (Choudhary, 1995; Green et al., 2003; Chiusolo et al., 2008, 2010; Brüschweiler et al., 2010; Sadeghnia et al., 2013; Zhang et al., 2019).

3.10 Pentachlorophenol (PCP) and Its Salts and Esters

Pentachlorophenol (PCP) is a chlorine containing anthropogenic substance. PCP can be obtained by the chlorination of phenol in presence of anhydrous aluminum chloride ($AlCl_3$) or ferric chloride ($FeCl_3$) as catalyst. The main sources of PCP, its sodium salt (sodium pentachloro phenolate or Na-PCP), and laureate ester (pentachlorophenyl laureate or PCPL) are the wastes from the industries (Fig. 8). PCPs (i.e., PCP, NaPCP, and PCPL) were used as wood preservative (for fences, posts,

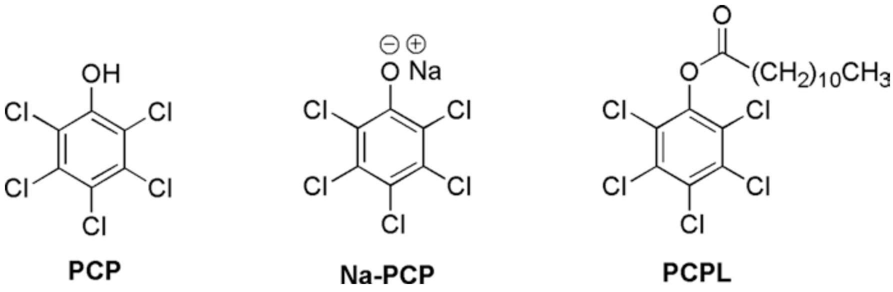


Fig. 8 Structures of PCP and related derivatives

etc.), cotton preservative in textile industry, insecticide, disinfectant, herbicide, pesticide, algaecide, and as a reagent in antifouling paint (Jorens & Schepens, 1993; Fiege et al., 2000). Technical PCP consists of a large number of impurities (e.g., other chlorophenols, polychlorodiphenyl ethers, polychlorophenoxyphenols, HCBs, PCBs, PCDDs, PCDFs, as well as chlorinated cyclohexenones and cyclohexadienones) with their compositing depending on the manufacturing unit.

PCPs have been detected ubiquitously in different environmental media such as rainwater, surface water, drinking water, soil, sediments, food materials as well as in human milk, urine, and adipose tissue (Zheng et al., 2012). PCPs are generally decomposed in the environment through photolysis, and they do not bioaccumulate that easily as does other POPs. People may be exposed to PCPs through drinking water contaminated with PCPs, inhalation of air polluted with PCPs, and dermal contact with products and soils treated with these chemicals. Exposure of PCPs has been reported to result in harmful effects on the immune system, blood, liver, nervous system, respiratory tract, eye irritation, gastrointestinal tract, reduced male fertility, and kidneys. They are considered as probable carcinogen and clastogen and are also associated with kidney cancer, multiple myeloma, non-Hodgkin's lymphoma, and long-term behavioral and learning impairment. Profuse sweating, decreased body weight, muscle twitching, leg pain, high body temperature, nausea, uncoordinated movement, loss of appetite, tremors, and coma are some of the additional side effects (Blakley et al., 1998; Chang et al., 2003; Demers et al., 2006; Guo & Zhou, 2013; Yu et al., 2013; Cheng et al., 2015; Fraser et al., 2019).

3.11 Polychlorinated Naphthalenes (PCNs)

Polychlorinated naphthalenes (PCNs) are the chloroderivatives of naphthalene with the generic chemical formula $C_{10}H_{8-(m+n)}Cl_{(m+n)}$. They are structurally related to polychlorinated dibenzodioxins (or PCDDs). The number of congeners possible for mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octachloro-naphthalenes is 2, 10, 14, 22, 14, 10, 2, and 1, respectively. Commercially available PCN consists of a mixture of these congeners with the concentration and ratio depending on the manufacturing plant. Of the 75 total congeners, some can bioaccumulate, are toxic with potential to be transported over long distances, and are persistent in the environment. They originate through combustion process, inadvertent defilement in many industrial chemicals and releases from old electrical equipment. They also occur as contaminants in many industrial chemicals such as PCBs or PCDDs.

PCNs were used as dielectrics; insulation for electric cable; cutting fluids; lubricants; preservatives for fabric, paper, and wood; plasticizers; and grinding fluids. Exposure to human can occur through dietary pathway, inhalation, and skin contact. Cereals, bread, fats, oils, meat, meat products, fruit, vegetables, milk, eggs, poultry, and fishes are rich in PCNs and are the main source of PCN intake in humans. PCNs were also detected in breast milk, liver, adipose tissue, and blood in humans (Fernandes et al., 2010; Jin et al., 2019). Exposure to PCNs results in teratogenic effects, depression, immunotoxicity, endocrine disruption, disruption to the gastrointestinal system with abdominal pain, substantial body mass loss, hepatotoxicity, chloracne, embryotoxicity, neuropathy, teratogenicity, carcinogenicity, dermal lesions, fetotoxicity, developmental toxicity, and mortality in humans and laboratory animals (Villeneuve et al., 2000; Kilanowicz & Skrzypinska-Gawrysiak, 2010; Kilanowicz et al., 2011; Gregoraszczuk et al., 2016; Fernandes et al., 2017).

3.12 Short Chain Chlorinated Paraffins (SCCPs)

Another family of organochloro anthropogenic pollutants are the short chain chlorinated paraffins (SCCPs). They are a complex mixture of polychlorinated n-alkanes having 10–13 carbon atoms. The molecular formula is given by $C_xH_{2x-y+2}Cl_y$ (where $x = 10$ to 13, $y = 3$ to 12) with $C_{10}H_{19}Cl_3$ and $C_{13}H_{16}Cl_{12}$ being the limiting molecular formulae. SCCPs are synthetic compounds and their natural source is unknown. They can be prepared by the action of chlorine gas on unbranched alkanes. They are water insoluble, but dissolve in mineral oils and chlorinated organic solvents. SCCPs find application as adhesives, paints, rubber conveyor belts, tubes for outdoor decoration bulbs, flame retardants for plastics, lubricant additives, and leather and plasticizer in rubber (Xu et al., 2019).

SCCPs are resistant to hydrolysis, have potential for long-distance transport, are persistent in the ecosystem of sufficiently long time, and can easily bioaccumulate in biota, thereby increasing the duration and probability of exposure (Ma et al., 2014; Li et al., 2016). SCCPs have been measured in marine animals, air, surface water, sediment, aquatic species, freshwater, terrestrial wildlife, a variety of food items as well as in human breast milk, maternal cord serum, and placenta (Li et al., 2017; Qiao et al., 2018; Lee et al., 2020). SCCPs are toxic to marine organisms even at low concentrations and are also categorized as possible human carcinogen. In laboratory test animals and marine organisms, SCCPs can cause renal tumor, developmental toxicity, irregular thyroid functioning, estrogenic effects, changes in metabolism, immunomodulatory effects, genetic damage, and hepatotoxcity (Tomy

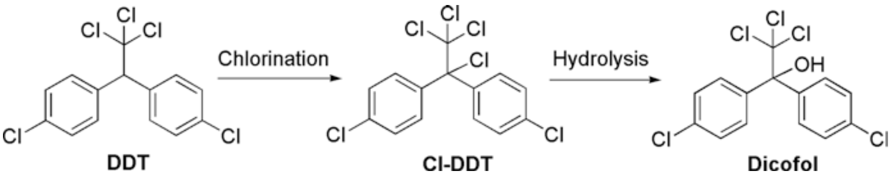


Fig. 9 Synthesis of Dicofol

et al., 1998; Bezchlebová et al., 2007; Geng et al., 2015; Zhang et al., 2016; Ren et al., 2018; Du et al., 2019; Wang et al., 2019; Zheng et al., 2020).

3.13 Dicofol

Dicofol is an organochloro pesticide, especially to prevent crops from mites. It a chemical which is structurally related to DDT and can be synthesized from DDT (Fig. 9) by chlorination (to get chloro-DDT) followed by hydrolysis (Qui et al., 2005). Dicofol was used as an acaricide on a wide variety of crops such as apples, strawberries, tomatoes, cucumbers, cotton, mint, beans, citrus fruits, stone fruits, and tomatoes. It is persistent, with capacity for long-distance transport and bioaccumulation in fatty tissues (Kumari & Duhan, 2011; Li et al., 2015). It is an example of a contact poison, killing pests after ingestion.

Dicofol is dangerous to many birds and animals. With only limited data available on Dicofol, it was inferred that it results in thinning of egg shell, reduced offspring survival, increase of liver weight, muscle twitching, hemolysis, overstimulation of nervous system, rupture of erythrocytes, reduced fertility, endocrine disruption, seizures, numbness, weakness in hands and feet, unconsciousness, and in some cases even death. In addition, Dicofol can cause skin irritation by dermal contact, conjunctivitis by eye contact, vomiting, nausea, headache, and poor appetite (Schwarzbach, 1991; Jadaramkunti & Kaliwal, 2002; Kamata et al., 2010; Ahmad & Ahmad, 2017; Haeba et al., 2008; Xu et al., 2020).

3.14 Perfluorooctanoic Acid (PFOA) and Related Compounds

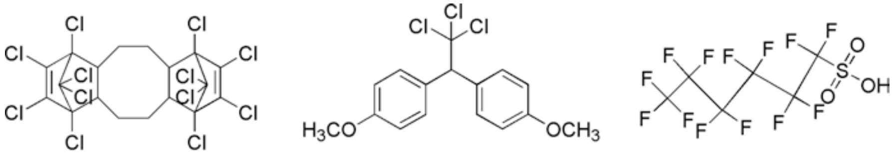
Perfluorooctanoic acid (PFOA) is a perfluorinated carboxylic acid consisting of eight carbon (in a linear chain) and 15 fluorine atoms. It can function as a fluorosurfactant consisting of a carboxylate “head group” (which interacts with polar groups) and n-octyl “tail group” (which interacts with non-polar and lipophilic part). PFOA-related compounds are any chemicals (salts, esters, or amides of PFOA; except for PFOS and its derivatives) that can be easily degraded or converted to PFOA. Electrochemical fluorination or telomerization are the two major methods involved in the synthesis of PFOA (Savu, 2000). For the past six decades, these anthropogenic chemicals were incorporated in a variety of useful products.

Several industrial applications of PFOA and related compounds include surfactants, thread sealants, floor wax, protecting agents for leather and upholstery, dental floss, fire-fighting foam, cleaners, stain-resistant textiles and apparels, emulsifier, wetting agents, grease-resistant food packaging, apparel membranes, and stain-resistant carpeting. They can also be employed to manufacture commercially relevant side-chain polyfluorinated polymers which are oil, water, and stain repellent and find applications in adhesives, floor waxes, stone sealants, paints, lacquers, surface finishes (for apparels and textiles), paper, cardboard, paper, wood sealants, etc. PFOA and related compounds have potential for long-range transport, are persistent in the environment and bioaccumulate in many air-breathing and water-breathing species, making their presence ubiquitous in the ecosystem (Lindstrom et al., 2011). Industries manufacturing side-chain polyfluorinated polymers, fire-fighting foams, textiles, and apparels are the primary source of pollution of PFOA and related compounds (Prevedouros et al., 2006).

Exposure of PFOA and related compounds in humans typically occurs through consumption of food, drinking water, inhalation of dust and air, as well as dermal contact with products contaminated with these pollutants. They do not accumulate more in fatty tissues but are found in blood, maternal milk and can be transferred to the fetus through the placental membrane (Conder et al., 2008; Monroy et al., 2008). Major adverse effects associated with these pollutants include impaired neurodevelopment, pregnancy-induced hypertension, testicular cancer, reproductive effects, neonatal mortality, liver toxicity, ulcerative colitis, endocrine disruption, immunotoxicity, kidney cancer, developmental effects, thyroid disease, and high cholesterol (Kennedy et al., 2004; Lau et al., 2007; Fei & Olsen, 2010; Nelson et al., 2009; Melzer et al., 2010; Steenland et al., 2010; Jacquet et al., 2012; Stein et al., 2014; Pierozan et al., 2018; Shane et al., 2020; Zhong et al., 2020).

4 The POPs of the Future

A few other chemicals such as Dechlorane Plus, Methoxychlor as well as Perfluorohexanesulphonic acid (PFHxS), its salts, and related compounds (Fig. 10) are proposed for review to be considered as POPs under the Stockholm Convention



Dechlorane plus **Methoxychlor** **PFHxS**

Fig. 10 Structures of the POPs under review for future inclusion to be held in future. This section briefly summarizes the adverse effects of these proposed POPs.

4.1 Dechlorane Plus

Dechlorane Plus is a polychlorinated high-production-volume (HPV) anthropogenic chemical and can be prepared by the Diels-Alder reaction of one equivalent of 1,5-cyclooctadiene with two equivalents of hexachlorocyclopentadiene (Garcia et al., 1991). Technical mixture of Dechlorane Plus consists of the syn- and the anti-isomers. Dechlorane Plus was used as a flame retardant and was introduced in the market as a substitute for Mirex. It was also used in industrial polymers (e.g., polybutylene terephthalate, acrylonitrile butadiene styrene, nylon, polypropylene), synthetic elastomers, plastic roofing materials, computer accessories, and electrical cables and wires (Zheng et al., 2010).

Dechlorane Plus has poor solubility in most of the solvents and if stored properly has an infinite shelf life. It is persistent in the environment, subject to transport over long distances in the ecosystem with potential to bioaccumulate and biomagnify. The presence of Dechlorane Plus was observed in air, dust, water, aquatic biota, tree bark, eggs of birds, sediments, soil, human serum, and human hair, raising concern over its usage (Xian et al., 2011). Inhalation and oral and dermal routes of exposures were described. Reported effects of the exposure of Dechlorane Plus include endocrine disruption, lesions in muscle fibers, neurotoxicity, effects on sex hormones, liver impairments oxidative stress, thyroid issues, induced cell apoptosis, and oxidative damage. It is also known to cross the blood-brain barrier (Ben et al., 2014; Chen et al., 2017; Gagné et al., 2017; Gong et al., 2018; Peshdary et al., 2019).

4.2 Methoxychlor

Methoxychlor is structurally similar to DDT with the chlorine atoms on the aromatic ring being replaced with methoxy groups. It was used to protect pets, livestock, forage crops, fruits, vegetables, and ornamentals against cockroaches, fleas, mosquitoes, and other insects. It was supposed to be a replacement for DDT. Methoxychlor is a contact insecticide. Methoxychlor can be prepared by the action of two equivalents of methoxybenzene (or anisole) with one equivalent of chloral, in presence of sulphuric acid. It can be absorbed or ingested by living organisms and has the potential to bioaccumulate in food chains. It is persistent in the environment and has the ability for long-distance transport. Exposure to this pollutant on fishes and laboratory animals can result in endocrine disruption, developmental toxicity, neurotoxicity, reproductive toxicity, disruption of spermatogenesis, and birth defects (Reuber, 1980; Miller et al., 2006; Lafuente et al., 2007; Ali & Azhar, 2013).

4.3 *Perfluorohexanesulphonic Acid, Its Salt, and Related Compounds*

Perfluorohexanesulphonic acid (PFHxS) is an organofluoro compound previously used in fire-fighting foam and stain coatings for paper, carpets, and textile. It can also be used in the manufacture of side-chain fluorinated polymers. Its usage is now banned in many countries. Inhalation of air and through skin contact are the two major sources of exposure to these pollutants. It is observed in human maternal milk and blood (Beesoon et al., 2012; Mondal et al., 2014). The toxicity of PFHxS, its salts, and related compounds can be compared to that of PFOS, its salts, and related compounds. Major adverse effects related to PFHxS, its salts, and related compounds include asthma, liver damage, behavioral problems, immune system impairments, learning problems, reproductive toxicity, as well as altered human cholesterol and triglyceride levels (Hoffman et al., 2010; Lee & Viberg, 2013; Power et al., 2013; Lee et al., 2014; Webster et al., 2014).

5 Summary

Persistent organic pollutants (POPs) are considered as “forever chemicals” due to their semi-volatility, lipophilicity, potential for long-distance transportation, ability to biomagnify and bioaccumulate, resistance to degradation, and high persistence in the environment. The world is under great threat due to the use of POPs. These “silent killers” have created various adverse on health of the living beings (plants, animals, and humans) and the environment. Endocrine disruption, carcinogenic effects, reproductive dysfunction, teratological effects, obesity, diabetes, cardiovascular issues, and sometimes even death are some of the major health concerns associated with the POPs on humans and other living beings. In the overall picture, the data at one’s disposal indicate reason for concern.

6 Future Outlook

In short, the POPs are the unvoiced enemies to mankind due to their extensive use in agricultural and industrial sector. A collective fight should be there to avoid or reduce the exposure of these POPs globally. Educating people of all sectors about the adverse effects of POPs on the environment is essential. Industries should try to phase out the production of POPs, try to look out secure substitutes, and also develop the utility of cleaner and more efficient processes to reduce the manufacture of unintentional POPs. There is need for the development of cheap, effective, and fast techniques for the removal of the POPs from the environment. Early identification of any adverse effect as well as facile degradation of the suspected POPs is essential. Development of novel degradation techniques without the use of toxic chemicals and resulting in complete degradation to less toxic compounds may be a good method for the removal of the existing POPs. A global solution in as cost-effective and eco-friendly manner, tailored to the socioeconomic considerations of the different countries, should be implemented for this problem by working together. POPs are expected to continue to furnish exceptionally fertile field of research for the foreseeable future. Research should be carried out to understand a finer mechanism of the processes involving POP emission, deposition, quantification, and degradation in the environment. A thorough knowledge associated with the sources, behavior, effects, and fate of the POPs (currently listed and those that are subject of study) is highly essential to prevent mankind from replicating the mistakes of the past.

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Environmental Deterioration Due to Existing and Emerging Persistent Organic Pollutants: An Overview

H. Thilagam and S. Gopalakrishnan

Abstract Due to increase in industrialization and rapid civilization, excessive numbers of chemicals are being discharged into the atmosphere. Persistent organic pollutants (POPs) are worldwide concern due to their widespread occurrence, enhanced persistence, distant transference, greater biomagnification and bioaccumulation which could affect the human health and other organisms in the ecosystems. Organic pollutants accumulating in aquatic sediments can adversely affect the benthic organisms, and the same can be thrown back into the ecosystem during resuspension and/or through the food chain from benthic to pelagic organisms and so on. This chapter summarizes the recent findings on the impact of existing and emerging POPs on ecosystem and various organisms including human. In recent years, some of the emerging contaminants including polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonate (PFOS) are classified under POPs, and these contaminants have been widely reported in environment. Though the concentrations of emerging POPs in the environment are presently very low, it has been estimated that they would dramatically increase owing to social and economic development. The impact of these pollutants on humans varies from skin rashes to cancer. Congenital disorders and metabolic diseases due to POPs could have significant health impacts for future generations as well. This chapter also addresses studies looking at the relations between the exposure and consequences of POPs to human health emphasizing the impact of these pollutants with reference to their gender-specific effects. This chapter also reviews a wide array of methods which can be used as markers to identify the effect of persistent pollutants on different organisms. Biomagnification and bioaccumulation were used as a tool for revealing the impact on the aquatic systems. Overall, studies in this field relating to POPs are not abundant, and hence extensive studies need to be conducted to increase our

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understanding on the health and ecological consequences of these contaminants in order to devise strategies for not only preventing exposure but also for ecological remediation.

Keywords POPs · PBDEs · PFOS · Bio-magnification · Bio-accumulation · Aquatic systems

1 Introduction

Environmental pollutants are not only harmful to our ecosystem but also lead to several health concerns disturbing the human population worldwide. Among the xenobiotics, concern over the potential impact of organic contaminants to the ecosystem and human has increased tremendously during last five decades. Anthropogenic activities, industrial and agricultural runoffs, have led to the introduction of these xenobiotics to the environment, and most of these pollutants are man-made synthetic organic compounds. The ultimate sink for these pollutants is the aquatic environment; it could be either due to direct releases or to hydrologic and atmospheric processes (Stegeman & Hahn, 1994). A portion of these organic compounds comprise greater impact to the living beings and apparently alter the construction and function of the ecosystem. The occurrence of these contaminants in an aquatic ecosystem does not, by itself, indicate adverse effects, but presumably reflect the level of accumulation in the tissues of the organism. Further, the physicochemical properties of these hazardous substances could determine their distributions and fate in the environment (Turner, 2001).

Organochlorine pesticides are one among the most important components of chemical contaminants present in both aquatic and terrestrial ecosystems. They are more vulnerable to all organisms including human beings. Though the adverse effect of organic pollutant has been revealed, less attention has been paid to the lack of awareness among the people about the impact of these contaminants especially in developing countries. Persistent organic pollutants (POPs) are of universal concern due to their persistency, greater transportability, and higher affinity toward fatty tissues and are highly toxic even at very low concentrations (Xu et al., 2013). Their characteristic features are their hydrophobicity, lipophilicity, and resistance to biological and chemical degradation, and these features make them highly persistent which enhance their chemical inclination to bioaccumulate and biomagnify to concentrations which could cause deleterious effects. Such biomagnification and bioaccumulation processes permit the organisms at the top of the food chain have the highest concentrations of POPs (Giesy et al., 2002).

In the early 1950s, the discovery of new persistent chemicals began and the use of such chemicals in the environment increased, though researchers were aware that these compounds were very stable and could have the long-term effects in the environment. As per WHO reports, the most common POPs encountered are organochlorine and organobromine pesticides including DDT, tetrabromobisphenol-A, (TBBPA) industrial chemicals, polychlorinated biphenyls (PCBs) and their derivatives, especially polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are frequently measurable contaminants in the atmosphere. It is well known that a wave of POPs which includes the PCB congeners has spread over the globe. Jensen (1966) first reported PCBs in environmental samples, and due to its persistent nature, it is freely transported from limited or local sites of contamination to remote regions through the atmosphere (Reinhardt & Wodarg, 1988). The atmospheric transport of such contaminants has led to their presence everywhere in the environment (Tanabe et al., 1987, 1988).

A number of organic contaminants including organochlorine pesticides (OCPs), PCBs and hexachlorobenzene (HCB), and their derivatives such as PCDD and PCDF were included in POPs list by the Stockholm Convention in 2001. Recently, few more contaminants such as polybromodiphenyl ether (PBDEs), perfluorinated compounds (PFCs), short-chain chlorinated paraffins (SCCPs), hexabromocyclododecane (HBCDs), perfluorooctane sulfonic acid (PFOS), commercial pentabromodiphenyl ether (penta-BDE), and commercial octabromodiphenyl ether (octa-BDE) were referred as emerging POPs and added to the list. Most of the organic substances are semi-volatile and can be easily transported even at low concentrations by movement of fresh and marine waters which were hundreds of miles away from the discharged places, and owing to their lipophilic nature, they eventually get deposited in any form in the fatty tissues of living organisms including humans. The organic contaminants could be transformed by hydrolysis, photolysis, and biodegradation process (Giesy et al., 2002), in which case the composition of the organic contaminant will not be the same as the technical grade (Giesy & Kannan, 1998; Newman et al., 1998), and this may be due to several processes collectively known as environmental weathering. These components could be synergistically more toxic to the organisms and indirectly could cause ecological imbalance. Once they are bioaccumulated and biomagnified, they may not easily depurate from the tissues and become more persistent.

Organisms are inevitably exposed to these contaminants in multiple ways: primarily through the food it takes and also through the environment it survives in. Human beings are routinely exposed to these chemicals since the products we use in our daily lives possibly contain many different POPs inevitably added to improve the characteristic of the products, and this could be one of the reason for being constantly present in the environment. Though the production of POPs were banned in number of countries since 1970s, due to their persistence in the environment, they get bioaccumulated through food chains and continue to pose significant health risks for the organisms in the ecosystem. POPs are not only hazardous to our environment and ecological balance but also lead to numerous health issues. Various studies have revealed that exposure to organic compounds could result in ailments including cancer, cardiovascular disease, and pulmonary disease. Furthermore, exhaustive research has confirmed the toxic effects of these contaminants in both in vivo and in vitro models.

The objective of this chapter is an attempt to shed light on these issues and collate recent available information relating to the environment deteriorating organic contaminants and their existence in different environments, especially on the approaches which utilize exposure models, biomarker of exposure and their limitation. This chapter critically assesses the literature with relevance to POPs and their impacts on biological and physiological systems in different organisms and ecosystems. We review the evidence from epidemiological and experimental studies on the association between exposures to POPs and other metabolic disorders in humans. Additionally, we also emphasize the possible metabolic derangements and molecular mechanisms underlying such an association. This chapter also reviews the existence of POPs in the environment causing complications such as learning disabilities, birth defects, disorders related with behavior, neurological, reproductive, and immunology in wildlife species and humans.

This chapter analyzes whether the POPs and the emerging POPs could play a role in cross and transgenerational effects and also addresses whether these organic contaminants have any gender-specific effects in the organisms. This chapter covers the biomagnifying and bioaccumulation tendency of POPs in different organisms with respect to single or multiple ecosystems at different trophic levels. In addition, we have also looked at the limitations with regard to the various management as well as legislation approaches formulated to tackle POP usage and remediation.

2 POPs: Classification and Uses

POPs are the chemicals which became a cause for universal concern due to greater persistence, long-range transport in the atmosphere, bioaccumulate and biomagnifying factor leads to adverse effects on organisms and their environment. POPs are intentionally produced once for the usage in agriculture, disease control, manufacturing, or industrial processes. The intentional uses of POPs have been listed in Table 1. POPs can be classified into two types: intentionally produced pollutants and unintentionally generated contaminants. Some of the existing POPs in the environment are aldrin, chlordane, dieldrin, dichlorodiphenyltrichloroethane (DDT), dioxins endrin, heptachlor, hexachlorobenzene (HCB), mirex, polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans, and toxaphene, and the emerging POPs or new POPs listed on the Stockholm Convention were chlordecone, endosulfans, α-hexachlorocyclohexane (α-HCH) and β-hexachlorocyclohexane (β-HCH), hexabromodiphenyl ether (hexaBDE) and heptabromodiphenyl ether (heptaBDE), hexabromocyclododecane (HBCD), lindane (γ-hexachlorocyclohexane, pentachlorobenzene (PeCB), tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE), and perfluorooctanesulfonic acid (PFOS).

Table 1 Chemicals listed by Stockholm Convention as persistence organic pollutants, uses and probable half-life periods of POPs

S.no	Name of the chemicals	Uses	Half-life
1.	Aldrin	Insecticide	5 years
2.	Chlordane	Insecticide	1 year
3.	Dieldrin	Pesticide	5 years
4.	Endrin	Pesticide	12 years
5.	Heptachlor	Pesticide	1–2 years
6.	Hexachlorobenzene	Fungicide	3–6 years
7.	Mirex	Insecticide	10 years
8.	Toxaphene	Insecticide	12 years
9.	Polychlorinated biphenyls	Heat exchange fluids, additives in paint, carbonless copy paper, and plastics	10 years
10.	Dichlorodiphenyltrichloroethane	Insecticide	15 years
11.	Dioxins	Exist as by-products of industrial processes such as bleaching paper pulp, pesticide manufacture, and combustion processes such as waste incineration	9–10 years
12.	Polychlorinated dibenzofurans	Insulators and lubricants in electrical equipment	8–10 years
13	Chlordecone	Pesticide	3.8–46 years
14	α-Hexachlorocyclohexane (α-HCH) and β-Hexachlorocyclohexane (β-HCH)	Insecticides	7–8 years
15	Hexabromodiphenyl ether (hexaBDE) and heptabromodiphenyl ether (heptaBDE)	Used in polymers, textiles, electronic equipment, construction materials, and furniture	3–6 years
16	Lindane	Pesticide	1–4 years
17	Pentachlorobenzene (PeCB)	Pesticide	4–6 years
18	Tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE)	Used in polymers, textiles, electronic equipment, construction materials, and furniture	1–3 years
19	Perfluorooctanesulfonic acid (PFOS)	Used in the production of fluoropolymers	2–3 years
20	Hexabromocyclododecane (HBCD)	Used as thermal insulation	2 days–2 months

2.1 Sources of POPs

In both aquatic and terrestrial ecosystems, they strongly bind to solids, predominantly to organic matter, evading the aqueous segment (Buccini, 2003) (Fig. 1). Since most of these chemicals are lipophilic, they get accumulated in fatty tissue of

Fig. 1 The environmental discharge of POPs, causes, and consequences

the organism easily and further metabolism is low in fatty tissues, and POP accumulation in these tissues enables their preservation and persistence in living organisms. Burning of flora, be it natural, unintentional, or planned, is considered as a very important source of POPs in the environment (Wong & Poon, 2003) (Fig. 1). Other important sources include power stations, household furnaces, landfill transport, and agricultural sprays (Thornton et al., 2002) (Fig. 1). Aquatic environments, including coastal and estuaries, are under significant anthropogenic pressures globally because a considerable part of the universal population is residing in areas near to the aquatic environment. More concern about POPs arises because of their potential toxicity and occurrence in the ecosystem even at remote topographical regions. Several studies reported that POP residues in several fresh and processed foods have posed risks to human health including the increasing incidence of birth defects. Exposure of organisms even to very minimal doses of POPs could cause chronic adverse impacts due to their chemical properties and mechanisms of action (Ashraf, 2017). In recent years, more research is being focused on the impact of organic pollutants on humans as well as and other organisms, since there is a general lack of information of such persistent environmental pollutants. In addition, there are the uncertainties in approach and interpretation about these contaminants and their patterns of accumulation and toxicity levels.

Most of the countries banned the usage of aldrin and dieldrin in 1987. They were used on corn product and citrus product and also for timber preservation. Other uses of aldrin were termite-proofing of timbers, building boards, and rubber coverings of electrical and electronic equipment and cables. This contaminant assessed to be comparatively less persistent in the atmosphere with a short half-life of about 4 months. Further, the precise arithmetic models measure that aldrin could degrade up to 70% to dieldrin in about 12 weeks. Compared to water, aldrin and dieldrin bind to the soil very easily because of their low solubility in water (186µg/L at 25–29 °C). Further, aldrin is more volatile and gets degraded into dieldrin in the environment and gets into soils strongly and withstand leaching to ground water systems and could be traceable in surface run-offs and waterborne sediments (ATSDR, 2000; Devi, 2020).

Initially 12 POPs were recognized as environmental contaminants, which cause adverse effects on humans and the ecosystem under the Stockholm Convention, 2001. Later, in 2009, few other pollutants have been regulated and included as emerging POPs that include the mixtures of PBDEs, PFOS, and salts of PFOS as representative PFASs and HBCDs. Between 2015 and 2017, poly-chlorinated naphthalenes (PCNs) and short-chain chlorinated paraffins (SCCPs) were listed as emerging POPs. Apart from the existing POPs, which are also known as dirty dozen, emerging POPs such as chlordecone, HCH, HBDE, lindane, pentachlorobenzene, tetra and penta bromodiphenyl ether, PFOS, endosulfans, and HBCD have received less consideration particularly concerning their fate and bioaccumulation potentials (de Boer et al., 2016; Sanganyado et al., 2018; Kim et al., 2019).

In spite of regulations issued from environmental act, the distribution and fate of POPs in the aquatic environment continue to have greater concern due to their potential toxicity and persistence in ecosystem (Aljerf & Al Masri, 2018). The fate of the contaminant in the aquatic environment depends on their manufacture, usage, duration of regulation, physicochemical properties, and persistence in the environment (Wang et al., 2019a). Several studies revealed that precipitation events lead to loading in sediments and accumulation in various biotas (Jiang et al., 2016). In most of these studies, fish have been taken as representative organism to predict the level of major accumulation routes (Wang et al., 2019a, b); moreover, fish have been used as a main food source for human and many other organisms which were placed in higher trophic level.

3 Biomagnification and Bioaccumulation of POPs

Being near to the contaminated zone or being exposed to the chemical contaminants or being taken as a food could be the principal factors for determining the extent of POPs that gets accumulated in the aquatic organism (Good et al., 2014; O'Neill & West, 2009). Conversely, the exposure period and nature of body condition and position of the trophic levels could be the main factor which plays a role in bioaccumulation (West et al., 2017). Though the contamination of POPs could adversely affect the organism’s health, the amount of exposure of different types of POPs may serve as the contaminant tracer in elucidating the information about the environment, population of the species involved migration, and pattern of migration (Svendsen et al., 2009). Based on the proportion of different types of the POPs accumulated in the organisms, the sources of POPs could be identified (Deshpande et al., 2016). In general, there is a higher possibility to find halogenated organic pollutants (HOPs) in a typical contaminated area closer to industrial regions (Jepson & Law, 2016), and these include polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs). The regulations on the production and usage of these halogenated organic pollutants have led to the development and usage of alternative flame retardants that include dechlorane plus (DP), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), and decabromodiphenyl ethane (DBDPE) (Covaci et al., 2011), but due to similar physicochemical properties with traditional POPs they newly made alternative chemicals that tend to be bioaccumulative and get biomagnified through food chains resulting in the environmental risks (Tao et al., 2019).

To assess the ecological risk of contaminants like POPs, biomagnification is one of the potential tools to be used (Gobas et al., 2016). To compare the existence of the same POPs in both aquatic and terrestrial regions, biomagnification factors and trophic magnification factors have been used widely (Walters et al., 2016: Morris et al., 2018). A few studies have analyzed the differences due to biomagnification potential shown by POPs in these two environment (Liu et al., 2020). Research on PBDEs has demonstrated that in contrast to aquatic food chain, they were stronger and biomagnified in the terrestrial food chains (Liu et al., 2020). However, many of these studies have either made use of simple models or analyzed data from a very few organisms studied in the trophic levels. Hence, it is vital conducting more field-based studies to assess biomagnifcation and to provide the critical data on the emerging organic contaminants (Gobas et al., 2016). Furthermore observations on HOP biomagnifications through food chains in the terrestrial ecosystem have primarily focused on higher trophic level predators and middle-level organism were ignored, especially the role played by insects (Morris et al., 2018). Insects form an essential link in the terrestrial food chains especially between primary producers and secondary consumers and hence will be important in bioaccumulation and trophic transfer of contaminants (Rosenberg et al., 1986).

Nie et al. (2015) reported that the biomagnification factor (BMF) of PBDEs in insects (grasshopper, ant, butterfly, and dragonfly) and turtledove's food web ranged between 0.20 and 11.6. Similarly, Fremlin (2018) documented in his study that the trophic magnification factor values of POP contamination in the food chain in case of terrestrial ecosystem ranged between 1.20 and 15.66. Further the BMF values of halogenated POPs in insects were found to be significantly higher than vertebrate animals such as toads and lizards, and these observed differences may be attributed to the differences between the physiology of poikilotherms and homeotherms. All these studies indicate that the mechanism of bioaccumulation of POPs in aquatic organisms showed clear differences with terrestrial organism, and thus care needs to be taken while interpreting data.

The additive brominated flame retardants, PBDEs, have been widely used around the world. The concentration of PBDE in surface sediment from Bohai Sea and Laizhou Bay was found to be 220 to 990 and 660 to 12,000 pg/g dw. The PBDE levels in the riverine, estuarine, and intertidal zone sediments of Bohai Bay were found to be in the range between non-detectable level to 870 pg/g dw (Chen et al., 2011, 2012). PBDEs were also found in fish oil supplements, poultry meat, fat and liver shellfish, plant oil blend supplements, eggs, and in baked products ranging from 164 to 13,862 pg/g (Boucher et al., 2018). Not surprisingly, the PBDE levels were comparatively very lesser in all plant-based food groups compared to animal-based products. Products from poultry meat or eggs were shown to have PBDE (149–414 pg/g); poultry liver had 1045–1860 pg/g. Even dairy product was reported to contain PBDEs below 100 pg/g. Compared with the majority of the contaminants, HBCD was found to be highly bioaccumulative. Bioconcentration factor ranges from 18,100 to 19,200 in fathead minnows and rainbow trout, respectively

(Drottar et al., 2001). HBCD in eggs from wild falcons have been reported indicating that HBCD may also bioaccumulated in terrestrial organisms and food chains (Lindberg et al., 2004).

3.1 Emerging POPs in Animals

In the last five decades, several studies have documented the potential effects of POPs in the environment and bioaccumulation pattern exist. Recent research has documented that contaminants such as perfluorooctane sulfonamide (PFOSA), PFOA, and PFHS are frequently observed in the tissues of wildlife organisms. Sample collected from remote regions of the marine environment shows PFOS accumulation of about >1 ng g^{-1} (Muir et al., 2019). A grey seal from Canadian and Norwegian Arctic showed 3–50 ng mL^{-1} of PFOS (Muir et al., 2019) and Alaskan polar bear liver contained 180–680 ng g^{-1} of PFOS (wet wt), similarly liver tissues of birds collected from Canada, Italy, Japan, and Korea showed up to 10–1000 ng g^{-1} PFOS (Giesy & Kannan, 2002).

4 Impact of POPs on Human Health and Other Organisms

It has been well documented that POPs could interrupt most of the systems of organisms and directly affect the organ functions which target endocrine system, immune system, and nervous system (Dai et al., 2020) (Fig. 2). Exposure to POPs alters gene expression and inflammatory changes which could directly or indirectly affect the physiological system of the organism (Tuomisto, 2019) (Fig. 2). However, the magnitude of changes produced by POPs predominantly depends on the source and route of exposure to POPs and age and sex of the individual (Sexton & Hattis, 2007) (Fig. 2).

4.1 POPs and Neurotoxic Effects

Several neurobehavioral tests with POPs have been conducted using various animals including mice and rats which demonstrated that the developing nervous system is a potential target of POP toxicity (Eriksson et al., 2002). In an experiment using zebrafish, Hill et al. (2003) showed that TCDD exposure adversely affects the key expression of certain developmental genes during brain development. Kuriyama et al. (2008) reported mice (gestational day 6) exposed with low doses of BDE-99 gave hyperactive offspring postnatal days 36 and 71. The doses used were relevant to human exposure levels. Interestingly, rats exposed to one single dose of 10 g HBCD/kg bw showed hypoactivity and a lower dose of 5 g/kg bw was set as NOAEL

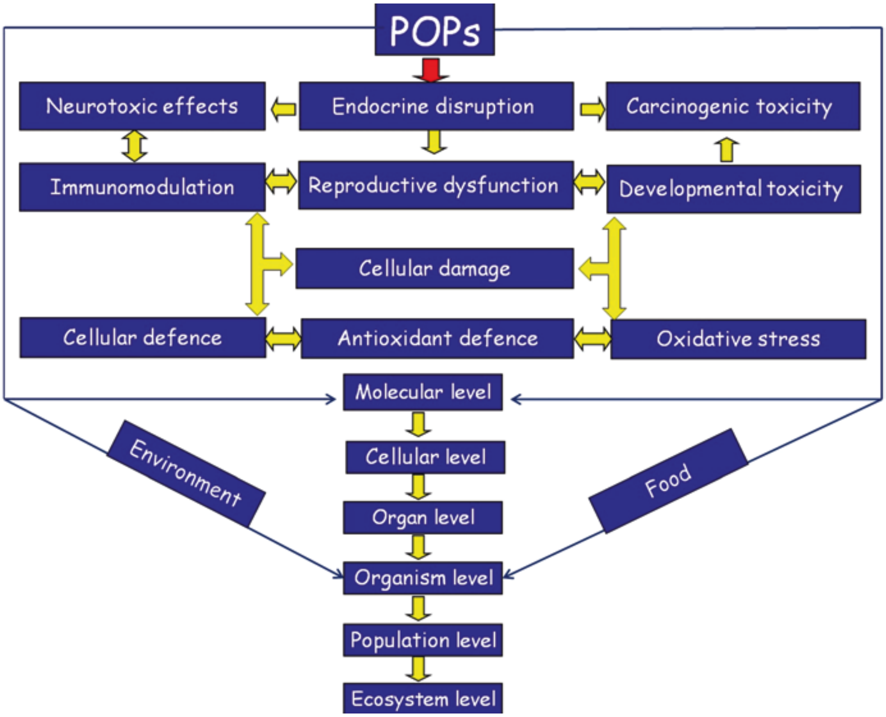

Fig. 2 The impact of POPs on several biological function of the organism. All the biological function can be modulated by POPs, since most of the functions are interrelated

(Geyer et al., 2004). The observed behavior changes were similar to earlier reports using PCBs (Eriksson et al., 2002). Dioxins in mice exert neurotoxic effects including on learning, memory, motor development, and emotion, and sex specificity of such effects has been reported (Haijima et al., 2010). Several studies have demonstrated that industrial workers exposed to chlorophenol or TCDD-containing phenoxyacid herbicide exhibit higher rates of psychological disorders, fatigue, and headache (Pelclova et al., 2009, 2018). Mariussen and Fonnum (2006) revealed that PCBs and PBDE exposure exert adverse neurological effects. Wild life species which prey on fish could biomagnify the contaminants like PCBs and PBDEs, which have been shown to elicit the similar effects with neurological impacts (Basu, 2012, 2015). A very few studies have been published which assessed the relationship between POP exposure and adverse effects in infants, which have been critically reviewed by Winkens et al. (2017). Studies using mice have reported that single oral exposure to PCBs leads to drastic reduction in levels of dopamine, and vesicular monoamine transporter 2 protein expressions were inhibited due to PCB (Caudle et al., 2006).

Studies on accidental exposure to human showed that PCBs have been associated to cognitive and behavioral disorders in infants (Ribas-Fitó et al., 2001), whereas exposure to adult has been associated to a greater incidence of Parkinson’s disease mortality (Hatcher-Martin et al., 2012). Since early 2000s, the levels of PBDEs significantly increased in the environment and also in human tissues have been consistently increased especially in the region of North America which were comparatively higher than Europe and Asia (Chen et al., 2014b). It was documented clearly that developing brain (infants) is more sensitive to POPs than the adult's brain, and hence the neurotoxicity was observed even at low exposure levels. However, in fewer cases, the developmental exposure to POPs results in morphological alteration of central nervous system with the diverse modulation of functions. Exposure to POPs has been shown to affect vulnerably on nervous system with numerous developmental disabilities such as learning, attention, hyperactivity, dyslexia, sensory, mental retardation, and autism that were diagnosed in children at a higher rate (Abdullahi et al., 2017; Neugebauer et al., 2015; Tue et al., 2013, 2016). Predominantly the rate was higher in infants due to exposure through breast milk, house dust, and food intake in toddlers (van den Berg et al., 2017). Studies using various animals also evidenced that the exposure to different PBDEs during the prenatal and/or postnatal periods cause behavior abnormalities (van den Berg et al., 2017). Few studies also showed dopaminergic dysfunction caused due to organochlorine insecticide dieldrin (Gezer et al., 2020). All these studies clearly showed that POPs have the ability to cause developmental neurotoxic effects in various organisms.

4.2 POPs and Reproductive Toxicity

Exposures to PCBs have shown to affect the reproductive functions in humans by altering the sperm quantity and quality (Mocarelli et al., 2008, 2011). Several studies revealed POPs retarded reproduction in humans and other mammals by influencing the reproductive hormones, sexual maturity, and fertility (Eskenazi et al., 2010; Burns et al., 2016). In rats, PCB congeners reduced sperm motility and velocity and penetration capability into oocytes (Hsu et al., 2004). Similarly, Arocolor 1254 has been shown to change the sperm characteristic in mice (Jiang et al., 2016). Mocarelli et al. (2008) reported a significant modulation of LH and FSH in the people who were exposed to POPs and reduced estradiol and increased FSH in infants and adolescents. Infants exposed to TCDD showed a negative relation with sperm concentration and motility; however, during puberty, the same reflected the changes in hormone regulation (Mocarelli et al., 2008). Women exposed to TCDD showed ovarian functional impairment, and this also leads to increase the incidence of birth defects in their offspring (Pilsner et al., 2017). Women have been reported to be more sensitive to the contaminants when exposure occurs before menarche leading to onset of menopause, prolonged menstrual cycle, infertility (Eskenazi et al., 2010), and endometriosis (Cano-Sancho et al., 2019).

In polar bear, PCBs and other organochlorine have shown gender-specific effect by decreasing the male androgenic hormones and also the testis size (Milon et al., 2017). PCBs were also shown to reduce the reproductive success in polar bear drastically (Haave et al., 2003). Though disruptions in male fertility have been demonstrated in several animal models (Sonne et al., 2020; Dai et al., 2020), human studies lend more support to these studies (Dai et al., 2020). As evidenced by recent research, PCB contamination continue to threaten marine animals in European waters (Jepson et al., 2016). This could be main reasons for impaired reproduction and one of the reasons for declining population that have been documented (Jepson et al., 2016; Dai et al., 2020). PCBs even at low concentrations in plasma have been reported to disrupt the mechanisms of the major hormones in mammals and thus preventing the ovulation process and retard the reproductive success (Haave et al., 2003). Ciesielski et al. (2017) reported that POPs could disrupt endocrine functions and impair the reproductive success in male polar bears. The relationship between the size of reproductive organs and POPs has been negatively correlated in polar bears, and the impact leads to decrease the sperm and egg quantity/quality drastically. The risk of POP contamination for polar bear cubs is very high comparatively with adult polar bears (Routti et al., 2019).

Severe environmental and health problems in most of the organisms including birds have been attributed to DDT and its metabolites, and the major metabolites such as 4, 4′-DDE have been associated to eggshell thinning and reduced the reproductive success in several birds (Ottinger et al., 2011). In humans, abnormalities of male sexual development have been shown to be associated with DDT exposure. The metabolites of DDT, especially 4,4′-DDE, do not directly effect by binding with estrogen receptor; it inhibits androgen receptor resulting in androgenic effects in mammals. Earlier studies on POPs impact on wild life species revealed that grey and ringed seals population dramatically reduced during 1960s and 1970s in the Baltic Sea region due to observed reproductive impairment in the populations. Though the contaminant input has been restricted by several measures adult animals at present show slight renal Baltic seal diseases complex symptoms due to low levels of POPs exist (Sonne et al., 2020). Roos et al. (2012) reviewed in his article that white-tailed eagle's population in the Baltic Sea increased as the level of POP contamination decreased. This was further supported by the chemical contaminants in the environment and the observed reproductive impairment in seals and eagles during that period (Roos et al., 2012), though the level of PCBs was comparatively higher than the DDT and pp-DDT that have less impact on white-tailed eagle's reproduction (Sun et al., 2020).

4.3 POPs and Immunotoxic Effects

One of the more sensitive targets for POPs includes the immune system of the organism. Especially, POPs produce severe alterations to the immune system during their development and maturation stages, which is quite different from the adult stages (Nowak et al., 2019). Several studies reported that POP exposure caused a wide range of immunotoxicity in several species tested affecting both the humoral and cellular responses (Vorderstrasse et al., 2003; O'Driscoll et al., 2019). Humans exposed to dioxin like compound demonstrate a dysfunctional immune response causing enhanced susceptibility to infections and allergies especially during the childhood (Miyashita et al., 2011), which leads to later consequences of maturation of immune systems (Weisglas-Kuperus et al., 2004). Several studies reported that prenatal exposure to TCDD could increase the development of infectious diseases by decreasing the immune response (Miyashita et al., 2011, 2018). Dioxin exposure leads to immune system dysfunction in humans by modulating T-lymphocyte subpopulations and levels of immunoglobulins which increase the susceptibility to infectious diseases (Kim et al., 2018). Baccarelli et al. (2002, 2004) documented that TCDD exposure suppress the antibody production in humans.

Destruction in immune response is of a major concern for aquatic organisms since a proper function of the immune system is important for survival (Segner, 2011; Segner et al., 2011). Exposure to POPs could reduce the survival rate in aquatic species due to immunosuppression and by increasing the susceptibility to infections, and parasitic disease could indirectly increase mortality in aquatic and terrestrial animals (Gopalakrishnan et al., 2011; Segner, 2011; Segner et al., 2011). Arkoosh et al. (1998) documented that exposure of salmonids to POPs could work in conjunction with parasites increasing their susceptibility to marine pathogens which potentially affects the population of the species. PCB concentration of 17μg /g w significantly modulated the immune system in marine mammals (Sonne et al., 2020). All these studies on POP exposure to marine species revealed that POPs proved to be immune suppressive agents even at very low concentrations. Desforges et al. (2016) documented in their review that the threshold level for suppression of lymphocyte proliferation is 0.001μg/g PCBs for several species in aquatic environment. Further, the threshold levels for the suppression of immune activity like phagocytosis were 0.6 to 1.4μg/g PCBs. All these studies clearly imply that an immune function is drastically modulated by POPs and suggest implication for future risk assessment (Lehnert et al., 2018).

4.4 POPs and Developmental Toxicity

POPs exposure occur during prenatal period, infants, childhood, and puberty is considered to be development toxicity in humans and these periods are more sensitive because of rapid growth and development (Beszterda & Franski Endocrine, 2018). POPs such as PCDD/Fs and DL-PCBs are reported to be responsible for poor birth rates and decreasing male to female birth ratio and growth retardation (Mocarelli et al., 2008; Pesatori et al., 2003). Dioxin, PCB, and PCDF contamination have been linked to poor birth rate, higher incidences of miscarriages, congenital birth defects, pregnancy loss, preterm deliveries, and decreasing ratio of male to female births (Ngo et al., 2006; Knafl, 2018). Exposure to higher concentrations of POPs in women results in lower birth weight especially in male babies (Tsukimori et al., 2012). Male infants, upon exposure to dioxin like compounds, were found to be more sensitive to growth restriction than females (Tsukimori et al., 2012).

4.5 POPs and Carcinogenic Effects

Several studies documented that POPs were classified under carcinogenic compounds; DDT was probably carcinogenic to humans and HCB is presumed to be carcinogenic to humans; TCDD, 2,3,4,7,8-PeCDF, PCBs, and DL-PCBs are proven to be carcinogens (IARC, 2016). Further, several authors revealed that TCDD is the most carcinogenic among the POPs, and it has been documented as the most frequently associated contaminant with majority of the cancers (Warner et al., 2011; Xu et al., 2016). Moreover, several studies documented that POP exposure in humans are associated with breast cancer (Koual et al., 2019), testicular cancer (Giannandrea et al., 2011), and colorectal cancer (Lee et al., 2018). Pesatori et al. (2003) reported Seveso population exposed to TCDD showed greater risk of having cancers linked to lympho-hemopoietic neoplasms, gastrointestinal tract, respiratory system, and the endocrine especially the thyroid. TCDD at higher concentrations have been shown to increase the reproductive cancers in cohorts (Revich et al., 2001). POP exposure to female rodents has shown to increase mammary, ovarian, and hepatic tumorigenesis (Cameron & Foster, 2009; Filgo et al., 2015), and colorectal tumors were found on direct exposure to POPs (Song et al., 2014; Hansen et al., 2019). A study on POP exposure showed that it could mediate epigenetic modifications thereby influencing carcinogenesis. Further OCP exposure showed gene-environment interactions with breast cancer (Rodgers et al., 2018). Studies revealed that dioxin-like compounds do not produce genotoxicity directly, but their carcinogenic effect is through the activation of the AhR leading to tumor promotion (Baccarelli et al., 2006; Knerr & Schrenk, 2006).

4.6 POPs and Endocrine Disruption

It is well known that POPs alter hormones and growth, and hence they are also known as environmental endocrine disruptors. Once they accumulate in the environment, they get incorporated into the body through bioaccumulation and affect normal functioning of endocrine system and other growth factors (Bergman et al., 2013). Dioxin altered the thyroid hormone levels and insulin leading to change to glucose metabolism and diabetes in humans (Kern et al., 2004). Some in vivo studies on epidemiology have demonstrated that dioxin like compounds cause diabetes through destruction of pancreatic beta cells (Alonso-Magdalena et al., 2011; Chang et al., 2011). Studies on cohorts exposed to high concentrations of PCDD/F and DL-PCB showed the presence of hormonal disorders in men involved in Vietnam War (Kim et al., 2003, 2018) and also in workers occupationally exposed to these chemicals in Czech Republic (Pelcl et al., 2018), New Zealand ('t Mannetje et al., 2016), and the United States (Calvert et al., 1999).

Among all the hormones, thyroid hormone is critical for growth development and physiological status in mammals. Modulation of this hormone during brain development could lead to major impairment and growth retardation (Ahmed et al., 2008). Dioxins have been documented to modulate the thyroid hormone in humans and other mammals. Exposure of PCDD/Fs and PCBs has also been reported to affect thyroid hormone in neonates and children (Baccarelli et al., 2008). Various studies revealed that both aldrin and dieldrin could disrupt the endocrine system in mammals. These two contaminants change the hormone level in both male and female, lead to degeneration of male germ cells and seminiferous tubules in the testes of male, and effect the estrus cycle and cells lining the uterus of female. Since endocrine system is important for higher vertebrate to respond the ecological stress, any contaminants which disrupt the endocrine system could interfere with the adaptations to increase the environmental stress (Jenssen, 2006).

Thyroid hormone could regulate growth, reproduction success, and thermoregulation in mammals, and to certain extent, it also regulates immune system, and any destruction of this hormone could lead to imbalance (Allen et al., 2016; Wu et al., 2019). Several research studies have documented the effects of POPs on thyroid hormones in most of the organisms including Greenland sledge dogs (Yu et al., 2011; Allen et al., 2016; Wu et al., 2019), domesticated Arctic foxes (Rogstad et al., 2017), seals (Imaeda et al., 2014), toothed whales (Noël et al., 2014), and polar bears (Bourgeon et al., 2017). Few studies have reported that PBDE exposure modulated thyroid hormones in animals (Fernie et al., 2005) and disturb the thyroid system during development which leads to the reduction of circulating thyroid hormone (Fernie et al., 2005; Kuriyama et al., 2008). PBDE and PCB exposures have been showed to decrease T_4 level in mothers, which could indirectly affect the neurological development in children, impair growth, and also contribute to developmental neurotoxicity (Pinson et al., 2016). Rats exposed to PCBs such as hexa-chlorinated biphenyls and their metabolites were reported to have lower T_3 and T_4 levels in serum (Kato et al., 2003). Overall, thyroid hormones play an important role in mammalian fetal development, and these POPs (PCB and PCDD/PCDF metabolites) are known to accumulate in fetal tissue after maternal exposure and could cause adverse health effects (Kato et al., 2003; Pinson et al., 2016; Yilmaz et al., 2020).

5 Emerging POPs and Its Impact

Perfluoroalkyl substances (PFASs) are wide groups of contaminants listed under emerging POPs. They are with long alkyl chain fluorinated either in part or completely with diverse functional groups attached. These chemicals have been used in many industries and household products such as non-stick cooking utensils, food wrappers, garments, and carpets. These chemicals are highly persistent due to their carbon-fluorine bonding nature, and hence they could not be degradable and recently added in the list of emerging POPs. Long chain compounds of PFAAs are a major concern due to high persistence and bioaccumulation and have shown toxicity in various studies using animals. Perfluoroocta sulfonate (PFOSs) is one of the most widely used PFAS compounds which have both hydro- and lipophobic perfluoroalkyl chain and also a sulphonic acid group which confers polarity. The Stockholm Convention added PFOS and its salts in Annex B. Due to high persistence and toxicity, these chemicals have been banned in the United States from the year 2000; Canada and European Union banned these chemicals in 2006 and 2008, respectively. PFASs easily get accumulated in the animal tissues by binding through blood protein. In recent years, PFASs have been detected in food items, drinking water, house dust, human blood, and even in breast milk (Domingo et al., 2012; Ao et al., 2019). Both in vivo and in vitro studies documented that PFOS could lead to adverse effects on human health similar to other POPs (Zeng et al., 2019). Few studies reported that PFAAs may exert genotoxic and neurotoxic effects in animals (Fuentes et al., 2008). They also affect the antibody production in mice and human population (Torres & August, 2018) and also cause immunosuppressive effects (Peden-Adams et al., 2008). Several studies proved that PFCs are immunotoxic and lead to immunomodulatory functions which lead to increase in the susceptibility to infection and favoring the development of autoimmune disease (Corsini et al., 2014). Rats exposed to PFOA showed a considerable growth in mammary fibroadenomas and Leydig cell adenomas (Kennedy et al., 2004). PFOA-exposed female pups showed underdeveloped mammary gland and affect the mechanism required for epithelial outgrowth and branching (White et al., 2006). Several studies documented that PFOS get bioaccumulated more in liver than any other organs, and this leads to hepatotoxicity in animals and humans which results in severe hepatic damage (Hagenaars et al., 2008; Yeung et al., 2009; Xu et al., 2016). PFOS also caused oxidative stress in liver which leads to excessive ROS generations in hepatocytes that cause damage to hepatic cells, which could further lead to effect lysosomal membrane stability and cellular protein breakdown in rat (Khansari et al., 2017).

Marine medaka larvae exposed to PFOS (1 and 4 mg/L) induced immunosuppression have been reported by Fang et al. (2013). Apoptosis have been shown to be induced by PFOS in the splenocytes and thymocytes of mice (Zhang et al., 2013). Lv et al. (2015) reported that mice exposed to PFOS for a period of 28 days showed reduced T cell proliferation. PFOS have been shown to exert neurotoxic effects in various studies. Exposure to this contaminant has been shown to cause dysfunction in motor behavior, cognition, learning, and memory (Wang et al., 2015a, b). Exposure of *Caenorhabditis elegans* to PFOS (~10 mg/L) for 48 h leads to reduction in locomotor behavior (Chen et al., 2014a). On the contrary, zebrafish larvae exposed to PFOS (1 ppm) showed hyperactivity due to dopaminergic shortfall (Spulber et al., 2014). Some of the authors demonstrated that in vitro studies using PFOS as toxicant-induced neuroinflammation damage in nerve cells (Zeng et al., 2011). Neuroinflammation due to PFOS has been shown to cause activation of immune cells in the central nervous system resulting in induced cytokines inflammation that leads to severe nerve damages (Kim et al., 2016; Chen et al., 2018). PFOS exposure caused damages in reproductive organs of male and female leading to poor pregnancy outcomes (Zeng et al., 2019). Apoptosis in placental syncytiotrophoblast in humans exposed to PFOS has been reported (Zhang et al., 2015). Similarly, several studies reported that PFOA exposure also caused reproductive toxicity (Lee et al., 2017; Kang et al., 2019). PFOS exerts cardiovascular diseases in several organisms which includes arterial hypertension, anomalies of the heart, instability heart rate, and cardiomyocytes apoptosis (Liang et al., 2017; Tang et al., 2017). Occupational exposure of humans showed increased level of PFOS concentration in blood serum, and it was positively correlated with alanine transaminase, which directly indicates that PFOS exposure induces hepatotoxicity in humans (Gallo et al., 2012). PFOS concentration in blood serum also shown to be associated with kidney function, and it has been reported that glomerular filtration rate was drastically reduced and the serum uric acid was increased (Kataria et al., 2015).

Though PFOA production has been reduced and PFOS manufacture has been stopped in United States, their persistence in the environment and resistance to degradation have resulted in their widespread bioaccumulation in organisms especially in humans. Most of the developing countries have been using these pollutants, and hence it has been detected worldwide. Exposures to these contaminants are reported to associate with ponderal index in humans (Kobayashi et al., 2017). PFOS and PFOA modulate the thyroid hormone signaling and interfere with thyroid hormone function and homeostasis (Long et al., 2013). This leads to developmental and maternal hypothyroidism which directly associates with low birth weight as reported by Bach et al. (2015). Several authors reported that PFCs could interfere with estrogen receptors (Kjeldsen & Bonefeld-Jørgensen, 2013; Sonthithai et al., 2016), and prenatal exposure to these pollutants could affect postnatal growth (Mildred Maisonet et al., 2012).

Several studies reported that POPs have potential adverse environmental and human health effects. HBCD and PBDEs have been identified as endocrine-disrupting chemicals which suggest that they can induce enzymes and modulate the thyroid homeostasis even at relatively low exposure levels (Palace et al., 2008). These contaminants are also reported to be related with premature puberty and also have severe impact on neurological development (Darnerud, 2008). PBDE and HBCD exposure to humans and other organisms are inevitable due to their presence everywhere (Darnerud, 2008; Palace et al., 2008; Saegusa et al., 2009). Several studies reported that PBDE and HBCD exposure could result in impaired reproductive function, developmental neurotoxicity, and endocrine disruption (Noyes & Stapleton, 2014). Though these contaminants are not reported to be acutely toxic, they retard several developmental functions in most of the organisms (Costa & Giordano, 2007; Deng et al., 2010). Laboratory exposure studies using rats and mice showed decreased fertility, behavioral effects, and malignant transformation of mammalian cells (Legler, 2008). In some developed countries, organophosphate flame retardants (OPFRs) and Tris(1,3-dichloroisopropyl)phosphate (TDCPP) were used as alternative components for flame retardants. Later several studies reported that OPFR and TDCIPP as carcinogenic agents which caused tumor development in liver, kidneys, and testes of rat (Wang et al., 2019a, b). Recent studies have demonstrated that TDCIPP produced neurotoxicity, inhibited DNA synthesis, and dysregulated neurodifferentiation (Wang et al., 2019a, b). Even at very low concentrations, HBCD induces endocrine disruption in humans by modulating thyroid homeostasis (Vos et al., 2003).

Halogenated flame retardants (FRs) such as PCBs and PBDEs have been reported to retard reproductive functions including decreased sperm motility, abnormal sperm morphology, and affected male fecundity (Meeker & Stapleton, 2010). Their toxicity is a concern which requires a search for replacement of these chemicals. Chemicals which have similar functions were used as replacements. HBCD and TBBPA are the chemicals used as replacements, and they are used as additives to products including electrical and electronic and household equipment (Stapleton et al., 2011; Betts, 2013). After a few countries started using HBCD and TBBPA as a replacement, these chemicals have been detected in environment showing prominence of their distribution in the ecosystem (Johnson et al., 2013; Wang et al., 2015a, b). Similar to other POPs, these emerging contaminants demonstrated to affect the endocrine functions in human and other mammals (Johnson et al., 2013). Further, these contaminants also shown to have negative impact on mitochondria in A_{549} cell lines and in pancreatic islet cells (An et al., 2014; Suh et al., 2017). Recent research reports revealed that young infants exposed to these contaminants have been shown to have decreased sperm count and other disorders in reproductive system in adult stage (Bonde et al., 2016).

6 Transgenerational Effects of POPs

Environment and genetic predisposition are two factors deciding the health life of an organism. It has been documented that environment could pose an extensive impact on the heredity of an organism without much changes on the genetic information. The chemical contaminants could mediate the trangenerational effects through epigenetic mechanisms (Skinner et al., 2010, 2011). Though the impact of POPs on several systems including molecular changes are known, epigenetic effects of persistence contaminants are largely unstudied. Song and yang (2018) reported that p,p'-DDE (100 mg kg^{-1} body weight) exposure to pregnant rats decreased the sperm fertility in F_2 and F_3 generation. The impact of POPs was similar in cross-generational observation as well. Dietert (2014) reviewed the impact of POPs on transgenerational effects; in his review, he clearly documented that epigenetic modifications occur due to the exposure of persistence contaminants. Some of the earlier reports documented that exposure to PBDE; PCB leads to histone modification of the DNA in brain and liver of rats (Desaulniers et al., 2009; Casati et al., 2012). Manikkam et al. (2012) observed that female rats (F_0) exposed to TCDD during the period of embryonic development leads to spermatogenic cell apoptosis in male and early onset puberty in female in F_1 and F_2 generations. Zebra fish exposed to TCDD showed reduced egg production in the F_2 generation drastically (King Heiden et al., 2009). All these studies clearly reveal that environmental influences of these contaminants could alter the DNA methylation and histone modifications which leads to the transgenerational effects.

7 Conclusion

POPs have been used for decades and most of them are highly persistent and accumulative. We speculate that enforcement of law and increased awareness among the people have generally kept the POPs under control in developed countries. However, some of the countries replaced the POPs with other similar chemicals in order to continue their usage. The repeated usages of these chemicals and their physicochemical properties have enabled these chemicals to get accumulated in the environment; the slow degradation of these chemicals made them highly persistent in the environment. Over the past few years, these emerging contaminants have posed potential environmental and health risks to humans and other organisms. It is unfortunate that most of the developing countries are fighting yet to get away from accumulated contaminants, and the enduring production of these components goes without any reduction. This chapter clearly shows that exposure to existing and emerging POPs could cause health hazards in humans and other higher vertebrates targeting the neuroendocrine system; hepatic system; reproductive and developmental system; and pulmonary, cardiovascular, and renal system. Available toxicological evidence indicates that these existing and emerging contaminants could increase the risk level for cancer in most of the organs in most of the organisms. Extensive experimental and epidemiological approaches are necessary to understand the magnitude of impact of POPs on human and other organisms. Furthermore, identification of markers and an in-depth understanding of the consequences of POPs would help to develop population exposure prevention strategies in order to control and manage the emerging contaminants. Though numerous remedial techniques have emerged for POP degradation, most of them are in pilot stages and no conclusive and effective techniques are presently available. Moreover, available information and most of the current research primarily focus on the impact of POPs on health and other physiological functions only, and thus there is an urgent need for extensive research to be conducted on degradation and eradication of these contaminants from the ecosystem. In addition, laws and regulations need to be enforced strictly together with creating awareness for people in developing and under developed countries to not only protect people but also their environment.

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Management of POPs: A Caribbean Perspective

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Abstract In the twenty-first century extensive use and production of hazardous chemicals referred as persistent organic pollutants (POPs) have raised significant concerns owing to their widespread environmental, health and ecosystem impacts. Although, the manufacture and usage of many POPs have been discontinued by many developed counties in many developing counties the usage and production of POPs is not as restricted. In the Caribbean region, POPs management efforts are problematical due to the lack of appropriate legislation and limitations in research and monitoring; hence these developing countries find it difficult to manage POPs and comply with international singed conventions. This poses a local, regional and global treat because of the POPs long-range transport characteristics. In an effort to have a more holistic perspective and a better understanding of the developments that have occurred subsequent to the approval of the Stockholm Convention this book chapter aims to discuss the types and impact of POPs, the analytical methods employed for the determination of POPs, the removal of POPs and an overview of POPs management in the Caribbean Region, specifically a case study of Belize.

Keywords POPs · Belize · Caribbean · POPs Management · Stockholm Conventions

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1 Introduction

In the twenty-first century, the environment, human health, and ecosystems face enormous challenges due to industrialization, rapid economic growth, and urbanization (Nguyen et al., 2020). In particular, the extensive use and production of hazardous chemicals referred as persistent organic pollutants (POPs) are of concerns due to their widespread health, environmental, and ecosystem impacts. POPs include organochlorine pesticides, polychlorinated biphenyls, and other by-product substances originating from human activities (Deribe et al., 2011). The characteristics and properties of POPs such as long-range transport, environmental persistence, bio-magnification, and bio-accumulation have rendered these pollutants as hazardous to human health and environment. Although the manufacture and usage of many POPs have been discontinued by many developed counties, these pollutants still pose a risk as they are still present in the environment. In many developing counties, however, the usage and production of POPs is not as restricted; thus, these pollutants are being released in the environment. For instance in the Caribbean region, POP management efforts are problematical due to the lack of appropriate legislation and limitations in research and monitoring; hence, these developing countries find it difficult to manage POPs and comply with international singed conventions. This poses a local, regional, and global threat because of the long-range transport characteristics of the POPs. For instance, persistent organic pollutants are found in places where there is little human or industrial activity (Kim et al., 2020). Even if the concentration of these pollutants is low, they can cause hazardous effects to health and environment due to their capability of bio-magnification throughout the food chain and bio-accumulation in organisms.

To decrease the effects of persistent organic pollutants on the environment, ecosystems, and humans, in May 1995 the Governing Council of United Nations Environment Program (UNEP) asked for an international assessment of 12 POPs. This led to the signing of the Stockholm Convention (SC) on POPs in Stockholm, Sweden, in May 2001. The convention was ratified by more than 152 countries; thus, it entered into effect in May 2004. The convention identified 12 POPs that affected the environment, human health, and ecosystems, including annex A, B, and C: Elimination, restriction and unintentional production, respectively. The convention also reviews proposals submitted by parties every 2 years for the addition of new POPs. Since then, the controlled list of POPs has increased. The objectives of the Stockholm Convention aim to eliminate dangerous POPs, target additional POPs for action, support the transition to safer alternatives, clear-out equipment with persistent organic pollutants and old stockpiles, and collaborate for a future free of persistent organic pollutants (United Nations Industrial Development Organization). The Stockholm Convention is important as it augments local, regional, and global efforts to control POPs.

In an effort to have a more holistic perspective and a better understanding of the developments that have occurred subsequent to the approval of the Stockholm Convention, this chapter aims to discuss the types and impact of POPs, the analytical methods employed for the determination of POPs, the removal of POPs, and an overview of POP management in the Caribbean Region, specifically a case study of Belize..

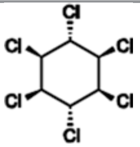
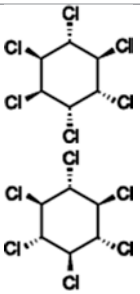
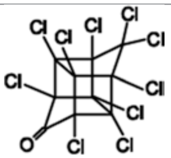
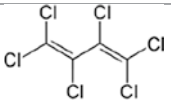
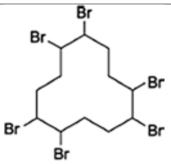
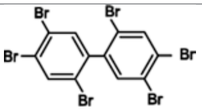
2 Types of Persistent Organic Pollutants

The initial 12 POPs that cause damage to human health and the environment fall in 3 categories: Industrial chemicals: polychlorinated biphenyls, hexachlorobenzene; Pesticides: DDT, dieldrin, endrin, heptachlor, aldrin, chlordane, mirex, toxaphene, hexachlorobenzene; and By-products: hexachlorobenzene; polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, and PCBs. In 2009, new POPs where added to the list of 12 and these include fire retardants such as hexabromobiphenyl, the insecticide lindane, and perfluorooctane sulfonyl fluoride, which are used in electronic products, hydraulic fluids, and textiles (Forde & Dewailly, 2015). Since then, the number of new POPs added to the list has increased to 16 and several other chemicals are being reviewed. These chemicals which are targeted by the Stockholm Convention are listed in either annexes A, B or C (United Nations Industrial Development Organization, n.d).

- Annex A: Parties must take measures to *eliminate* the production and use of the chemicals listed under Annex A. Specific exemptions for use or production are listed in the Annex and apply only to Parties that register for them.
- Annex B: Parties must take measures to *restrict* the production and use of the chemicals listed under Annex B in light of any applicable acceptable purposes and/or specific exemptions listed in the Annex.
- Annex C: Parties must take measures to reduce the *unintentional release* of chemicals listed under Annex C with the goal of continuous minimization and, where feasible, ultimate elimination.

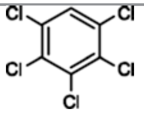
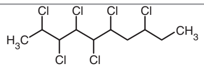
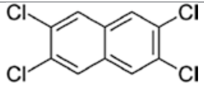
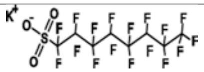
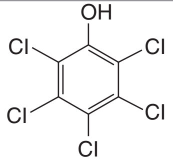
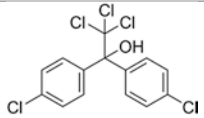
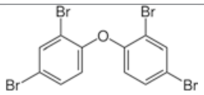
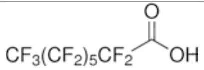
In order for a chemical to be listed as a persistent organic pollutant, there has to be convincing scientific evidence of its potential for bioaccumulation, persistence, toxicity, and long-range transport. This aspect of the convention, which encourages parties to identify new POPs, will result in the continuous addition of new chemicals to the POP list. Table 1 summarizes the use and effects of the 16 newly added POPs to Stockholm Convention. Most of the information for the table was obtained from the Stockholm Convention Secretariat United Nations Environment 2017 16 New POPs booklet.

Table 1 Sixteen new chemicals: structure, use, and adverse effects

Name	Chemical structure	Use	Adverse effects
Gamma hexachlorocyclohexane		Insecticide and against parasites	Immunotoxic, causes reproductive and developmental effects
Alpha hexachlorocyclohexane; beta hexachlorocyclohexane		Alpha- and beta-HCH are by-products of lindane	Alpha- and beta-HCH are potentially carcinogenic
Chlordecone		Pesticide	Carcinogenic and toxic to aquatic organisms
Hexachlorobutadiene		Solvent for other chlorine-containing compounds	Toxic to aquatic organisms, birds, and carcinogenic
Decabromodiphenyl ether		Additive flame retardant, applications in polymers/composites, adhesives, and inks	Adverse effects to humans and animals such as birds, fish, frog, rat, and mice
Heptabromodiphenyl ether and hexabromodiphenyl ether		Flame retardants	Toxic to earth worms and health effects: fetus
Hexabromocyclododecane		As a flame-retardant additive on polystyrene materials	Toxic to aquatic organisms and human
Hexabromobiphenyl		Flame retardant	Human carcinogen and has chronic toxic effects

(continued)

Table 1 (continued)

Name	Chemical structure	Use	Adverse effects
Pentachlorobenzene		Fungicide and a flame retardant, chemical, and produced unintentionally during combustion	Toxic to humans and aquatic organisms
Short-chain chlorinated paraffins		Plasticizer, flame retardants, pressure lubricant	Affects environmental and human health
Polychlorinated naphthalenes		Insulating coatings, wood preservatives, additives, lubricants	Liver disease due to chronic exposure
Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride		Electric and electronic parts, firefighting foam, photo imaging, hydraulic fluids, and textiles	Binds to proteins in the blood and the liver. Toxic
Pentachlorophenol and its salts and esters		Herbicide, insecticide, fungicide, algaecide, disinfectant	Affects human health and/or environment
Dicofol		Pesticide	Toxic to aquatic animals, birds and human health
Tetrabromodiphenyl ether and pentabromodiphenyl ether		Flame retardants	Affects the liver, thyroid and neurobehavioral development
Perfluorooctanoic acid, its salts, and PFOA-related compounds	 $CF_3(CF_2)_5CF_2C(=O)OH$	Production of fluoroelastomers, fluoropolymers, non-stick kitchen ware, and food processing equipment	Toxic for environment and living organisms

3 Analytical Methods for Detecting Organic Pollutants

The list of Stockholm Convention POPs keeps increasing; thus, the need of novel analytical methods for detecting POPs. The analytical techniques and instrumentation used to analyze POPs continue to evolve as there is the need for accurate and precise determination of these chemicals. The analytical methods employed for the separation and identification of POPs are the liquid chromatography (LC) coupled to a ultraviolet light/fluorescence detector or mass spectrometry (MS) and the gas chromatography (or two-dimensional gas chromatography – GC x GC) coupled to an ionization detector (electron-capture detector), or an infrared spectrometry (Fourier-transform infrared spectrometry), or mass spectrometry (MS). Recently, the development of optical spectroscopy such as the Fourier-transform infrared resonance spectroscopy (FTIR) is being investigated for dioxins, furans, and related compounds (Patrizi et al., 2019).

However, with the new development the coupling of a gas chromatography and mass spectrometry and relatively inexpensive device compared to the liquid chromatography, the former has become the method of choice as can be seen by the vast amount of literature employing these devices (Table 2).

It is easier to identify compounds if they are fully separated from all others in the sample. To achieve this, several chromatographic techniques are useful. The most common chromatographic technique used for POPs are LC and GC. The purpose for the separation using either liquid or gas chromatography is to fully resolve the sample analytes.

In gas chromatography, the sample is injected through the sample inlet where the sample is vaporized. The vaporized sample will be transported by a gas called the carrier gas to the column for separation. After separation, the individual component gives rise to an electric signal which is detected by a detector device. The detector produces an output called a chromatogram. These detectors monitor the column effluents and produce a signal which is proportional to the analyte being eluted. Two universally accepted detectors are the flame ionization detector and the thermal conductivity detector. Some selected detectors are electron-capture detector, alkali-flame ionization detector, and the flame photometric detector (Poole, 2005). An electron capture detector (ECD), for instance, detects trace amounts of halogenated compounds.

The gas chromatography can be single dimensional (1 capillary) to multidimensional. It has been recognized that single capillary column cannot fully resolve to baseline, all components of many samples. Therefore, the multidimensional or comprehensive GC x GC are techniques that enhance selectivity and increase sensitivity. For instance, the GC x GC are connected sequentially, which are connected by a modulator. This modulator traps compounds from the first column and reinjects to the second column, and these compounds are subjected to two independent separations, thereby increasing separation capacity.

The mass spectrometer when coupled to liquid chromatography or a gas chromatography system becomes a powerful detector. The sample is ionized in the compartment of the mass analyzer by any of several techniques: electron impact (EI), chemical ionization (CI), fast atom bombardment (FAB)/ liquid secondary ionization (SIMS), atmospheric pressure ionization (API), matrix-assisted laser desorption ionization (MALDI), desorption ionization, and electrospray ionization (ESI). After ionization, the ions moved through the mass analyzer component of the mass spectrometer where individual ions are filtered according to their mass to charge ratio (m/z). There are different types of mass analyzers. These include magnetic

Table 2 Types of equipment used for the qualitative and quantitative identification of persistent organic pollutants (POPs)

POPs	Analytical methods used	References
OCP	GC-ECD	Fernández-Rodríguez et al. (2015), Tolosa et al. (2019)
	GC-MS	Malarvannan et al. (2013), Zhang et al. (2018)
	GC-MS/MS	Lara-Gonzalo et al. (2012), Tolosa et al. (2019)
	GC x GC-ECD	Tolosa et al. (2019)
	GC-MS(SIS)	Lara-Gonzalo et al. (2012)
	GC-HRMS	Ochiai et al. (2011), Tolosa et al. (2019)
	GC-QMS	Ochiai et al. (2011)
	GC × GC-HRTOFMS	Ochiai et al. (2011)
	GC-QqQMS	Pitarch et al. (2007)
	GC/Q-TOF	Wang et al. (2020)
PCBs	GC-ECD	Fernández-Rodríguez et al. (2015), Tolosa et al. (2019)
	GC-MS	Čvančarová et al. (2012), Tolosa et al. (2019), Yu et al. (2020)
	GC-HRMS	García-Bermejo et al. (2015), L'Homme et al. (2015); Li et al. (2015), Tolosa et al. (2019)
	GC-MS/MS	Tolosa et al. (2019)
	GC-QqQMS	García-Bermejo et al. (2015), Pitarch et al. (2007)
	GC-QqQMS/MS	L'Homme et al. (2015)
PCDDs, PCDFs	GC-HRMS	García-Bermejo et al. (2015), L'Homme et al. (2015), Li et al. (2015)
	HRGC-HRMS	Rivera-Austrui et al. (2017)
	GC x GC TOFMS	Focant et al. (2005), Organtini et al. (2014), Planche et al. (2015), Plaza-Bolaños et al. (2013)
	GC-QqQMS/MS	García-Bermejo et al. (2015), L'Homme et al. (2015), Rivera-Austrui et al. (2017)
	GC–MS/MS-FTICRMS	Taguchi et al. (2010)
PBB	GC-MS	Yu et al. (2020)
HBCD	LC-MS/MS	Malarvannan et al. (2013)
HCBD	GC-MS	Zhang et al. (2018)
PeCB	GC-MS	Zhang et al. (2018)
	GC-QqQMS	Pitarch et al. (2007)
PCP	GC-MS	"Pentachlorophenol and Lindane [Air Monitoring Methods, 2003]"
PFOS, PFOS-F	LC-MS	Chen et al. (2013), Saito et al. (2010)
	LC-QqQ MS/MS	Villaverde-de-Sáa et al. (2012)
PFOA	LC-MS	Chen et al. (2013), Saito et al. (2010)
PCNs	HRGC-HRMS	Guo et al. (2008), Li et al. (2015, 2012)
	GS-QqQMS	Li et al. (2014)
SCCPs	GC-(Q)TOFMS	Gao et al. (2016)

(continued)

Table 2 (continued)

POPs	Analytical methods used	References
	GC-QqQ-MS/MS	Carro et al. (2018)
PBDEs	GC-ECD	Tolosa et al. (2019)
	GC-MS	Malarvannan et al. (2013), Tolosa et al. (2019), Yu et al. (2020)
	GC-HRMS	Mackintosh et al. (2012), Tolosa et al. (2019)
	GC-QqQMS	Mackintosh et al. (2012), Pitarch et al. (2007)

LC liquid chromatography, *GC* gas chromatography, *MS* mass spectrometry, *HR* high resolution, *ECD* electron-capture detection, *GC x GC* comprehensive two-dimensional gas chromatography, *QMS* quadrupole mass spectrometry, *TOFMS* time-of-flight mass spectrometry *FTICRMS* fourier transform ion cyclotron resonance mass spectrometry, *MS/MS* tandem mass spectrometry, *QqQ MS/MS* triple quadruple tandem mass spectrometry, *(Q)TOF* quadrupole time-of-flight, *MS/MS-FTICRMS* tandem quadrupole-fourier transform ion cyclotron resonance mass spectrometer

OCP[a] organochlorinated pesticides, *PCBs* polychlorinated biphenyls, *PCDDs* dioxins, *PCDFs* furans, *HBCD* hexabromocyclododecane, *PeCB* pentachlorobenzene, *PCP* pentachlorophenol and its salts and esters, *PFOA* perfluorooctanoic acid, its salts, and related compounds, *PFOS* perfluorooctane sulfonic acids and its salts, *PFOS-F* perfluorooctane sulfonyl fluoride, *PCNs* polychlorinated naphthalenes, *PBDEs* polybromodiphenyl ethers, *PBB* hexabromobiphenyl, *HCBD* hexachlorobutadiene, *SCCPs* short-chain chlorinated paraffins

[a] OCP -aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), hexachlorocyclohexanes (alpha, beta, or gamma hexachlorocyclohexane-lindane), chlordecone, dicofol, endosulfan, mirex, toxaphene

sectors, quadruple mass filters (Q), time-of-flight (TOF), and ion-trap analyzer. Moreover, there are many configurations of the mass analyzers that combine different designs and are called "hybrid instruments." A design that combined a quadrupole and a TOF is called a Q-TOF, whereas a triple quadrupole analyzer (QqQMS) consist of three quadrupoles.

The *quadrupole mass analyzer* (Q MS) consists of four parallel rods. Ions travel down the quadrupole between the rods and for a given voltage will reach to the detector, while others collide and not reach the detector. It is filtering the mass with a specific voltage. Direct current and radio frequency electric fields will be applied to the rods (Nollet & Lambropoulou, 2017). *Time-of-flight mass analyzer* (TOFMS analyzer) is based on movement of ions possessing the same energy but different mass travelling through a flight tube at different velocities and the lighter ions arrives before the heavier ones (Nollet & Lambropoulou, 2017). *Magnetic sector mass analyzer* deflects the trajectories of the ions into circular paths of radii that depends on the momentum-to-charge ration of these ions (Poole, 2005). *Ion trap mass analyzer* is similar to a quadrupole mass analyzer but also captures or "traps" ions inside the mass analyzer using a combination of electric or magnetic fields to. Ion trap analyzer includes "2D trap, 3D ion traps, electrostatic trap (Orbitrap), or a magnetic field-based trap (ion cyclotron resonance)" (Clarke, 2017). MS/MS which uses two mass analysers were the first instruments which were double sector consisting of magnetic (B) and electrostatic (E) sectors arranged in series, with either an BE or EB configuration. Now there are multisector instruments with more than two sectors with magnetic and electric analyzers in series. The most widely used MS/MS configuration has been the tripe quadrupole, QqQ. Hybrid instruments have been developed which combines a magnetic sector and quadrupole analyzer, BEqQ. Also both of these have been combined with a time-of-flight analyzer, BE-TOF, and QqTOF. Depending on the sensitivity and selectivity for the POPs analysis, different possibilities exist for the selection of analytical instruments (Table 2). The multisector instruments are the most selective and sensitive but most expensive. When selecting an analytical instrument, several factors must be considered. Some of the considerations are as follows: capital investment cost, operating costs, sample throughput, number of analytes per unit time, instrument LOD (sensitivity), instrument selectivity – elemental composition, instrument selectivity – isomeric compounds, skill and training level of analyst, suitable for ultra-trace, detect and measure unknown compounds, detect and quantify target compounds, analyze multiple analyte groups in same run, and reduced cleanup extract (Reiner et al., 2014).

3.1 Removal of Persistent Organic Pollutants

These novel analytical methods will help us to better understand the fate and effects of POPs in the environment, thus, aiding in the development of better techniques for the removal of POPs from the environment. Presently, there exist different techniques for the removal of organic pollutants. The conventional methods employed are electrochemical oxidation, membrane process, coagulation, adsorption, precipitation, and sonochemical degradation. There is also other oxidation process and this include ozonation, UV mediated, UV/H2O2 mediated, O3/UV/H2O2 mediated, fenton reactor, photofenton reaction, and heterogenous photocatalysis (Barot & Kumar, 2021). The conventional techniques systems are very costly and more cost-effective techniques are required. Bioremediation and biodegradation are emerging technologies and are environmentally friendly. There exist potential candidates for this process such as fungi, bacteria, and plants (Table 3).

Fungal bioremediation, also called mycoremediation, uses the extracelluar and intracellular enzymatic systems of fungi to breakdown polycyclic aromatic hydrocarbons. For instance, lignolytic fungi release extracellular lignin transforming enzymes which degrade organic compounds that resemble lignin. These enzymes consist of three major peroxidases (lignin, manganese, and versatile) and an oxidase (laccase, a phenol oxidase)(Čvančarová et al., 2012). A study conducted by Cvancaarova showed that *Pleurotus ostreatus* is capable of biotransforming PCB and that both intracellular and extracellular (ligninolytic enzymes) enzymatic systems could be involved in the process (Čvančarová et al., 2012).

Cordyceps sinensis strain A, a cyclic ether-degrading fungus, has been used to degrade dioxins (Nakamiya et al., 2005). A white-rot fungus *Phlebia lindtneri* was studied to biodegrade polychlorinated naphthalenes (PN) into six metabolites (Mori

Table 3 Organisms used for the bioremediation/biodegradation of persistent organic pollutants (POPs)

Type of organism	POPs	Bioremediation/ biodegradation	Reference
Fungi	OCP	*Aspergillus niger*	Bhalerao and Puranik (2007)
	PCBs	*Pleurotus ostreatus*	Čvančarová et al. (2012)
	PCDDs, PCDFs	*Cordyceps sinensis* strain A	Nakamiya et al. (2005)
	PeCB	*Psilocybe* cf. *castanella* CCB444	Matheus et al. (2000)
		Lentinus cf. *zeyheri* CCB274	Matheus et al. (2000)
	PCP	*Anthracophyllum discolor*	Cea et al. (2010)
	PCNs	*Phlebia lindtneri*	Mori et al. (2009)
Plants	PCBs	*Salix alaxensis*	Slater et al. (2011)
		Amaranthus retroflexus	Ficko et al. (2010)
		Ambrosia artemisiifolia	
		Barbarea vulgaris	
		Brassica nigra	
		Capsella bursa-pastoris	
		Chenopodium album	
		Chrysanthemum leucanthemum	
		Cirsium arvense	
		Cirsium vulgare	
		Daucus carot	
		Echinochloa crusgalli	
		Echium vulgare	
		Lythrum salicaria	
		Medicago lupulina	
		Polygonum convolvulus	
		Polygonum persicaria	
		Rumex crispus	
		Setaria pumila	
		Sisymbrium officinale	
		Solanum nigrum	
		Solidago canadensis	
		Sonchus asper	
		Symphyotrichum ericoides	
		Symphyotrichum novae-angliae	
		Trifolium pratense	
		Verbascum Thapsus	
		Vicia cracca	
Bacteria	OCP	*Streptomyces*	Fuentes et al. (2017)
		Alcaligenes faecalis JBW4	Kong et al. (2013)

(continued)

Table 3 (continued)

Type of organism	POPs	Bioremediation/ biodegradation	Reference
	PCBs	*Ensifer adherens* R2	Xu et al. (2016)
		Rhodococcus R04	Yang et al. (2004)
		Dehalococcoides mccartyi Strain JNA	LaRoe et al. (2014)
		Alcaligenes xylosoxidans	Murínová et al. (2014)
		Ochrobactrum anthropic	
		Pseudomonas stutzeri	
		Pseudomonas veronii	
		Arthrobacter sp. strain B1B	Munawar et al. (2021)
		Burkholderia xenovorans	
		Pseudomonas aeruginosa	
		Ralstonia eutropha H850	
		Rhodococcus sp. strain RHA1	
	PCDDs and PCDFs	*Actinobacteria*	Huang et al. (2019)
		Bacteroidetes	
		Firmicutes	
		Proteobacteria	
		Sphingomonas sp. strain RW1	Keim et al. (1999), Wittich et al. (1992)
	HBCD	*Rhodopseudomonas palustris* YSC3	Chang et al. (2020)
	PFOA, PFOS, and PFOS-F	*Acidimicrobium sp*. strain A6	Huang and Jaffé (2019)
	PBDEs	*Rhodococcus jostii RHA1*	Robrock et al. (2009)
		Burkholderia xenovorans LB400	

OCP[a] organochlorinated pesticides, *PCBs* polychlorinated biphenyls, *PCDDs* dioxins, *PCDFs* furans, *HBCD* hexabromocyclododecane, *PeCB* pentachlorobenzene, *PCP* pentachlorophenol and its salts and esters, *PFOA* perfluorooctanoic acid, its salts, and related compounds, *PFOS* perfluorooctane sulfonic acids and its salts, *PFOS-F* perfluorooctane sulfonyl fluoride, *PCNs* polychlorinated naphthalenes, *PBDEs* polybromodiphenyl ethers

[a] OCP -aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), hexachlorocyclohexanes (alpha, beta or gamma hexachlorocyclohexane- lindane), chlordecone, dicofol, endosulfan, mirex, toxaphene

et al., 2009). *Aspergillus niger*, a soil fungus has been identified to biodegrade endulfan, a organochlorinate pesticide (OCP) (Bhalerao & Puranik, 2007).

Phytoremediation is the uptake of organic contaminants from soil through the roots, translocated to the tissues and stored (Munawar et al., 2021). Ficko et al. (2010) conducted an assessment of 27 species of weed to extract PCBs from contaminated soil, and they found that these species are able to grow in soil-contaminated areas and found various species completing their life cycle by producing weeds or spreading rhizomes. The weed species investigated that show strong potential to phytoextract PCBs are *Chrysanthemum leucanthemum, Daucus carota, Polygonum* *persicaria, Solidago canadensis*, and *Vicia cracca* (Ficko et al., 2010). Slater et al., 2011 used *Salix alaxensis* (felt-leaf willow) and *Picea glauca* (white spruce) to identify if they were capable of removing PCB from contaminated soils. They were looking if the phytochemicals released by the dead root will promote the biodegradation of PCB (Slater et al., 2011). *S. alaxensis* was identified as a plant for rhizoremediation since it alters the microbial community structure which enhances the loss of PCB congeners.

In microbial degradation, the bacteria possess specific catabolic pathways which helps degrade persistent organic pollutants (POPs). Biodegradation by bacteria is either aerobic (in the presence of oxygen) or anaerobic (dehalogenation). Since POPs are recalcitrant organic compounds which have sulfo, halogen (Cl/Br), and/or aromatic moieties, biodegradation may be employed in their removal. During the anaerobic process, the chlorine is usually degraded through organohalide respiration, which is a natural process and mitigates the harmful impacts of hazardous chemicals by exclusion of chlorine. Here the chlorine atom is substituted by a hydrogen atom (Munawar et al., 2021). *Sphingomonassp* RW1 can catabolize chlorinated dibenzofurans (Keim et al., 1999) and metabolize Dibenzo-p-Dioxin (Wittich et al., 1992). Aerobic biotransformation of polybrominated diphenyl ethers (PBDEs) has been performed by *Rhodococcus jostii* RHA1 and *Burkholderia xenovorans* LB400 (Robrock et al., 2009). A study conducted in paddy soils revealed that various *Rhodopseudomonas palustris* are able to biodegrade hexabromocyclododecane (HBCD) (Chang et al., 2020). A soil contaminated with pentachlorophenol can be degraded by *Anthracophyllum*, and it shows that agricultural residues, such as wheat straw, can be used as growth substrate by bacteria (Cea et al., 2010). Defluorination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by *Acidimicrobium sp*. strain A6 (S. Huang & Jaffé, 2019) has shown that under the right conditions can be used as a bioremediation process.

Although, the list of POPs continues to grow and novel analytical and removal techniques are being developed to address the environmental and health hazards and risks of POPs, the developing world is still struggling to manage legacy POPs. In order to have a better perspective of what countries in the developing world are doing to manage POPs, the next section of this chapter will look at an overview of persistent organic pollutant management in the Caribbean Region, specifically a case study of Belize.

4 Overview of POP Management in the Caribbean

Although most countries have officially banned the usage of the legacy persistent organic pollutants (POPs), these chemicals (DDT and aldrin) were used in the Caribbean for different purposes including agriculture and vector control (UNEP, 2002). While several of these chemical compounds are banned from production and use, some of them are still produced outside of the Caribbean region and imported and used in the Caribbean for acceptable purposes through exemptions permitted under the SC. The chemicals that have exemptions and may still be used include the following: a. Lindane. b. Polychlorinated naphthalenes. c. Short-chain chlorinated paraffins (SCCPs). d. Pentachlorophenol and its salts and esters. e. Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride. f. Perfluorooctanoic acid (PFOA), its salts, and PFOA-related compounds. g. Hexabromocyclododecane, hexabromodiphenyl ether, and heptabromodiphenyl ether (commercial octabromodiphenyl ether). h. Decabromodiphenyl ether (commercial mixture, c-decaBDE). i. Technical endosulfan and its related isomers. j. Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether) (http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx). Furthermore, there are unintentional releases of POP chemicals listed under Annex C of the SC (http://chm.pops.int/Convention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx).

In response to the myriad of problems caused by POPs, countries in the Caribbean region have signed on to several international conventions. Among the most prominent are the Stockholm Convention (SC) which aims to eliminate or restrict the production and use of POPs (The Stockholm Convention on persistent organic pollutants (POPs), 2020), the Rotterdam Convention which aims to promote shared responsibilities in the trade of certain hazardous chemicals (Rotterdam Convention on the Prior Informed Consent (PIC) procedure for certain hazardous chemicals and pesticides in international trade, 2020), and the Basel Convention on the Control of Transboundry Movements of Hazardous Wastes and their Disposal (The Basel convention on the control of Transboundary Movements of hazardous wastes and their disposal, 2020). These international conventions and their associated commitments have synergies in their approach and aims for effective POP management and have supported and driven POP management efforts at the national level in Caribbean countries.

The existing capacity and efforts to manage POPs in the wider Caribbean vary significantly from one country to another, in part because POPs may not be necessarily considered a priority for the smaller Small Island Developing States (SIDS), particularly those with limited industrial development (UNEP/GPA, 2006). Additionally, POP management efforts are further complicated because of lack of appropriate legislation and limitations in research and monitoring among others (Fernandez et al., 2007); hence, creating gaps in data availability to harness the financial, human capital, and informational resources are needed to achieve management goals. While these challenges to effective management of POPs in the Caribbean persist, the region has experienced increased consumerism and a shift in regional economies from agriculture to tourism and industrial economies resulting in greater usage of these chemicals and the generation of larger, more complex categories of solid, hazardous, and chemical wastes containing POPs (BCRC Caribbean, 2020).

Given the need to find venues to effectively manage POPs, the Caribbean region has taken a regional approach to acquiring financial resources to finance POP management. Most recently in 2013, eight countries in the Caribbean successfully acquired funds and are implementing a large-scale project under the GEF-5:

"Development and Implementation of a Sustainable Management Mechanism for Persistent Organic Pollutants (POPs) in the Caribbean." The countries participating in the project Saint Kitts and Nevis, Barbados, Belize, Saint Lucia, and Saint Vincent to name a few. The GEF-5 project was funded by the Global Environment Facility (GEF) and is being implemented by the United Nations Industrial Development Organization (UNIDO) and executed by the Basel Convention Regional Centre for Training and Technology Transfer for the Caribbean (BCRC-Caribbean). According to the project mid-term review (as cited in United Nations, 2018), to date the project has achieved the following:

1. Review and update of National Implementation Plan (NIP) under the Stockholm Convention: In line with the national requests in fulfillment of the SC, the project is supporting the countries through a regional approach with the aim of efficient information management and knowledge exchange.
2. Sound chemicals management mainstreamed into all national policies and plans for all eight project countries: Via virtual inception meetings and through regional information exchange and knowledge management, the countries benefitted from experiences on the national levels.
3. Regional information system available: ICT infrastructural upgrades within the BCRC-Caribbean and the development of an ICT policy and protocols were done in order to aid in the development of a POP Regional Information System.
4. Evaluate potential POP contaminated sites and estimate the level of contamination, and thus, develop appropriate remediation strategies: The assessment of potentially contaminated sites will be done in each country; however, through the regional information system, knowledge and experience will be shared to ensure regional harmonization of soil assessment and potential remediation strategies.
5. Demonstration of technically and environmentally sound management of POPs. Selected countries are on the way of assessing or implementing environmentally sound management procedures for dealing with U-POPs from open burning of waste and/or dealing with polychlorinated biphenyls (PCBs).

Similarly, 11 Caribbean countries acquired funds for a large-scale regional project which was undertaken by the FAO, with support from the GEF for the identification, collection, and disposal of obsolete and unwanted pesticides. In 2017, the project saw the removal of 319 tons of obsolete pesticide stocks and related wastes in 11 Caribbean countries (FAO, 2017).

While POP management differs from country to country in the Caribbean, the case of POP management in Belize presented next provides insight into management status and challenges occurring in the Caribbean region.

4.1 Current Status of POPs in Belize

Uses and Emissions

Belize, a small Caribbean country located on the northeastern coast of Central America, does not produce any of the POP chemicals listed under the SC (Avella et al., 2008). However, POPs have historically been imported and used in Belize and until as recent as 2016 stock piles of legacy POP pesticides such as DDT (approximately 24 metric tons) and minor quantities (less than 1 kg) of aldrin existed in country (Carrias & Alegria, 2016).

In regard to current usage, some legacy POP pesticides (DDT) and newly added POP pesticides to the SC (pentachlorophenol [PCP], lindane, and sulfluramid) have restricted use exemptions in Belize as afforded by the SC. Currently, the Vector Control Unit (VCU) of the Ministry of Health (MOH) of Belize uses DDT alternatives with commercial names, such a deltamethrin, temophos, and cyhalothrin for the malaria eradication program in Belize; however, the MOH maintains a policy of reserving the right to import DDT for emergency use during an outbreak of malaria (CARPHA, 2017a). Currently in Belize, PCP is exempted for wood treatment of utility poles and cross arms. However, a recent inventory identified that none of the potential major users of PCP have used the chemical in recent years (CARPHA, 2017b). According to the Pesticide Control Board, the last known imports of PCP were in 2000 (N. Canto, personal communication, November 2, 2020). Lindane is still used in Belize as a human health pharmaceutical for control of head lice and scabies. Mirex-S (sulfluramid) is not a prohibited pesticide and has restricted importation and use designation in Belize (Pesticides Control Act, chapter 216, revised edition, 2011). While there are a number of registered alternative pesticides that can be used in its place (e.g., boric acid, carbaryl, and malathion), sulfluramid (0.5%) is used for the treatment of leaf cutting and fire ants in Belize (CARPHA, 2017d). Of all POP pesticides with restricted use designation in Belize, sulfluramid is the most extensively used POP pesticide in Belize, most notably in the citrus and banana industries (N. Canto, personal communication, November 2, 2020).

POP polybrominated diphenyl ethers (POP-PBDEs), which are present in waste electrical and electronic equipment, were imported and are either stored or are still in use in households, government institutions, and private businesses in Belize. Most of the sources of POP-PBDEs in Belize are from cathode ray tubes (CRTs) and TVs imported years ago but are either stored or still in use (CARPHA, 2017e). For 2016, the total amount of in use and/or stored CRT computer monitors and TVs for the consumers sampled (households, government institutions, and private businesses) in Belize was 718 t. The estimated total amount of polymer fraction POP-PBDE (c-octaBDE) contained in use and/or stored CRT casings of computer monitors and TVs for consumers sampled in Belize was 253 kg and the estimated total of the impacted polymer fraction was 212 t (CARPHA, 2017e). Similarly, POP-PBDEs in the form of c-pentaBDE are or were historically imported into Belize in vehicles. The total estimated amount of c-pentaBDE in historic vehicle imports (produced before 2005) and vehicles imported for the inventory year (2016) and produced before 2005 was 3 t (CARPHA, 2017e).

Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride have also been imported into Belize in firefighting foams. Best estimates indicate that the low net PFOS content in these current stocks of firefighting foams were 0.12 kg and the high net content was 0.35 kg, based on quantity of 22.73 L/23.41 kg of foam (CARPHA, 2017c).

According to recent POP inventories carried out for Belize, there are practices in Belize which contribute to emissions of unintended organic pollutants (UPOPs) (CARPHA, 2017a). These practices result in three main causes of UPOPs emissions: heat and power generation, open burning and waste incineration (CARPHA, 2017a). The emissions for polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) and other UPOPs were calculated for the year 2016. With today's best knowledge, emissions for PCDD/PCDF and other UPOP emission in Belize for the inventory year 2016 were 4.47 g TEQ/a (CARPHA, 2017a). The emission of PCDD/PCDF was made up of emissions for group 1 (waste incineration) which comprised 0.3217 TEQ/a, emission for source group 3 (heat and power generation) which comprised 0.5273 g TEQ/a), and emission for source group 6 (open burning processes) which comprised 2.9189 g TEQ/a) (CARPHA, 2017a). Additionally, the emissions for source group 4 (transportation) which comprised of 0.0196 g TEQ/a and for source group 9 (disposal) which comprised 0.6565 g TEQ/a was calculated (CARPHA, 2017a).

Stockpiles and Disposal

Belize does not have appropriate and approved disposal facilities for POPs; therefore, stockpiles have to be shipped and disposed of at international facilities. In 2017, the existing POP stockpiles in Belize at the time (i.e., DDT and aldrin) were packaged and shipped to the Tredi Saint Vulbas incineration facility in France for final disposal (Ysaguirre, 2017). While the stockpiles of legacy POP pesticides (i.e., DDT and aldrin) have been disposed, there are stockpiles and contaminated sites in country of other POPs particularly from the waste and articles in use of newly added list of POPs to the SC. According to recent POP inventories carried out for Belize by one of the authors (i.e., Abel Carrias) of this chapter on behalf of the Caribbean Public Health Agency (CARPHA), unknown quantities of polychlorinated biphenyls (PCBs) are likely present in 55 old (some manufactured pre-1970s) decommissioned transformers and two capacitors at a power generation facility (CARPHA, 2017d). Similarly, quantities of POP polybrominated diphenyl ethers (POP-PBDE) present in EEE and WEEE are still in circulation and are present in waste disposal sites in different parts of the country (CARPHA, 2017e).

Contaminated Sites

In regard to contaminated sites, according to the Chief Environmental Officer of the Department of Environment (DOE) of the Government of Belize, a proper assessment including testing of sites for the presence of POP contaminants has not been done in Belize (M. Alegria, personal communication, November 11, 2020). Nonetheless, as precautionary measures, waste management sites and dumpsites are considered important sites of POP contamination in Belize (M. Alegria, personal communication, November 11, 2020). While there are typically no major population centers in the immediate surroundings of approved dumpsites, a recent assessment of these dumpsites shows that waste is disposed in open areas that may be prone to leaching (Hydea, 2016). Therefore, the potential of leachates from these dumpsites contaminating soil and groundwater is possible. According to POP inventories done in 2016, the potentially contaminated sites of priority concern in Belize are as follows:

- Sites associated with use of PFOS-containing firefighting foams, sulfluramide application, and dumpsites and landfills (CARPHA, 2017c).
- Storage site of potentially PCB containing transformers located at Farmers' Light Plant Corporation (FLPC) in the Spanish Lookout, Cayo District (CARPHA, 2017d).
- Any sites, including waste management facilities, where POP-PBDEs and HBCD containing residues or products, which have been discarded of, are, for precautionary measures, considered contaminated sites in Belize (CARPHA, 2017e). Belize has numerous open or partially controlled dumpsites where waste is deposited. Additionally, three major recycling sites were identified (Belize Recycling Company, Caribbean Paper Mill Company, and Orange Walk Metal Recyclers) as potentially contaminated. These have at one point in their existence received and processed vehicles WEEE (computer parts, cell phones, etc.) and non-ferrous vehicle parts.
- While minor quantities of the sulfluramide have been used in various places in Belize, the bulk has been used in the citrus industry, which is primarily located in the Stann Creek District. Sites of sulfuramide use are considered potentially contaminated sites in Belize (CARPHA, 2017b); therefore, soils potentially contaminated with sulfluramide are largely confined to the citrus industry.
- Potentially PCDD/PCDF and other UPOP contaminated sites include sites where historical activities could result in contamination (CARPHA, 2017a). In Belize, potentially contaminated sites include sites where: a. PCB equipment has been used or stored or PCB containing oil has been managed; b. chlorinated phenols (PCP, 2, 4, 5 -T or 2, 4-D) have been used; c. fires have occurred (dumpsites and cane production areas); d. old vehicles are stored/disposed; and e. accidental fires with materials polluted with PCDD/PCDFs have occurred.

4.2 Legal Framework

The prohibition, elimination, and restriction of the production and/or use, import, and export of listed POPs in the SC continues to be tackled in Belize through various mechanisms. One mechanism is through legislative framework. Presently, Belize has no legislation addressing POP chemicals directly. However, the Pesticides Control Act, which prohibits or restricts several POP pesticides and the Customs (Prohibited and Restricted Goods) (Consolidation Order), 1988, which includes a consolidated list of goods that are either prohibited or restricted under the Customs Regulation Act or any other law or regulation are considered the most relevant Acts to POP management (Pompey & Mendoza, 2018).

The Pesticides Control Act and Its Amendments

The Pesticides Control Act (PCA) and subsequent amendments established and grants authority to the Pesticides Control Board (PCB) to control the importation, manufacture, storage sale, transportation, and use of pesticides in Belize (Pesticides Control Act, 1985, Pesticides Control Act, chapter 216, revised edition, 2000 Government of Belize and Pesticides Control Act, chapter 216, revised edition, 2011).

Under the PCA, pesticides registered for use in Belize are categorized as "general use" or "restricted use." As it pertains to POPs, a list of restricted pesticides including DDT and mirex can be found in the Third Schedule to the Pesticides Control Act. DDT has restricted use since the MOH currently has a policy of reserving the right to import DDT for emergency use during the outbreak of malaria. Similarly, Mirex-S (sulfluramid) has restricted importation and use designation in Belize (Pesticides Control Act, chapter 216, revised edition, 2011). In Belize, sulfluramid (0.5%) is used for the treatment of leaf cutting and fire ants. Prohibited pesticides are listed in Schedule IV of the PCA. Most POP pesticides have been listed as prohibited pesticides since the passing of the PCA. Prohibited pesticides also include those pesticides that have not been duly registered for use in Belize.

In 1989, the Government approved a Statutory Instrument, the Registered and Restricted Pesticide (Manufacture, Import and Sale) Regulations, 1988, S.I. No. 8 of 1989. This was followed by the Registered and Restricted Pesticides (Registration) Regulations, 1995, S.I. 77 of 1995. Further Legislation passed includes the Registered and Restricted Pesticides (Manufacture, Import and Sale) (Amendment) Regulations, 1996, S.I. 30 of 1996. Collectively, these regulations provide the legal requirements for importation, registration, labeling, and sale of pesticides.

Customs (Prohibited and Restricted Goods) (Consolidation Order) 1988

Customs (Prohibited and Restricted Goods) (Consolidation Order) 1988 expressly prohibits the importation of prohibited pesticides. Section 15 of Part I of the Schedule (Prohibited Goods) prohibits the importation of pesticides listed in the Fourth Schedule to the Pesticides Control Act and restricts those pesticides, which are listed in the Third Schedule to the Act. The list of restricted goods in Part II of the Schedule (Restricted Goods) includes registered or restricted pesticides under the Pesticides Control Act (Customs Regulation, 1999).

Other Relevant Pieces of Legislations

With regard to UPOPs, there is also no existing legislation in Belize. The Pollution Regulation, 1996 addresses air emission control from both mobile and stationary sources. The Pollution Regulation sets standards for NOx, SOx, Cox, and particulate matter; however, it does not address UPOPS such as dioxins and furans. Nonetheless, several provisions in the Pollution Regulations can be used to regulate the emission or discharge of contaminants which also can address/cover unintended POPs. For example, regulation 6 of the Pollution Regulations states that it is not for a person/source to emitted or discharged contaminants either directly or indirectly into the environment. Likewise, regulation 8 prohibits persons, installations, factories, or plants from emitting or discharging air pollutants into the environment, in contravention of the permitted levels specified under regulation 6 or 7 unless specifically permitted by the Department. In addition, regulation 12 states that burning in is not permitted in any urban area or the burning in a commercial area. Regulation 13 (1) also provides that the DOE can permit the use of disposal sites where burning of solid waste and combustible material can be done.

The Environmental Protection Act Chapter 328 and its amendments of 2009 are also relevant to POPs management in Belize (EPA, 2011). The Environmental Protection Act has overarching responsibility for environmental protection and pollution control; therefore, its mandate covers all classes of chemicals including POPs, although there are other pieces of legislation that are specific to various groups of chemicals.

4.3 Challenges to POP Management in Belize

The sound management of POPs remains a challenging proposition in Belize. According to the National Chemical Profile for Chemicals Management Belize 2015, Belize faces four major challenges to sound chemicals management (BCRC, 2015). As the DOE, these challenges also apply to POP management (M. Alegria, personal communication, November 11, 2020). The major challenges to POP management in Belize, are the following:

1. Lack of POPs-specific legislation coupled with lack of comprehensive policy and legislation that allows for harmonization and uniformity among the various existing legal instruments and efforts that are applicable to chemicals management in general. The current applicable legislation related to the integrated management of chemicals is fragmented among various institutions with limited coordination among them.
2. Insufficient systemic and institutional capacity inclusive of lack of a coordinated, cross-cutting, and comprehensive system for sound waste and chemicals management, and limited collaboration.
3. Professional and technical limitations for chemicals management from a regulatory and administrative perspective. While laboratory facilities exist, these are not currently utilized to its full capacity due to insufficient human resources inclusive of trained personnel.
4. Financial limitations within the different Ministries of Government involved in chemicals management; hampering the institutional strengthening and development of a sound legal framework to further improve their role in chemicals management in Belize.

4.4 Current POP Management Activities/Actions in Belize

As signatory to the SC, Rotterdam, and Basel conventions, Belize continues to progress the agenda and commitments under these conventions. According to the Chief Environmental Officer of the DOE, Belize has recently taken some major steps toward achieving sound management of chemicals, inclusive of POPs (M. Alegria, personal communication, November 11, 2020). Among the major accomplishments recently achieved are the following:

1. The Integrated Chemicals Management Bill and its Industrial Chemicals Management Regulations have been drafted and are pending enactment. The bill would allow for improved management of POPs and other hazardous chemicals.
2. Training and capacity building in various aspects of chemicals management, inclusive of POPs, was received and continues to be received through the Basel Convention Regional Centre for Training and Technology Transfer for the Caribbean Region (BCRC-Caribbean).
3. Inventories of the five categories of POPs under the SC were carried out in 2016.
4. Disposal of chemical stockpiles (i.e., DDT and obsolete pesticides including POPs) was carried put in 2017.
5. The National Implementation Plan (NIP) for Belize has been updated and is pending approval from the Government of Belize. Under Article 7 of the Stockholm Convention, Parties to the Convention are required to prepare a plan on how they are going to implement the obligations under the Convention and make efforts to put such plan into operation.

Once approved, the NIP will give life to Belize's plan to implement its obligations under the SC convention through a series of recommended action plans, including strategies and activities (M. Alegria, personal communication, November 11, 2020).

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Aldehydes' Sources, Toxicity, Environmental Analysis, and Control in Food

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Abstract Aldehydes are highly reactive carbonyl compounds that are widespread in the nature. Aldehydes are broadly distributed in the indoor and outdoor environment sourced from the industrial, restaurant, and motor vehicular exhausts. Besides, aldehydes are thought to be a major cause of the photochemical smog in the air. Aldehydes are also present in rainwater and the surface water due to their washing away from the atmosphere owing to their high-water solubility. In addition, microbial or photochemical degradation of organic chemicals leads to the formation of aldehydes in the surface water. Furthermore, chlorination and ozonation sterilization of drinking water lead to aldehydes' formation. On the other hand, aldehydes could be formed during cooking upon high-temperature frying and also could be

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sourced from cigarette smoke and/or other combustion operations. Besides, aldehydes are present in wine and vegetable oils, and they are formed as by-products during deterioration, maturing, or microbial fermentation of food. Human exposure to aldehydes from the environment or food could bring many adverse health effects either acute or chronic ones. Aldehydes are highly reactive with biological molecules; thus, they are considered highly toxic. The aldehydes' biochemical modification could lead to the disruption of biological functions, and consequently, cause many diseases. Thus, aldehyde monitoring in the surrounding environmental and food samples is vital to control the toxic aldehydes' possible health risk on humans. Aldehydes' different sources in the environment, molecular toxicity mechanisms, possible effects on human health, and recently developed analytical methods for determination and control of aldehydes in environmental and food samples will be summarized in this chapter.

Keywords Aldehydes' sources · Environmental sources · Aldehydes in food · Human exposure · Aldehydes' toxicity · Toxicity mechanisms · Environmental analysis · Food analysis

1 Introduction

Aldehydes are highly reactive naturally ubiquitous carbonyl compounds that are widespread in the surrounding indoor and outdoor environments. They are classified according to their side chain into different categories including saturated aldehydes (e.g., alkanals), unsaturated aldehydes (e.g., alkenals, oxo-alkenals, hydroxy-alkenals, and dialkenals), dialdehydes (malondialdehyde (MDA) and glyoxal (Gly)), and aromatic aldehydes (e.g., benzaldehyde, cinnamaldehyde, vanillin, and anisaldehyde). The chemical structures of different kinds of aldehydes are shown in Fig. 1.

Environment aldehydes are sourced from industrial activities, and exhausts from restaurants and stores kitchens, and motor vehicles. Additionally, most of the aldehydes are hydrophilic compounds; thus, they are washed away from the atmosphere into rainwater and surface water. Another source for aldehydes in the surface water is the microbial and photochemical degradation of some chemical compounds that are spread in nature (Zhang et al., 1994a; Altemose et al., 2015; Kuykendall, 2010). Besides, aldehydes are also formed inside the human body mainly through lipid peroxidation, and to a smaller extent from autoxidation of carbohydrate and ascorbate, and as reaction products of oxidases, peroxidases, and some metabolic enzymes (Kuykendall, 2010). In addition, aldehydes are present in many foods including many fruits and vegetables (e.g., acetaldehyde), cinnamon and peas (e.g., cinnamaldehyde), almonds and cherries (e.g., benzaldehyde), anise extract (e.g., anisaldehyde), and vanilla extract (e.g., vanillin). Furthermore, aldehydes are employed as additives in cosmetics, detergents, and food industries (e.g., C_7–C_{13}

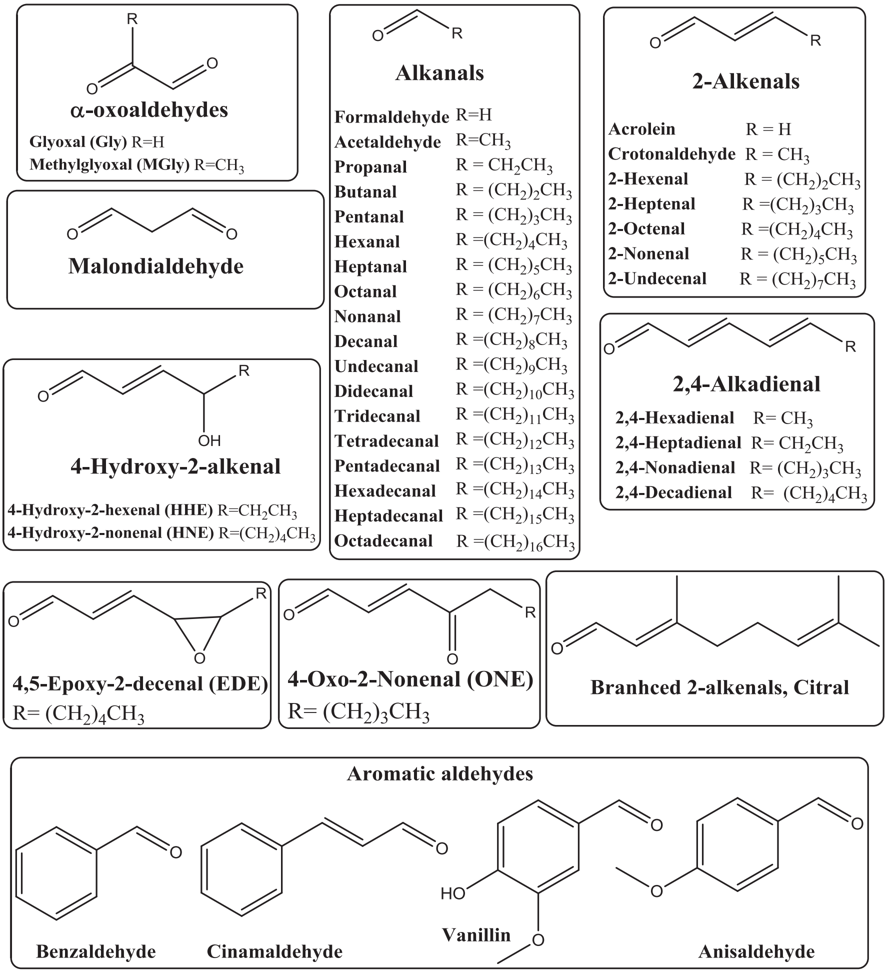

Fig. 1 The chemical structures of different categories of aldehydes

aliphatic aldehydes, benzaldehyde, 4-hydroxybenzaldehyde, cinnamaldehyde, anisaldehyde, vanillin, and furfural) (O'Brien et al., 2005; Feron et al., 1991). Aliphatic and aromatic aldehydes have also been identified in drinking water sourced from leakage from surface water. Additionally, aromatic aldehydes and alpha ketoaldehydes were detected in many beverages (Cancho et al., 2002; Serrano et al., 2013a; Osório & Cardeal, 2013; Lachenmeier et al., 2013). Besides, aldehydic function group exists in some antibiotics such as tylosin, josamycin, streptomycin, and spiramycin. Furthermore, some anticancer agents, such as cyclophosphamide and ifosfamide, produce the reactive toxic aldehyde acrolein and crotonaldehyde, upon their metabolism, causing neurotoxicity and hemorrhagic cystitis (O'Brien et al., 2005; Sood & O'Brien, 1996). In the same context, the medicinal drugs sudoxicam, felbamate, misonidazole, and abacavir were found to be metabolized also into reactive aldehydes, such as Gly, atropaldehyde, or reactive aldehydes intermediate, causing various side effects including hepatotoxicity and aplastic anemia (O'Brien et al., 2005; Kapetanovic et al., 2002; Heimbrook & Sartorelli, 1986; Walsh et al., 2002). As can be seen, aldehydes surround us everywhere, in the environment, in food, in beverages, and even in some medicines, in addition to their in vivo formation through various oxidative and metabolic processes. Meanwhile, aldehydes are very reactive due to the presence of the polarized carbon-oxygen double bond imparting them substantial dipole moments resulted from the high difference in electronegativity between the oxygen and carbon atoms. Thus, the carbon atom possesses high electrophilicity rendering it very reactive toward nucleophilic sites such as nucleotide bases and protein amino acids producing many toxic effects inside the human body when present in high concentration. This reactivity and toxicity are augmented in α,β-unsaturated aldehyde, such as acrolein and crotonaldehyde, as the double bond is conjugated with the carbonyl group, employing positive polarization for the β-carbon; thus, it becomes another site for nucleophilic attacks. Furthermore, the presence of γ-hydroxy group substitution with electron-withdrawing power, such as in 4-hydroxy-2-nonenal (HNE) and 4-hydroxy-2-hexenal (HHE), employs more electrophilicity to the β-carbon (Feron et al., 1991; McMurry, 1984) making these aldehydes more reactive and more dangerous. Given these facts, the main objective of this chapter is to summarize and discuss different sources of aldehydes in the environment and food, possible effects on human health, their molecular toxicity mechanisms, and recently reported method for analysis and control of aldehydes in environmental and food samples.

2 Aldehydes' Sources in the Environment and Food

Aldehydes are emitted indoor and outdoor and released into the environment and act as dangerous pollutants as they cause adverse health effects on humans in rural and even in urban areas (Araki et al., 2020). They are produced either naturally or due to industrial activity. Also, they are present in many kinds of foods. Their sources will be discussed in detail in the following sections.

2.1 Natural Environmental Source of Aldehydes

Naturally, aldehydes are resulted from the photooxidation of volatile organic hydrocarbons that are produced from the metabolism of the plants. They are released from the dark reactions of ozone with any volatile organic compound (VOC), which contains unsaturated carbon-carbon bonds (unsaturated VOCs), as well as organic acids (Zhang et al., 1994b; Villanueva et al., 2015). The unsaturated VOCs include benzene, ethylbenzene, limonene, *p*-dichlorobenzene, styrene, toluene, and xylene, and many of them are present in paints, thinners, adhesive agents, printing inks, cleaning agents, and petrochemical oils such as gasoline and kerosene (Araki et al., 2020; Kanazawa et al., 2010). According to their boiling points (BPs) and volatility, Godish T. classified these VOCs into very volatile organic compounds that have BP ranged from <0 °C to 50–100 °C, volatile organic compounds with BP ranged from 50–100 °C to 240–260 °C, semi-volatile organic compounds with BP ranged from 240–260 °C to 380–400 °C, and particulate organic matter with boiling points above 380 °C (Godish, 2016). Unfortunately, these compounds and their products of aldehydes have many adverse health impacts including irritation, wheezing, and other common allergic symptoms, according to the World Health Organization, 2009 guidelines for indoor quality (Heseltine & Rosen, 2009).

2.2 Industrial Sources of Aldehydes

Aldehydes are also derived from urban and industrial activities such as biomass burning, fossil fuel combustion, and household activities (Nguyen et al., 2020). Aldehydes enter as raw materials or additives in many industrial activities including the manufacturing of building materials, flooring wallpaper, adhesives, and furniture (Zhang et al., 2020). Aldehydes are exchanged in the indoor and outdoor air; however, their indoor levels are generally more than that of outdoor levels (Gilbert et al., 2008). The indoor air aldehydes' pollution has a major public health concern due to the continued elevation in their indoor level and at the same time, general populations spend most of their time in indoor environments. Aldehydes and other VOCs were reported to be emitted from building materials, and they are considered as a major source of sick building syndrome (Takeda et al., 2009; Takigawa et al., 2010, 2012). Also, cleaning and maintenance agents, furniture, paints, particle boards, fabrics, carpets, and others were the main sources of the increased levels of indoor as a local emission of aldehydes more than outdoor (O'Brien et al., 2005; Brown, 1999). Therefore, due to the known hazardous effects of aldehydes and VOCs on humans, the World Health Organization (WHO) set a guideline to prevent their health risks. In addition, in Japan, the Ministry of Health, Labor, and Welfare developed air quality guidelines for formaldehyde and 12 VOCs (Araki et al., 2020; Heseltine & Rosen, 2009).

The circulated anthropogenic aldehydes are mainly formaldehyde and acetaldehyde. Relatively, formaldehyde is the most abundant aldehyde in indoor air compared to its presence in outdoor air, followed by acetaldehyde (Zhang et al., 1994a). Zhang et al. (1994a), and Baez et al. (2003) reported that aldehydes are present in high concentrations (2–10 times) in indoor than their presence in outdoor, related to the multiple varieties in the sources of aldehydes in indoor air such as direct emissions and chemical formation than their sources in outdoor air. Moreover, temperature, humidity, and the low air exchange rates in the indoor environment resulted in high concentrations of aldehydes and total VOCs more than that of the outdoor ones (Zhang et al., 2020; Salthammer et al., 1995; Chi et al., 2016). On the other hand, the outdoor VOC concentrations are affected by season and temperature which indirectly affect the presence of the total aldehydes, as well as proximity to emission sources such as industry, traffic and gas stations, and meteorology, such as mixing height, wind speed, and precipitation (Kwon et al., 2006; Jia et al., 2008; Cheng et al., 1997).

The sources of aldehydes in the urban areas are motor vehicle wastes in air, either via direct aldehydes emission, or indirect through hydrocarbon emission, which then undergo photochemical oxidation and converts into aldehydes (Cecinato et al., 2002; Destaillats et al., 2002). The urban areas' vehicular fleet involved the vehicles fueled with hydrated ethanol, gasohol (gasoline and anhydrous ethanol mixed in a ratio of about 4:1), and diesel, as reported in a study in Londrina (Pinto & Solci, 2007). In these fuel hydrocarbons, the oxidation and/or ring breaking of benzene, ethylbenzene, toluene, and xylenes in the internal combustion motor or the exhaust gave the largest carbonyl emissions, as a source for aldehydes and other pollutants. O'Brien et al. (O'Brien et al., 2005) divided these carbonyl emissions into four groups according to their chemical structure, namely, alkanals, alkenals, aromatic aldehydes, and α-oxoaldehydes. The chemical structures of these types of aldehydes are illustrated previously in Fig. 1. The crowdedness in the urban areas allowed aldehyde to be present in residential, workplace environments, and the confined spaces as spacecraft and airline cabins (National Research Council, 2002). Modern industrial settings use aldehydes as raw materials or they are released during the manufacturing process as a source of humans to be exposed to aldehydes. In different synthetic products such as resins, resin coating, lubricating oils, polyurethane, polyester plastics, and plasticizers, formaldehyde is used in their manufacture (O'Brien et al., 2005).

The sources of aldehydes in the rural areas are hydrocarbons' photooxidation and ozonolysis, especially for the naturally emitted one, named as nonmethane (Rottenberger et al., 2004). For this reason, aldehydes are thought to be a major player in the formation of air photochemical smog (Granby et al., 1997). The burning processes, such as the agriculture productions, photochemical decomposition of hydrocarbons and other organics in the air, and incomplete combustion of oxygenated fuels in engines, resulted in increased emissions of aldehydes in indoor air (Pinto & Solci, 2007). Moreover, naturally generated through tropospheric reactions of the terpenes and isopropene emitted by foliage also react with hydroxyl radicals to contribute to the formation of aldehydes (O'Brien et al., 2005; Leikauf, 2020). The rural areas are apart from the industrial operations; therefore, they receive minimal impact from local anthropogenic sources of aldehydes, just from alcohols incomplete combustion or polymeric materials aldehydes leakages.

In both rural and urban areas, cooking oil fumes, which are a mixture of chemicals contain aldehydes (acrolein, and *t*,*t*-2,4-decadienal), acid, alcohol, and polycyclic aromatic hydrocarbons (e.g., benzo(a)pyrene) (Peng et al., 2017), are suspected as indoor pollutant carcinogens. These fumes were emitted from high-temperature frying and classified as group 2 A by the International Agency of Research on Cancer (IARC WHO, 2017). Aldehydes are the major components in cooking oil fumes, as they are produced by the decomposition of the fatty acids of the cooking oils at the cooking temperature (Fullana et al., 2004a; Lin & Liou, 2000; da Silva & Pereira, 2008; Katsuta et al., 2008).

Another source of aldehydes is cigarette smoke which is considered a potential risk for indoor aldehyde pollution (Baez et al., 2003). Acetaldehyde is the major component of the cigarette smoke with a concentration of 709µg/cigarette, followed with acrolein (82µg/cigarette), then formaldehyde (54µg/cigarette), and then crotonaldehyde (15µg/cigarette) (O'Brien et al., 2005). In general, the released aldehydes from cigarette smokers are categorized into a mainstream (the part inhaled by the smoker), a side-stream (a part released from the burning cigarette), and an environmental (indoor or/and outdoor) tobacco smoke (a combination of the smoke of aged side-stream and breathed out mainstream). It was found that acetaldehyde is the most abundant saturated aldehydes in environmental tobacco smoke, followed by formaldehyde and propionaldehyde. As the smokers inhale about less than 50% of each cigarette, therefore, the side-stream smoke could be a significant contributor to the indoor aldehyde release (Fujioka & Shibamoto, 2006; Stabbert et al., 2017). In order to overcome this problem, alternative electronic cigarettes (e-cigarettes), have been activated in the United States in 2007, to decrease the indoor smoking restrictions. These were analyzed to assess their potential health impacts, compared to the standard tobacco cigarettes. For all by-products measured in e-cigarettes, the results revealed that they considerably lowered the level of aldehydes and they could help in the decrease of the indoor aldehyde pollutants (McAuley et al., 2012).

Regarding the aqueous environment, the formaldehyde concentrations have been reported to be about 1.38 mg/L, 6.8 mg/L, and less than 0.1 mg/L in rainwater, fog water, and in drinking water, respectively (O'Brien et al., 2005). The presence of formaldehyde in rainwater is from its scavenging from the gas phase and aerosol on which formaldehyde is absorbed in the polluted areas and has no correlation with rainfall.

Aldehydes are washed away from the atmosphere into the rainwater and surface water due to their high solubility in water. Furthermore, the natural microbial and photochemical degradation of organic chemicals could lead to the formation of aldehydes in the surface water. An aqueous photoproduction of dissolved organic compounds, absorption from the gas phase, transportation on the regional scale, and degradation such as the activity of microorganisms, all resulted in the existence of different types of aldehydes, especially formaldehyde, in rainwater (Southwell et al., 2010).

2.3 Aldehydes' Sources in Food and Cosmetics

The reactive aldehyde, formaldehyde, is present in the fish and seafood naturally resulted from some oxidative enzyme reactions, such as amine oxidases and the oxidation of lipids by some microorganism activities. Besides, formaldehyde is produced also inside the frozen fish due to the breakdown of trimethylamine into dimethylamine and formaldehyde (Cui et al., 2007; Gram et al., 2002; Arashisar et al., 2004). Furthermore, aldehydes are usually used in the form of formalin (37% formaldehyde), as a preservative for meats and frozen fishes, to extend the shelf life and stiffness and to preserve their fresh look for a longer time (Jaman et al., 2015; Kibria, 2007). As fish is a favorite diet in different areas, the presence of formalin contributes to the accumulation of formaldehyde more than the carcinogenic threshold to humans (LD_{50} 30 gm) (Jaman et al., 2015). Improper freezing and time-consuming transport force the sellers of fish to indulge in malpractices, as they dip the whole fish in or inject their body cavities with formalin or spread formalin mixed water as a preservative (Bhowmik et al., 2020; Sumon et al., 2020).

Moreover, aldehydes have a sensory relevance to be added to the most foodstuff products (e.g., cheese, seafood, and meat), usually added in low concentration and in limited types. Moreover, the presence of certain aldehydes could be an indication of temperature overheating, microbial fermentation, quality deterioration, and off-flavor (Schultheiss et al., 2000). Alcohols (methanol, ethanol) are present in vegetables, fruits, fruit juices, and fermented beverages (a substantial amount of ethanol or contaminated with methanol) (Ohimain, 2016). They are converted in vivo to aldehydes (mainly, formaldehyde and acetaldehyde) through the action of dehydrogenase enzymes. As well, aspartame (an artificial sweetener) undergoes intestinal conversion forming aspartic acid-methyl ester (10% of all compounds), then upon further hydrolysis of the methyl ester, methanol is formed and which is then transported through the portal vein to the liver (Hill & Belsito, 2003). Methanol is then oxidized to formaldehyde and formic acid by alcohol and aldehyde dehydrogenases, and microsomal oxidases. Regarding acetaldehyde, it is either naturally present or added as a flavoring substance to many fluids such as vegetables and fruits, and alcoholic products.

As we mentioned previously, the cooking of fat-containing foods or frying using oil or fats could produce acetaldehyde, formaldehyde, and acrolein (Kundu et al., 2020; Lynch et al., 2008; Zamora et al., 2015). Many other common foods and soft drinks have different types of aldehydes and their derivatives, such as peas (contain acetaldehyde), cherries and almonds (contain benzaldehyde and hexanal, during their unripe seeds), cinnamon (contains cinnamaldehyde), anise (contains anisaldehyde), and vanilla extracts (contain anisaldehyde and vanillin). The environmental aldehydes are mainly represented by formaldehyde, but the dietary aldehydes have multiple forms and with variable concentration levels (O'Brien et al., 2005; Hellwig et al., 2018).

Other sources of aldehyde pollution are cosmetics and hair salons, as aldehydes, especially formaldehyde, are used there as fumigating agents. Different regulatory practices are set for cosmetics, in which formaldehyde is used as a preservative, as it is highly biocidal, pungent, and skin-irritant (Wu et al., 2003).

In conclusion, aldehydes in food could be classified according to their sources and concentrations in brief into the following:

1. Aldehydes derived from phospholipid and fatty acid hydroperoxide decomposition, namely, alkanals, alkenals, hydroxyalkenals, glycolaldehyde, Gly, and acrolein (from cooked vegetables). They are formed endogenously through lipid

peroxidation of the food products (Spiteller, 2001), mainly vegetables and fruits. They distribute their aldehydes in vivo through the enzymatical hydrolysis of their unsaturated fatty acids with lipoxygenase-hydroperoxide lyases (Gardner et al., 2004).

2. Aldehydes and ketones derived from monoterpene of essential oils of some odoriferous plants. They are mainly added to foodstuff and beverages as flavoring additives (Baines & Seal, 2012). An example of these monoterpenes aldehydes is citral, a reactive alkenal present in all citrus fruits and forms about 3% of lemon peel essential oil (Cimanga et al., 2002; Umano et al., 2002). Citral is commonly used as an additive flavor agent in cosmetics, detergents, and some sweet food industries, after its approval from the US Food and Drugs Administration (FDA) as safe additive "generally recognized as safe, GRAS 182.10 coding" (Mori et al., 2019).
3. Aromatic aldehydes, such as benzaldehydes, cinnamaldehyde, salicylaldehyde, vanillin, and furaldehyde. Benzaldehyde is the main component present in the fixed essential oils of the kernels and seeds of apricots, peaches, plums, bitter almonds, and cherries (Prabuseenivasan et al., 2006). It is believed that it has antibacterial, antiviral, antifungal, insecticidal, and antioxidant properties (Kordali et al., 2005). Cinnamaldehyde is commonly used in baked goods and sweets, ice cream, and juices, chewing gums, condiments, and meat preparations, as a flavoring additive (Friedman et al., 2000; Cocchiara et al., 2005). Salicylaldehyde and vanillin have antimicrobial properties (Petrović et al., 2015). Furaldehyde is present in abundance in coffee and cocoa (Yang et al., 2016).
4. Dialdehydes (MDA), α-oxoaldehydes (3-deoxyglucosone, Gly, and methylglyoxal (MGly)), formed from advanced glycation end products and peroxidation of lipids (O'Brien et al., 2005).

The major aldehydes that could exist in food and cosmetics are listed in Table 1 with a hint about their nature and their potential sources.

3 Human Health Risks Related to Aldehydes and Molecular Mechanisms of Their Toxicity

3.1 Aldehydes' Adverse Impacts on Human Health

Aldehydes' adverse effects on humans are caused by their endogenous production (i.e., bio-formation through oxidative stress or metabolic processes) and exogenous sources (National Research Council, 2014). As we mentioned in the previous section, the continuous contact or exposure to carbonyl aldehydes is higher in indoor air than outdoors, and the most abundant aldehyde there is formaldehyde (Zhang et al., 1994a; Baez et al., 2003). Formaldehyde is a widespread crucial allergen, as well as it is reported to be toxic and irritating to the respiratory tract, eyes, and skin, and its effects depend on its ambient levels (de Groot & Flyvholm, 2020; Clarisse

Table 1 Aldehydes' sources from food and cosmetics

Aldehyde	Properties	Sources	Ref
Formaldehyde	Short-chain saturated aldehyde	Environmental pollutant, metabolic by-product, natural constituents Formed during the cooking process of oils and fats, as well as sugars Fumigating agents in cosmetics and hair salons	Feron et al. (1991) and Abraham et al. (2011)
Nonanal	Medium-chain saturated aldehyde	Human and plant metabolites Present in many natural oils (e.g., lemongrass, citrus, cinnamon, and rose oils) Produced from ozonolytic processes that induce oxidative cleavage in the unsaturated oils from plant origin	Omonov et al. (2014)
Vanillin	Aromatic aldehyde	The major component of natural vanilla and it is used in the food and fragrance industry Used as a flavoring agent in pharmaceutics	Walton et al. (2003)
Acrolein and crotonaldehyde	α, β, unsaturated aldehydes (very reactive and toxic)	They are produced during the preparation of various foods such as fried potatoes, old cheese, and salted fish They originate from petrochemical combustion, smoke from cigarettes, and coal and wood incineration Acrolein is also a lipid peroxidation by-product in the human body	Woodruff et al. (2007), Leikauf (2002), and Werley et al. (2008)
Citral	α, β, unsaturated branched aldehyde	Added as a flavoring agent in food and beverages Added as an odorant to cosmetics and detergents	Adams et al. (2008)
Cinnamaldehyde	Aromatic alkenal	A component of plant essential oils, added as a preservative to provide antimicrobial properties against many strains Used as a flavoring agent	Otoni et al. (2014)
HNE	Very reactive α, β, unsaturated aldehyde	A toxic aldehyde, found mainly in vegetable oils and oil-cooked or derived foods Lipid peroxidation by-product	Ma and Liu (2017)

(continued)

Table 1 (continued)

Aldehyde	Properties	Sources	Ref
Gly and MGly	Very reactive α-oxoaldehydes	Metabolic by-product naturally present in dietary foods and drinks such as bread, rice, yogurt, soy sauce, beer, wine, tea, coffee; as well as in oils Formed products in smog, fog, cigarette smoke, vehicle exhaust, as well as some household cleaners Formed in vivo via carbohydrates and ascorbate autoxidation, glycated proteins degradation, and peroxidation of lipids	O'Brien et al. (2005) and Lange et al. (2012)

et al., 2003). Formaldehyde contact allergy occurs frequently in women associated with hand dermatitis, and the sensitization is caused, especially in nurses, metalworkers, para-medical professionals, and cosmetologists. Women patients are allergic to formaldehyde induced eczema by about 1.5 times more than men. In 2013, the European community discovered a patch testing to measure the traces of formaldehyde in such individuals (Pontén et al., 2013). In formaldehyde-rich areas, if the susceptible individuals are trying to avoid aldehydes or substances containing it, the dermatitis will frequently heal entirely and constantly (de Groot & Flyvholm, 2020). Among the domestic individuals, formaldehyde aggravates the frequent nocturnal breathlessness, as it affects different respiratory system parameters and might cause bronchial hyper-responsiveness, with or without smoking tobacco (Clarisse et al., 2003; Rumchev et al., 2002).

Related to the central nervous system, there is a disease of unknown etiology named multiple chemical sensitivity (MCS) (Kreutzer et al., 1999), resulted from repeated exposure to the aldehydes and VOCs in an indoor environment. MCS symptoms are termed a sick building syndrome, involving headache, nose, eyes, and throat irritation, mental fatigue, and respiratory distress, among the new building owners with newly constructed homes (Hayashi et al., 2004). The olfactory system is responsible for the expression of MCS symptoms. The olfactory epithelium, which consists of olfactory bulb neurons and higher center, receives the airborne chemical information. Chemical signals collected by the olfactory epithelium are transported into olfactory bulb neurons, periglomerular cells, and granule cells. Various signaling substances are responsible for the olfactory system functioning, such as tyrosine hydroxylase (as well responsible for dopamine synthesis), is present in abundant in periglomerular cells (McLean & Shipley, 1988). Formaldehyde causes the olfactory nerve threshold defect in a concentration is higher than 60μg/m^3. Long-term exposure to a low level (80 ppm) of formaldehyde in rats' experiments, resulted in a particular localized variation in the MOB in the brain and changed its neuronal function that is caused by increases in the number of periglomerular cells that are immune-positive to tyrosine hydroxylase (Hayashi et al., 2004).

In addition to the allergic and inflammatory effects of aldehydes, some of them possess potential carcinogenic and mutagenic properties (Pinto & Solci, 2007). The International Agency for Research on Cancer (2008) (IARC) (Crosignani, 2008) categorized formaldehyde as group 1 carcinogen (confirmed human carcinogen). Regarding acetaldehyde, it was first classified as group 2B carcinogen (agents probably carcinogenic to humans) (Villanueva et al., 2015); however, this was then revised by IARC (1999) and acetaldehyde was classified as a group I carcinogen owing to the carcinoma risk correlated with its release after consumption of ethanolic beverages. Like formaldehyde and acetaldehyde, many other aliphatic (acrolein), aromatic (benzaldehyde), and low-molecular weight aldehydes have been found to be genotoxic to many biosystems including microbial, mammalian, and even insect ones (Liu et al., 2007; Feng et al., 2006). Moreover, formaldehyde has an impact in teratogenicity, embryotoxicity, gene mutations, and chromosomal abnormalities in mammalian cells in animals (Thrasher & Kilburn, 2001; Hashim & Fatimah, 2016; Yang et al., 2010); therefore, the US Environmental Protection Agency (EPA) determined the daily maximum dose reference of formaldehyde to be 200μg/kg human body weight per day (Kundu et al., 2020).

The exposure to aldehydes from the surrounding environment can potentiate the occurrence of many diseases, called collectively as the oxidative stress ailments, namely, cardiovascular illness, diabetes, rheumatoid arthritis, Alzheimer's illness, cataract, Werner's syndrome, and neurodegenerative diseases such as amyotrophic lateral sclerosis, and Parkinson's disease, and other hundreds of clinical disorders that are correlated to oxidative stress ailments. Oxidative stress results from a disturbance that promotes the formation of reactive oxygen species that exceeds the organism's antioxidant capacity, which can be significant for cancer prognosis (O'Toole et al., 2008; LoPachin et al., 2008a, b; Bhatnagar, 2006; Fedorova et al., 2014).

As previously discussed, aldehydes are formed upon oxidation processes of polyunsaturated fatty acids in cooking food systems and the formed aldehydes include Gly, acrolein, formaldehyde, acetaldehyde, pentanal, hexanal, and HNE (Zhu et al., 2001; Fullana et al., 2004b). These aldehydes are confirmed as the main causes of food rancidity and lead to the loss of nutritional quality in foods (Zhou & Decker, 1999). Moreover, their presence in a concentration of 10μg/m^3 is associated with mucus and respiratory stress, headaches, nausea, dizziness, and/or lung carcinogen. Also, these aldehydes have caused repeated chronic symptoms in some individuals in closed indoor areas, such as conjunctivitis, bronchitis, laryngitis, or dry cough, and even they can provoke contact-type dermatitis and aggravate the effect of pollens or other allergen sensitivities (Garrett et al., 1998).

As mentioned previously, fish and seafood are major sources of exposure to aldehydes, mainly formaldehyde, for the populations (Kuehl et al., 1994). Moreover, fish preservation via salting or smoking, in the presence of formaldehyde, may raise the probability of stomach carcinoma, even after cooking in high temperatures. Epidemiologic studies confirmed the relation between high consumption of fish and pickled vegetables with the incidence of adenocarcinoma in the stomach (Tsugane, 2005; Wu et al., 2011; Yoo et al., 2020).

3.2 Molecular Mechanism of Aldehydes' Toxicity

Owing to their electrophilic nature, aldehydes could bond covalently with the electron-rich sites (nucleophiles) on the human body. These reactions potentially impair many enzyme functions, proteins, DNA, and various macromolecules, thereby leading to cellular process inhibitions and subsequent cellular toxicity (Esterbauer et al., 1991; Kehrer, 2000). In vivo aldehyde toxicity through adduct formation occurs with a second-order rate reaction kinetics. This reaction rate is dependent on aldehyde levels and nucleophilic biological target amount, as well as, their electronic energies that affect the rate constant (LoPachin & Gavin, 2014).

The aldehydes can be categorized to relatively soft or hard according to the electron distribution on the atoms of the molecule and subsequent polarizability. The hard-electrophilic aldehydes such as alkanals and formaldehyde are characterized by relative non-polarizability where their weak electron density is concentrated on the carbonyl carbon atom. On the other hand, the soft-electrophilic aldehydes such as α,β-unsaturated aldehydes, including acrolein and crotonaldehyde, are more polarizable since they show several spots with weak electron density. Meanwhile, the biological nucleophiles (e.g., lysine and histidine amino groups) are comparatively hard since they have a more localized charge due to their lesser atomic radii and larger electronegativity. The hard and soft acid and base (HSAB) theory realized that covalent adducts are favorably and rapidly formed between electrophiles and nucleophiles having similar softness or hardness. On the other hand, the reactions of electrophile and nucleophile with substantially different softness or hardness are less favorable and slower (O'Brien et al., 2005; LoPachin & Gavin, 2014; LoPachin et al., 2012; Schwöbel et al., 2011).

In addition to the degree of softness or hardness, the electrophilic index, an electrophilicity measure that unites chemical potential with softness, is related to the adduct reactions' rate constant (k) and consequently directly correlates to toxicant power (LoPachin et al., 2007a, b, 2009). The toxicity of aldehydes is also influenced by physicochemical factors such as steric hindrance, acid-base equilibrium, and solubility. The less hindered aldehydes, e.g., monosubstituted, reacted quicker than the more hindered, e.g., disubstituted aldehyde (Chan & O'Brien, 2008). Meanwhile, the solubility of the toxicant is a determining factor of tissue distribution that controls its effective concentration at the target site and the overall rate of adduct formation (Mccarthy et al., 1994; Böhme et al., 2009). On the other hand, the acid-base equilibrium has a direct influence on the electrophilic index and consequently the toxicant potency (Schopfer et al., 2011).

Hard aldehydes such as formaldehyde and acetaldehyde are known genotoxic compounds that trigger nasopharyngeal cancer in humans and nasorespiratory epithelial carcinoma in rodent models. The cause of this toxicity is the ability of the two aldehydes to react with amines through 1,2-addition mechanism forming aminols which go then through dehydration producing imines. Therefore, formaldehyde and acetaldehyde react favorably with comparatively hard nucleophiles (e.g., deoxyguanosine N_2 nitrogen). Besides, alkanals can undergo hard−hard interactions with lysine residues ε-amino and DNA exocyclic amino groups inducing the formation of cross-links with proteinaceous amino acids and deoxynucleosides, respectively (Kuykendall & Bogdanffy, 1994; Lu et al., 2010).

Soft aldehydes can undergo Michael addition with soft nucleophiles, such as the cysteine residues (sulfhydryl groups) present in the biological systems. Additionally, the deprotonated cysteine thiolate (RS^-), which exists in equilibrium with the proteins' sulfhydryl moiety, is characterized by softness and high nucleophilicity, and thus, favorably interact with the soft unsaturated aldehydes. Furthermore, the histidine imidazole side chain and lysine ε-amino group have nucleophilic amine groups that are favorable to react with unsaturated aldehydes via 1,4-Michael addition (LoPachin et al., 2012). α-Oxoaldehydes (e.g., Gly) can interact with nucleophilic sites on proteins producing advanced glycation end products (AGEs), which are strongly linked to diabetes pathogenesis (El-Maghrabey et al., 2018a). The favorable nucleophilic groups for interaction with oxoaldehyde derivatives include the side chains of lysine and arginine that contain hard nitrogen groups (Lo et al., 1994) as well as the cysteine thiolate sites on proteins (Zeng & Davies, 2005).

The unsaturated aldehydes belong also to the conjugated type-2 alkenes that comprise also the α,β-unsaturated amides, esters, and ketones. Type-2 alkenes are electrophilic compounds that have variable electrophilic properties and softness and reveal a common toxicity mechanism. In consequence, experiencing an environmental combination of unsaturated carbonyl compounds can lead to "type-2 alkene toxicity" via combined interactions (Martyniuk et al., 2011).

4 Analysis of Aldehydes in the Surrounding Environment and Food Samples

4.1 Challenges in Analytical Determination of Aldehydes and How to Overcome Them

Aldehydes' determination in environmental and food samples at trace levels is a challenge to the analyst due to many factors. At first, most of the aldehydes are very hydrophilic and with small molecular sizes; thus, they are not well retained in reversed-phase columns commonly used in HPLC. Second, aldehydes, especially aliphatic ones, have very weak absorbance in the UV region rendering their spectrophotometric detection problematic. Despite the fact that *α,β*-unsaturated aldehydes possess UV absorbance at 220 nm, due to the presence of the C=C chromophore group conjugated with the carbonyl one, its UV detection is also limited due to the low obtained sensitivity and repeatability. The third limiting factor for aldehyde determination is their high polarity and hence their poor ionization and fragmentation behavior that render them nearly undetectable by mass spectrometry (Long & Picklo, 2010). The fourth limiting factor for aldehyde determination is their high chemical reactivity toward amines; thus, they form amide adducts with amines and amino acids present in the sample. Hence, their recovery in intact form from a complicated matrix (food samples) becomes tedious. Also, these adducts are usually water-soluble which complicate their recovery using organic solvents. The fifth factor is their volatile nature which hinders their complete recovery from the sample matrices (Shibamoto, 2006). Finally, the sixth property for aldehydes that render their analysis very difficult is their poor stability and their possible degradation to aliphatic carboxylic acids upon their treatment with harsh extraction conditions (Eggink et al., 2010).

All these limiting factors for aldehyde determination could be partially or fully overcome through derivatization with suitable reagents. Derivatization will help to decrease aldehyde polarity and consequently improve their retention behavior on LC columns and allow their recovery from aqueous samples (El-Maghrabey et al., 2016). Moreover, derivatization forms adducts with strong UV absorption (Gonçalves et al., 2010; de Lima et al., 2018), fluorescence (El-Maghrabey et al., 2014, 2015), or chemiluminescence (Ali et al., 2014) properties. In the same context, a new form of derivatization called dual-labeling, in which a purification tag and a fluorophore are reacted with aldehydes at the same time, was recently reported by El-Maghrabey et al. (2018b). Labeling of aldehydes with a purification tag such as taurine produced an adduct that possesses a sulfonic acid group. This group is known to be easily retained selectively on anion exchange sorbents, allowing the easy recovery of the reaction product in a pure form free from the excess fluorescent derivatizing reagent and other interfering matrix components (Fig. 2) (El-Maghrabey et al., 2018b).

Additionally, aldehydes' derivatization could improve their MS detectability by enhancing their ionization efficiency and fragmentation properties (El-Maghrabey et al., 2016, 2018c). Despite the fact that LC-MS is very selective, the sample coexisting substances could cause matrix effects that might affect the analytes' ionization extent leading to an error in the measurement. In order to overcome this problem, derivatization with isotope-coded reagent has been employed. The sample is derivatized with the reagent light form, while the standard is derivatized with its heavy type. Afterward, both are combined in a certain ratio and then analyzed by LC-MS/GC-MS giving relative and absolute quantification for the samples at one LC-MS run (El-Maghrabey et al., 2020a, b; Kishikawa et al., 2019). For this purpose, many isotope-coded reagents were designed for aldehydes, including the normal and deuterium (D) or ^{15}N substituted dinitrophenyl hydrazine (Zurek & Karst, 2000; Prokai et al., 2012), D_0/D_3-4-(1-methyl-1H-phenanthro[9,10-d]imidazol-2-yl) phenylamine (D_0/D_3-MPIA) (Sun et al., 2014), and most recently, the commercially available ^{14}N/^{15}N-ammonium acetate combined with 9,10-phenanthrenequinone (El-Maghrabey et al., 2018c).

Another advantage gained by derivatization is the improved stability of the produced aldehyde adduct over the original aldehyde, thus facilitating their recovery from complex matrices (Eggink et al., 2010; Kishikawa et al., 2019). At last, we can

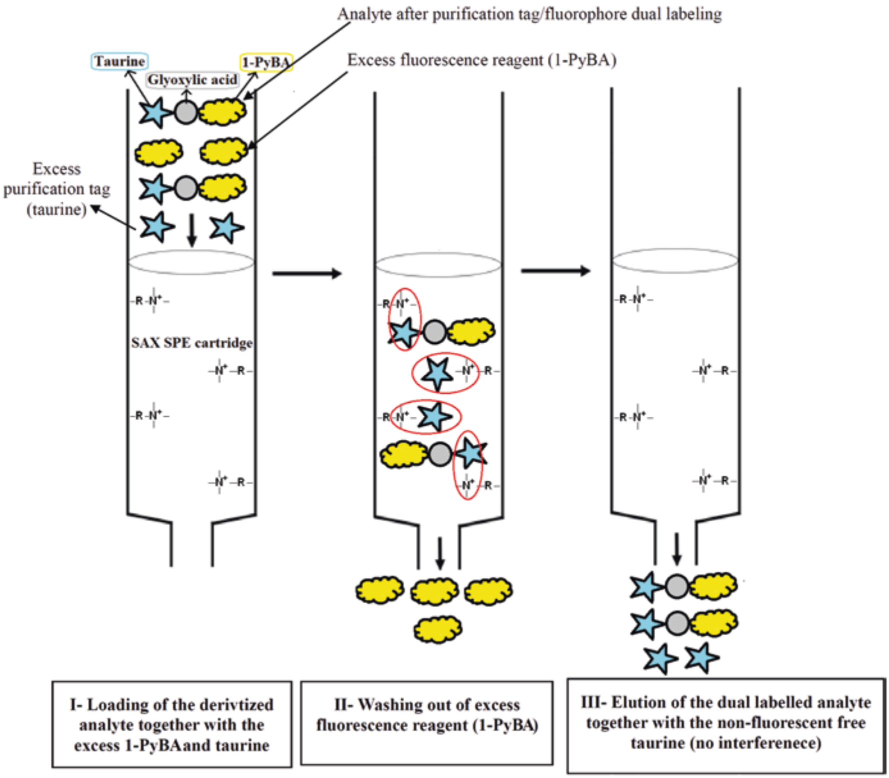

Fig. 2 A diagram showing the purification tag/fluorophore dual-labeling followed by solid-phase extraction. (Reprinted with permission from Ref. El-Maghrabey et al. (2018b) © Elsevier)

conclude that the choice of the derivatizing agent, the extraction technique, and the applied analytical platform are crucial for obtaining a selective and sensitive detection method for aldehydes. Next, we will discuss the recent analysis techniques applied for aldehydes' control and determination in the surrounding environment and food.

4.2 Analytical Methods for Aldehydes' Monitoring in Environmental Samples

Aldehydes' monitoring in the surrounding environment is vital for the evaluation of their exposure risk and assess their potential adverse effect on human wellbeing. As we mentioned previously, derivatization approach is almost essential for aldehydes prior to their determination. 2,4-Dinitrophenylhydrazine (DNPH) is the most commonly used reagent in this approach. DNPH reacts with the carbonyl group of the aldehydes forming colored hydrazones that could be easily analyzed with UV detector (Kishikawa et al., 2019). Prieto-Blanco et al. derivatized different types of aldehydes such as the aliphatic aldehydes, formaldehyde, hexanal, decanal, and acrolein and the aromatic aldehyde, benzaldehyde, with DNPH and then determined them in particulates from the atmosphere utilizing HPLC-UV. A surprising data resulted stating that the levels of aldehydes in industrial sites are not higher than their levels in rural ones but even it is slightly lower (Prieto-Blanco et al., 2010). Rosenberger et al. analyzed a similar group of aldehydes to those analyzed by Prieto-Blanco after DNPH derivatization; however, Rosenberger et al.'s method was targeting determination of aldehydes in commercial aircraft cabin air (Rosenberger et al., 2016). They used a DNPH-coated silica gel cartridge for solid-phase extraction (SPE) of aldehydes to make simultaneous adsorption and derivatization of aldehydes present in the cabin air. The formed colored hydrazones were monitored using HPLC-UV. They found that the maximum highest level of aldehydes in the air of cabin was reached at the phase of taxi-takeoff-climb. DNPH was also used for aliphatic aldehyde derivatization, especially those with short chains, for their analysis in rainwater by HPLC-UV. Aldehyde extraction and derivatization were performed simultaneously via solid-phase microextraction (μSPE) using polypropylene membrane porous sheet loaded with C_2-coated silica. The authors found that formaldehyde is present plentifully in rainwater followed by acetaldehyde and propanal and at last pentanal (Basheer et al., 2010).

In addition, Liu et al. extracted DNPH-derivatized aldehydes using ionic liquid via single-drop liquid-liquid microextraction (LLME) (Fig. 3). 1-Octyl-3-methylimidazolium-hexafluorophosphate was used for extraction, and the extracted hydrazones were analyzed using HPLC-UV. The authors stated that there were no aldehydes found in the river water. On the other hand, they found that formaldehyde was present in seawater and snow water in a mild and trace amount, respectively (Liu et al., 2010).

Additionally, DNPH was used for the derivatization of aldehydes in water samples spiked with heavy metal before their analysis with HPLC-UV. This study demonstrated that the formation of aldehydes was induced upon illumination of the complex of Cu(II) with amino acids (Lin et al., 2009). At last, DNPH was used for the derivatization of aldehydes prior to their determination with micellar electrokinetic chromatography (MEKC). The method was applied for aldehydes' determination in drinking water and swimming pool samples employing μSPE. According to this study, the level of aldehydes in chlorinated swimming pool water is similar to its level in ozonated drinking water, which highlights the danger of water ozonation (Fernandez-Molina & Silva, 2014).

Apart from the DNPH derivatization and HPLC-UV analysis methods, GC-MS was utilized for aldehydes' determination in environmental matrices. Another hydrazine reagent, namely, 2,2,2,-trifluoroethylhydrazine (TFEH) was used for derivatization of aldehydes in drinking and surface water prior to their GC-MS analysis. TFEH is used in GC-analysis as its derivatives have high volatility; thus, they

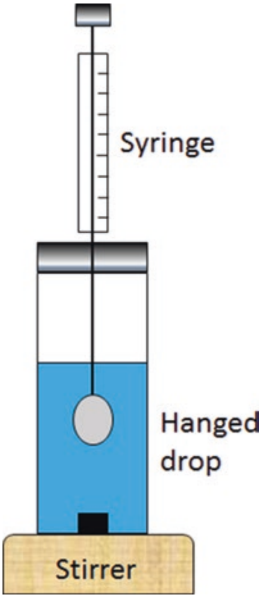

Fig. 3 Illustration for single drop LLME

provide a strong response in GC-MS. The TFEH-derivatized aldehydes were extracted with µSPE prior to their GC-MS analysis. It was reported that the level of aldehydes in the commercialized mineral water is surprisingly higher than that present in the surface waters (Kim & Shin, 2011). Additionally, hydroxylamine reagents, such as *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA), were used for aldehydes' derivatization before their GC-MS analysis to increase their volatility and ionization. Serrano et al. used PFBHA for the derivatization of aldehydes employing an micro liquid–liquid extraction (MLLE) method for their extraction from the pool and environmental water samples. The extracted formed derivatives were then analyzed by GC-MS. The authors found that the level of aldehyde was substantially elevated in swimming pool water than environmental samples such as tap and well water (Serrano et al., 2013a). The same research group derivatized the same group of aldehydes using the same reagent but instead of MLLE, they used the classical static headspace for aldehydes' extraction and derivatization combined in one step and they applied their method to drinking water samples. Their study revealed that drinking water disinfection prompted aldehydes' formation in water. They also stated that disinfection via ozonation forms more aldehydes than disinfection through chlorination and chloramination (Serrano et al., 2013b). Recently, Zhang et al. determined acetaldehyde, hexanal, acrolein, and crotonaldehyde in cigarette mainstream smoke gas phase by GC-MS directly in derivatization-free approach. They found that the aldehydes' levels are higher in the smoke of US cigarettes than that of China cigarettes (Zhang et al., 2019). Collectively, the reported methods for determination and control of aldehydes in environmental samples are summarized in Table 2.

4.3 Analytical Methods for the Determination of Aldehydes in Food Samples

In order to judge the quality and safety of food, aldehydes' monitoring is one of the most vital procedures. Aldehydes were found in considerable amounts in different human consumable food and beverage products. As mentioned previously in detail, aldehydes' food sources include vegetable oils, cooked food, alcoholic beverages, and even drinking water. In the next paragraphs, we will summarize the analytical methods used for the analysis of aldehydes in each of those sources.

Aldehydes' analyses in vegetable oils have been performed by several chromatographic methods, and in most of them, the used extraction method was LLE. Butylated hydroxytoluene was mixed with the analyzed samples during the extraction as an antioxidant to prevent the artificial formation of aldehydes during extraction. Ma et al. developed a chromatographic method coupled with a dual-channel photodiode array detector for aldehydes' determination in oil samples and French fries before their derivatization with DNPH. The analyzed aldehydes by this method included HHE, HNE, and MDA (Ma & Liu, 2017). Douny et al. used also DNPH for derivatization of the same group of aldehydes; however, liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) was used to monitor the formed hydrazones. The role of DNPH here is to increase the ionization efficiency of aldehydes (Douny et al., 2015). In addition, another hydrazine reagent, pentafluorophenylhydrazine (PFPH) was used by Gabbanini et al. for derivatization of HNE, and they also used LC-MS/MS instrumentation for the determination of the formed hydrazine (Gabbanini et al., 2015).

Ramezani et al. reported a GC system linked to flame ionization detector (GC-FID) for aldehydes' determination without derivatization, prior to their extraction from the oil samples using a smartly designed reverse micelles technique (Ramezani et al., 2015). When surfactants are dispensed in a non-polar organic phase accompanied with a little volume of water, reverse micelles are formed as nano-inverted aggregated surfactant molecules forming water cores inside the organic phase. This water core extracts the hydrophilic analytes, such as aldehydes, then, centrifugation is employed for achieving phase separation. The sedimented surfactant-rich phase is then transferred to a centrifuge tube in which back extraction is performed through mixing it with chloroform and water followed by sonication of the mixture and then centrifugation. Phase separation occurs and the upper organic layer is the surfactant-rich phase, while the lower organic layer contains the

Table 2 Summation of the previously reported methods for aldehydes' analysis in the surrounding environment

Sample	Analytes	Instrument	Derivatizing agent	Extraction	Recovery (%)	Detection limit (unit)	Ref.
Atmospheric particulates	Acrolein, C_1–C_{10} alkanals, benzaldehyde	HPLC-UV	DNPH	Ultrasonic extraction	86–110	3–10 (ng/mL)	Prieto-Blanco et al. (2010)
Cabin air	Acrolein, C_1–C_6 alkanals, benzaldehyde	HPLC-UV	DNPH	SPE	98–103	8–20 (ng)	Rosenberger et al. (2016)
Rainwater	C_1–C_5 alkanals	HPLC-UV	DNPH	µSPE	85–107	0.03–0.15 (ng/mL)	Basheer et al. (2010)
River, sea, and snow water	Acrolein, crotonaldehyde C_1–C_5 alkanals,	HPLC-UV	DNPH	Single drop LLME	84–107	0.04–2.0 (ng/mL)	Liu et al. (2010)
Environmental water	C_1–C_9 alkanals	HPLC-UV	DNPH	None	93–115	7–121 (nM)	Lin et al. (2009)
Drinking and pool water	C_1–C_{10} alkanals, benzaldehyde	MEKC-UV	DNPH	µSPE	Not mentioned	65–775 (pg/mL)	Fernandez-Molina and Silva (2014)
Drinking water	C_1–C_{10} alkanals	GC-MS	TEFH	µSPE	Not mentioned	0.1–0.5 (ng / mL)	Kim and Shin (2011)
Swimming pool water, tap, and well water	Gly, M Gly, C_1–C_5 alkanals, benzaldehyde	GC-MS	PFBHA	LLE	96–99	0.7–80 (pg/mL)	Serrano et al. (2013a)
Drinking water	Gly, MGly, C_1–C_5 alkanals, benzaldehyde	GC-MS	PHBHA	Headspace	97–99	2–80 (pg/mL)	Serrano et al. (2013b)
Cigarette smoke	Acetaldehyde, hexanal, acrolein, crotonaldehyde	GC-MS	None	Headspace	79–115	0.014–0.12 (µg/cigarette)	Zhang et al. (2019)

targeted analytes which are then injected into the GC-FID. The scheme for the reverse micelle technique is illustrated in Fig. 4 (Ramezani et al., 2015). Results obtained by these methods show that aldehydes' levels are elevated in oil samples upon thermal treatment due to the induced lipid peroxidation. Thus, we can conclude that the aldehydes' levels in oil may possibly be considered as a good monitor for its quality and its lipid deterioration status.

Aldehydes were also determined in different types of food including cooked meat, canned vegetables, yogurt, and baby food. Different aldehydes including alkanals, acrolein, and benzaldehyde were determined by Gosseti et al. in different cooked food samples by LC-MS/MS prior to their derivatization with DNPH. The authors inspected the effect of food matrices, used frying matrices (olive oil or butter), and way of cooking on the level of aldehydes in food (Gosetti et al., 2011). It was found that the levels of some aliphatic aldehydes are increased upon cooking in olive oil than in the case of cooking with butter. In addition, the oil cooked steak contains most of the tested aldehydes; however, the butter or oil in which the steak was cooked has much lower levels of aldehydes. Another LC-MS method was developed for aldehydes' determination in food, but this time targeting α-dicarbonlys including Gly and its methylated and dimethylated forms. *O*-Phenylene diamine (OPD) was used for the derivatization of these compounds, forming highly ionizable quinoxaline derivatives easily detectable by MS. In this study, it was found that dimethylglyoxal (DMGly) was detected in higher amounts in baby foods than Gly and MGly (Kocadağlı & Gökmen, 2014). Donegatti et al. developed a

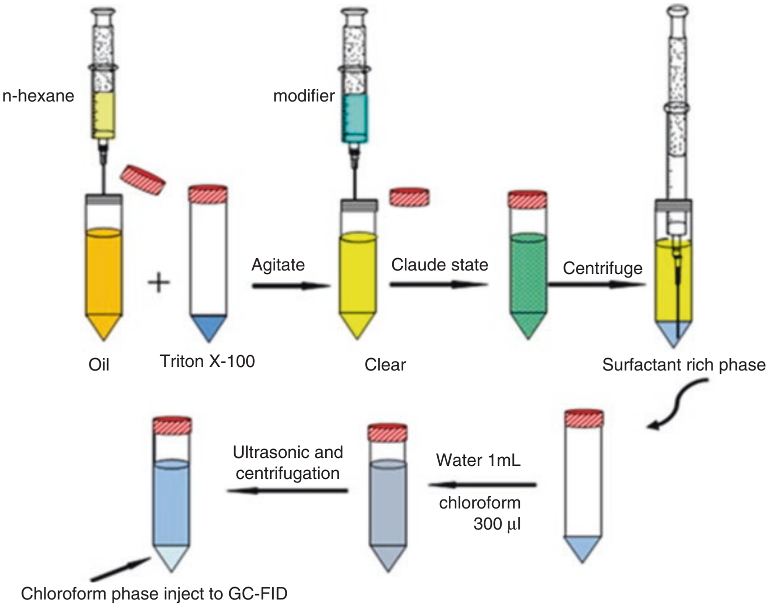

Fig. 4 Schematic illustration of the reverse micelle device. (Reprinted with permission from Ref. Ramezani et al. (2015) © Elsevier)

chromatographic capillary micellar electrokinetic method coupled with UV detection for aldehydes' determination in milk products prior to their derivatization with benzhydrazide. As a result, acetaldehyde was the only aldehyde that could be found in yogurt (Donegatti et al., 2017). In addition, volatile aldehydes were analyzed in canned vegetables using headspace sample extraction prior to their derivatization with PFBHA and and GC-MS analysis. It was found that reactive toxic aldehydes including Gly and formaldehyde were detected only in the liquid phase of the canned vegetable, which is a non-edible portion (Serrano et al., 2017).

Various techniques were also developed for aldehydes' determination in different juices and beverages. An HPLC-UV method was reported for the analysis of the aromatic aldehydes, furfurals, in samples from fruit-based juices, using the natural absorbance for the detection of these aromatic aldehydes. They used vortex assisted-salting out LLME for extracting furfurals from the juice samples prior to their analysis. In this study, they found that the concentrations of 5-hydroxymethylfurfural in some grape and apple juice samples are higher than the maximum allowed level stated by the Fruit Juice Producers International Federation. These could have resulted from improper storage, or prolonged heating during the juice production (Abu-Bakar et al., 2014).

Goncalves and coworkers have developed a novel extraction method for aldehydes from alcoholic beverages called gas-diffusion microextraction (GDME) (Gonçalves et al., 2010). In GDME, an extractor device, composed of a small-sized tube made from Teflon containing a microporous semipermeable membrane with hydrophobic nature, is used. The rule of this semipermeable membrane is allowing the volatile analytes' mass transfer while preventing their solvent diffusion. This device is then immersed inside the sample as shown in Fig. 5. Then, the extraction solvent containing the derivatizing agent is put inside the extractor device, followed by volatilization of the aldehydes through heating the sample with agitation, thus, facilitating the transfer of the aldehydes from the samples to the extracting solvent through the semipermeable membrane. The derivatization reagent in the solvent will react with the aldehydes; hence, extraction and derivatization occur simultaneously. This technique allows substantial enrichment for the targeted analytes, yielding high sensitivities, as the extracting solvent will not be saturated due to the continuous draw of the analytes from the solvent through the derivatization reaction. Goncalves and coworkers simultaneously DNPH derivatized and extracted a group of versatile aldehydes, including furfural, acetaldehyde, and methylpropionaldehyde, from beer samples prior to their determination with HPLC-UV. In addition, they used LC-MS to confirm the presence of the aldehyde in beer through detecting the masses corresponding to the DNPH derivatives (Gonçalves et al., 2010). Furthermore, free and bound acetaldehydes in wine were simultaneously extracted and derivatized using the same technique by the same research group, and many more carbonyls were identified in wine using hyphenation of HPLC-DAD and tandem MS (Cruz et al., 2012). At last, Lima et al. used the same extraction technique, GDME, but this time coupled with newly developed aldehydes' colorimetric reagent, 4-hydrazinobenzoic acid, for analysis of aldehydes in wine (de Lima

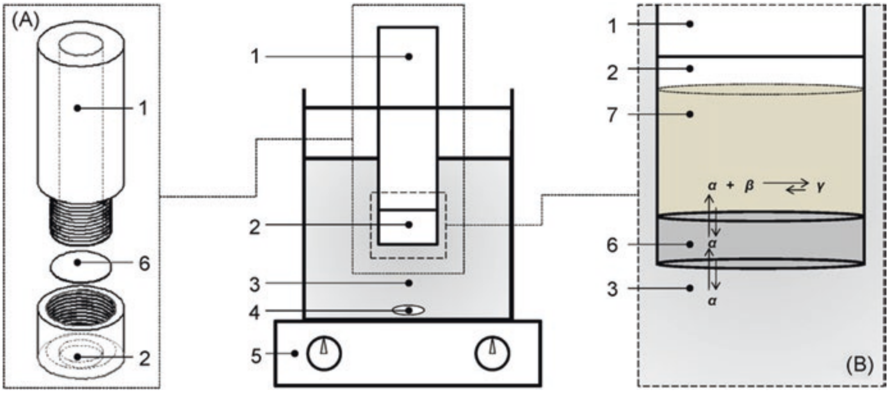

Fig. 5 Illustration for GDME where (**a**) a magnified view of the extractor, (**b**) detailed diagram for the chemical equilibria; in which the numbers from 1 to 7 represent extractor's superior piece and lower piece, sample solution, stir bar, heater with stirring capability, the membrane, and the acceptor solution, respectively, while α, β, and γ represent the analyte, the derivatizing agent, and the formed product. (This figure is reprinted with permission from Ref. Gonçalves et al. (2010) © Elsevier)

et al., 2018). They stated that the GDME method necessitates the use of the standard addition method to decrease the matrix effect (de Lima et al., 2018).

Olivero and Trujillo have designed a derivatization free GC-MS method for aldehydes' determination in the wine after their headspace microextraction. Their results indicated that the level of aldehydes is more elevated in red wines than in white ones (Pérez Olivero & Pérez Trujillo, 2010). Besides, an HPLC-FL method was designed by You et al. for the purpose of C_1–C_{10} alkanals analysis in alcoholic beverages. They used the derivatization fluorescence labeling hydrazine reagent, 2-[2-(7*H*-dibenzo[*a,g*]carbazol-7-yl)-ethoxy]ethylcarbonylhydrazine (DBCEEC), for derivatization of aldehydes. They found that the very short-chain aldehydes, namely, formaldehyde and acetaldehyde were the major aldehydes in these beverages among the tested alkanals (You et al., 2009). The reported analytical for aldehydes in food and drinks is summarized in Table 3.

5 Conclusion

Human exposure to aldehydes from the surrounding environment and food forms represents a high toxicological alert. In this chapter, different sources of aldehydes in the environment and food are discussed in detail. Aldehydes could be formed from the photooxidation of volatile organic hydrocarbons emitted for the plants or from biomass burning and fossil fuel combustion. Aldehydes are also present in rainwater and the surface water sourced from the upper atmosphere. Besides, chlorination and ozonation of drinking water for sterilization purposes could lead to the

Table 3 Summation of the previously reported methods for aldehydes' analysis in food and drinks

Sample	Analytes	Instrument	Derivatizing agent	Extraction	Recovery (%)	Detection limit (unit)	Ref.
Vegetable oil and French fries	HHE, HNE, MDA	HPLC-UV	DNPH	LLE	96–101	9–14 (ng/mL)	Ma and Liu (2017)
Linseed oil	HHE, HNE, MDA, 2,4-decadienal	LC-MS/MS	DNPH	LLE	79–101	20–140 (ng/g)	Douny et al. (2015)
Vaseline, sweet almond, and olive oil	HNE	LC-MS/MS	PFPH	LLE	91–105	7 (ng/g)	Gabbanini et al. (2015)
Vegetable oil	C_3–C_7 alkanals	GC-FID	None	Reverse micelles technique	80	20.0–80.0 (ng/g)	Ramezani et al. (2015)
Smoked salmon, grilled or cooked meat	Acrolein, C_1–C_{10} alkanals, benzaldehyde	LC-MS/MS	DNPH	On-line SPE	71–100	2–272 (pg/g)	Gosetti et al. (2011)
Baby food	Gly, MGly, DMGly	LC-MS	OPD	Protein precipitation	89–110	3–27 (ng/g)	Kocadağlı and Gökmen (2014)
Yoghurt	C_1–C_5 alkanals except butanal	MEKC-UV	Benz-hydrazide	Filtration	80–125	0.4–0.5 (μg/mL)	Donegatti et al. (2017)
Canned vegetable	C_1–C_9 alkanals, GO, MGO, benzaldehyde	GC-MS	PFBHA	Headspace	89–99	0.02–0.1 (ng/g)	Serrano et al. (2017)
Fruits juice	Furfurals	HPLC-UV	None	Vortex assisted salting-out- LLME	82–105	0.3–3.5 (ng/mL)	Abu-Bakar et al. (2014)
Beer	Acetaldehyde, furfural, and methyl propanal	HPLC-UV	DNPH	GDME	Not mentioned	1.5–12 (ng/mL)	Gonçalves et al. (2010)
Wine	Acetaldehyde	HPLC-UV & LC-MS/MS	DNPH	GDME	Not mentioned	0.8–1.1 (ng/mL)	Cruz et al. (2012)
Wine	Acrolein, C_1–C_3 alkanals, furfural, benzaldehyde	HPLC-UV	4-Hydrazinobenzoic acid	GDME	Not mentioned	5–210 (ng/mL)	de Lima et al. (2018)

Sample	Analytes	Instrument	Derivatizing agent	Extraction	Recovery (%)	Detection limit (unit)	Ref.
Wine	Alkanals, alkenals, furfural, benzaldehyde	GC-MS	None	HS- µSPE	20–190	2.0–8.0 (ng/mL)	Pérez Olivero and Pérez Trujillo (2010)
Alcoholic beverage	C_1–C_{10} alkanals	HPLC-FL	DBCEEC	None	99–104	0.20–1.8 nM	You et al. (2009)

abundant formation of aldehydes. In food, aldehydes could be formed during high-temperature frying. Besides, they are present in wine and vegetable oils, and they are formed as by-products during food deterioration or microbial fermentation. The adverse health effects of aldehydes are many varying from allergic and inflammatory effects to carcinogenicity and mutagenicity. The molecular mechanism of aldehydes' toxicity was discussed in order to make a truthful risk assessment. Aldehydes with side short chain or with long saturated chain cause toxicity through forming adducts with the lysine side chain amino groups (hard nucleophiles) owing to their hard-electrophilic properties. On the other hand, aldehydes with conjugated unsaturated side chain, such as alkenals and α-oxoaldehydes, possess soft electrophilic properties; thus, their main toxic effect is due to their reaction with cysteine sulfhydryl group (soft nucleophile). Other factors such as side chain steric hindrance and aldehydes' solubility may affect the toxicity extent of aldehydes as they might limit their accessibility to the targeted biomolecule.

As aformenioned above, aldehydes are toxic compounds that are highly reactive towards biological molecules leading to biochemical modifications that disturb many biological functions. Thus, aldehydes' determination in environmental and food samples was heavily reported in order to control their possible health risks. Practically, derivatization for aldehydes is essential to improve their extraction, chromatographic behavior, stability, and detectability. The most reported aldehydes' derivatizing agent is DNPH, and additionally, there are some recent reagents, such as PFPH, 4-hydrazinobenzoic acid, and DBCEEC, that were developed to employ some advantages such as increasing sensitivity or allowing fluorescence detection of aldehydes. Owing to aldehydes' high reactivity, polarity, instability, and volatility, their extraction from complex matrices is a challenging process. Thus, different sample pretreatment procedures for aldehydes such as GDME, fluorophore-purification tag dual-labeling, μSPE, and inverse micelles extraction were recently reported. Regarding their analysis techniques in food and the surrounding environment, various chromatographic methods were reported for this purpose including HPLC methods coupled with UV, FL, or MS detection, in addition to GC coupled with either FID or MS detection. At last, we can conclude that the aldehydes' determination in the surrounding environment and heavily consumed food and drinks is a crucial matter, and the research in this area is growing fast. For developing an integrative aldehyde assay, the choice of appropriate derivatization and extraction technique is very important, and it mainly depends on the targeted aldehydes and matrices. Having the right analytical tool for aldehydes in hand, we can study and control the possible risks and adverse effects of toxic aldehydes on human health.

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Phthalate Esters and Their Ecotoxicological Risks from the Rivers of India

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and Babu Rajendran Ramaswamy**

Abstract A category of new chemicals, phthalic acid esters (PAEs), are used primarily as plastic additives that can be easily leached out of plastics and released into the environment and can create risks when exposed by the humans and other living organisms. The distribution and ecotoxicological risk assessments based on risk quotient (RQ) of six phthalic acid esters (PAEs) including dimethyl phthalate, diethyl phthalate, dibutyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, and di-n-octyl phthalate in surface water and sediment collected from the Kaveri, Vellar, and Tamiraparani Rivers, Tamil Nadu, India. As far our knowledge is concerned, this is the first comprehensive study that examines phthalate contamination seasonally in these three rivers. This chapter confirms ubiquitous phthalate contamination of fresh water ecosystems in India, and the data contribute for better understanding and managing the pollution from emerging contaminants.

Keywords Phthalic acid esters · Emerging contaminants · GC-MS ·
Ecotoxicological risk assessment

1 Introduction

Phthalates are a category of chemicals commonly used for softening and improving plastic products' strength and toughness, mostly polyvinyl chloride (PVC). They are also utilized as dispersants, gelling and emulsifying agents, stabilizers, lubricants, binders, and so forth in numerous user items such as personal care products and cosmetics, plastic and vinyl supplies, vinyl flooring, food packaging and wraps, cleansers, adhesives, plumbing accessories, and medical equipment (NIH, 2019).

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Phthalates were initially used in the 1920s, which greatly improved production with the advent of PVC in the 1930s. PVC items may have up to 50% of plasticizers, usually phthalates, by weight. The estimated total worldwide production of phthalates is 11 billion pounds (EUROPA, 2011; Holland, 2018). Asia Pacific region itself uses 52% plasticizers globally, and phthalates make up 87% of the produced plasticizer (Selvaraj et al., 2015). Phthalates are not directly linked to the polymer however by means of secondary molecular interactions. Therefore, they leach out of plastic items over time and might migrate and contaminate the air, water, food, house dust, and soil; particularly under conditions involving heat (Net et al., 2015a). Therefore, monitoring of phthalates in terrestrial and aquatic ecosystems and evaluation of the possible ecological threat is therefore highly significant (Li et al., 2017).

The 2008 US Consumer Product Safety Improvement Act (CPSIA) bans any infant toy or child care items containing amounts of >0.1% by weight of the following phthalates: di-(2-ethylhexyl) phthalate, dibutyl phthalate, benzyl butyl phthalate, diisononyl phthalate, diisobutyl phthalate, di-n-pentyl phthalate, di-n-hexyl phthalate, and dicyclohexyl phthalate (US-CPSC, 2018). Similarly, as set out in revised entry 51 of Annex XVII to the REACH regulation of European Union, the restriction was put in place on things comprising the four phthalates, di-(2-ethylhexyl) phthalate, dibutyl phthalate, benzyl butyl phthalate, and diisobutyl phthalate in an amount equivalent to above 0.1% by weight exclusively or in any blend in plasticized material (EU, 2018).

Long-term exposure to phthalates may lead to health problems, such as altered semen quality, birth defects, hormonal and endocrine disturbances, asthma, breast cancer, and so on (Diamanti-Kandarakis et al., 2009; Mathieu-Denoncourt et al., 2015).

Ceaseless human exposure to phthalates may affect liver-detoxifying enzymes (Praveena et al., 2018). In male rats, chronic exposure of phthalates altered spermatogenesis by altering androgen metabolism even with long-term exposure below the no observed adverse effect level (NOAEL) (Gao et al., 2018). Phthalates have harmful effects on aquatic organisms even at exposure to environmental concentrations (i.e., ng/l to μg/l) (Oehlmann et al., 2009). Chronic exposure to DEHP (20–200 μg/l) has altered fish growth and locomotion in medaka fish *Oryzias latipes* perhaps by a cumulative impact of neurotoxicity, oxidative stress, and apoptosis pathways (Yang et al., 2018). In addition, chronic DEHP exposure (100–500 μg/l) in juvenile yellow catfish *Tachysurus fulvidraco* shows disturbance of normal lipid metabolism processes at the enzymatic and molecular levels (Meng et al., 2018). Xu et al. (2013) suggested that DBP and DEP (5–500 μg/l) could induce antioxidant stress and immune response in zebra fish embryos. Further, DBP exposure (0.36–3.6 μM) reported to cause developmental toxicity and adverse effects on the embryo heart (cardiac structure deformities, pericardial edema, and altered cardiac function) in zebrafish (*Danio rerio*) (Sun & Li, 2019).

Phthalates are shown to affect primary producers in aquatic ecosystems. Acute exposure (0–20 mg/l) of DBP on freshwater algae (*Chlorella pyrenoidosa* and *Scenedesmus obliquus*) showed inhibition of photosynthetic activity by disrupting cell membranes and organelles with elevated ROS levels in lipid peroxidation and oxidative stress (Gu et al., 2017). Further, DEHP exposure (1–10 μg/l) on the marine dinoflagellate *Alexandrium pacificum* showed a noteworthy reduction in cell density and abundance (1.2–50 times lower) with inhibition of photosynthetic activities (M'Rabet et al., 2018).

Rivers are vulnerable to synthetic organic pollutants released into the river as a result of anthropogenic activities. In India, mostly treated/untreated wastewaters are discharged directly to the rivers. Therefore, the water quality is substandard in the majority of the rivers, and they act as major sinks of organic pollutants (Ramaswamy, 2015). Although persistent organic pollutant contamination has been well studied in environmental matrices (Patil et al., 2015), information is scare on phthalates.

Recently, emerging contaminants such as triclosan, triclocarban, benzotriazoles, carbamazepine, nonsteroidal anti-inflammatory drugs, parabens, phenolic compounds, synthetic musks, perfluorinated compounds and phthalates were reported by us in water, sediment, and fish from the rivers such as Kaveri, Vellar, and Tamiraparani (Ramaswamy et al., 2011; Selvaraj et al., 2014, 2015, 2021; Shanmugam et al., 2014a, 2014b; Vimalkumar et al., 2018, 2021). However, until now phthalates have not been studied in the Tamiraparani and Vellar Rivers in Tamil Nadu, India. Therefore, this study aims to investigate the distribution profile and risk assessment of six phthalates in water and sediment gathered from 30 locations from the Vellar and Tamiraparani Rivers along with the Kaveri River. This is the first report on the occurrence of phthalates in the Tamiraparani and Vellar Rivers of Tamil Nadu, India.

2 Materials and Methods

2.1 Study Area and Sample Collection

The surface water and sediment samples were collected from 30 locations (Fig. 1) in three rivers (Kaveri: 16; Vellar: 3; and Tamiraparani: 11) during dry season (1–15 September 2017) and wet season (19 November–11 December 2016). See Table 1 for details of the sampling locations. Amber glass bottles (1 l) were washed consecutively before sampling with liquid detergent, running tap water, ultrapure deionized water, and sample water prior to water sampling. Bags made of polypropylene were used for grab sampling of the sediment. The sampling station was particularly far from wastewater/effluent mixing point in the river stream to get realistic contamination levels. The samples obtained were put in iceboxes and then transported to the laboratory, where water samples were kept at 4 °C and analyzed within a week, and sediment samples were kept in deep freezer at −20 °C up to chemical extraction.

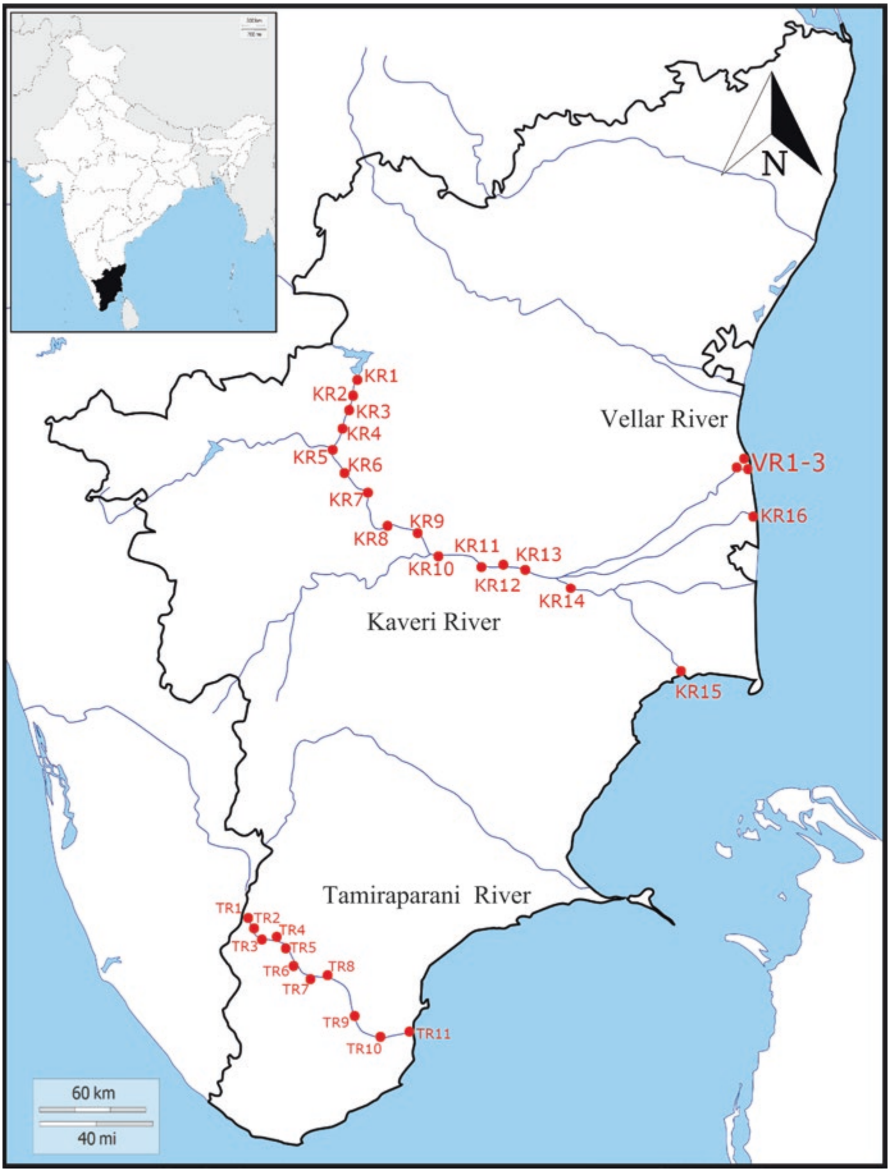

Fig. 1 Map displaying the sampling stations of water and sediment from the Kaveri, Vellar, and Tamiraparani Rivers, India

Table 1 Sampling locations from the Kaveri, Vellar, and Tamiraparani Rivers, India

River	Sample ID	Location	Lat. (N)	Long. (E)	Area
Kaveri	KR1	Mettur	11° 47′	77° 48′	Rural/industrial
	KR2	Neringipettai	11° 38′	77° 45′	Rural
	KR3	Ammapettai	11° 36′	77° 44′	Rural
	KR4	Singampettai	11° 35′	77° 40′	Rural
	KR5	Bhavani	11° 25′	77° 44′	Urban/industrial
	KR6	Erode	11° 21′	77° 53′	Urban/industrial
	KR7	Jedarpalayam	11° 09′	77° 53′	Semi urban
	KR8	Vellur	11° 05′	78° 07′	Semi urban
	KR9	Vangal	11° 02′	78° 14′	Rural
	KR10	Mayanur	10° 57′	78° 25′	Rural
	KR11	Kulithalai	10° 56′	78° 34′	Rural
	KR12	Mukkombu	10° 53′	78° 41′	Rural
	KR13	Tiruchirappalli	10° 50′	78° 69′	Urban
	KR14	Tanjore	10° 46′	79° 08′	Urban
	KR15	Muthupet	10° 24′	79° 30′	Estuary
	KR16	Pichavaram	11° 29′	79° 49′	Mangrove
Vellar	VR1	Customs	11° 48′	79° 76′	Rural
	VR2	Railadi	11° 47′	79° 74′	Rural
	VR3	Parangipettai	11° 49′	79° 76′	Rural
Tamiraparani	TR1	Kutralam	08° 93′	77° 27′	Rural
	TR2	Tenkasi	08° 95′	77° 30′	Urban
	TR3	Ambasamudram	08° 69′	77° 46′	Urban
	TR4	Alwarkurichi	08° 76′	77° 39′	Rural
	TR5	Papanasam	08° 71′	77° 36′	Rural
	TR6	Cheranmahadevi	08° 70′	77° 56′	Urban
	TR7	Tirunelveli	08° 72′	77° 71′	Urban/industrial
	TR8	Srivaikuntam	08° 62′	77° 90′	Urban
	TR9	Aeral	08° 61′	78° 01′	Rural
	TR10	Athur	08° 62′	78° 06′	Rural
	TR11	Punnaikayal	08° 63′	78° 02′	Estuary

2.2 *Preparation of Stock Standards and Chemicals*

Stock solution of phthalates was made by dissolving EPA phthalate esters mix (4S8231) consisting of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DnOP) in solvent ethyl acetate. EPA phthalate esters mix was procured from Supelco Analytical (Philadelphia, USA). Phenanthrene d-10 was used as internal standard which was bought from Cambridge Isotope

Laboratories (Andover, USA). Ethyl acetate, hexane, and methanol used during experiments were of HPLC grade, whereas other chemicals used were of analytical grade. Solid phase extraction cartridges Strata C18-E (1000 mg/6 ml) were bought from Phenomenex (California, USA), whereas, glass vials (2 ml) for GC-MS analysis were obtained from Agilent Technologies (Waldbronn, Germany). Water purification system (ELGA, UK) was used to get ultrapure water for analytical experiments. Silica gel (60–120 mesh), sodium sulfate, and glass wool were dried overnight in hot air oven (Heco, Chennai, India) at 200 °C prior to use.

2.3 Standards Preparation

The purchased standard mix of phthalates was considered as stock solution. Working solutions were prepared by diluting the stock solution at appropriate concentrations in ethyl acetate. These were used for instrumental calibration and procedural recovery check. Standard solutions were stored in deep freezer at −20 °C.

2.4 Preparation of Glassware

Initially the glassware was washed with 10% liquid detergent solution (Laboline, Fischer Scientific, Mumbai, India) followed by tap water, 50% hydrochloric acid, and ultrapure water (ELGA, USA). After air drying, the glassware was wrapped in aluminum foil (Hindalco, Mumbai) and baked overnight in a hot-air oven (Heco, Chennai, India) at 200 °C. To decrease the background concentration of phthalates, safety measures were taken to evade plastics contact.

2.5 Extraction of Phthalates from Water by Solid Phase Extraction

Phthalates were extracted from water samples based on the method developed by Selvaraj et al. (2015). C18-E cartridges were preconditioned and 500 ml water sample (pH 7) was passed at the rate of 5 ml/min using a vacuum manifold. The cartridge was then air dried and eluted with 20 ml of ethyl acetate. Sodium sulfate (anhydrous) was added to the eluate to remove the moisture content. Then the eluent was condensed using rotary vacuum evaporator (Buchi) and stored in teflon-lined screw cap glass vials until GC–MS analysis.

2.6 Extraction of Phthalates from Sediment by Ultrasonication

Sediment samples were extracted for phthalates by following the method established in our laboratory (Selvaraj et al., 2015). The sediment samples were air dried and homogenized using mortar and pestle. One gram sediment sample was taken in an amber glass bottle; 20 ml of ethyl acetate was added to it and ultrasonicated for 30 min. The extract was dehydrated (using sodium sulfate) and condensed using rotary vacuum evaporator to dryness. Finally, the analyte was put back together with 1 ml of ethyl acetate and the column clean-up was performed to remove interfering molecules.

2.7 Column Clean-Up

The glass column was plugged with glass wool at its base. Silica gel (2 g) slurry was prepared using 15 ml of ethyl acetate and added to the glass column. Silica gel was layered (1 cm) with anhydrous sodium sulfate; 20 ml of ethyl acetate was then passed through the column to wash away the impurities. Subsequently, the sediment extract was eluted with 20 ml of ethyl acetate. The eluate was condensed to 1 ml using rotary vacuum evaporator. Then, it was stored in 2 ml glass vials with teflon-lined screw cap until GC–MS analysis.

2.8 Instrumental Parameters

Phthalates were identified and quantified by gas chromatograph mass spectrometer (GCMS QP-2010) (Shimadzu Corporation, Japan) equipped with electron impact mode operating at 70 eV; 1 μl of the final extract was loaded onto the column in splitless mode using auto injector (AOC-20i). RTX-PCB fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness) (Restek, Pennsylvania, USA) was used to resolve the analytes. The injection port temperature was 280 °C. The column temperature program was as follows: 150 °C for 1 min and then at the rate of 8 °C/min raised to 300 °C and further to 320 °C at the rate of 7 °C/min and maintained for 10 min. The transfer line temperature was maintained at 270 and ion source temperature was 230 °C. Ultrapure (99.999%) helium gas was used as the carrier phase (flow rate – 2.25 ml/min). Identification of the analytes were performed based on the retention time (RT) and mass spectrum obtained in full scan acquisition mode (m/z 50–500). Individual peak for six phthalates and internal standard is shown in Fig. 2. Quantitative analysis was performed using the selected-ion monitoring (SIM) mode where one target ion and two characteristic ions (Table 2) were used for quantification. Additionally, external calibration method was adopted for quantification purpose.

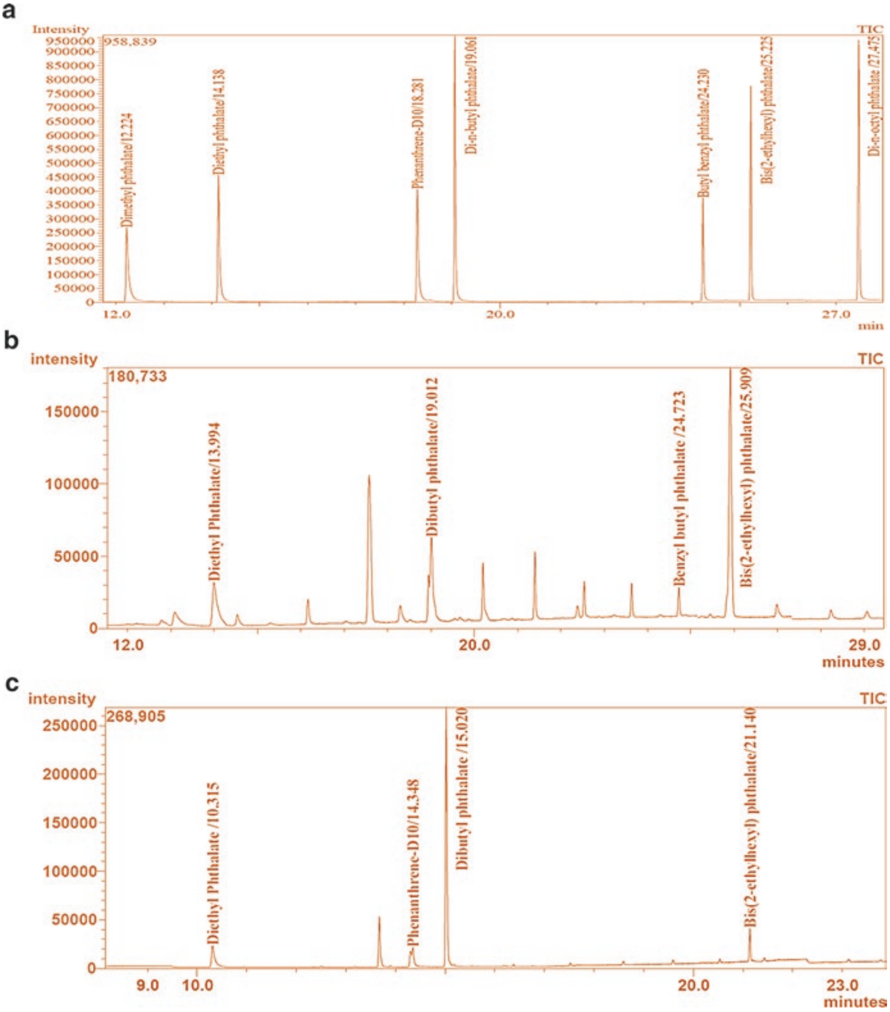

Fig. 2 GC-MS SIM chromatograms of phthalate standard (**a**), and water (**b**) and sediment (**c**) samples

2.9 Quality Assurance and Quality Control

Validation of the solid phase extraction method for water was performed by spiking 1000 ng of phthalate standard mix in 500 ml of river water. Correspondingly, ultrasonic extraction method for sediment was validated by spiking 100 ng of phthalate standard mix to 1 g of sediment. The recovery rate was satisfactory for both the extraction methods. Linear correlations ($R^2 > 0.999$) were obtained for six phthalates and internal standard using external calibration method in the range of 1–200 µg/l. The limit of detection (LOD) and limit of quantification (LOQ) for each

Table 2 Quality assurance/quality control parameters for extraction and analysis of phthalates

Phthalate	Target ions (m/z)	Retention time (RT)	Linearity R^2	LOD ($n = 7$) ng/ml	LOQ ($n = 7$) ng/ml	Sediment recovery (%) (100 ng/g) ($n = 3$)	Water recovery (%) (1000 ng/l) ($n = 3$)
DMP	163,164,133	12.22	0.999	0.80	2.68	85	109
DEP	149,177,150	14.14	0.999	0.47	1.55	108	118
DBP	149, 150, 104	19.06	0.999	0.75	2.49	105	121
BBP	149, 206, 123	24.23	0.999	1.22	4.07	108	33
DEHP	149, 167, 150	25.22	0.999	0.94	3.15	79.4	116
DnOP	149, 150, 279	23.49	0.999	0.75	2.49	93	45

of the phthalates were assessed with a signal-to noise ratio of 3 and 10 times, respectively. For every set of five samples, one solvent blank was analyzed to look for interference and/or cross-contamination. The target ions, recovery, retention time, LOD, and LOQ are shown in Table 2, whereas, Fig. 2 shows the standard and sample chromatograms.

2.10 Freshwater and Sediment Risk Assessment

For selective organisms which are representative of the ecosystem of interest, ecological risk assessment as risk quotient (RQ) was conducted. RQ was estimated as the ratio of the measured environmental concentration (MEC) to the predicted no effect concentration (PNEC) of aquatic organisms as per formula (1). The methodology is given in detail elsewhere in our previous studies (Ramaswamy, 2015; Ramaswamy et al., 2011; Selvaraj et al., 2015; Selvaraj et al., 2014; Shanmugam et al., 2014b).

$$\mathrm{RQ} = \mathrm{MEC} / \mathrm{PNEC} \tag{1}$$

The PNEC values were calculated from the chronic NOEC toxicity values of algae, invertebrates, and fish retrieved from literature. An assessment factor of 10 was applied to NOEC values. Further, PNEC values for sediment was adopted from the European Chemicals Agency (ECHA) website (echa.europa.eu). The RQ value greater than one indicates associated risk for the respective chemical of concern, whereas the RQ value less than one indicates no associated risk.

3 Result and Discussion

3.1 *Phthalates in River Water*

Dry Season

Phthalates are the primary category of plasticizers used globally, so knowing their fate in riverine ecosystem is very much warranted. Aiming to know the distribution of phthalates, water samples collected from 30 locations at the Kaveri, Vellar, and Tamiraparani Rivers and tested for six major phthalates. Phthalates, namely, DMP, DEP, DBP, BBP, DEHP, and DnOP were detected ranging from ND (not detected) to 3,58,694 ng/l as shown in Fig. 3a. The detection frequency for these compounds

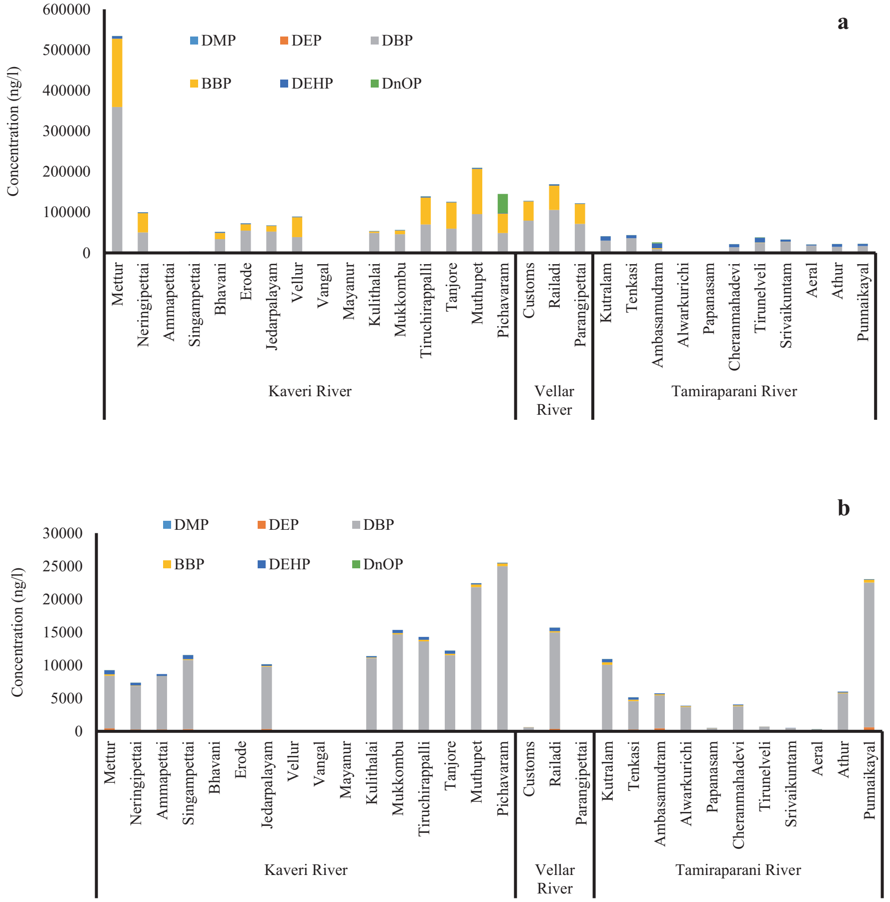

Fig. 3 Concentration of phthalates in water from the Kaveri, Vellar, and Tamiraparani Rivers, India, during dry season (**a**) and wet season (**b**)

varied between 0% and 100% in Kaveri, Vellar, and Tamiraparani: three major rivers of Tamil Nadu. Furthermore, total phthalates in all the samples were found between ND and 5,34,324 ng/l with mean level of 2,51,376 ng/l.

The concentration of phthalates in the Tamil Nadu river waters (Fig. 3a) indicates that DEHP, DBP, and DEP were ubiquitous in the Kaveri and Vellar River water samples, whereas BBP was detected only in 75% and 27% of Kaveri and Tamiraparani River water samples, respectively. Among 30 locations, 18 locations were found with all the phthalates, signifying widespread occurrence of phthalates in the riverine environment. The calculated mean level of DBP (1,52,489 ng/l) and BBP (1,03,617 ng/l) were two orders greater in magnitude than DEHP (6016 ng/l) and DnOP (4467 ng/l), whereas four orders of magnitude higher than DMP (22 ng/l). From the above mean values, it is understood that DBP (57%) and BBP (39%) contribute more for total phthalates than DEHP (2%) and DnOP (2%). The contribution of other phthalates (DMP and DEP) was not significant (<1%).

The total phthalates in the Kaveri River were quantified in the range of 128–5,34,324 ng/l which was three orders greater in magnitude than our previous report (ND–822 ng/l) indicative of the increased use over the period of 5 years (Selvaraj et al., 2015). The mean total (1,03,354 ng/l) was comparable to the Vellar River (1,39,874 ng/l) and one order greater in magnitude than in the Tamiraparani (24,444 ng/l) River. The major contributing phthalates were DBP (51%), followed by BBP (44%) and DnOP (4%) which were comparable to our earlier study BBP (92%) and DBP (67%) (Selvaraj et al., 2015). Among the individual phthalates, DBP was quantified very high up to 3,58,694 ng/l in Mettur (Stanley reservoir) and up to 95,348 ng/l in Muthupet. Similarly, BBP also quantified more at Mettur (1,68,200 ng/l) and Muthupet (1,11,358 ng/l). It could be because chemical effluents and household discharge were dumped into the river at several sites near these places. Other emerging pollutants, such as Bisphenol A and nonyl phenol, have already been identified at higher rates in Muthupet (136 ng/l and 2200 ng/l, respectively) compared to other locations of the Kaveri River (Selvaraj et al., 2014).

In the Vellar River, the total phthalates were observed in the range of 1,22,344–1,69,089 ng/l (Fig. 3a). All the phthalates were quantified in all the locations (i.e., 100% detection frequency). Mean concentrations of all the phthalates except DnOP calculated in the Vellar River was comparable to the Kaveri River. The major contributing phthalates were DBP (61%), followed by BBP (38%) as in the case of the Kaveri River. Like the Kaveri River, DBP was quantified at higher concentration (1,05,366 ng/l) followed by BBP (59,917 ng/l) at Railadi.

In the Tamiraparani River, the distribution of phthalates was slightly different from the other two rivers with DBP (68%) and DEHP (25%) followed by trivial contribution from BBP (4%) and DnOP (2%) (Fig. 3a). It was in agreement with the finding of Selvaraj (2015) who reported contribution of DBP and DEHP as 56% and 31%, respectively, in the Tamiraparani River. The total phthalates were observed ranging from ND to 43,857 ng/l, which reveals the Tamiraparani River is less contaminated compared to other two rivers. This may be due to the fairly low population of the region. Similar to the Kaveri and Vellar Rivers, DBP was quantified highest in Tenkasi (35,525 ng/l), whereas, DEHP was quantified maximum in

Tirunelveli (11,769 ng/l) among all the river locations. Ramaswamy et al. (2011) also reported higher concentration of a well-known antibacterial agent, triclosan (3800 ng/l) in Tirunelveli. Apart from DEHP, concentration of DEP found in Tenkasi (765 ng/l), Kutralam (583 ng/l), Srivaikuntam (684 ng/l), and Aeral (624 ng/l) was indeed greater than any other river locations.

Wet Season

The total phthalates in all the water samples collected during wet season were found between 6 and 25,511 ng/l (mean: 18,993 ng/l). Individual phthalates were detected ranging from ND (not detected) to 24,946 ng/l as shown in Fig. 3b. This concentration was less than dry season, the similar trend was also observed by Lee et al. (2019) while studying distribution of phthalates in waters of the Asan Lake of South Korea. Wet deposition and runoff will greatly influence the concentration of phthalates in water (Gao & Wen, 2016). Furthermore, the detection frequency of these compounds varied between 17% and 100% in three rivers. The occurrence of phthalates during wet season (Fig. 3b) indicates that DBP was ubiquitous in the Kaveri and Tamiraparani River water samples, whereas DEP was omnipresent in the Vellar and Tamiraparani River samples. Moreover, DMP and DnOP were among the least detected compounds (33–56%). Unlike the dry season, among 30 locations only 9 locations were found with all the phthalates. The mean level of DBP (25,029 ng/l) was two orders greater in magnitude than DEP (407 ng/l), BBP (453 ng/l), and DEHP (892 ng/l), whereas three orders greater in magnitude than DMP (15 ng/l) and DnOP (11 ng/l). Based on the above results, DBP (93%) was found to be the single most contributor to total phthalates relative to other compounds.

The Kaveri River exhibited total phthalates between 45 and 25,511 ng/l (Fig. 3b). This was one order of magnitude less than the amounts recorded in the dry season with the mean total concentration of 9296 ng/l. The major contributing phthalate was DBP (93%), followed by DEHP (3%), DEP (2%), and BBP (4%) consisting the minor portion. Among the phthalates, DBP (24,946 ng/l) and BBP (414 ng/l) were quantified at elevated level in Pichavaram mangrove forest area.

Total phthalates in the Vellar River were detected between 6 and 15,696 ng/l (Fig. 3b). This was one order magnitude lower than the levels observed during dry season. The detection frequency of phthalates varied between 33% and 100%. DEP was detected at all three sampling stations of the Vellar River. Similar to the dry season, mean concentrations of all the phthalates in the Vellar River was comparable to the Kaveri River. The key contributing phthalate was DBP (94%), while other five phthalates comprising the negligible portion. Highest individual phthalate concentrations were recorded at Railadi for DBP (14,593 ng/l), DEHP (528 ng/l), DEP (359 ng/l), BBP (205 ng/l), DMP (7 ng/l), and DnOP (4 ng/l).

Unlike dry season, phthalate distribution in the Tamiraparani River was similar to the other two rivers with DBP (91%) followed by slight contribution from DEP (4%), BBP (3%), and DEHP (2%) (Fig. 3b). The total phthalates were within in the range of 327–23,011 ng/l, which was comparable to the other two rivers. Similar to the Kaveri and Vellar Rivers, DBP was quantified highest in Punnaikayal (21,901 ng/l). In the harbor city of Punnaikayal, DEP and BBP were also reported at highest levels of 620 ng/l and 416 ng/l, respectively. These levels were higher than the ones recorded at the Kaveri and Vellar Rivers.

3.2 Phthalates in River Sediment

Dry Season

The distribution and composition of six major phthalates in southern Indian rivers were recorded in this study. The study of chemicals in sediment provides clues on their prolonged occurrence in environment than water where the concentration flux is high. Phthalate concentration in the Tamil Nadu river sediments during dry season (Fig. 4a) specifies that DBP was ubiquitous in all the samples, whereas DEHP was pervasive in the samples collected from the Vellar and Tamiraparani Rivers. The same pattern was also observed by Selvaraj et al. (2015) with DBP (100%) and DEHP (96%) occurring predominantly. The levels of individual phthalates ranged from ND to 673 ng/g dw, whereas the total phthalates were in the range of 6–725 ng/g dw. In comparison, DEHP (mean 99 ng/g dw) was quantified at higher concentrations at several of the sites, followed by DBP (66 ng/g dw), DMP (62 ng/g dw), BBP (11 ng/g dw), DEP (9 ng/g dw), and DnOP (5 ng/g dw). As observed, the phthalate that contributed most to the total concentration was as follows: DEHP (39%) > DBP (26%) > DMP (25%) > DEP (4%) > BBP (4%) > DnOP (2%). The total mean phthalates were found in the decreasing in the order of Kaveri (112 ng/g dw) > Tamiraparani (81 ng/g dw) > Vellar (32 ng/g dw) Rivers.

Among the locations in the Kaveri River, all the phthalates were detected only at Ammapettai. The major contributing phthalates for total concentration were DEHP (39%), followed by DBP (26%) and DMP (25%) (Fig. 4a). The minimum and maximum concentration of total phthalates were found at Pichavaram (6 ng/g dw) and Ammapettai (725 ng/g dw), respectively. Not only total phthalates, DEHP (673 ng/g dw) and DEP (8 ng/g dw) (highest among all the rivers) were also recorded maximum at Ammapettai. In mangrove forest area like Picharavam, the overall phthalates were found to be 6 ng/g dw with maximum input from DBP (4 ng/g dw). This could be attributed to the discharge of domestic waste into the mangrove waters.

The total phthalates quantified in the Vellar River ranged from 27 to 39 ng/g dw. DEP, DBP, and DEHP were detected at all three locations, whereas DMP, BBP, and DnOP were not detected in sediments of the Vellar River. The maximum phthalate concentration was observed for DBP at Railadi (30 ng/g dw) which much lower than the Kaveri River. The major composition of phthalates consisted more of DBP (53%) and DEHP (34%) with less DEP (13%) (Fig. 4a). The Vellar River sediment showed lower concentration of phthalates than the Kaveri and Tamiraparani Rivers.

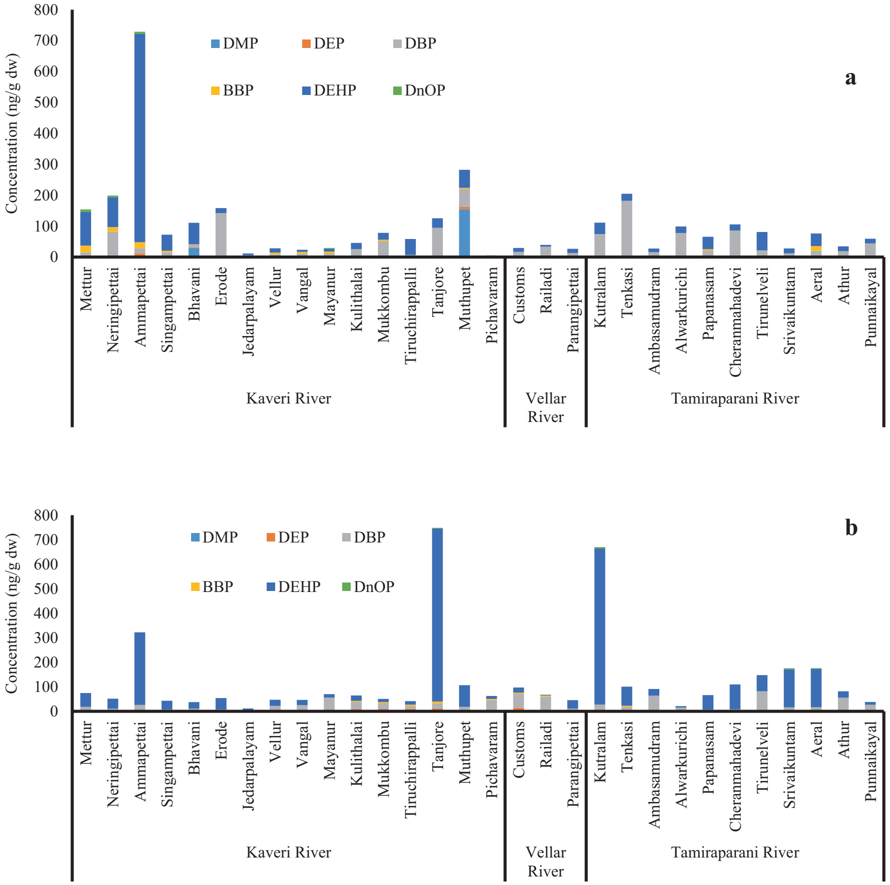

Fig. 4 Concentration of phthalates in sediment from the Kaveri, Vellar and Tamiraparani Rivers, India, during dry season (**a**) and wet season (**b**)

The maximum concentration of overall phthalates was witnessed at Tenkasi (205 ng/g dw) on the Tamiraparani River with major contribution from DBP (182 ng/g dw), whereas Ambasamudram was lowest at 27 ng/g dw. The phthalate composition consisted of DBP (56%) contributing higher than DEHP (30%) and BBP (11%), whereas, DMP and DnOP were not detected in sediment samples of the Tamiraparani River. The mean of DBP, DEHP, BBP, and DEP was calculated as 51 ng/g dw, 27 ng/g dw, 10 ng/g dw, and 2 ng/g dw. The signature of phthalates (mean: 59 ng/g dw) in Punnaikayal signifies the potential load of phthalates drained into the estuary and thereby into the open sea.

Wet Season

Total phthalates in all the sediment samples collected during wet season were found between 12 and 748 ng/g dw (Fig. 4b) with an average level of 236 ng/g dw which was comparable with the dry season. Individual phthalates were detected in the range of ND to 705 ng/g dw. Furthermore, the detection frequency for phthalates varied between 0% and 100% in the Kaveri, Vellar, and Tamiraparani Rivers. Phthalate occurrence indicates that DBP and DEHP were ubiquitous in all three rivers unlike DMP which was not reported during wet season. DMP was more frequently detected in water than in sediments, which can be due to its relatively higher water solubility (4000 mg/L) (Howard et al., 1985).

Furthermore, no location had reported all the phthalates in sediment samples. DEHP (60%) was the contributor for total phthalates followed by DBP (28%). The mean concentration of DEHP and DBP was 149 and 70 ng/g dw, respectively.

The Kaveri River showed total phthalates in the range of 12–748 ng/g dw (Fig. 4b) with the average total concentration of 115 ng/g dw. The major contributing phthalates were DEHP (73%) followed by DBP (16%) with DEP (4%), BBP (5%), and DnOP (2%) consisting of the small portion. Among the phthalates, DEHP (705 ng/g dw), DEP (12 ng/g dw), BBP (8 ng/g dw), and DnOP (3 ng/g dw) were quantified highest in Tanjore area. Furthermore, DnOP was only detected at Tanjore.

Total phthalates in the Vellar River ranged from 45 to 97 ng/g dw. Similar to the dry season, DEHP and DBP were detected across all three locations, while DMP and DnOP were not detected in the Vellar River sediments. Furthermore, like dry season, the maximum phthalate concentration was observed for DBP at Railadi (60 ng/g dw) which was much lower than the Kaveri River. The composition of phthalates comprised more of DBP (56%) and DEHP (26%) with a smaller amount of DEP (11%) (Fig. 4b). Similar to the dry season, the Vellar River sediments showed lower concentration of phthalates than the Kaveri and Tamiraparani Rivers.

In the Tamiraparani River, total phthalates ranged from 21 to 670 ng/g dw (Fig. 4b) with the average total concentration of 152 ng/g dw. Similar to the Kaveri River, the main contributing phthalates were DEHP (75%) followed by DBP (17%). DEHP was quantified at highest concentration (636 ng/g dw) at Kutralam. Ramaswamy et al. (2011) also reported significant presence of triclosan and parabens in Kutralam.

For the most part, the recent sources of phthalates are indicated by the levels of phthalates in water phase, while the sediment trend demonstrates the accumulation/persistence of phthalates over the years. Therefore, the concurrent occurrence of phthalates in water and sediment at higher level in most of the locations indicates contamination of rivers for years.

Phthalates Comparison with Indian and Global Studies

The concentration of total phthalates recorded in the rivers Kaveri, Vellar, and Tamiraparani was comparable to the studies carried out around the world (Table 3). The Kaveri River water reported the highest concentration of total phthalates (5,34,324 ng/l) which was greater than other studies globally. Net et al. (2015b) reported the highest level (1,79,100 ng/l) of total phthalates ($n = 6$) at Nivelles on the Scarpe River which was comparable to the Vellar River (1,69,089 ng/l). Upper levels reported in the Tamiraparani River (43,857 ng/l) were comparable to the levels reported (28,000 ng/l) in Cochin estuary, Kerala, India (Ramzi et al., 2020). The total phthalate concentration of the water and sediment samples of the Yellow River in Lanzhou was ND to 6040 ng/l and ND to 9898 ng/g dw, respectively, with the concentrations of two priority phthalates (DBP and DEHP) higher in all samples (Zhao et al., 2020). This observation is similar to the present study. In case of sediment, the levels reported in the Kaveri River (6–748 ng/g dw) and the Tamiraparani River (21–670 ng/g dw) were comparable with the levels reported by (Selvaraj et al., 2015) in the Kaveri River (2–1438 ng/g dw) and recently reported levels in the Adyar River (52–1796 ng/g dw) and the Cooum River (28–856 ng/g dw). Concentrations reported in the Vellar River (27–97 ng/g dw) were lower compared to the Kaveri and Tamiraparani Rivers, which were comparable with the levels seen in eight urban lakes (17–242 ng/g dw) of Guangzhou, China (Zhang et al., 2018).

Ecotoxicological Risk Assessment

Risk assessment for freshwater organisms was performed based on RQ calculated from MEC and PNEC. To determine the ecological toxicity by risk quotient, the highest determined environmental concentration of phthalates in the rivers was used. List of organisms, end point, and NOEC for phthalates were given in Table 4.

The risk to aquatic habitat from phthalates was assessed for invertebrates, fish, and algae as shown in Fig. 5. The calculated RQs of DMP and DEP in the Kaveri, Vellar, and Tamiraparani Rivers for *Daphnia magna*, *Oncorhynchus mykiss*, and *Selenastrum capricornutum* were well below unity, whereas RQs of DBP for *Oncorhynchus mykiss* were in decreasing order of the Kaveri River (35.9) > the Vellar River (10.5) > the Tamiraparani River (3.6). The RQ of DBP for *Daphnia magna* was 3.7 and 1.1 for the Kaveri and Vellar Rivers, respectively. Furthermore, the RQ of DBP for algae *Chlorella emersoni* was 1.3 in the Tamiraparani River. The RQs of BBP in the Kaveri and Vellar Rivers for *Daphnia magna*, *Oncorhynchus mykiss*, and *Selenastrum capricornutum* ranged from 2.1 to 16.8 indicating risk to all three taxonomic groups. Higher levels of DEHP in the Tamiraparani River mirrored the risk for *Daphnia magna* (RQ 1.5) and *Selenastrum capricornutum* (RQ 1.2). In case of DnOP, *Daphnia magna* was found to be at risk in the Kaveri River (RQ 1.5). Therefore, these results indicate that DMP and DEP pose little or negligible risk, and potential risk can be anticipated due to higher water concentrations of DBP, BBP, DEHP, and DnOP in South Indian rivers. In Cochin estuary, India,

Table 3 Comparison of phthalates recorded in major Indian rivers and elsewhere

Country	River	Number of phthalates analyzed	Water (ng/l)	Sediment (ng/g dw)	References
China	Yangtze River	5	34–91,220	76,300–450,000	Wang et al. (2008)
	Qiantang River	16	NP	590–6740	Sun et al. (2013)
	Pearl River Delta	16	NP	567–47,300	Liu et al. (2014)
	Pearl River	6	500–28,100	880–13,600	Li et al. (2016)
	Jiulong River	6	3500–18,000	4–1600	Li et al. (2017)
	Eight lakes of Guangzhou	6	273–1173	17–242	Zhang et al. (2018)
	Yangtze River	6	2650–39,310	930–34,700	Chen et al. (2019)
	Pearl River	14	13–6717	72–17,340	Weizhen et al. (2020)
	Yangtze River Estuary	16	588–22,900	1650–48,300	Zhang et al. (2020)
	Yellow River	22	ND–6040	ND–9898	Zhao et al. (2020)
Taiwan	Dianbao River	6	NP	<1–1949	Yang et al. (2015)
South Korea	Asan Lake	14	ND–2290	3.6–8973	Lee et al. (2019)
Iran	Anzali Wetland	6	NP	4180–20,710	Shariati et al. (2019)
France-Belgium	Fifteen transboundary rivers	6	17,200–179,100	1100–11,900	Net et al. (2015b)
France	Rhône River	8	182–615	NP	Paluselli et al. (2018)
	Rhône River	7	70–405	NP	Schmidt et al. (2020)
India	Gomti River	5	NP	ND–364	Srivastava et al. (2010)
	Kaveri River	6	313–1640	2–1438	Selvaraj et al. (2015)
	Cochin estuary	6	NP	44–3121	Ramzi et al. (2018)
	Cochin estuary	6	ND–28,000	NP	Ramzi et al. (2020)
	Adyar River	7	NP	52–1796	Mukhopadhyay et al. (2020)
	Cooum River	7	NP	28–856	Mukhopadhyay et al. (2020)
	Kaveri River	6	45–5,34,324	6–748	Present Study
	Vellar River	6	6–1,69,089	27–97	Present Study
	Tamiraparani River	6	ND–43,857	21–670	Present Study

ND not detected, *NP* not performed

Table 4 Derived PNEC values for phthalates based on toxicity values in aquatic organisms

Chemical	Species	Endpoint (Duration)	NOEC Value (µg/l)	PNEC Value (µg/l)	References
Dimethyl phthalate	*Daphnia magna*	NOEC (21 d)	9600	960	Rhodes et al. (1995)
	Oncorhynchus mykiss	NOEC (102 d)	11,000	1100	Rhodes et al. (1995)
	Selenastrum capricornutum	NOEC (6 d)	64,700	6470	Adams et al. (1995)
Diethyl phthalate	*Daphnia magna*	NOEC (21 d)	25,000	2500	Rhodes et al. (1995)
	Oncorhynchus mykiss	NOEC (96 h)	3800	380	Adams et al. (1995)
	Selenastrum capricornutum	NOEC (8 d)	3650	365	Adams et al. (1995)
Di-n-butyl phthalate	*Daphnia magna*	NOEC (21 d)	960	96	Rhodes et al. (1995)
	Oncorhynchus mykiss	NOEC (102 d)	100	10	Rhodes et al. (1995)
	Chlorella emersoni	NOEC (7 d)	2780	278	Melin and Egnéus (1983)
Butyl benzyl phthalate	*Daphnia magna*	NOEC (21 d)	280	28	Rhodes et al. (1995)
	Oncorhynchus mykiss	NOEC (109 d)	200	20	Rhodes et al. (1995)
	Selenastrum capricornutum	NOEC (6 d)	100	10	Adams et al. (1995)
Di-2-ethylhexyl phthalate	*Daphnia magna*	NOEC (21 d)	77	7.7	Rhodes et al. (1995)
	Oncorhynchus mykiss	NOEC (90 d)	502	50.2	Defoe et al. (1990)
	Selenastrum capricornutum	NOEC (6 d)	100	10	Adams et al. (1995)
Di-n-octyl phthalate	*Daphnia magna*	NOEC (16 d)	320	32	McCarthy and Whitmore (1985)
	Pimephales promelas	NOEC (20 d)	3200	320	McCarthy and Whitmore (1985)

parallel trend was observed where DBP and DEHP risk quotient values were large enough to pose moderate to high risk to aquatic biota (Ramzi et al., 2020).

Sediment risk assessment of phthalates showed all the calculated RQs did not exceed unity (Fig. 6). This assessment determines that phthalates are not expected to pose a risk to environmentally sensitive benthic communities in sediments.

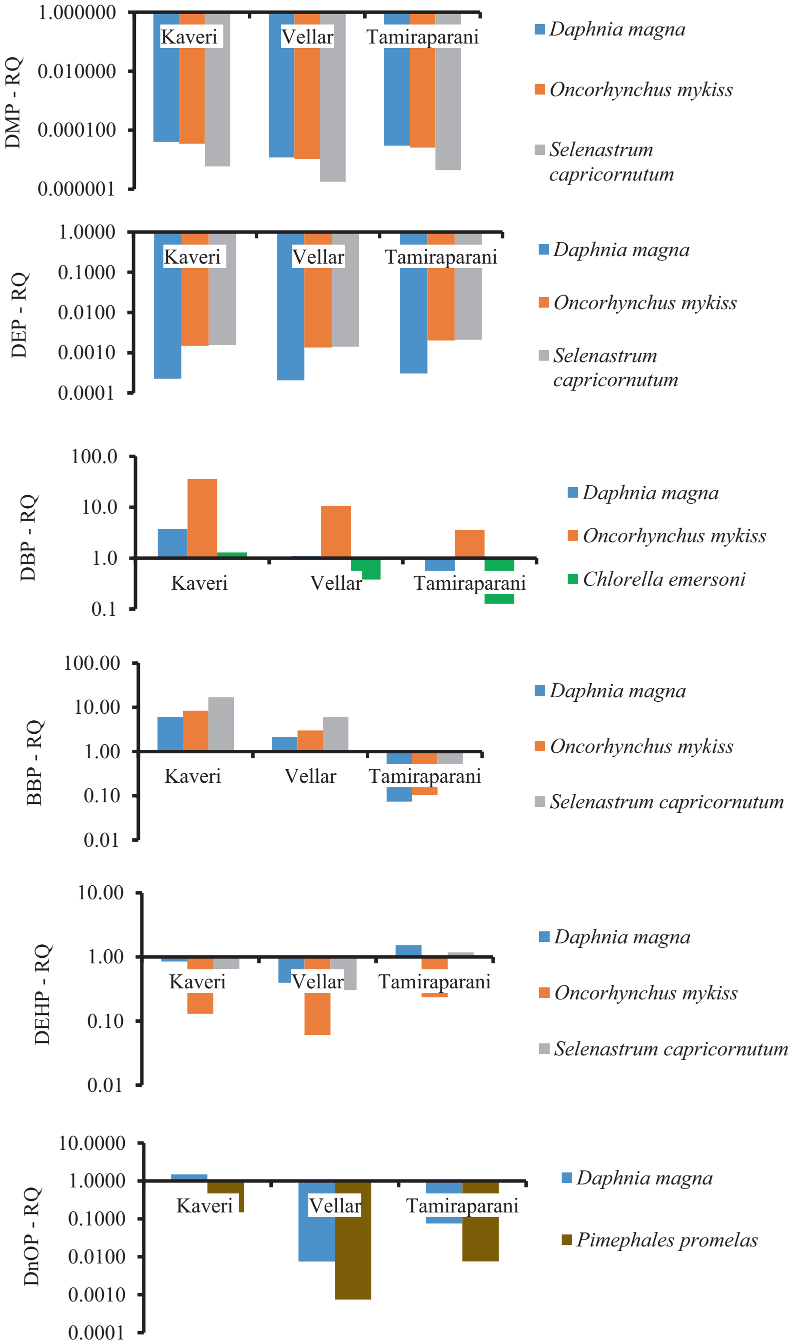

Fig. 5 Ecotoxicological risk assessment of phthalates in water based on RQ values

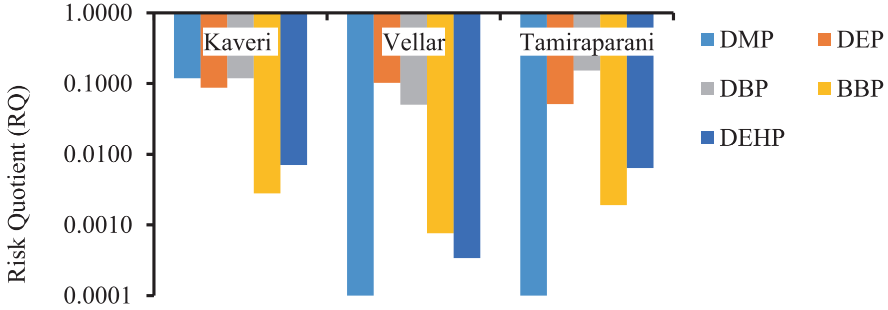

Fig. 6 Ecotoxicological risk assessment of phthalates in sediment based on RQ values

4 Conclusion

Phthalates were ubiquitously detected in three major rivers of southern India. Furthermore, this study reports these contaminants for the first time in the Vellar and Tamiraparani Rivers, confirming the anthropogenic influence throughout the river stretch. Among the contaminants analyzed, higher levels of DBP were observed in water. Among the rivers, Kaveri seems to be contaminated at higher proportion than others. Aquatic risk evaluation indicated potential vulnerability because of DBP, BBP, DEHP, and DnOP. The results indicate the need for water quality guidelines to manage the discharge of domestic/industrial sewage effluents containing estrogenic compounds into the river system. In addition, this study will also act as basic data for future environmental monitoring, fate, and toxicological investigation initiatives relating to emerging contaminants.

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Development of Various Strategies for the Removal of Phenol Pollutant

S. Radha Thirumalaiarasu and G. K. Mahalakshmi

Abstract Phenol is hydroxybenzene, an organic aromatic compound consisting of the attached hydroxyl group to aromatic hydrocarbon group. Phenol is hazardous to environment that is added mainly through wastes waters of textile, pharmaceuticals industries, and automobile waste. Phenolic compounds in the aquatic system harm flora and fauna of water bodies and they also interfere with biotransformation. Various forms of phenolic compounds influence the ozone layer, cause acid rain, and disturb the atmospheric temperature balance. Phenol is difficult to degrade, and hence, it is retained in air, soil, and water for a long period. Thus, for protection of the ecosystem and human health, it necessary to adapt effective strategies to eliminate the phenolic pollutant. This chapter depicts various physicochemical methods analyzed for degradation of phenol that include partial electrocatalytic degradation, photo-Fenton processes, electro-polymerization, and advanced nano systems. This chapter focuses on the relevant eco-friendly techniques such as adsorption, immobilization, and fuel cell technology using microorganisms employed for phenol removal and various physical, chemical, and biological factors evaluated by optimization studies designed using statistical tools for enhancing phenol degradation.

Keywords Phenol · Pollutant · Immobilization · Microorganism · Optimization

1 Introduction

Phenolic compounds are hazardous organic environmental pollutants which are added to through the decomposition of biomass of plants and effluents of leather, oil refinery, pharmaceutical industries, coal processing, motor fuel production unit, etc. (Arutchelvan et al., 2006). A few quantities of phenolic compounds are present in stains, sterilizers, and synthetic resins, and phenol is also added as indicator in chemical laboratory (Kafilzadeh & Mokhtari, 2013). Phenol can decrease the

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enzyme activity and is lethal to fish even at low concentration of 5–25 mg L^{-1}. The polychlorinated phenols formed are toxic when they contaminate chlorinated water and make municipal water unfit for drinking. The United States Environmental Protection Agency (USEPA) has set phenol less than 1.0 mg L^{-1} as standard for water purification (Chung et al., 2003). Phenol in high concentration affects central nervous system and causes muscle weakness, which leads to paralysis, coma, and arrest respiration (Jame et al., 2010). It causes irritation of eyes, swelling, corneal whitening, blindness, and also cancer (Nair et al., 2008; Mangukiya et al., 2015).

Due to the adverse effect of this organic pollutant on health of humans and environment, proper treatment of phenolic waste materials is a prerequisite; hence, many physicochemical methods were employed for the degradation of phenol. To further remove phenolic wastes more effectively in an eco-friendly manner, much research is focused on biological methods. Microbial degradation is employed through various strategies such as adsorption, immobilization, and bioreactor system. The basic mechanism behind involves an enzymatic process which was optimized for maintaining a suitable physiological condition for maximum phenol degradation (Pradeep et al., 2015). Microbial fuel cell (MFC) is a current advanced novel technique employed for the bioremediation of phenolic pollutant. This bioelectrochemical technology used successfully for the production of electrical energy through biodegradable chemical compounds by microbial-mediated enzymatic process (Khan et al., 2018).

2 Sources of Phenol Pollutant

Phenol or hydroxybenzene is an organic aromatic compound with the attached hydroxyl group to aromatic hydrocarbon group. Phenol stays in the environment by two main processes: chemical and natural (Table 1). Naturally, it was formed by the part of coal-tar and creosote, decomposition product of organic matter and as secondary metabolite in plants. Phenol exists as free or bound form in foods such as red grapes, cocoa, and tomatoes. It is also produced during plant decomposition processes, usually in the form of intermediates such as ρ-cresol or lignin (Gami et al., 2014). Phenol is also synthesized during chemical reaction such as toluene oxidation, fusion process of sodium benzenesulfonate with sodium hydroxide, or heating

Table 1 Sources of phenol pollutants

Natural sources	Anthropogenic sources
Coal-tar and creosote	Oil refineries and petroleum-based processing plants
Decomposition of plant	Resin manufacturing and plastic and varnish industries
Oxidation of toluene	Pharmaceutical industries
Environmental transformation	Agricultural wastes
Photo-oxidation	Domestic wastes

monochlorobenzene with sodium hydroxide under high pressure (Basha et al., 2010). Due to microbial enzymes, phenol and chlorophenols are transformed into catechol and chlorocatechols. The compound 4-tert-buthylcatechol, which inhibits the polymerization process of synthetic materials, is produced using catechols. The process of chlorination of catechol forms dichloroaniline and chlorinated biphenyls (Michalowicz & Duda, 2007).

Large quantities of phenol are discharged as wastes of resin production unit, plastic synthesizing and varnish companies, etc. (Liu et al., 2009). Phenol pollutant also enters soil and food through water, as it can be desorbing from the soil sediment in water source and re-enters the water phase where it can accumulate inside living organisms (Singh et al., 2013). The anthropogenic sources for pollution of water with phenolic compounds come from industries and domestic, agricultural, and municipal discharge (Anku et al., 2017). Photo-oxidation of aromatic hydrocarbons produces nitrated phenol in the atmosphere which includes benzene oxidized to 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP), and toluene oxidized to methylnitrophenols (MNP) (Yuan et al., 2016). Phenolic compounds react with OH produced by the increasingly popular UV/ hydrogen peroxide (H_2O_2) water treatment process or UV light to form toxic enedials and oxoenals (Prasse et al., 2018).

3 Phenol Degradation

3.1 Physicochemical Methods

Phenol is converted into organic acid by partial electrocatalytic degradation performed utilizing PbO_2 anode containing fluorine resin. During degradation of phenol, there is a decrease in the concentration of benzoquinone (BQ), and the conversion of phenol in to organic acids were enhanced utilizing an optimized operational condition (Wu & Zhou, 2001). Pismentel et al. (2008) reported that electro-Fenton process using carbon felt cathode with metal cations as catalyst of Fenton reaction proposes a complete mineralization of phenol in aqueous media. Huang et al. (2010) implemented low concentration of ferric ions with photo-Fenton process and removed COD below 100 mg L^{-1} at 365 nm UV light in Taiwan. Saputra et al. (2013) investigated that the chemical state of Mn influences the catalytic properties of Mn oxides. Mn_2O_3 effectively activates peroxymonosulfate PMS to produce sulfate radicals for phenol degradation. Phenol is completely removed in 60 min at the conditions of 25 mg L^{-1} phenol, 0.4 g L^{-1} catalyst, 2 g L^{-1} PMS, and 25 °C.

Electropolymerization at an anode is employed for removing phenol in alkaline solution. Due to oxidation of HO at Ta/-PbO_2 surface incineration of polymeric substances occur partially. The permeability of polymeric films governs the mass transfer rate (Tahar & Savall, 2009). Medel et al. (2012) constructed a boron-doped diamond electrode that used to selectively eliminate phenolic compounds of hydrocarbon industry. Li et al. (2017) found that Sn-Sb-Ce modified granular-activated carbon particle electrode has been employed in removing phenol from effluent. Recently RC8 and RCpH were investigated as a carrier in polymer inclusion membrane (PIM). The complex is formed by hydrogen bonding and/or intermolecular interactions between the phenol and calix resorcinarene which is simple to implement and hence most widely used for the removal of phenol from waste water (Benosmane et al., 2018). Aqueous phase oxidation processes (AOPs) are used for the treatment of pollutant, and further the cost can be reduced using solar energy (Esplugas et al., 2002). Degradation and mineralization efficiency of phenol was increased in photo-Fenton processes as compared to conventional Fenton process (Kavitha & Palanivelu, 2004). Fenton's reaction increases phenol degradation by direct or indirect photolysis and pyrolysis destruction using pulse field electric discharges (Shen et al., 2008).

Titanium dioxide (anatase, TiO_2) nanoparticles of less than 7 nm in diameter is deposited on carbon nanotubes (MWCNTs) by hydrolysis of titanium isopropoxide. This TiO_2/MWCNT degrades phenol by irradiation of visible light and exhibits higher efficiency compared to a mixture of TiO_2 and MWCNTs (An et al., 2007). Yehia et al. (2014) reported that nanosized zero-valent copper (NZVC) or nanosized zero-valent nickel (NZVN) in combination with H_2O_2 and 20 kHz ultrasound irradiation degrades phenol. Lee et al. (2017) designed the boron-doped diamond nanowire (BDDNW) electrode with metal-assisted chemical etching (MACE) of Si and electrostatic self-assembly of nano-diamond (ESAND) that allows large surface area for the electrochemical oxidation. With the increased chemical oxygen demand (COD), total organic carbon (TOC) removal behavior, current efficiency, and enhanced oxidation performance, the BDDNW electrode consumes low energy during phenol oxidation process.

3.2 *Biodegradation of Phenol*

Usually, bacteria and fungi are well known to degrade various forms of aromatic compounds. Microorganisms have the capability to produce a wide variety of enzymes that degrade phenol. Enzyme such as oxygenase includes monoxygenases and dioxygenase, which exhibit potential to cleave the benzoid ring by hydroxylation and fission under aerobic condition. The aromatic metabolism can be grouped as catechol pathway depending on variation in ring cleavage. Catechol 1,2dioxygenase is an ortho cleavage enzyme, and catechol 2,3 dioxygenase is an meta cleavage enzyme which on cleavage forms the product cis-muconic acid and 2-hydro cismuconic semi aldehyde (Supriya & Neehar, 2014; Jayachandran et al., 2008).

Bacteria of aquatic and terrestrial environments perform degradation of phenol in aerobic environment through a few metabolisms. The degradation of phenolic compounds initially produces catechol or protocatechuate that follows the ketoacid and ketoadipate pathways and further oxidized to ketoadipate which enters two sequential steps to form Krebs cycle intermediates (Tian et al., 2017). Mei et al.

(2019) reported that *Cobetia* sp. SASS1 shows phenol-degrading ability of following ortho-cleavage pathway catalyzed by catechol 1,2-dioxygenase and benzoic acid pathway.

3.3 Phenol-Degrading Microbes

The degradation of phenol by bacteria can be grouped into two based on its ability to utilize phenol as a source of carbon. They possess phenol-degrading enzyme and they can thrive in phenol-contaminated polluted environment. Another group of bacteria degrade phenol through co-metabolism pattern that is influenced by the availability of other sources of carbon. Sometimes degradation of phenol is performed by two or more bacteria (Zhao et al., 2018).

Many indigenous strains of *Pseudomonas* sp. are involved in the degradation of various forms of phenolic compounds, which has the ability to degrade a maximum of 600 ppm of phenol (Jame et al., 2008). Bacteria such as *Rhodococcus, Stenotrophomonas, Lysinibacillus, Comamonas, Microbacterium, Halomonas* (Ahmad et al., 2015), and *Streptococcus* sp. (Parihar & Dubey, 2016) were identified in a sample collected from a polluted region and found to perform effective degradation of phenol. Kafilzadeh and Mokhtari (2013) isolated several phenol-degrading Gram-positive and Gram-negative bacteria from the mangrove sediments (Table 2).

Many algae are effectively degrading polycyclic aromatic hydrocarbons. The molecular characteristics of pollutant and metabolic process of the algae governs the mechanism of phenol degradation (El-Sheekh et al., 2012). Degradation of phenol by algae is an aerobic process, and availability of other carbon source like glucose reduces the phenol degradation due to the competition for oxygen. Subashchandrabose et al. (2013) reported the potential dechlorinating and degrading ability of *Chlorella* sp. after 5 days of incubation. Comparison of degradation process by *Chlorella* sp. records that it degrades 2,4-dichlorophenol more effectively than 2,4-dimethyl phenol and 2-chlorophenol. Its degrading potentiality is due to the presence of two intracellular enzymes like polyphenol oxidase and laccase enzymes. Zhao et al. (2018) determined the degradation rate alkylphenol and correlated it with growth rate of *Tolypothrix*. Due the degrading efficacy on wide range of organic pollutants, many fungi are widely employed for waste water treatment systems, and the potentiality of a yeast strain was also reported to degrade phenol even at high initial concentration (Stoilova et al., 2006; Karimi & Hassanshahianc, 2016).

Table 2 Various microorganisms involved in phenol degradation

Microorganism	Sources of microbial isolates	References
Bacteria		
Bacillus brevis	Phenol–formaldehyde resin manufacturing industrial wastewater	Arutchelvan et al. (2006)
Sphingomonas sp. FG03	Activated sludge	Liu et al. (2009)
Bacillus cereus	Fuel refining region	Banerjee and Ghoshal (2011)
Acinetobacter sp. AQ%NOL1, *Acinetobacter calcoaceticus*	Pesticide-polluted site, oil refinery effluent	Ahmad et al. (2012), Liu et al. (2016)
Pseudomonas fluorescens PU1	Contaminated soil sample	Mahiudddin et al. (2012)
Alcaligenes odorans *Bacillus subtilis* *Corynebacterium propinquum* *Pseudomonas aeruginosa*	Dissolved air Floatation outlet in refinery	Singh et al. (2013)
Rhodococcus phenolicus *Stenotrophomonas geniculata* *Rhodococcus zopfii* *Lysinibacillus sphaericus* *Comamonas thiooxidans* *Microbacterium paraoxydans* *Pseudomonas plecoglossicida* *Halomonas elongata*	Sludge at bioremediation site	Ahmad et al. (2015)
Halomonas campisalis	Near soap lake	Alva and Peyton (2003)
Variovorax	Aquifer soil	Futamata et al. (2005)
Aeromonas sp.	Industries and workshop soil	Jame et al. (2008)
Brevibacterium iodinum *Staphylococcus aureus*	Mangrove sediments	Kafilzadeh and Mokhtari (2013)
Streptococcus sp. PDM5	Municipal sewage water	Parihar and Dubey (2016)
Pseudomonas sp.	Sewage water, paper mill wastewater	Mohanty and Jena (2017), Sachan et al. (2019)
Bacillus thuringiensis	Olive mill wastes	Ereqat et al. (2017)
Cobetia sp. SASS1	Natural pyrite site	Mei et al. (2019)
Fungi		
Fusarium sp.	Bentonite	Cai et al. (2007)
Aspergillus flavus	Polluted soil at cars reparation's area	Ghanem et al., 2009
Alternaria sp.	Painted sick-building walls	Jacob and Alsohali (2010)
Phaenerochaete sp. *Penicillium* sp.	Soil and sewage sample	Kaur and Rani (2015)
Aspergillus terreus	Pollutant contaminated sites	Ibrahim and Al-Ghamdi (2019)

(continued)

Table 2 (continued)

Microorganism	Sources of microbial isolates	References
Yeast		
Candida tropicalis, *Pichiaguillier mondii*, *Meyerozyma guilliermondii*	Soil and waste-water samples from the coking plant	Karimi and Hassanshahianc (2016)
Candida subhashii *Candida oregonensis* *Schizoblastosporion starkeyi-henricii*	Raised bog	Filipowicz et al. (2017)
Algae		
Volvox aureus *Nostoc Linckia* *Oscillatoria rubescens*	Polluted site	El-Sheekh et al. (2012)
Chlorella pyrenoidosa	Effluent treatment plant	Priyadharshini and Bakthavatsalam (2016)

4 Optimization of Phenol Degradation

The pH of medium has a significant role influencing the oxidation process photo-Fenton process at pH 3, 5 mg L^{-1} Fe (III), 1080 mg L^{-1} H_2O_2 using 3 UV lamps (365 nm). In the UV/ H_2O_2 system, the phenol degradation reduces to 25% in 1 h (Huang et al., 2010). The haloalkaliphilic bacterium *Halomonas campisalis* utilizes phenol as carbon source under alkaline condition at pH 8–11 and 0–150 g L^{-1} NaCl (Alva & Peyton, 2003). Arutchelvan et al. (2006) reported that phenol biodegradation in *B. brevis* was optimized for various environmental conditions and was found to be maximum at pH 8.0, 5% (v/v) of inoculum density.

The pH of the solution has great impact on surface charge and degree of ionization of absorbent thereby influencing the phenol biodegradation. The rate of phenol degradation increases with the pH of the media from acidic to alkaline condition at 30 °C. Further increase in the pH denatures proteins and metabolic process of microorganism (Mohanty & Jena, 2017). Liu et al. (2016) investigated that *Acinetobacter calcoaceticus* PA can degrade phenol at initial 800 mg L^{-1} and even grow well at 1700 mg L^{-1} phenol concentration. Ereqat et al. (2017) found that the pH 6.57 and temperature 30 °C as optimum for *Bacillus thuringiensis* J20 and on increasing the temperature from 25 °C to 30 °C while increasing the temperature above 30 °C, the phenol degradation was about to decrease from 88.6% to 62.1%.

Phenol degradation is also influenced by temperature that is required at optimum level and increasing temperature may denature enzyme (Leven & Schnurer, 2005). Polymenakou and Stephanou (2015) reported that when the temperature is decreased by 10 °C leads to decrease in activity of *Pseudomonas* sp. The bacteria *B. brevis* degrade phenol effectively at 34 ± 0.1 °C and with biomass concentration 5% (v/v) (Arutchelvan et al., 2006). Higher phenol removal was attained on shifting to increased temperature. Phenol is degraded completely at temperature of 25 °C in 60 min (Saputra et al., 2013).

5 Techniques to Enhance Phenol Removal

5.1 Response Surface Methodology

Response surface methodology (RSM) is a combination of statistical and mathematical tool for designing model to perform optimization of different variables. It avoids the time-consuming classical one step optimization process. This statistical technique also used to study the interaction between various parameters and analyze the results obtained with a few number of experiments. The Box-Behnken design was effectively used to study degradation of phenol by *Pseudomonas putida* (ATCC 31800) in sludge and evaluated the interaction of four factors involved in the degradation of phenol showing maximum of 80.1% degradation (Annadurai et al., 2002). Ferreira et al. (2007) reported that compared with central composite design and three-level full factorial designs, more efficient output was observed with Box-Behnken design and Doehlert matrix. Agarry et al. (2008) studied the removal efficiency of phenol from liquid medium with *Pseudomonas aeruginosa* with response surface methodology and recognized optimized process condition as 30.1 °C, 3.0 vvm and 301 rpm for increased phenol removal of 94.5%. Agarry et al. (2010) found temperature of 30 °C, aeration of 3.0 vvm, and agitation of 300 rpm for degradation of 60.7% phenol using response surface methodology with *Pseudomonas fluorescence*. Sridevi et al. (2011) reported the optimization of glucose, ammonium sulphate, and metal ion concentration for 98.24% degradation of phenol employing CCD model. Suhaila et al. (2012) used CCD for evaluating the optimized parameters for phenol degradation with parameters such as phenol, $(NH_4)_2SO_4$ concentrations, and temperature. With initial phenol concentration of 500 mg L^{-1} of phenol and 300 mg L^{-1} growth and degrading ability of *Rhodococcus* UKMP was enhanced on maintaining incubation temperature of 36 °C. Prabu and Narendrakumar (2015) used nano zero-valent iron with cashew nut shell for optimization of parameters such as pH, dose, phenol content, time, and temperature applying Box-Behnken design for removing phenol from solution.

The two-level Plackett–Burman design (PBD) was used to study the factors involved in degradation of phenol which showed 97% efficiency with 4 g L^{-1} of algal biomass, initial phenol content of medium was maintained as 0.8 g L^{-1}, and it took 4 days for complete degradation. Reaction time of 4 days (Priyadharshini & Bakthavatsalam, 2016). Nawawi et al. (2016) reported the increased phenol degradation efficiency of 1.2 fold with cell density of 1.3 fold by *Rhodococcus* sp. NAM 8. Studies carried out using BBD experiment with Serratia *marcescens* NSO9-1 evaluated the efficacy of seven components that had significant impact on phenol degradation. The result depicts relevance of media components such as $MgSO_4$, NaCl, $CaCl_2$, and molybdenum salt that showed degradation of 90.12%. Interaction studies performed with quadratic model supported the optimal pH of 8.94, temperature of 22 °C, time period 4.19 days, and inoculum density of 4.68% (v/v) (Sarac et al., 2017).

5.2 Adsorption

Adsorption is a well-known currently applied cost-effective method used for water treatment. A wide variety of absorbents are employed such as activated carbons, zeolites, clay, and silica beads (Hararah et al., 2010). Chen et al. (2015) used modified XAD-4 resin which exhibits 1.5 times increased phenol removal.

Recently natural adsorbent is intensively used for the removal of phenol from waste water (Amin et al., 2012). In general, physical adsorption method is efficient, eco-friendly, and cost-effective which includes biological source and agricultural wastes. This by-product provides increased area for absorption, easy availability and exhibit suitable structural characteristic that make them to be employed as excellent absorbent (Sahua et al., 2017). Many wastes generated by agriculture processing are employed as low-cost materials for adsorption (Namane et al., 2012). The carbon content of rice straw has the ability to adsorb phenol, and hence it is considered to be the cheapest material that is effectively applied for adsorption (Sarker & Fakhruddin, 2017). Abdelkreem (2013) found the increased removal of phenol from 52% to 85% with 1 g olive mill waste as adsorbent. Afsharnia et al. (2016) proved that pomegranate peel has adsorption capacity of 148.38 mg g^{-1} (98%). Auwal et al. (2018) used tamarind seed powder for removal of phenol. Batch experiments carried out for various concentrations of phenol (1.0–10.0 ppm) for about 1 h under different initial concentrations suggested pH 8.0 as optimum of phenol degradation and recovered up to 94.90% of adsorbed phenol.

5.3 Immobilization

Immobilization is the process of physical trapping or holding of live microorganism to an inert material to restrict mobility of cell, enhance catalytic properties, and reuse for production (Martins et al., 2013). Degradation of phenol implementing immobilized microbes is an important and successful technique that has been applied for the reason of easy recovery and reuse of microbial population (Sheeja & Murugesan, 2002). By immobilization technique, the enzyme activity and required condition are unaltered; however, it shows increased stability that can tolerate high initial phenol concentration. Compared with free cells that show degrading ability only up to 600 mg L^{-1}, the immobilized cell has increased phenol degradation even at concentration of 1000 mg L^{-1} (Chung et al., 2003). El-Naas et al. (2009) reported the immobilization of *P. putida* with polyvinyl alcohol (PVA) gel at increased amount of 300 mg L^{-1}. Ying et al. (2006) have proved the strength of immobilized *Acinetobacter* sp. using poly vinyl chloride and employed it for degradation of phenol. Al-Zuhair and El-Naas (2011) utilized bubble column reactor for immobilizing bacteria using bacteria with poly vinyl chloride. Banerjee and Ghoshal (2011) reported the increased degradation of phenol with different strains of *Bacillus cereus* at increased phenol concentration of 2000 mg L^{-1}. Ahmad et al. (2012)

reported that when *Acinetobacter* sp. strain AQ5NOL 1 was immobilized by encapsulation using gellan gum showed increased phenol degrading ability and compared to free cells, immobilized bacterial took less time to degrade phenol. Cheng et al. (2012) worked on the characterization of immobilized cells with SEM analysis and has shown increased absorption of crystal violet from liquid solution with immobilized cells. Kaur and Rani (2015) investigated improved phenol degradation by fungi from 68% to 89% by immobilizing the cells with alginate.

Different species of *Pseudomonas* were tested for phenol degradation at 500 mg L^{-1} and they show enhanced degradation compared with free cells (Mohanty & Jena, 2017). Ereqat et al. (2017) reported that the degradation of phenol by *B. thuringiensis* was improved with alginate at 30 °C and pH 6.57. Recently, *Sphingomonas* sp.GY2B has shown to degrade phenol more effectively with least pH of 1 to alkaline pH of 12 (Ruan et al., 2018). Encapsulation of more than 80% of cell of *A. niger*, *P. griseofulvum,* and *A. terreus* into calcium-alginate beads has proven to increase the efficiency of the microbial cell viability and growth and promote better survival and activity of some microorganisms (Ibrahim & Al-Ghamdi, 2019).

5.4 Bioreactors

Bioreactors have been designed to degrade and remove toxic compounds (Table 3). Membrane bioreactors (MBRs) are designed precisely with appropriate immobilized system for wide application in different fields to remove pollutants with semipermeable membranes (Luke & Burton, 2001). Chung et al. (2004) reported removal of phenol upto 1000 mg L^{-1} with *Pseudomonas putida* CCRC14365 using hollow-fiber membrane bioreactor. Ersu and Ong (2008) used ceramic membrane-mediated bioreactor for removal of phenol till 600 mg L^{-1}. Boonnorat et al. (2014) employed two-stage membrane bioreactor for treating municipal solid wastes contaminated with phenol compounds which showed greater than 95% phenol degradation.

Several hybrid membrane bioreactors were designed to enhance the removal of phenol (Rafiei et al., 2014). Boonyaroj et al. (2016) constructed a two-stage MBR bioreactor using nitrifying bacteria that showed removal of 75% of bisphenol A. The fluidized-bed bioreactor is considered to be more efficient and has an advantage of using immobilized cells that contact directly with gas, liquid, and solid phases and exhibits high percentage of removal of phenol up to 1034 ppm (Vinod and Reddy (2005). Erhan et al. (2004) used micro-cellular polymers as fixed bed material in bioreactor working continuously. Juang et al. (2010) demonstrated phenol removal from acidic and saline solutions using *Pseudomonas* strain at 30 °C in two phase system. Tomei et al. (2011) prepared beads of the polymer Hytrel 8206 in two phase system and showed enhanced phenol removal. Anaerobic/anoxic processes exhibit low operation cost and are highly efficient in removing 95.5% and 96.75% of phenol and nitrate (Zhu et al., 2006). A submerged membrane bioreactor (SMBR) can be employed for the removal of phenolic wastes of petroleum refineries. This

Table 3 Utilization of various bioreactors for phenol degradation

Reactor type	Microorganisms used	Purpose	References
Membrane bioreactor (MBR)	*Neurospora crassa*	Phenol degradation	Luke and Burton (2001)
	Sludge	Wastewater treatment	Ersu and Ong (2008)
	Mixed culture	Enhanced phenol removal	Ahn et al. (2008)
	Micrococcus luteus, *Rhizobium* sp., *Pseudomonas* sp.	Waste water treatment	Su et al. (2019)
Hollow fiber-membrane bioreactor (HFMBR)	*Pseudomonas putida*	Phenol degradation	Chung et al. (2004)
Immersed membrane bioreactor	Mixed culture	Phenol biodegradation	Marrot et al. (2006)
Fluidized bed bioreactor	*Pseudomonas putida* ATCC17484	Industrial phenolic wastewater treatment	Gonzalez et al. (2001)
Fixed bed bioreactor	*Pseudomonas syringae*	Phenol degradation	Erhan et al. (2004)
Membrane electro-bioreactor	Activated sludge	Waste water treatment	Wang et al. (2016)
Enriched nitrifying membrane bioreactor sludge	Nitrifying sludge	Phenol removal from leachate of Landfill	Boonyaroj et al. (2016)
Extractive membrane bioreactor (EMBR)	Activated sludge	Waste water treatment	Loh et al. (2016)
		Removal of organics such as phenol	Jin et al. (2017)
		Phenol degradation	Ren et al. (2017)
Two-phase partitioning bioreactors	*Acinetobacter baumannii*, *Acinetobacter johnsonii*, *Pseudomonas alcaligenes*, and *Pseudomonas putida*	Rapid and complete phenol degradation	Prpich and Daugulis (2004)
Airlift inner loop bioreactor	*Achromobacter* sp.	degradation of 2,4-dichlorophenol and phenol	Quan et al. (2004)

(continued)

Table 3 (continued)

Reactor type	Microorganisms used	Purpose	References
Fluidized bed bioreactor	Methanogens	Removal of Trichlorophenol and Phenol from synthetic toxic wastewater	Orijel et al. (2005)
	Pseudomonas sp.	Treatment of phenolic wastewater.	Vinod and Reddy (2005)
	Mixed bacterial culture	Treating aqueous phenol	Sevillano et al. (2007)
Expanded granular sludge bed (EGSB)	Anaerobic sludge	Anaerobic biological treatment of phenol	Scully et al. (2006)
Anaerobic bioreactor	Anaerobic sludge	Removal of Phenol and nitrate	Zhu et al. (2006)
Internal loop airlift bioreactor	*Candida tropicalis*	Modelling of batch phenol biodegradation	Jia et al. (2006)
Two phase bioreactor	*Pseudomonas putida* BCRC 14365	Phenol removal under extreme condition	Juang et al. (2010)
	Mixed culture	Treatment of substituted phenol mixtures	Tomei et al. (2011)
Submerged membrane bioreactor	Activated sludge	High phenol removal efficiencies	Viero et al. (2008)
Spouted bed bioreactor	*Pseudomonas putida*	Waste water treatment	El-Naas et al. (2010)
Spouted bed bioreactor (SBBR)	*Acinetobacter baumannii*	Cyclodextrin used for microbial degradation of phenol	Safont et al. (2012)
Bubble column and spouted bed bioreactor (SBBR)	*Pseudomonas putida*	Phenol biodegradation	Zuhair and El-Naas (2011)
Aerobic moving bed bioreactor	Mixed culture	Kinetic analysis of phenol	Sahariah and Chakraborty (2011)
Air pulsed bioreactor	*Trametes versicolor*	Removal of Total Phenol and color removal in hydrous ethanol vinasse	Gamboa et al. (2015)
Forward osmotic hollow fiber membrane bioreactor (FOHFMB)	*Pseudomonas putida* ATCC 11172.	Treatment of high strength saline phenolic wastewater	Praveen et al. (2015)
Packed bed bioreactor	Soybean seed coat	Phenol removal	Rezvani et al. (2015)

process is used to remove COD and TOC to 17% and 20%, respectively (Viero et al., 2008). Internal loop airlift bioreactor (ILAB) has advantages of excellent processing capability with less time and enhanced transfer of oxygen (Jia et al., 2006). Due to the movement of particle in cyclic motion, spouted bed bioreactor

(SBBR) shows fine mixing (El-Naas et al., 2010). Pulsed plate column, provided with plates piled together connected with electric motor, is suitable for easy scale up process (Shetty et al., 2007). Continuous operation of air pulse bioreactor removed phenol and COD of 80% and 60% (Gamboa et al., 2015). Bavandi et al. (2019) investigated cyanobacteria *Oscillatoria* in a bubble column bioreactor that showed removal of trinitrophenol by 12%.

5.5 Fuel Cell for Phenol Degradation

Recently, microbial fuel cell (MFC) technology is considered an extensively researched area that utilizes electroactive bacteria which degrade organic wastes for electricity production. The main advantages of MFC is that the reduction in wastes volume and conversion of that the same for energy production (Zhang et al., 2019). Different variations in MFC are produced based on methods used for electricity generation and type of functioning of the microbial population (Song et al., 2014).

The culture of *Cupriavidus basilensis* bacterial cells was used in MFC using acetate or phenol as substrate produced current of 541 and 228 mA m^{-2} (Friman et al., 2013). Buitron and Moreno-Andrade (2014) reported single-chamber microbial fuel cell with *Pseudomonas* sp. as predominant culture showed power and current densities of 49.8 mWm^{-2} and 292.8 mA m^{-2} were obtained, respectively. Zhang et al. (2017) investigated on graphite electrodes as both the anode and cathode, which operated with anaerobic bacteria for phenol degradation. Khan et al. (2018) found that 2,4,6-trichlorophenol (TCP) was bioelectrochemically treated in anodic and cathodic compartments with two identical dual-chambered microbial fuel cells with maximum power density for MFC-A with bio-anode was 446.76 mW/m^2 while for MFC-B with bio-cathode it was 1059.58 mW/m^2. Moreno et al. (2017) found that in batch-operated MFCs, phenol can be removed effectively at initial 1000 mg L^{-1} concentration. The output of current and power densities was 3444.4 mA m^{-3} and 777.8 mW m^{-3}. Hassan et al. (2018) evaluated the mixture of different microbial population showed removal of 2,4-dichlorophenol (2,4-DCP) and producing electricity.

Recently a multistage microbial fuel system was designed that has sensor anode with fermentative bacteria that produce fatty acids and hydrogen that were consumed by electrogenic *Geobacter* spp. (2.76–21.39% of the anode community), which generated the electrical signal in the sensor (Godain et al., 2020). Ullah and Zeshan (2020) studied that among various carbon substrates used with chemical oxygen demand (COD) of 2000 mgL^{-1}, acetate source showed power density and COD removal of 114 mW/m^2 and 79%, respectively, in double-chamber microbial fuel system. Xu et al. (2020) record the removal of 94% Triclosan using microbial fuel cells which produced 60 mV electricity generation.

Recently, microbial electrochemical system (MES) uses diffusion of oxygen and electrode potential for phenol degradation. In MES, population of electro active bacteria (EAB) and phenol-degrading bacteria (PDB) were increased which there by enhance degradation of phenol. Degradation of phenol upregulate four metabolic pathway such as benzoate degradation via CoA ligation, pyruvate metabolism, glyoxylate and dicarboxylate metabolism, and glycolysis or gluconeogenesis (Zhou et al., 2020).

6 Conclusion

The research works reviewed in this chapter concluded that large quantities of phenolic wastes discharged from various factories and industries add more organic pollutant to the environment if it has been not treated properly. Besides causing adverse effect on the soil and aquatic life, phenolic pollutants are also toxic to human beings. Even though many physicochemical methods were applied for phenol degradation, alternatively eco-friendly biological methods of phenol degradation are gaining significant application. Many microorganisms have been explored, optimized using statistical tool, and employed for waste water treatment containing phenolic compound. Much research efforts were put on enhancing phenol degradation using adsorption and immobilization. Immense work on bioreactor has proven an advanced bioprocess strategy for complete mineralization of phenol pollutant. Available literature on phenol degradation emphasized the needs for utilizing emerging microbial fuel system as low-cost eco-friendly energy production technique for maintaining sustainable ecosystem.

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Bioremediation of Lindane-Contaminated Soil and Water Ecosystems: A Review

T. R. Shanthi, M. Vasanthy, and A. A. Mohamed Hatha

Abstract The usage of fertilizers and pesticides has increased to meet the increasing needs of exploding population. Pesticides refer to the chemicals which are widely used for destroying the pests that could affect the produce of the agricultural fields. One such organochlorine pesticide is lindane, which is widely employed all over the world. The pesticides and fertilizers applied to the fields with an intention to destroy the pests and to increase the production respectively result in the ground water pollution due to the leaching of the compounds and pave way for surface water pollution contaminating the rivers, lakes, and reaches the sea too. Not only the water gets polluted, the soil also gets polluted. However, the rate of degradation of the compound of interest, namely, lindane is of utmost importance as it makes us understand the time for which the risk exists with the exposure to the compound.

Hence, this chapter elucidates the details on lindane-contaminated soil and water ecosystems and the remediation strategies that can be implemented. However, the natural microbiota present in the lindane-contaminated ecosystems is continuously exposed to this pesticide. So, one could expect that the microorganisms that inhabit in such polluted environments are equipped with the resistance and would be capable of removing the toxic compounds. As it is proved that the process of bioremediation is an effective strategy for the removal of many number of xenobiotics, it could be an effective solution for lindane pollution too. This chapter also intends to explain the potential of certain microorganisms which could facilitate the degradation of lindane.

Keywords Lindane · Groundwater · Soil · Pollution · Bio-remediation

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1 Introduction

The chemical compounds used for protecting the crops from the various pests are termed as pesticides. They are used as a part of agricultural produce protection strategy and as a part of health protection program aimed for the public. These farm chemicals, which are termed as the agro chemicals, aim to destroy pests and to minimize the impact caused to the agricultural products.

Pests refer to a wide variety of insects, animals, weeds, and microbes such as bacteria, fungi, and viruses which generally affect the humans and human concern. The synthetic compounds, namely, the pesticides are invented and used to check such organisms and they include rodenticides, herbicides, fungicides, and even insecticides. These compounds have become a part and parcel of modern agriculture, without which pest management is thought to be completely impossible. They are widely used all over the world to not only safeguard the product quality but also to prevent the economic losses.

Though pesticides have helped in combating the diseases caused, their application to the fields have increased the level of pollution, to the water, air, and soil too. The quality of the ground and surface water along with the soil quality has been put under threat. Hence the life depending on these ecosystems has lost their quality and is facing life-threatening diseases too. Irrespective of the impacts caused by these chemicals to the ecosystem, their usage has increased day by day, as their property of killing pest and improving the produce is alone considered worldwide. Though the usage of chemical with pesticidal activity is recorded to have occurred by 2500 BC, their usage has been the maximum during the last 50 years as per Day et al. (1997). Earlier by the seventeenth century, nicotine derived from tobacco plants has been used as an insecticide. Later by the nineteenth century, pyrethrum and rotenone obtained from plants were used as pesticides. But a marked significant contribution toward pest control was noticed with the invention of DDT. This compound had a huge importance in controlling the pest and increasing the agricultural produce during the Second World War, thereby paving a way for the wide usage of the same, following which a number of pesticides were discovered. The low cost, ease of use, and effectiveness have made them to be given the highest preference of usage. Such crop protection and increased crop yield for a longer period has thus become a truth and has thereby improved the production of food and longevity of life.

2 Classification of Pesticides

Pesticides are broadly divided into many classes and based on the chemical structure as the organochlorines, organophosphates, and carbamates. The organochlorine pesticides (OCPs) are widely used and considered to be most important.

2.1 *Organochlorine Pesticides (OCPs)*

The organochlorine pesticides are categorized as broad-spectrum chlorinated hydrocarbons but are reported to be one of the POPs. The persistent organic pollutants (POPs) refer to the chemicals of global concern, as they could be persistent in the environment for a longer time and could be transported to a long range and has the possibility to bioaccumulate and undergo biomagnification too. Such chemicals were used with higher preference from 1940 in the agricultural fields and also to control the deadly vector, namely, mosquitoes. Since then, these chemicals are used in many countries. Organochlorine pesticides are also highly persistent in the environment.

Normally the chlorinated derivatives of diphenyl ethane namely DDT, DDE, and DDD are all organochlorine pesticides. Even the group of hexachlorocyclohexane and hexachlorobenzene falls under this category. Aldrin, heptachlor, endrin, etc., fall under cyclodiene, and toxaphene, dodecachlorine, and chlordecone were included under chlorinated hydrocarbons. The organochlorine pesticides are reported to be highly stable and are found to resist chemical and biological degradations. Even DDT is reported to undergo degradation for a period of 4–30 years and certain other compounds were found to exist as such in the soils even after a long time from the period of application.

When the usage of different pesticides is considered, about 40% of the pesticides used is reported to belong to organochlorine chemicals. And due to the wide range of toxicity and on the basis of economy, the insecticides highly preferred are aldrin, dieldrin, DDT, and hexachlorocyclohexane, which are some of the highly preferred pesticides in Asia (Gupta, 2004).

2.2 *Organophosphate Pesticides*

These are esters of phosphoric acid and they are the group first discovered by chemists who originated from Germany by about 1983. Examples of these pesticides include parathion, malathion, temephos, and chlorpyrifos. Their toxicity against various animals, mammals, and insects made them to be used not only against pests but also in warfare as chemicals for destruction. Till about 1930–1940, these pesticides were proved to be highly toxic to even mammals, but later these compounds were resynthesized and were made to be target specific, which was preferred by the users. These pesticides were reported to be neurotoxic and their mode of action involves the inhibition of acetylcholine esterase in an irreversible manner. The effect is found to be on the nervous system as the acetylcholine esterase is a key enzyme involved in the functioning of CNS (Singh & Walker, 2006). These insecticides deactivate the acetylcholine esterase enzyme by binding and deactivating or inhibiting the enzyme. Hence, the acetylcholine (ACh) levels in the neuromuscular junctions get elevated in its content (Kwong, 2002).

2.3 *Carbamates*

By 1950s, yet another organic compound with broad spectrum of biological activity was introduced and were used for the pest control even today. These compounds were the carbamate esters prepared from carbamic acid. Such carbamate pesticides were characterized with higher polarity, toxicity, solubility in solvent like water, and of course with thermal instability. Examples of carbamates include terbucarb, oxamyl, aldicarb, and carbaryl. The thiocarbamates include benzimidazole-, *N*-methyl-, *N*-phenyl-, and carbamates. The carbamates were reported to differ in certain properties such as their persistence and toxicity to mammals. Hence they were found to undergo hydrolysis, oxidation, photolysis, biodegradation, and even biotransformation and get converted into different products whose stability is relatively lesser. These carbamates were found to undergo degradation after certain weeks or months. Even these pesticides affect the enzyme, acetylcholinesterase, which is involved in the regulation of acetylcholine and hence disturb the nervous system followed by the accumulation of acetylcholine. This reaction causes hypersalivation, lacrimation, sweating, and convulsions. But fortunately reports exist to prove that the effects of the enzyme are of course reversible.

3 Effects of Pesticides

Though the pesticides were invented to target the pests that are toxic to agricultural produce, they also get released into the environment and thereby affect the organisms of the food chain and of the food web. The possible routes by which the human beings get exposed to pesticides include ingestion, inhalation, and even through the skin which is reported to result in both acute and chronic health issues. The impacts on health normally range from acute effects to certain chronic effects such as cancer, reproductive disorders, and even developmental disorders. Such pesticides were found to be highly carcinogenic, and their usage has contaminated the air, water, and soil ecosystem. These chemicals have longer half-life, their residual metabolites are toxic, and major part of the chemical reaches the non-target organism. The comparatively higher usage of pesticides has induced the resistance toward the widely used pesticides in the natural soil organisms. Reports exist for confirming the pest resurgence too. Such pesticides were studied for their bioaccumulation and biomagnification processes too.

Pesticides applied to the soil are found to pose threat to the soil microbial population. Some of the pesticides applied have longer persistence and thereby find its way in the food chain and food web, affecting many different organisms. The persistence of pesticides in soil depends upon their characteristics such as their chemical properties and the ease with which they react with the soil constituents. The pesticides could be persistent in soil for a week to several years. But, the pesticides finding its way into the soil affect the soil microbes and also the plant growth get affected by the excess usage of the pesticides.

Soil microorganisms gets actively involved in the biogeochemical cycling of S, C, N, Fe, O_2, P, etc. When the pesticides affect such microbes, the nitrogen fixation gets affected, and thereby the nitrogen balance gets affected, and thus the soil loses its fertility. Such imbalance in due course impacts the soil microflora and alters the ecological balance too. As the role of microorganisms in influencing the soil fertility and crop productivity is well known, it becomes more important that the natural microbiota of the soil is to be taken care and the toxicity of pesticides must not affect the indigenous organisms of the soil to ensure the soil fertility.

On consuming the pesticide-contaminated food, the wild life gets poisoned indirectly and sometimes they get exposed directly to pesticides. The beneficial natural organisms and other living organisms also get adversely affected by pesticides. At times, the ordinary pests get destroyed, but this paves way for the secondary pests to develop, which needs other powerful treatments in order to safeguard the crops. Though there exists certain benefits due to pesticides, they pose considerable hazards to the environment.

4 Degradation of Pesticides in the Environment

Whether we prefer or not, the pesticides applied targeting the pests find their way to the soil and undergo various processes. The pesticides reaching the soil undergo transport and degradation. The transport of the chemicals down the soil profile occurs through leaching, their transport across the soil happens and the pesticides reaches the runoff, and also they reach the atmosphere due to their possibility of volatilization. On discussing the degradation, we could include the chemical reactions which result in breaking down of toxic chemical form into nontoxic compounds and sometimes into less toxic forms too. This breaking down is reported to be effected by chemicals, microbes, or in presence of light termed as photodegradation. Comparatively the photodegradation is reported to degrade the pesticidal residue present in the soil and even the pesticides present on foliage and even in air. Such photodegradation is normally influenced chiefly by the sunlight intensity. Whereas the chemical degradation of the pesticides involves not the living organisms but is influenced by the temperature, moisture, pH, and even certain characteristics such as adsorption. The light, heat, and certain other properties may act as a limiting factor thereby affecting the rate of chemical degradation of pesticides. Contrarily, the degradation of pesticides which depends on the activity of the involved microbes such as bacteria, fungi, and any other suitable microbes happens as the microbes utilize the pesticides as a source of energy and convert them into less toxic or at times nontoxic compounds.

Such microbes inhabit the soil and they actively take part in the biodegradation of the toxic pesticides. However, the rate of pesticide biodegradation in the soil is determined by the characteristics of the microbes including the physiology of microbes to tolerate the pesticides and also depend on their capability to proliferate in presence of the pesticides and is also determined by the physicochemical characteristics of the soil such as the percentage of moisture, pH, content of organic matter, temperature, and the availability of aeration. Compared to different types of pesticidal degradation, biodegradation due to microbes is reported to be a major process favoring the degradation.

Whatever may be the means of degradation of pesticides, the process is commonly termed as "remediation." Hence, remediation refers to the physical, chemical, or biological process intended to reduce the concentration of pesticides from a contaminated site. Remediation processes generally fall under two categories: controlled and uncontrolled. Controlled processes are those where variables that affect remediation can be initiated, maintained, and terminated. Uncontrolled processes typically involve in situ decontamination using processes that are initiated or enhanced but which are much less controlled.

There exist various remediation processes such as incineration, thermal desorption, land farming, photochemical processes, biostimulation, phytoremediation, and direct and radical oxidative processes. Of all these, bioremediation is one of the highly preferred strategies for the cleanup of contaminated aquatic ecosystems and contaminated soils. In recent years, the quest for clean environment has stimulated interest in finding an alternative method of waste disposal, pollution reduction, and decontamination of toxic residues. Biological remediation of ecosystem contaminated with toxic chemicals is an efficient and preferred technology due to its higher efficiency.

4.1 Bioremediation

Bioremediation refers to the process that is initiated and performed by the biological agents. These biological agents perform the degradation and help in the transformation of the contaminated area and restores the original environment. These bioremediation processes work based on certain principles. This process as said earlier, is based on the microorganisms and based on their enzymes. Mostly these microbes are indigenous and their growth is enhanced by the addition of required nutrients and at times due to the optimization of various conditions such as pH, temperature, and nutrients. Such modification and optimization of the required conditions enhance the process of bioremediation resulting in degradation of contaminants. However, bioremediation is found to be effective than the physical and chemical treatment technologies for the removal of diluted contaminants. Microbes have the capacity to degrade a wide range of synthetic compounds. Bioremediation technologies are widely classified as in situ and ex situ. In situ technology aims to treat and degrade the contaminants on the contaminated zone itself, whereas the ex situ technology aims at the degradation of contaminants at a treatment facility meant for the same. Further the in situ bioremediation happens by two methods. Intrinsic bioremediation involves the indigenous microbes present in the contaminated zone, and the accelerated bioremediation involves the addition of either necessary substrate or nutrients to effect the process resulting in the cleanup of the contaminated zone.

The various in situ bioremediation process available are as follows:

- Bioventing: It is the most preferred in situ treatment technology. This process involves the addition of air and nutrients to the contaminated zone to support the indigenous organisms.
- In situ biodegradation: As the name implies, it is targeted to degrade the contaminants with the indigenous organism by the adequate supply of nutrients and oxygen too.
- Bioaugmentation: Augmentation of biological organisms, either indigenous or exogenous, for the decontamination of the polluted sites.
- Biosparging: Biosparging refers to the injection of air under pressure below the water table in order to enhance the groundwater oxygen concentration to improve the rate of contaminant biodegradation.

The various ex situ bioremediation process available are as follows:

- Land farming: This technique involves the spreading of the contaminated soil on a prepared bed, followed by a periodical tilling until the required degradation of the contaminants happen.
- Composting: Composting of the contaminant flooded soil is done by permitting the waste to undergo composting by the addition of organic wastes such as agricultural wastes.
- Bioreactors: Bioreactors are employed for the ex situ treatment. This is employed for the treatment of both contaminated soil and water.

When the environmental factors and conditions were favorable for the microbes, especially bacteria and fungi, the process of degradation occur. These microbes could degrade the pollutants when their physiological and metabolic capability supports the degradation of pollutants. Currently, we are aware of the disadvantages of conventional waste management landfilling and incineration practices. With this information, we could appreciate the bioremediation process which is characterized with lesser disadvantages. It is claimed as a safe remediation strategy for both soil and groundwater as it involves the immobilization of contaminants and is found to be economical in comparison with yet other technologies.

Normally the in situ bioremediation is preferred as it is less expensive and also the damage to the contaminated site is comparatively small. This process helps in the complete elimination of the wastes and is also found to be widely accepted among the users. Bioremediation can be done on site, and it is economical along with less disturbance to the site even. This process has helped to permanently eliminate the waste and has earned wide acceptance among the users too. Another important aspect is that it can be added as an additional treatment along with chemical or other physical treatments. Any method has its own limitations and advantages. The foremost limitation focuses on the contaminants that pose challenge as they are not biodegradable. These types of contaminants include radionuclides, mostly heavy metals and certain chlorinated compounds. Yet another limitation is that the process could result in toxic metabolites. But it is certain that the bioremediation process needs optimization of parameters before being implemented in the contaminated sites. Some of the major factors which influence bioremediation include microbial characteristics, environmental conditions, and bioavailability of pollutants. Even though bioremediation has its limitations, it has emerged as a promising technology for pesticide degradation.

5 Bioremediation of Lindane-Contaminated Soil and Water Ecosystems

Organochlorine pesticides, which are anthropogenic contaminants with ubiquitous distribution, cause severe damage to the ecosystem, and as they are resistant to degradation, these chemicals got accumulated in the members of the food chain. Large-scale application of these pesticides has successfully boosted the production of food grains and vegetables, but their residues have brought unimaginable health issues to human and irreversible damage to the ecosystem. The chemical stability of these organochlorine pesticides reflects their persistence in the environment, and the lipophilic nature contributes to their tendency to be magnified in the lipid fractions in the tissue. DDT was the major pesticide used in different agricultural fields. Since the ban for the usage of DDT began in 1940s, the usage of a pesticide, namely, lindane started.

5.1 Lindane

The organochlorine chemical lindane refers to the γ-isomer of hexachlorocyclohexane, in short γ-HCH. It was first synthesized in 1825, although it was only in 1940 Dr. Teunis van der Linden, a Dutch scientist, understood its insecticidal properties (Hardie, 1964). Later by 1945, the insecticide was started to be prepared commercially. This insecticide is prepared by chlorinating the benzene molecule in presence of the UV light. Actually, this process results in technical grade HCH, with stereoisomers, eight in number termed as α- to θ-HCH based on the chlorine atoms position. On comparing the fraction isomers present in the reaction mixtures, it was understood that a major proportion, that is, about 55–80% was α isomer, 5–14% was β isomer, about 8–15% was the γ isomer, about 2–16% was δ isomer, and about 3–5% was ε isomer, respectively. Other isomers, three in number are found in trace amounts. Normally the chlorine atom position varies in the isomers. Commercial lindane (>99% 8-HCH) is purified from technical grade HCH by multiple extractions with methanol.

Of the highly preferred and used organochlorine pesticides, hexachlorocyclohexane and lindane occupy a prominent position, and their usage all over the world is estimated to be 7,20,000 and 5,50,000 tons per year, respectively (Dominguez et al., 2018). Around 4,50,000 tons of lindane is reported to be used for agricultural purposes before 20–50 years. It was during the 1960s and the early 1970s, peak production of lindane occurred.

Further, about 150,000 tons of lindane was used in various sectors such as in forestry, pharmaceuticals, and even for certain livestock (Vijgen, 2006), thereby the global figure reaching about 600,000 t. The γ-isomer of HCH had insecticidal properties and so by 1950s in certain countries, well-known companies started isolating such isomer and was sold under the brand name of lindane. This isomer was found to be superior to other isomers as they resulted in crops, fruits, and vegetables which are inedible as they had organoleptic property. In India during 1997, a ban on HCH was effected, and later the production and usage of lindane commenced.

5.2 Applications of Lindane

Lindane has numerous applications, because of its broad range of action. It was used on crops, in warehouses, for seed treatment, and for the protection of public health. In domestic and agricultural sector, lindane has also been used for livestock and domestic pets in different forms. Lindane is further used even in personal care products such as lotions, creams, and shampoos to check the growth of lice and mites.

5.3 Effects of Lindane

Though the range of activity of lindane and technical HCH was quite high, their usage has resulted in the contamination of the entire biosphere. Enough publications exist to prove the health effects of HCH (γ isomer) on living organisms and proof exist to explain the pesticidal residues in water, air, soil, and also in animals and plants (Tao et al., 2005). However, the lipid solubility and stability of lindane has made to categorize it to be a chemical which is highly toxic and persistent. Lindane is also found to get spread to longer distances and cause higher level of contamination.

The toxicity of lindane has made the chemical to get a score of 25, based on its toxicity, and it is assigned a score of 5 as it registers impact on all the categories of environment. The high score corresponding to the toxicity of the chemical to human makes it to be placed in Class Ia or Ib, and it is assigned the name of danger/poison. As discussed earlier, lindane not only affects the living organisms, it also affects the environment. Even the ingestion of lindane is found to cause acute toxicity resulting in certain symptoms such as seizure, diarrhea, headache with dizziness, and even irritation of the lungs, throat, and nose. Whereas the long-term exposure is said to result in chronic toxicity including certain discomfort in gastrointestinal tract, cardiovascular, musculoskeletal and nervous systems, and at times death too. Evidence of such death has been recorded by 1953 (Nolan et al., 2012).

Basically, residues of lindane find their way through the food chain, and due to its lipid solubility it is toxic to animals and human beings as it can get infiltrated and gets accumulated in the brain, breast milk, and in organs rich in fat in particular. It is also found to exhibit carcinogenicity, genotoxicity, teratogenicity, and is also an endocrine disruptor (Muniz et al., 2017). Its carcinogenic property has caused breast, lung, stomach, colon, rectum, bladder cancers (Abolhassani et al., 2019). Agrahari et al. (2019) have reported that lindane acts on γ-aminobutyric acid (GABA) receptor/chloride ionophore complex, leading to CNS excitation and making paralysis, convulsion, and even death possible.

5.4 *Occurrence of Lindane*

Though, due to its wide spread toxicity, lindane is either banned or restricted in about 40 different countries, its usage is declared to be illegal in about 65 countries, but it is often used under certain exemptions. Unfortunately, India takes a leading role in both consuming and producing lindane. Hence it is very clear that it is indiscriminately produced in industries and is used at a higher rate (Abhilash & Singh, 2010). Kanoria Chemicals & Industries Limited and India Pesticides Limited (IPL, Lucknow) are reported to produce 1300 t per annum. However, Kanoria Chemicals & Industries Limited is reported to end up the lindane production, and the other company is found to continue the production (Abhilash & Singh, 2009). As per the Rotterdam Convention on Prior Informed Consent, lindane is listed as moderately hazardous by WHO and its trade is restricted and even regulated.

Though, lindane is categorized as a pesticide which deserves restricted usage by the Central Insecticide Control Board, it is not strictly followed in the market, restricting its utilization. It is on May 10, 2009, the fourth meeting of the Conference of Parties (UNEP, 2009) was conducted and about nine new persistent organic pollutants (POPs) were accepted, following which they were included in the Stockholm Convention of POPs list on August 26, 2009. Under this convention, the production and usage of lindane were banned too. Out of the nine POPs, three POPs were the α, β, and γ isomers of HCH (lindane). It was further understood that the stockpiles of waste contain lindane and hence contaminate the soil too (Vijgen et al., 2019). As lindane is highly used in the past decades, it is found in different quantities at the solid waste dumping sites and also in agricultural areas (Franciskovic-Bilinski et al., 2005). Hence, it becomes utmost important to clean up the contaminated soil as well as the water ecosystem. HCH isomers were found in different countries all over the world including Brazil, Canada, China, Germany, Greece, India, Spain, the Netherlands, and the United States (Kumar & Pannu, 2018). In Kerala, India, one of the important pesticides used in the food crops is lindane, and it is actually permitted for restricted use only. However, it is consumed at a higher rate, and its annual increase in the consumption of lindane is as high as 107.54% (Devi, 2010).

The property which makes lindane to remain for a longer time in the soil matrix is its ease of interaction with the soil organic matter and its lower solubility in water (7 mg per L). As lindane is one of the highly used pesticide throughout the world, we need to understand the factors which control its distribution and fate in the soil such as volatilization, loss along with the surface runoff and also by the biodegradation. Lindane on application on water bodies, for the control of mosquitoes, finds its way into the water and from the manufacturing plants finds its way into the atmosphere too. Thus, lindane reaches soil, water, and atmosphere through wet, dry deposition and by gas exchange across the interface between air and water. Though the vapor pressure of lindane is high, its loss from the surface water through evaporation is found to be insignificant. This loss occurs during the warmer months. However, the biodegradation of lindane is reported to be the possible mechanism for its removal from aquatic systems. Its half-live period for its degradation in different aquatic ecosystems range from 3 to >300 days (Padma et al., 2003). Beyer and Matthies (2001) has reported that the half-life for lindane as 708 days in soil and 2292 days in water. The derivatives of HCH from aquatic systems contaminated with lindane in central Germany was determined by Berger et al. (2016). The surface and ground waters are polluted as the lindane contaminants have leached underground for decades.

6 Degradation of Lindane

Certain properties of γ-HCH, such as its toxicity and persistence, enable us to understand the need for better technologies to make the soil and water contaminated with lindane free from the pesticidal contamination. Though there exist certain physical, chemical, and biological methods to degrade lindane, there exist certain limitations. The process such as ozonation could help in the degradation of lindane, but the rate reaction constant with ozone is reported to be very low (Ikehata & Gamal, 2005). Further, the microwave-induced oxidation, chemical oxidation, electro oxidation, and incineration are certain physicochemical methods available for lindane degradation, but these methods require expensive infrastructure and also result in generation of toxic compounds during the process (Huang et al., 2019). Compared to the above mentioned treatments, the microbe-mediated degradation of lindane is both cost-effective and environmental friendly (Bhatt et al., 2019). The treatment utilizing microbes is now a proven technique on comparison with other technologies, for the biodegradation of contaminants including pesticides in polluted soil and solid waste too. However, it becomes mandatory to isolate and understand the potential of the microorganisms to bioremediate the polluted sites. The possibility of isolating a diverse group of microbes offer a positive chance for the transformation and mineralization of the contaminants into metabolites which are relatively less toxic. The success of the biodegradation technology purely depends on the microbial strain and its efficiency to degrade the contaminants, namely, the pesticide residues. The rate of degradation also plays a predominant role in decontaminating the polluted sites.

Halogenated compounds were found to be the growth substrate promoting the growth of different microbes. During the microbial degradation of the halogenated compounds, the removal of halogen atom is effected. The removed halogen atom is usually replaced by either hydroxyl or hydrogen group. During such reaction, less chance is found to exist for the formation of toxic intermediates. In both aerobic and anaerobic soils, contaminated with lindane, the possibility of biodegradation by microbes such as aerobic and anaerobic bacteria, cyanobacteria, algae, fungi is reported. Though the lindane biodegradation is predominantly an anaerobic process, certain isomers of HCH is found to get degraded under aerobic condition. The enzyme-mediated aerobic or anaerobic bacterial degradation of lindane is well studied, and only few bacterial species were reported to mineralize lindane to either nontoxic and less toxic compounds.

6.1 Aerobic Degradation

Reports exist regarding lindane biodegradation under aerobic conditions. Senoo and Wada (1989) reported the aerobic degradation of HCH using *Pseudomonas paucimobilis* SS86 isolated in Japan by about 1990. Imai et al. (1989) reported *Sphingomonas paucimobilis* UT26, a nalidixic acid-resistant strain of *Pseudomonas paucimobilis* SS86 to degrade isomers of HCH aerobically. Further a HCH-degrading species of *Pseudomonas* was isolated especially from the Indian sugarcane fields (Sahu et al., 1990). *Pseudomonas* sp. (Tu, 1976) and *Escherichia coli* (Francis et al., 1975) were isolated and identified to convert the γ-isomer of HCH into 2,3,4,5,6-pentachloro-1 cyclohexene (g-PCCH). A species, *Rhodanobacter lindaniclasticus,* of a new genus *Rhodanobacter,* was identified for the strain RP5557T (Nalin et al., 1999). During the HCH biodegradation, the role of *lin* genes was encoded during the characterization of aerobic HCH biodegradation in *Sphingomonas paucimobilis* strain UT26 (Miyazaki et al., 2006). Nagasawa et al. (1993) identified and stated about the bacterial species *Sphingomonas paucimobilis* SS86, as capable of utilizing γ-isomer of HCH as carbon and energy source needed for its survival. The lindane (γ-isomer of HCH) degradation using bacterial consortia isolated and identified from the sediment collected from the polluted site of the Suquia River, Cordoba, Argentina, is reported. Evaluation of the ability to grow and to degrade γ-isomer of HCH present in mineral salt medium (100 mg/L) by the bacterial strain *Arthrobacter citreus* BI-100 was done (Datta et al., 2000). Nagata et al. (2007) have extensively studied the aerobic lindane degradation employing *Sphingobium japonicum* UT26. Many of the strains such as UT26 and also other strains similar to the strain mentioned use lindane as a sole carbon and energy source aerobically. Cuozzo et al. (2017) reported major reactions involved during the lindane microbial degradation which are hydroxylation, dehydrogenation, dehydrochlorination, dechlorination, and even mineralization. Dechlorination of lindane is reported to involve the enzymes such as dehydrochlorinase (LinA), halidohydrolase (LinB), and dehydrogenase (LinC). During such reaction, 1,2,4-trichlorobenzene (1,2,4-TCB), 2,5-dichlorophenol (2,5-DCP), and 2,5dichlorohydroquinone (2,5-DCHQ) are found to be the end products following the lindane degradation. And the conversion of lindane to 2,5-DCHQ is called as the upstream pathway, and its metabolization is referred to as downstream pathway (Endo et al., 2005). The conversion of 2,5-DCHQ to β-ketoadipate always involves ring-cleavage dioxygenase (LinE), reductive dechlorinase (LinD), and maleylacetate reductase (LinF). The succinyl-CoA: 3-oxoadipate CoA transferase (LinGH) and β-ketoadipyl CoA thiolase (LinJ) help to convert β-ketoadipate into acetyl-CoA and succinyl-coenzyme A (CoA). The TCA cycle involves the metabolization of the above mentioned compounds (Camacho-Pérez et al., 2012). Cuozzo et al. (2017) explained the lindane conversion into 3, 4, 5, 6-tetrachloro-1-cyclohexene (TCCH), pentachlorobenzene (PCB), and pentachlorocyclohexene (PCCH).

6.2 Anaerobic Degradation

The in situ degradation of pesticides becomes possible by employing the proper indigenous microbial strain. Even the possibility of emergence of autochthonous microbial populations tolerable to the contaminants exists with time. There are many strains reported to possess the capability to degrade lindane, but the degree of degradation varies. The most commonly observed phenomenon is its partial degradation to its metabolites and not the complete degradation. *Pseudomonas paucimobilis* commonly referred to as *Sphingomonas paucimobilis* isolated from the plant roots is the most reported bacterial stain to degrade lindane.

Bacterial strains such as *Rhodanobacter lindaniclasticus, Pandorea* species, and *Escherichia coli* were known to degrade lindane with a varying capacity ranging from 10% to 90%. Different species of *Bacillaceae* and *Enterobacteriaceae* were reported to degrade lindane in an anaerobic environment. LIN-1 and LIN-3, two bacterial strains that could use γ-isomer of HCH as a source of required carbon and energy, were isolated from the enrichment culture (Okeke et al., 2002). The same isomer was also reported to be degraded in an anaerobic condition by different bacterial cultures isolated from sediments of lake, sludge, and soil flooded with water and also by *Clostridium* spp. (Ohisa et al., 1980). Not only individual bacterial strains even consortia of bacterial species were reported to degrade lindane in an anaerobic environment (Silvia Pesce & Daniel Wunderlin, 2004).

Bashir et al. (2018) have also stated that the possibility of lindane degradation exist in both aerobic and anaerobic conditions and they differ from each other. The main mechanism that which occur during the transformation of lindane to chlorinated compounds is reported to be dichloroelimination and dehydrochlorination. This process is found to occur under anoxic condition prevailing in the sediments of the aquatic ecosystem normally by two different pathways (Lal et al., 2010).

Dichloroelimination of lindane is found to result in 3, 4, 5, 6-tetrachloro-1-cyclohexene (γ-TCCH) and later 5,6-dichlorocyclohexa-1,2-diene is formed due to two dichloroelimination, and later chlorobenzene is reported to be formed as a result of dehydrochlorination reaction (Saez et al., 2017). Quintero et al. (2005) reported that yet another anaerobic degradation pathway produces not only pentachlorocyclohexene (PCCH) but also 1,2-dichlorobenzene (1,2-DCB) and 1,3-dichlorobenzene (1,3-DCB).

6.3 Potential Lindane-Degrading Bacteria

Either structural changes or complete degradation of lindane molecule occurs through physical and chemical interaction between the compound and the bacterial strains. *Microbacterium*, *Paracoccus*, *Achromobacter, Burkholderia*, *Rhodococcus*, *Chromohalobacter, Kocuria, Staphylococcus*, *Streptomyces*, *Arthrobacter, Azotobacter*, *Sphingomonas*, *Xanthomonas*, *Pseudomonas*, *Pseudoarthrobacter*, *Klebsiella, Pleurotus*, and *Actinobacteria* were some of the reported lindane-degrading bacterial strains (Kumar & Pannu, 2018).

The degradation of lindane by various bacterial strains was reported not to occur at same rates but the rate varies. A rhizospheric bacteria *Microbacterium* spp. strain P27 from *Phragmites karka* was isolated by Singh and Singh (2019), and the organism was found to degrade about 83% of lindane when its concentration was about 50 mg/L. But yet another study reported the possibility of 90% degradation of lindane when its concentration was about 100 mg/L after a time period of 8 days with *Paracoccus* sp. NITDBR1 was isolated from the Manipur agricultural fields (Sahoo et al., 2019). Similarly, *Burkholderia* spp. strain IPL04 isolated from the pesticide-contaminated site using enrichment culture method was reported to degrade 98% lindane in about 8 days (Kumar, 2018). Further, the degradation of lindane by both in situ and ex situ methods with different concentrations of (10 and 100 ppm) lindane by *Azotobacter chroococcum* was studied by Anupama and Paul (2010) and observed that the lindane was completely degraded by the end of the period. And about 47% mineralization of lindane in sediment of aquatic systems was studied by Kalsch et al. (1998).

Even the strain isolated from agricultural field, namely, *Alkaligens faecalis* is reported to degrade the γ-isomer of HCH (Gupta et al., 2000). Manickam et al. (2006) isolated and characterized the γ-isomer of HCH degrading *Microbacterium* sp. strain ITRC1. The authors also isolated *Xanthomonas* sp. which degraded γ-isomer of HCH by successive dechlorination (Manickam et al., 2007). Benimeli et al. (2008) have studied the degradation of lindane using *Streptomyces* sp. M7, and the authors have studied the impact of the same on the growth of *Zea mays*.

Kiran Bala et al. (2010) have isolated *Sphingobium quisquiliarum*, P25 (T), a HCH degrading yellow-pigmented bacteria from a HCH-contaminated site located in North India. Similarly, Dadhwal et al. (2009) isolated another yellow-pigmented bacterium, *Sphingobium chinhatense* capable of degrading the compound. For cold regions, *Sphingobium indicum* B90A was reported to be an apt candidate for degrading γ-isomer of HCH from soil/waters thereby implementing the bioremediation of the contaminated site (Zheng et al., 2011). Abhilash et al. (2011) have studied extensively and have reported the degradation potential of bacterial strains isolated from the rhizosphere. They are identified as *Staphylococcus equorum* and *Staphlococcus cohnii* along with *Kocuria rhizophilla* and *Microbacterium resistens*.

Actinomycetes are potential organisms for bioremediation of lindane. Benimeli (2004) has subjected the wild-type *Streptomyces* strains isolated from river sediments to degrade lindane, and the species has shown tolerance to the compound and has degraded the same. Cuozzo et al. (2009) have further reported the dechlorinase activity of *Streptomyces* sp. M7 along with the end products obtained as a result of catabolism of lindane. The *Streptomyces* sp. has resulted in lindane degradation with no intracellular accumulation under aerobic condition. During such process, no accumulation of products obtained after lindane transformation is noticed (Benimeli, 2004), though report exists to prove that lindane could be degraded by both individual actinomycete and by a mixed consortia under laboratory conditions. Fuentes et al. (2010) have reported the capacity of mixed cultures of Actinomycetes to be more suitable for the same due to their diversity enhancing the survival of the organisms facilitating the biodegradation of the contaminant. Thereby the authors suggest Actinomycetes as the potential candidate for lindane degradation.

6.4 Functional Enzymes Involved in Lindane Degradation

Dehalogenases were reported to be the functional enzymes that degrade the halogenated compounds. These enzymes perform the dehalogenation of the compounds through the cleavage of the bond between carbon and chlorine atoms effectively. As lindane has about 6 Cl- atoms per molecule, dechlorination is found to be the important step during the degradation of the same. However, the enzymes reported responsible to carry out the dehalogenation are the dehalogenases such as (LinA) dehydrochlorinase, reductive dechlorinase (LinD), and (LinB) dehalogenase (Nagata et al., 2007). Further, dehalogenases were stated to include certain other enzymes such as maleylacetate reductase (LinF), ring cleavage oxygenase (LinE), and dehydrogenase (LinC).

The enzymes such as Lin A (dehydrohalogenase class) along with LinB and C are reported to follow the upstream pathway during the lindane degradation (Cuozzo et al., 2017), and LinA is found to mediate the dehydrochlorination steps. The authors also reported that Lin A requires no cofactors for catalyzing the degradation. Janssen (2004) has reported that the enzyme LinB belongs to α/β-hydrolase family and is a haloalkane dehalogenase enzyme and reported to possess wider specificity for substrate. This enzyme is found to catalyze lindane degradation through dehalogenation. Further this enzyme is reported to dechlorinate 1,3,4,6 tetrachloro-1,4-cyclohexadiene (1,4-TCDN) to 2,5-dichloro2,5-cyclohexadiene-1,4-diol (2,5-DDOL) during the lindane aerobic degradation (Jan et al., 2005). Rinku et al. (2005) have reported the activity of 28 kDa enzyme LinC, as a member of dehydrogenase family and it is 2,5-DDOL dehydrogenase. Further NAD-conversion to NADPH through the hydride transfer is explained to be general catalytic mechanism which also includes the conversion of 2,5-DDOL to 2,5-dichlorohydroquinone. But reports do not exist regarding the third upstream pathway enzyme, LinC or about certain downstream pathway proteins.

6.5 Role of Algae in Lindane Degradation

Use of algae for bioremediation is effective as algae is autotrophic and has low nutrient requirements. *Cyanobacteria*, *Anabaena* sp. strain PCC7120, and *Nostoc ellipsosporum* were reported to degrade lindane into trichlorobenzenes (both 1, 2, 3 and 1, 2, 4). This reaction was found to involve penta chlorocyclohexene as an intermediate. Kuritz and Wolk (1995) reported the enhancement of the process due to nitrate ions. El-Bestawy et al. (2007) reported that certain cyanobacterial strains could degrade lindane at a faster rate. Kumari et al. (2002) identified cyanobacterial species isolated from two lakes in Egypt namely, Qaroun and Mariut, and exposed the organisms to about 5–10 ppm of lindane for 7 days, and the degradation potential of the organisms both individually and as a mixture was found. This study thus highlighted the possibility of using cyanobacterial strains for lindane degradation. González et al. (2012) reported the ability of microalgae to degrade lindane. Lindane and diflubenzuron degradation using a macroalgae *Laminaria digitata* was studied by Anacleto et al. (2017).

6.6 Role of Fungi in Lindane Degradation

The efficiency of fungi to degrade lindane from soil and aquatic systems was also studied extensively and was found to be suitable for the same. Nagpal et al. (2008) substantiated the possibility of utilizing fungi for lindane degradation due to the availability of larger surface area available for absorption and also the mycelia is reported to enhance deeper penetration of the compound. The white rot fungi *Phanerochaete chrysosporium* was reported, and it was published for the first time to degrade lindane by Bumpus and Aust (1987). Singh and Kuhad (2000) studied the ability of two different white rot fungi *Cyathus bulleri* and *Phanerochaete sordida*, to degrade the γ-isomer of HCH. On comparing the efficiency of the two species to degrade Lindane, *Cyathus bulleri* was found to be more efficient than *Phanerochaete sordida*. Not only these species, further Rigas et al. (2005) reported *Pleurotus ostreatus* and the authors Rigas et al. (2007) further evaluated the bioremediation capacity of polypore fungus, *Ganoderma australe* to degrade lindane doped in a mixture of sandy soil and wheat straw. Tekere et al. *(*2002) reported a subtropical white rot fungus *DSPM95* to possess the ability for lindane degradation.

A non-white rot fungus, *Conidiobolus* 03-1-56, a phycomyceteous fungus isolated from the degraded litter was reported to degrade lindane on the 5th day of incubation (Nagpal et al., 2008). Further, *Fusarium poae* and *Fusarium solani* were reported to tolerate and use lindane as a source of carbon and degrade the same. These two species were found to possess higher biodegradation potential when compared with the other fungal isolates identified from the same contaminated soil (Sagar & Singh, 2011). Kaur and Kaur (2016) investigated the capability of a white rot fungi isolated from rice bran substrate, namely, *Ganoderma lucidum* GL-2 to degrade lindane by about 76% after about 28 days. Fungal species isolated from the *Agave tequilana* leaves was *Fusarium verticillioides* AT-100, a non-white rot fungus was found to degrade lindane and was reported to produce benzoic acid derivatives (Guillen-Jimenez et al., 2012). *Candida* sp. *Rhodotorula* VITJzN03 identified from a field cultivated with sorghum was found to possess lindane-degrading ability and enzyme system involved in the degradation process was elucidated and was reported (Salam et al., 2013).

6.7 Factors Affecting Lindane Biodegradation

For bioremediation to be successful, there is the influence of a number of factors. The factors affecting degradation of lindane are given in the following section.

Effect of pH on Lindane Degradation

Environmental factor such as pH may affect the growth of microorganisms and their degradative abilities. It is an important factor which affects the lindane degradation and influences the survivability of microorganisms. The degradation of lindane is optimal at a neutral pH; however, the process may be slowed down with a considerable change in pH followed by the reduction in the growth of degraders. Accordingly, the growth of two different novel strains, namely, *Staphylococcus* sp. DAB-1 W and *Kocuria* sp. DAB-1Y in lindane-containing medium was found to be optimum at neutral pH (Kumar et al., 2016). Elcey and Kunhi (2010) studied the effect of pH on the degradation of HCH and understood that the degradation was optimum at a pH of 6–8. The acclimatized consortium was found to possess the degradation potential at a wide range of pH from 3 to 9. Further an increase in pH toward neutrality, the microbial survival was found to improve gradually. A reduction in the microbial population was noticed at pH 4, and at the same acidic pH, even with a consortium of ten microorganisms, no degradation of lindane was noticed (Murthy & Manonmani, 2007). Okeke et al. (2002) also studied the effect of pH on the lindane degradation potential of *Pandoraea* sp. and reported pH 9 to be facilitating the organism growth and degradation too. The efficiency of *Streptomyces* sp. M7 to degrade lindane at different pH was studied, and it was determined that the pH of 5 and 9 could not facilitate the degradation (Benimeli et al., 2007). About 70%

biodegradation was noticed at a pH 7 and in an yet other experiment the *Rhodotorula* sp. VITJzN03 was found to degrade lindane at an optimum pH of 6 (Salam et al., 2013).

Effect of Temperature

For different HCH-degrading species, the favorable temperature for their biodegradation was reported to range between 25 and 30°C under different experimental conditions. The variation in temperature was found to affect the biological activity thereby either increasing or decreasing the bioavailability of HCH for its degradation (Phillips et al., 2005). Lindane degradation was optimum at a temperature of 30°C (Zhang et al., 2012; Salam et al., 2013; Kumar et al., 2016). Zheng et al. (2011) reported the lindane degradation potential of *Sphingobium* strains even at 4 °C. Elcey and Kunhi (2010) assessed the lindane degradation potential at different temperatures ranging from 5 to 60°C and noticed a dehalogenation at about 30–35°C.

Effect of the Concentration of Lindane

Of the various factors affecting the lindane degradation, the concentration of lindane is one of the important factors that alter and affect the production of the biomass and also the rate of degradation. However, concentration of the contaminant may not prevent bacterial growth (Cunha et al., 2003), but there are only three possible effects of pesticides on microbes: inhibition, no effect, and stimulation.

The lindane concentration of the medium is reported to be directly proportional to the microbial dissipation in the medium. When the lindane concentration is too low, its concentration may not facilitate the production of necessary degradative enzymes and too high levels may become toxic to the organism itself Salam et al. (2013).

Salam et al. (2013) reported that mineralization of 600 mg/l of lindane is possible by 100% by *Rhodotorula* sp. VITJzN03; however, it becomes impossible for the yeast to grow when the concentration exceeds 600 mg/L. The degradation of lindane was also found to be possible using *Staphylococcus equorum* and *Staphylococcus cohnii* subspecies *urealyticus, Kocuria rhizophila, Microbacterium resistens* when the concentration of lindane was about 100 mg/L by about 33 percentage (Abhilash et al., 2011). A microbial consortium was developed to degrade about 25 ppm of HCH by Murthy and Manonmani (2007). Okeke et al. (2002) studied the efficiency of *Pandoreae* sp. to degrade lindane present in water and soil slurry systems. And the removal of lindane was found to increase with the increase in concentration until it reaches 150 mg/L and it was followed by a reduction in removal when the concentration reaches 200 mg/L. Pesce and Wunderlin (2004) stated that the bacterial consortia which could degrade lindane got its activity reduced when the concentration was increased from 0.07 to 0.4 mM. *Pseudomonas* *nitroreducens,* which is auto fluorescent strain which possess dehydrochlorinase activity was reported to degrade 10 gmL^{-1} γ-HCH in about 28 h (Zhang et al., 2010). *Achromobacter* sp. A3 was reported to degrade to a maximum when the concentration was 10 mg/L and when the concentration increased to 50–100 mg/L the degradation of the root epiphytic bacteria, Achromobacter got reduced (Singh & Singh, 2019). Saez et al. (2014) and Phillips et al. (2005) reported that the favourable concentration is about 50 mg/kg HCH which is mixed in the soil slurry by microbes and at the same time other microbes got their growth inhibited.

Effect of Inoculum

There exist various factors facilitating the degradation of the contaminants. One such parameter is the size of the inoculum. The inoculum would be rich due to the number of microbial cells which were in active growth phase. Studies have proved that the size of the inoculum does influence the degradation of lindane to certain extent, but further increase do not pose any significant impact. Saez et al. (2014) reported the degradation with an immobilized consortium of *Streptomyces,* at 107 CFU/g of inoculum strength was comparatively higher than the removal obtained with a lesser inoculum. But it is not that higher cell density could have additional benefit on the pesticide degradation. Even the inoculum size and the lindane removal rate were reported to be not directly proportional (Fuentes et al., 2010). But Salam and Das (2014) reported a direct relation between the inoculum size and the degradation percent. With the *Candida* sp. VITJzN04, an increase in degradation percentage from 40% to 100% was noticed with an increase in inoculum size from 0.02 to 0.06 mg/L at a particular incubation time.

Effect of Different Substrates and H_2O_2 on Lindane Degradation

Co-metabolism is a very important interaction factor to induce bioremediation process intended to degrade certain xenobiotics. Carbon source other than the target molecule can influence the degradation of lindane. Several studies demonstrate co-metabolism to be an effective tool to induce bioremediation. The capability of bacterial isolates to degrade lindane was improved on the addition of glucose as a carbon source (Pannu & Kumar, 2017). It was reported that both glucose and lindane were used by *Streptomyces* sp. M7 and their presence improved the lindane degradation (Benimeli et al., 2007). Addition of carbon source in the form of exudates of root (Alvarez et al., 2012) and agave leaves (Guillen-Jimenez et al., 2012) increased the degradation of lindane. But certain carbon sources were reported to impact the degradation rate negatively which is suspected to be the repression of catabolite. Similarly, the impact of nitrogen source on the degradation of lindane was studied, and it was understood that the presence of beef extract improved the lindane degradation followed by the malt extract and by peptone. Nagpal and Paknikar (2006) reported the enhancement of lindane degradation by *Conidiobolus*

03-1-56 and also they reported that the lindane degradation got affected on yeast and casein addition.

Even hydrogen peroxide (1%) addition to the broth containing culture is found to enhance the organochlorine pesticide in particular, lindane degradation from about 3–15% after 7 days of incubation (Pannu & Kumar, 2017). This may be due to an increase in the available electron donors facilitating the removal of chloride ion and enhance the degradation of lindane.

7 Different Approaches for Lindane Degradation

Various effective methodologies were used for the degradation of lindane sampled from different polluted sites. The studies involved the usage of either pure cultures or their consortia, metagenomic study, nanobiotechnology, microbial interaction with the plant, and phytoremediation. These factors are discussed below.

7.1 Pure Cultures

A large amount of lindane is used in agriculture and hence large amount of the lindane residue is present in the ecosystem. Therefore, it is planned to use pure cultures for the lindane degradation. As discussed earlier, microbial strains which have tremendous potential for lindane degradation are identified and characterized. The degradation rate varied among organisms which is dependent on inherent catabolic potential.

7.2 Lindane Degradation by Microbial Consortium

Both autochthonous and allochthonous microbes could facilitate the degradation and removal of different contaminants. They possess catalytic properties to degrade the compounds completely or partially. Different reports have shown the ability of consortia above a single culture.

Soil sample collected from a sugarcane field was used for microbial strain isolation, and about one fungal strain and nine bacterial strains were identified and were reported to degrade 10 g/L of γ-isomer of HCH individually and were found to degrade about 300μg/ml of lindane on acclimatization for about 108 hours (Elcey & Kunhi, 2010). Fuentes et al. (2011) evaluated the lindane degradation using about 57 mixed *Streptomyces* culture. The degradation was found to improve when a consortium is used instead of a single culture. A microbial consortium was reported to degrade four major isomers of HCH till 25 ppm at ambient temperature and pH under shaking condition. Sineli et al. (2016) studied the degradation of α -, β HCH and lindane by employing actinobacterium strain, *Streptomyces* sp. M7.

However, the γ-isomer (lindane) is reported to undergo degradation at all the concentrations at a faster rate (Murthy & Manonmani, 2007). It is also certain that in contaminated ecosystems, autochthonous microbes develop with time and positively degrade the pollutants of the area. A number of studies exist to prove the efficiency of native microbes to perform lindane and isomers of HCH degradation. Further a sponge *Hymeniacidon perlevis* associated with about seven different bacterial species has shown about 97% lindane degradation (Loredana et al., 2017). Kumar et al. (2017) studied the possibility of co-degradation of lindane and chlopyrifos on employing two or more strains. Similarly, simultaneous reduction of lindane and Cr (Vl) was experimented using five actinobacterial strains both individually and as consortia (Marta Polti et al., 2014).

7.3 Metagenomics

Studies associated with metagenomics of lindane degradation are few and are published. Normally the metagenomic study is carried out by the microbial communities isolated from the sites contaminated with the target pollutant/contaminant. Raju and Bidlan (2017) performed the metagenomic characterization of the microbial consortia capable of degrading lindane and DDT. About 870 species making up the consortia were identified using 16S amplicon sequencing. The consortia have degraded 30 ppm of both DDT and lindane simultaneously. Naseer Sangwan et al. (2012) characterized the microbial strains responsible for the biodegradation (in situ) of HCH contaminants in three different soil samples. The methods employed for studying the community function and structure of the responsible microbes were both 16S rRNA amplicon and shotgun metagenomic sequencing methods. Fang et al. (2014) studied the genes and the pathway responsible for the degradation of atrazine, DDT, and HCH both in sediments of marine and freshwater using metagenomic methodology. Two HCH-degrading species, *Sphingobium japonicum* UT26 and *Sphingobium indicum* B90A were subjected for metagenomic sequencing (Sangwan et al., 2014). Ivdra et al. (2017) even applied the multielemental (C, H, and Cl) stable isotope fingerprinting for studying the risk associated with the lindane degradation.

7.4 Nanobiotechnology

Nanobiotechnological approach is a new and effective solution for environmental cleanup and pollution prevention. It could be claimed as one of the existing technologies facilitating the degradation of pesticides, in particular the organochlorine pesticides. The studies using nanoparticles or granular iron have shown to effectively transform various organochlorine pesticides. FeS nanoparticles stabilized by fungal polymer were used for the elimination of pesticide residues from drinking water by Paknikar et al. (2005). This method was found to ensure a complete degradation of lindane (5 mg/L) from synthetic aqueous solution in about 9 hours. *Sphingomonas* sp. strain NM05 with bimetallic nanoparticles (CMC-Pd/Fe (0)) was employed to degrade γ-isomer of HCH from a Indian soil. Salam and Das (2015) reported the lindane degradation using nanoscale zinc oxide (n-ZnO). Even silica embedded with immobilized fungi laccase isolated from *Myceliophthora thermophila* was used for the degradation of lindane and within a day, the initial concentration was found to reduce by 57% (Bebić et al., 2020).

7.5 Degradation by Plant–Microbe Association and Phytoremediation

Some of the effective technologies reported to degrade certain organic pollutants are phytoremediation and also microbe-associated phytoremediation. Becerra-Castro et al. (2013) studied the possibility of HCH degradation using a mixture of microbe along with *Cytisus striatus*, a tolerant leguminous shrub. Salam et al. (2017) examined the efficiency of *Candida* VITJzN04 along with *Saccharum* sp., identified from doped garden soil was checked for lindane degradation. Even the dissipation of HCH was found to increase when microbial inoculum was added to the medium. Gianfreda and Rao (2004) reported that when fungi grow with plants forming a symbiotic relationship, they have unique enzymatic pathway degrading the targeted pesticides than what is noticed with bacterial strains alone. It is a well established fact that the mycorrhizal fungi forming symbiotic association with many plant species could enhance the plant growth and survival by making the plants tolerant to toxins and reduce the stress. Sainz et al. (2006) studied the impact of lindane on the arbuscular mycorrhiza and on the associated vegetation, and understood the effect of fungi in increasing the plant's tolerance to toxicity prevalent in the contaminated soil. *Zea mays* associated with *Streptomyces* strains was found to possess dechlorinase activity in the root exudates which helped the lindane degradation in liquid medium (Alvarez et al., 2012). Abhilash et al. (2011) conducted a study to understand the efficiency of *Staphylococcus cohnii* subspecies *urealyticus* grown on *Withania somnifera* which was cultivated in soil contaminated with lindane. The authors understood that the combination of plant with rhizospheric microbial strains can improve the degradation of lindane. Further the synergistic degradation of γ-isomer of HCH mediated by plant associated with fungi in rhizosphere was studied (Asemoloye et al., 2017).

8 Conclusion

Lindane has been extensively used worldwide since the ban of DDTs by about the 1940s. Higher usage, higher reactivity on pests, and persistence have made the soils all over the world contaminated with lindane. A number of microorganisms are found to exhibit the capacity to degrade lindane to different extent, and also its complete degradation is reported rarely. Thus more research could be focused on (1) the isolation, identification, and characterization of lindane degrading bacteria; (2) studies have to be undertaken for the complete mineralization of the compound; and (3) further application of novel approaches like nanobiotechnology, metagenomics, and plant microbe interaction in the field of bioremediation of lindane.

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A Review on Health Menace of Disinfectants and Its By-Products in Humans

S. Subha Ranjani

Abstract A disinfectant is a chemical agent and constitutes different group of products used to control the microorganisms in all surfaces except animates. These chemical compounds exterminate most of the pathogens excluding bacterial spores, a few will kill spores that lengthen the timing according to its vulnerability. Disinfectants were predominantly used in hospitals, industrial and institutional settings, but recently the usage of disinfectants reaches each and every house to get rid of communicable diseases. It is highly recommendable to have knowledge on proper usage of disinfectants, type of chemicals, and its concentration; otherwise, it will cause a severe health damage in humans from irritation in the eye and skin to acute, chronic defects in respiratory, nervous system, and even cancers. Government regulations require only limited labelling of cleaning products for the purpose of marketing. Hence, business people recognized the explicit loopholes in understanding fundamental information, choice and utilization of items and practices, risk correspondence, and more secure alternatives. This chapter bridges the gap by creating a clear understanding on classification of disinfectant, considerations, assessment, and implementation for a disinfection action plan, concentration of disinfectant, application methods, and contact time. This chapter also emphasizes, how overexposure or improper usage of disinfectant causes symptomatic and asymptomatic health hazards in humans and also creates awareness on clear management of disinfectants among the disinfectant handlers, health care workers, and public.

Keywords Disinfectants · Health risks · Action plan · Awareness · Management

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1 Introduction

Sterilizing operators are enrolled by the Environmental Protection Agency (EPA) as "antimicrobial pesticides" and are materials employed to manage, forestall, or devastate unsafe microorganisms (e.g., organisms, diseases, or parasites) on lifeless things and surfaces. These disinfectant materials have customarily included cleansing agent, disinfectants, and sterilants. Information on an item's science; adequacy; poisonous levels to people, creatures, and plants; and different boundaries must be tried and submitted to the EPA before the promoting of the compound (US EPA, 2004).

Disinfectant depicts an item applied legitimately to a lifeless thing. It devastates or irrevocably inactivates a good number of disease-causing microbes and few infections; however, it does not normally inactivate spores (Ewart, 2001; Quinn & Markey, 2001; Kennedy et al., 2000). In examination, germ-killers are put in to the outside of sentient life forms or tissues to forestall or stop the development of microorganisms by restraining the life form or by wrecking them (Ewart, 2001).

2 History of Disinfectants

Various key spearheading researchers in the course of the most recent 175 years made noteworthy discoveries in the battle against diseases. In 1913, Harper's Weekly article entitled "What publicity can do," Brandeis made his famous statement that "daylight is supposed to be the best of disinfectants." The historical backdrop of surface cleaning and sanitization is an interesting story that dates back to the time when Egyptians utilized wine or vinegar to clean. For example, in The Odyssey, Homer, composed that the hero, in the wake of crushing his adversary, requested that sulfur be scorched to detoxify the house and sanitize the surface (Blancou, 1995).

The filtering impact of sulfur dioxide exhaust (Block, 2001) was in this manner utilized in numerous events. In India, during the fourth century, a book named Susruta-tantra written by Susruta, recommended the consumption of sulfur in houses where careful tasks were to occur (Karasszon, 1988). During the human plague in Europe, pandemics of the medieval time, sulfur was likewise suggested for cleaning debased places and articles (Block, 2001). Nonetheless, with Antonie Van Leuwenhook's revelation of microbes in 1675, and his disclosure that vinegar executed a portion of these microbes in 1676, researchers began understanding that these already concealed living beings could be equipped for causing malady, and thus, synthetic substances might slaughter these life forms without an obvious response to the eye. This revelation opened the door for boundless examination in the investigation of the utilization of synthetics to slaughter microorganism(s) on an assortment of outdoors and environment. In 1745, during a pestilence of plague, infected items (and people) were exposed to sulfur fumigation (Blancou, 1994).

Disinfection by different substantial strategies was drilled in untimely occasions in an exact method. For the period of Greco-Roman relic, the circumstances were determined, and afterward the methods were recognized. The techniques can be gathered into four general classifications: raising of temperature, fumigation, drying, and filtration. A portion of the chronicled occasions of disinfectants is arranged in Table 1.

Today, numerous disinfectants can be securely utilized in the hospitals. There is an adaptability with regard to utilizing surface sterilants. A sterilant might be incredibly successful at accomplishing the gained log decrease and execute argues, however might be exceptionally hurtful and debasing to surfaces. Each medicinal service office must choose what is best for their office.

3 Grouping of Chemical Disinfectants

Disinfectants are grouped by their compound character, and each group has its special qualities, perils, poison levels, and adequacy against different microorganisms. Ecological conditions, for example, the nearness of natural issue, pH, or water hardness can likewise affect the activity of a sterilant. The significant classes of synthetic disinfectants and their qualities are as follows.

3.1 Phenols

The phenol parent compound C_6H_5OH is a white translucent strong solid (liquefying point 39–40 °C), which gets pink and dark on persistence. Phenols are dissolvable in water in the ratio of 1: 13 and are a feebly corrosive, pKa 10. It is active to both Gram-negative and Gram-positive microscopic organisms, yet it is just gradually powerful against bacterial spores and corrosive quick microorganisms.

Method of Activity

At low fixations, phenols cooperate with bacterial chemicals required for cell divider combination, bringing about cell lysis. High groupings of phenols cause general coagulation of the cytoplasm and go about as broad protoplasmic harms. What is more, phenols can influence the cytoplasmic layer (Judis, 1965) bringing about spillage of potassium particles first, at that point the cytosol. Hexachlorophene was found to have extra action as an inhibitor of the electron transport chain, subsequently repressing the metabolic exercises in microscopic organisms (Hugo et al., 2004).

Phenols can be *coal-tar subordinates* or *synthetic formulations* and for the most part have a smooth or overcast exterior with water, just as a solid pine scent (Pandey

Table 1 Historical background on usage of chemical and physical disinfectants

Period	Usage	Reference
Chemical method		
Fourth century AD	In India, Susruta in his book Susruta-tantra recommended the consuming of sulfur in rooms where careful activities were to happen	Karasszon (1988)
Fifth to the fifteenth century	In Europe, during the human plague scourges sulfur was additionally suggested for cleaning polluted site and items	Block (1991)
3000 BC–AD 500.	Mercurial mixes, similar to sulfur, were utilized as disinfectants and as a defensive paint or covering in China, India, Egypt, and Europe	Block (1991)
1429	Mercurial mixes were utilized especially for fighting syphilis in Italy	Leclainche (1936)
1676	Detection of microorganisms and disclosure that vinegar deactivates a portion of these microbes by Antonie Van Leeuwenhoek	Blancou (1994)
1705	Homberg treated wood with destructive control (mercuric chloride) to forestall decay	Blancou (1994)
1715	Concentrated soft drink lime is utilized to wash the wellsprings, beneficiaries, and potable water channels	Lancisi (1715)
1745	The scourge of steers plague, dirtied articles (and people) were exposed to sulfur fumigation	Blancou (1994)
1767	Bordeaux blend, containing copper sulfate, was prescribed by Boissieu and Bodenare to shield the wood from decay	Block (1991)
Eighteenth century	During the scourge of steers plague (rinderpest), soft drink lime was used to clean places. (Motivated by the first work of Giovanni Lancisi, doctor and private chamberlain to Pope Innocent XII and Pope Clement XI)	Block (1991)
Early twentieth century	Rockefeller Institute first revealed the antibacterial effect of quaternary ammonium salts.	Carl Lawrence (2014)
1935	Benzalkonium chloride (BZK) was the first available QAC which was acquainted as an option with carbolic corrosive for skin antibiotic and scour	Carl Lawrence (2014)
Physical method		
By temperature		
Fifth to the fifteenth century	The dress of people with the plague was scorched so as to forestall the spread of the dark passing	Castiglione (1931)
980–1046	In Persia, Avicenna showed in Book ill of his Cannon that water might be delivered potable by dissipation and refining, or just by bubbling	Tadjbakhsh (1992)
1718	Joblot had exhibited that it was conceivable to clean an imbuement of roughage by bubbling it for 15 minutes and afterward fixing the holder	Block (1991)

(continued)

Table 1 (continued)

Period	Usage	Reference
1776	Logically demonstrated by Spalanzani that “unconstrained age” of microorganisms was difficult to happen once the liquid is bubbled for 60 minutes	Blancou (1995)
By fumigation		
429 BC	Hippocrates suggested fumigation for controlling a pandemic that influenced creatures and people in Athens	Karasszon (1988)
Fifth century AD	Vegetius suggested sanitizing the air, additionally valuable for cleaning objects, dress, and so on for use against Morbus estranges In the same century, it is trailed by Hierocles against malleus	Smith (1976)
By drying		
Seventh century BC	Drying was suggested in the Avesta Vandidad, the Code of the convention of Zarathustra, for the refinement of land It was utilized in old Egypt to finish the preserving of carcasses, after absorbing a salt mixture This practice may have come about because of the perception of corpses normally preserved by drying in the desert	Karasszon (1988)
By filtration		
(1042–1135)	Egyptians utilized this technique to purify grape juice by going it through cloth materials In Persia, Sayyid Ismail Jorjani (1042–1135) saw that sifted (or heated) water took more time to go stale	Tadjbakhsh (1992)
1757	Filtration was likewise suggested by the British Navy for the sanitization of water (entry through sand and charcoal)	Theves (1993)

et al., 2020; Grooms, 2003). Dark liquids are basic coal-tar divisions solubilized with cleansers; white liquids are set up by emulsifying tar portions. The solubilizing materials are used to set up the dark liquids of trade incorporate cleansers arranged from the association of sap NaOH (possess sap acids) along with sulfate and sulfonate blend prepared by warming castor oil and H_2SO_4 (named sulfonated Turkey red oil or castor oil). White liquids vary from the previous details in being interfused, as unmistakable from emulsifiable, phenolic mixes. The solubilizing materials are utilized incorporate creature paste, casein, and the starch extractable from ocean growth called Irish greenery.

Non-Coal-Tar Phenols

Phenol itself is currently made in huge amounts by a manufactured procedure, similar to a portion of its subordinates. The three kinds of phenols, which are utilized in an assortment, are 4-tertiary octylphenol, 2-phenylphenol, and 4-hexylresorcinol.

4-Tertiary Octylphenol

Alcoholic arrangements of the phenol are more effective toward positive Gram life forms than the negative Gram microbes. Octylphenol also act against fungi, and has been utilized as an additive for items rich in protein, for example, pastes and non-food gelatins.

2-Phenylphenol (o-Phenylphenol; 2-Phenylphenoxide)

It is dynamic against the two microscopic organisms like bacteria and fungi and is utilized as an additive, particularly against growths, in a wide assortment of utilizations. The foremost function of this kind of sterilant having pine as a component is that it acts as additives for lubricants and as an overall horticultural disinfectant. It has been especially valuable against the organism that produces slimes and acts as antifungal compound in paper manufacturing factories and as an added substance to petroleum wax in the planning of waxed paper and liners for container and container tops.

4-Hexylresorcinol

In humans, because of its low poisonousness, it can be utilized as oral medication against roundworm and intestinal parasite like *Trichuris trichiura* diseases. 0.1 g of hexylresorcinol in 30 g of glycerol was used as membrane clean and in tablets and cured desserts for the cure of upper respiratory tract infections, where it has neighborhood sedative impact (Buchholz et al., 2009).

3.2 Natural and Inorganic Acids: Esters and Salts

Vast group of natural sour both sweet-smelling and aliphatic, and a couple of inorganic acids have discovered application as additives, particularly in the food business. A few, for instance, benzoic corrosive, are additionally utilized in the safeguarding of pharmaceutical items; others (salicylic, undecylenic, and benzoic acids) have been utilized as medication for contagious diseases of the skin. Vinegar as acidic corrosive is used as an additive and as an injury covering for pseudomonal diseases. Citrus extract is an affirmed decontaminator against foot-and-mouth malady infection. Because of its binding nature with metal ions, it expands the porousness of external layer of Gram-negative microscopic organisms. Except tartaric acid, malic acid as well as gluconic acid can function as permeabilizers at soluble pH.

Hydrochloric and sulfuric acids are two mineral acids, which for some time have been utilized in veterinary sterilization. Hydrochloric acid at elevated fixations is effective against spores, and it is utilized for sanitizing stows away and dermal layer defiled with *Bacillus anthracis* spores. Sulfuric acid, still at elevated fixations, is not sporicidal; however, in some countries it is utilized, generally in blend with phenol, for the disinfecting of grounds, food cartons, and manger (Ayres et al., 1993).

Method of Activity

The following researchers (Eklund, 1989; Gould, 1989; Cherrington et al., 1991; Russell, 1992) have evaluated the method of activity of acids utilized as food additive. Persuading proof has been delivered that numerous corrosive additives act by forestalling the take-up of basic materials, which rely upon a proton-motive force to enter the cell; at the end of the day, they go about as uncoupling operators. Notwithstanding acids, for example, benzoic, acidic, propionic, the p-hydroxybenzoic acids esters were additionally utilized for a portion of the above investigations; they also went about as uncoupling operators, yet additionally restrained electron transport.

3.3 Aromatic Diamidines

During 1920, the diamidines were first brought into medication as alternatives to insulin to bring down the serum glucose in people. Later, Thrower and Valentine (1943) and Wien et al. (1948) stated it was active against Trypanosomes. Through these examinations, both propamidine and dibromopropamidine developed as valuable microbicidal mixes, effective toward various microbes.

Method of Activity

Diamidines appeared to hinder oxygen take-up and actuate amino corrosive spillage (McDonnell & Russell, 1999). Also, they induced harm to the cell envelope of some Gram-negative microorganisms, and this has been depicted (Michael et al., 1993). Likewise, aromatic diamidines have been appeared to tie to DNA, and some of them are nucleoside grouping specific covers (Bailly et al., 1997).

3.4 Biguanides

Different biguanides show microbicidal movement, including chlorhexidine, alexidine, and polymeric structures.

Method of Activity

Different methods of activity have been found for various biguanide compound as depicted underneath.

Chlorhexidine

Chlorhexidine has a broad range of antibacterial activity against all kinds of Gram stained microbes. A few microscopic organisms, strains of species of *Providencia* and *Proteus*, might be exceptionally impervious to the biguanide (Russell, 1986; Baillie, 1987). It is not sporicidal at encompassing temperatures (Russell & Chopra, 1996; Opstrup et al., 2016; Russell, 2015). Chlorhexidine is not deadly to acid-fast microbes, despite the fact that it shows a serious extent of bacteriostasis (Russell, 2015), activity is decreased within the sight of serum, blood, discharge, and other natural issue. Due to its positive ionic in nature, its action is additionally decreased within the sight of cleansers and other negatively ionic mixes. Its principle functions in clinical and animal antisepsis (Holloway, 1986). A solution with an alcohol is an extremely viable skin disinfectant (Lowbury & Lilly, 1960; Traoré et al., 2000), in urinary water system, and in obstetrics and gynecology. Chlorhexidine is also suggested as an antibacterial agent for consideration in eye medicines and is generally utilized in eye contact lenses (Gavin et al., 1995).

Alexidine

Alexidine is a form of bisbiguanide which has ethylhexyl-bunches as discrete from chlorophenol-bunches established in chlorhexidine. It is significantly dynamic than chlorhexidine in instigating spillage of cell from *E. coli* over the minimal inhibitory concentration actuate lysis of cell (Chawner & Gilbert, 1989). The use of alexidine as an oral germicide and antiplaque compound was reported by Gjermo et al. (1973). It has amoebicidal action against a few pathogenic *Acanthamoeba* spp. and is utilized in contact lens cleansing compound (Alizadeh et al., 2009). In contrast to chlorhexidine, both alexidine and polyhexamethylene biguanide (PHMB) incite membrane lipid-stage division and domain arrangement.

Polymeric Biguanides

PHMB is certifiably not a surface-dynamic specialist, it very well may be utilized in the fermenting business, as it does not influence head maintenance on brews and lagers. It has additionally been utilized effectively for the sterilization of natatorium. Copper causes discoloration, but no harmful impact was observed with these polymeric biguanides on the majority of substances. PHMB is active against *Acanthamoeba castellanii* trophozoite and the blister (Khunkitti et al., 1998).

PHMB has a valuable impact in hindering plaque when utilized in mouth cleansers (Rosin et al., 2002). Because of its expansive range of action against both Gram-stained microorganisms and its less poisonousness, polyhexamethylene biguanide is utilized as a special microbicidal in different ophthalmic items.

3.5 Surface-Dynamic Operators

Surface-dynamic operators (surfactants) have two sub-atomic structures, such as a hydrophobic hydrocarbon and a hydrophilic set. Surface-dynamic operators are arranged as cationic, anionic, non-ionic, and amphoteric (ampholytic) mixes based on its ionization capacity of the hydrophilic gathering.

Cationic Operators

Cationic surfactants have solid bactericidal and frail cleanser properties. The expression "cationic cleanser" ordinarily connotes a quaternary ammonium compound (QAC, quat, or onium). The quaternary ammonium compounds might be considered as naturally subbed ammonium mixes of $NR^{+}4$, (R- alkyl or aryl radicals) and a small anion. Models incorporate mixes, for example, benzalkonium chloride, cetyltrimethylammonium bromide, and cetylpyridinium chloride.

Method of Activity

The quaternary ammonium compounds are essentially dynamic toward Gram-positive microorganisms, with fixations as short as 1 of each 200X deadly; 30X are deadly to Gram-negative microorganisms (Hamilton, 1971), although *P. aeruginosa* will, in general, be profoundly safe. The QACs have a trypanocidal movement yet are not mycobactericidal, apparently due to the lipid, waxy layer of these life forms. Gram-negative microbes, for example, *P. aeruginosa*, *Salmonella typhimurium,* and *E. coli,* reject quaternary ammonium compounds, yet profound harsh mutants are touchy. When compared with bacteria and fungi, viruses are safer to quaternary ammonium compounds. Grossgebauer (1970) stated that due to the huge protein failing quaternary ammonium compounds are active against the viruses like Vaccinia, Simplex, adeno, and flu which are lipophilic in nature. It shows week impact toward infections that display hydrophilic properties (enteroviruses, e.g., poliovirus, coxsackievirus, and echovirus). The quaternary ammonium compounds are suggested for use in cleanliness of food in emergency clinics and are frequently utilized in food-preparing businesses.

Benzalkonium chloride is utilized for the pre-surgical sanitization. About 0.2% of benzalkonium chloride is used for cutaneous, 0.1% is suitable for mucous layer, and 0.005% is applicable for bladder and urethra water system. Ointments are suitable for rashes caused by diaper brought about by smelling salts delivering life forms and capsules for the treatment of shallow mouth and throat diseases.

Cetrimide is utilized as skin cleansers before performing surgeries; it is also used for cleaning and sterilizing cuts and burns. Normally cetrimide incorporated with chlorhexidine is frequently utilized. *P. aeruginosa* is more to this product when it used at pH 6 (Bassett, 1971). In hair care purposes, cetrimide (1.3%) is used in shampoos (e.g., diluted Cetavlon) for *Seborrhea capitis* and *Seborrheic dermatitis*.

Cetylpyridinium chloride (0.1%) is utilized pharmaceutically, to sterilize the abrasions and as cutis antisepsis. 100–200 mcg of quaternary ammonium compounds as tablets was used as an oral and upper respiratory disinfectant and as an additive in gel fusions. Quack (1976) reported that 0.1–0.5% mixtures were prepared for hair care and in antiperspirants; minor fixations are used as facial moisturizers and in shaving creams.

3.6 Aldehydes

Three aldehydes are vital as disinfectants, specifically, glutaraldehyde, formaldehyde, and ortho-phthalaldehyde, despite the fact that others have been examined and appeared to have microbicidal movement. Aldehydes act by alkylating different substance bunches related with proteins and nucleic acids, which brings about ensuing cross-connecting of macromolecules.

Glutaraldehyde (Pentanedial)

Glutaraldehyde has high microbicidal action against microscopic organisms and their spores, hyphae and spore types of growths, and different kinds of infections (Borick & Pepper, 1970). Glutaraldehyde is viewed as a compelling antimycobacterial operator (Russell, 1994). The system of activity of glutaraldehyde includes alkylation of hydroxyl, amino, carboxyl, and sulfhydryl gatherings of microbes that influences to synthesize the RNA, DNA, and protein. Likewise, glutaraldehyde brings about cross-connecting of proteins and macromolecules in the phone envelope. The external cell layers of spores, the cell mass of organisms (chitin), and the mycobacterial cell divider are accepted to be the objective destinations for glutaraldehyde against bacterial spores, parasites, and mycobacteria, individually (McDonnell & Russell, 1999).

Formaldehyde (Methanal)

Formaldehyde is effective toward bacteria, viruses, fungi, and spores. Formaldehyde joins promptly with proteins and is less viable within the sight of protein-containing matter. Plasmid-interceded protection from formaldehyde has been depicted, probably because of aldehyde debasement (Heinzel, 1988). Formaldehyde fume might be discharged by dissipating formalin arrangements, by adding potassium permanganate to formalin or, on the other hand, by warming, under controlled conditions, the polymer paraformaldehyde (HO(CH_2O)nH), urea formaldehyde, or melamine formaldehyde. It is utilized as a sterilant in fluid and vaporous forms. Vaporous formaldehyde is utilized as sterilant of fixed rooms.

Ortho-Phthalaldehyde

In 1999, the US Food and Drug Administration declared OPA as sterilant at a significant point (Rutala & Weber, 2010). It has intense antibacterial and virucidal property (Alfa & Sitter, 1994; Akamatsu et al., 2005). It is additionally dynamic against mycobacteria, including glutaraldehyde-safe strains (Cabrera-Martinez et al., 2002). It acts better against vegetative forms than the spore. The spore-coat has all the earmarks of being a critical factor in this diminished action, yet it is not the main factor as OPA seems to exhibit sporicidal action by obstructing the spore germination process (Acosta-Gío et al., 2005).

3.7 Halogens

Iodine mixes, bromine, and chlorine mixes are the high significant microbicidal halogens in nature.

Iodine Mixes

Free Iodine

Iodine was first utilized in the management of lesion exactly more than 100 years prior, and it has demonstrated to be a proficient antimicrobial specialist with fast deadly impacts against all kinds of microbial infections and its spores (Russell, 1971). The dynamic operator in natural iodine (I_2) is just marginally dissolvable in water; iodide particles are expected to set up a fluid arrangement of iodine (Lugol's solution BP 1988, 5% iodine, 10% potassium iodide). Tincture of iodine (alcoholic arrangement of iodine) can be set up by utilizing 2.5% iodine, 2.5% potassium iodide, and ethanol (90%) (powerless solution of iodine BP 1988). Iodine has fewer responsive synthetically than chlorine. The microbicidal movement of iodine covers all Gram-stained microbes, spores of bacteria, acid-fast bacilli, parasites, and viruses. Its movement is less subject to temperature and pH.

Iodophors

Iodophors (iodine transporters) are buildings of iodine and aggravates that go about as transferors or solubilizers for iodine. They permit moderate, continued arrival of iodine from the complex. Iodophors were created to dispose of the unwanted properties of iodine while keeping up its microbicidal action. The grouping of free iodine in fluid or alcoholic iodine arrangements is liable for microbicidal action. Similarly, the iodophore of iodine is apt for its action. Iodophors might be utilized in the dairy business (when utilized in the purging of milk industry to keep the pH on the corrosive level to guarantee satisfactory evacuation of milkstone) and for cutaneous and abrasion antisepsis. Iodophors, for example, betadine, as alcoholic arrangements, are generally utilized in the USA for antisepsis of hands before intrusive methods, for example, operations and obstetrics.

Method of Activity

Iodine can infiltrate the cell mass of microorganisms rapidly. It responds with and oxidizes thiol bunches that occur in the cytoplasm. Hence, the deadly impacts are accepted as a consequence from the disturbance of production of nucleic acid and protein (Hugo et al., 2004).

Chlorine Complex

Chlorine-Liberating Substances

The sorts of chlorine exacerbates that are most, as often as possible, utilized are the hypochlorites and N-chloro mixes (Bloomfield, 1996). Chlorine mixes are generally utilized as purifying agents in the food business because of their high microbicidal adequacy, low poisonousness to people, scope of utilizations, and minimal effort. The organochlorines are more slow acting regarding bactericidal adequacy by correlation. The steadiness of free accessible chlorine in arrangement is subject to various components, particularly: (i) chlorine focus; (ii) pH of natural issue; and (iii) light (Dychdala, 1983).

Hypochlorites have a wide bactericidal range, with non-spore formers compared with the spore producers, and it has expressed less effectiveness toward mycobacteria. It has been proposed that chlorine mixes are among the most intense sporicidal specialists (Coates & Hutchinson, 1994). The hypochlorites show action against enveloped and non-enveloped viruses (Morris & Darlow, 1971). Sodium hypochlorite is regularly utilized for the sterilization of pools. Chloramine-T, dichloramine-T, and halazone are utilized to clean sullied drinking water (Rose et al., 2005). Blood dismissal with human immunodeficiency (HIV) or hepatitis B infection can be cleaned with sodium hypochlorite incorporated with 1% accessible chlorine.

Method of Activity

The specific system by which chlorine obliterates microbial cells is as yet obscure. In any case, it is accepted that chlorine movement against microorganisms includes a few targets, for example, oxidation of SH chemicals and amino acids, ring monochloramines; cell divider and film interruption by assaulting basic proteins, starches, and lipids; loss of intracellular substance; diminished take-up of supplements; restraint of protein amalgamation; diminished oxygen take-up; disturbance of oxidative phosphorylation and other layer-related catalyst exercises; direct protein corruption into smaller polypeptides and precipitation; diminished adenosine triphosphate creation; and breaks in DNA and discouraged DNA union (McDonnell, 2007).

Chloroform

Chloroform ($CHCl_3$) has been utilized as an additive in numerous pharmaceutical items planned for internal use, for over a century. Chloroform acts effectively against the vegetative cells than its spores, when it is diluted or the concentration gets decreased there will be a bacterial growth (Westwood & Pin-Lim, 1972; Lynch et al., 1977). It does not show up as an affirmed material in the most recent form of Cosmetics Directive (Anon, 2002); however, it is as yet recorded in the British Pharmacopeia (2012) as an overall sedative and an additive, and it is completely restricted in the USA.

Bromine

In 1930, the microbicidal movement of bromine was first seen, till then, it was utilized economically in purification of water. Normally chlorine is used as microbicide in water recycling; however, bromine can also be used as a choice (Elsmore, 1993).

3.8 Quinoline and Isoquinoline Subordinates

8-Hydroxyquinoline by-products, 4-aminoquinaldinium by-products, and isoquinoline by-products are the three primary forms.

8-Hydroxyquinoline By-Products

8-Hydroxyquinoline (oxine) has antibacterial action against Gram-positive microbes than Gram-negative life forms. It effectively interrupts the cell wall of *S. aureus* including MRSA and causes cell lysis (Short et al., 2006). The antifungal activity of this compound ensues at slow rate. Like oxine, clioquinol, chlorquinandol, and halquinol are extremely less soluble in water and are commonly utilized as skin ointments. An intriguing component of their function is it is the chelating operator, but it works well with the sight of metal particles.

4-Aminoquinaldinium By-Products

These are QACs, which likewise fall into the quinolone gathering. The most significant individuals are laurolinium acetic acid derivation and dequalinium chloride (a bis-QAC). The two mixes have antibacterial action, particularly against Gram-positive microorganisms (Cox & D'Arcy, 1963), just as huge action against numerous types of fungi and yeast. Dequalinium chloride is active against vaginal disease–associated microbes (Casa et al., 2011). It is also used as a medicine for upper respiratory tract infections.

Isoquinoline By-Products

Hedaquinium chloride is a significant by-product containing bisquaternary salt. This has antibacterial and antifungal movement (Collier et al., 1959), and it is viewed as one of the most dynamic quaternary ammonium compounds act against fungi.

3.9 Alcohols

A few alcohols have been appeared to have microbicidal properties. Mostly, it is a fast disinfectant (Morton, 1950), including mycobacteria, but not against spores. They are virucidal but not to all kind of viruses. Alcohols, as indicated by their synthetic structure, are separated into aliphatic and aromatic alcohols. The vast majority of the aliphatic alcohols (ethyl and isopropyl) are broadly utilized as cleaning agents and disinfectants. Some aliphatic alcohols can be utilized as additives (chlorbutanol and bronopol). Aromatic alcohols are utilized primarily as additives (benzyl liquor, phenylethanol, and phenoxy ethanol).

Method of Activity

The action of alcohol increments within the sight of water (as blends of alcohols and water are more microbicidally dynamic than supreme liquor) and since protein denaturation happens all the more quickly within the sight of water, it is accepted that alcohol damages cell membrane, denaturing fundamental microbial proteins and thus meddling with digestion and bringing about cell lysis. Moreover, a few reports have demonstrated that alcohols cause denaturation of dehydrogenases in *E. coli* and an expansion in the length of the slack period of *Enterobacter aerogenes*, an occasion which has been ascribed to hindrance of metabolic procedures (McDonnell & Russell, 1999).

Ethyl Alcohol (Ethanol)

Ethanol is promptly deadly to non-spore-forming microscopic organisms and devastates acid-fast bacilli, yet it is incapable at all focuses against bacterial spores. Setlow et al. (2002) indicated that a decrease in the feasibility of spores of *B. subtilis* can be accomplished by treating with ethanol heated at 65 °C. The best fixation is around 60–70% for skin antisepsis, instrument cleaning, and natural surfaces. Sanitizers made with alcohol are getting progressively famous for sterilizing hands. Hand cleanliness is of specific significance in the health care personnel to forestall nosocomial contaminations brought about by cross transmission of microorganisms.

Isopropyl Liquor (Isopropanol)

Isopropyl and n-propyl alcohols are good antibacterial agents than EtOH; however, they are not sporicidal. Isopropyl liquor has a marginally more prominent movement than ethanol, but at the same time it is twice as poisonous. It is less dynamic against infections, especially non-wrapped infections, and ought to be viewed as a constrained range virucide (Rutala, 1990).

3.10 Peroxygens

Hydrogen peroxide and peracetic acid are viewed as better sterilants by goodness of its creation of the exceptionally responsive R-OH radicals. The upside of this compound over the other microbicidal products is that their residual items are non-harmful and biodegradable.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a recognizable domestic disinfectant. Hydrogen peroxide solutions have disinfectant, germicide, and antiperspirant properties. It is an elevated level disinfectant. Numerous items containing hydrogen peroxide are endorsed by the FDA as chemisterilants. Hydrogen peroxide decayed living tissue and numerous metals by releasing O_2. It is active against both vegetative and spores

(Baldry & Fraser, 1988). It releases free hydroxyl radicals, causes assault of membrane lipids and fundamental cell segments, and can cause DNA strand breakage in developing microbes. In any case, the system of activity of hydrogen peroxide on spores is unique.

3.11 Heavy Metal By-Products

Salt is added as a meat additive in the silver and copper vessels which prevents the growth of microbes by keeping away from the water accumulation. Universally salting is the most preferable meat additive technique, and salts of metals like Cu, Ag, Hg, and even organic tin are used as antibacterial agents.

Copper Compounds

Although the pharmacopeias list various plans containing copper salts (sulfate, acetic acid derivation, citrate) as rudiments of germ-free astringent salves, the fundamental microbicidal utilization of copper subordinates as antifungal and antialgal compounds. The Cu(II) particle Cu^{2+} is a chief anti-algal particle, and at a dilution of 0.0005–0.0029 mg/ml, as $CuSO_4$, it is utilized to clean algae in swimming pools. On thiol, when Cu is in the form of Cu(II) particle, it showed the harming impact (chemicals with thiol bunches at the dynamic or vicinal locales) and perhaps other thiol bunches in microbial cells (e.g., glutathione and so on.). Zeelie (1998) revealed that the copper particles in the sterilants cetylpyridinium chloride and povidone-iodine enhance the microbicidal movement against emergency clinic removal of *Staphylococcus* sp., *Pseudomonas* sp., and *C. albicans*.

Silver Compounds

Historically there is evidence in usage of vessels made up of silver and its associated metals to keep the water consumable and also it has the antimicrobial properties (Weber & Rutala, 1995). Aside from these functions, the $AgNO_3$ in the treatment of ophthalmia neonatorum occurred in newborns. Silver mixes have been utilized in the anticipation of contamination in products, with variable adequacy. Brown and Anderson (1968) discussed the adequacy of bactericidal effect of silver ions.

Mercury Compounds

These days its utilization in medication has diminished, albeit various natural subordinates of mercury are utilized as antibacterial and antifungal specialists as well as additives and bactericidal in infusions; models incorporate mercurochrome, nitromersol, thiomersal, and phenylmercuric nitrate. Salts, for example, the stearate, oleate, and naphthenate were, until significantly more as of late, broadly utilized in the conservation of wood, materials, paints, and calfskin.

Tin and Its Mixes (Organotins)

Tin, SnO_2, was utilized as an oral medicine in the prophylaxis of throat infection caused by *Staphylococcus* sp. It was professed as discharge by means of sebaceous organs and, subsequently, aggregated at destinations of contamination. All the more as of late, natural tin subordinates are utilized as antifungal and antibacterial compounds and also as additives in cloth and wood industries (Schmith & Smith, 1975).

Titanium

In oral depression, titanium is used as an antimicrobial agent. Particles of titanium are tested in case of microbes present in mouth, yet demonstrated low antibacterial action. Titanium additionally has discovered use in clinical inserts including dental inserts. Titanium surfaces embedded with fluorine particles exhibited microbicidal movement (Leonhardt & Dahlén, 1995).

4 Elements Impacting Biocidal Action

A few components can influence the antimicrobial viability of concoction biocides (Table 2). Failure of a cleansing/sterilization process regularly all around portrayed for a considerable lot of these mixes (Russell, 2004). Nevertheless, their down-to-earth hugeness replicates the despite or absence of comprehension of the elements. Subsequently, it is imperative to consolidate the utilization of an appropriate microbicidal item/plan for a particular undertaking with the preparation of the end client. Since consistence to the producer's directions is especially significant, the adequacy of an antimicrobial item ought to be assessed with customary conventions that examine a scope of circumstances. Numerous microbicidal analyses, remarkably handy tests, remember different boundaries for their structure, for example, fixation, contact time, temperature, dirtying, type, and number of microorganisms. For the most part, these components can be partitioned into those innate to the biocide and those inborn to the microorganisms.

Table 2 Variables affecting the action of disinfectants

Factors	Observations
Concentration	The fundamental driver for malfunction of cleansing. Diluting the disinfectant deactivates the biocidal property, remarkably those with a low dilution
Contact time	Time of contact can bring about the endurance of microorganisms. It should be adjusted with state of utilization
Organic load	Especially significant in the industries dealing with food, and in the clinical setting with spillage of blood. Diminishes the microbicidal viability of disinfectants
Temperature	When disinfectants are used under cold storage room or in cold environment or with the efficiency of additives, it could be a problem
pH	Can influence both the microorganisms and the operators, particularly in the event that it is a corrosive or an alkali
Microorganisms type	Microorganisms shift in vulnerability to microbicides; virus particles and dormant stage are most impervious to cleansing
Number	Progressively hard to sterilize/clean substantial microorganism sullying
Phenotype	Microorganisms are developed as consortium, or having limited capacity to burn calories are highly impervious to microbicidal than development of plankton and microbes developed on rich media
Relative humidity	Especially significant for vaporous sterilants. Increasing the water vapor content of a gas influences the water content of the microbes
Neutralization/ incompatibility	The loss of activity of sterilant is totally/partially disturbed

4.1 Factors Integral to the Product

The adequacy of the disinfectant is dependent on the ratio of its dilution (Holah et al., 2002; Russell & McDonnell, 2000) called attention to that when the grouping of QACs stays high (e.g., 1000 mgL^{-1}) and endurance of vegetative microorganisms is far-fetched. Moreover, failure of significant level disinfectants, for example, glutaraldehyde to dispose of all microorganisms from endoscope washer disinfectors has been accounted. Griffiths (1997) and Van Klingeren and Pullen (1993) reported that the sterilant gluteraldehyde fails to be effective against the microbes present in the endoscope sterilizer.

The impact of changes in dilution on microbicidal adequacy is evaluated by the dilution (η) and the formula is:

$$\eta = \frac{\log t_2 - \log t_1}{\log C_{1-} \log C_2}$$

Where C_1 and C_2 is concentrations of two, t_1 and t_2 the time required to decrease the growth to a similar level. Concentration type changes among biocides (e.g., for phenolics η esteem is 4–9.9). It gives a sign of the impact of weakening being used in concentrations; for example, biocides with high fixation type will quickly lose action upon weakening, while those with a low concentration type will hold action upon weakening. This, as a result, permits the determination of suitable fixations is assessed with testing microbicidal conventions.

The time of contact is significant to microbicidal analyzing conventions, and the selection introduction time as a rule reflects conditions in analysis. There is no basic connection among movement and exposure timings, albeit lengthy presentation time influences the activity as well as the development of resistant microbes. Regular microbicidal analysis conventions, to producers and clean strategy, normally determine a maximum and minimum time of contact required. For example, the European Standard for analyzing the sterilants (CEN1276, 1997a) specifies that $5\log_{10}$ decrease in microbial focus have to be achieved inside 5 min of introduction time. Similarly, CEN1499 (1997b) suggests the methodology to wash the hands as well as its time of contact toward sterilants.

Organic burden/defiling interferes the efficacy of the disinfectant, whereas altering the dilution of the sterilant offered better activity against microbes. Undoubtedly, defiling influenced the microbicidal viability of disinfectants profoundly. The impact of dirtying accentuates the need of disinfecting areas and hardware that were previously disinfected, otherwise consolidating a sterilant with a cleanser is mandatory. The efficacy of biocides and the increase of temperature are directly proportional when using disinfectant and vaporized sanitization. Then again, decrease in temperature may diminish the antimicrobial adequacy of disinfectant. It is especially a problem when considering the shelf life of disinfectant and its by-products as well as in producing and storing the food in refrigerated condition (Taylor et al., 1999). The relationship of temperature and disinfectant efficacy can be determined with the temperature coefficient (Θ) with all the more advantageously by the Q_{10} esteem (alter in action by an ascent of 10 °C). The Q_{10} esteem is given by the condition:

$$Q_{10}\frac{\text{Time to kill at } T^{\circ}\text{C}}{\text{Time to kill at}\left(T+10\right)^{\circ}\text{ C}}$$

According to prescribed analysis procedure, analyzing the antimicrobials at certain temperature does not reveal the efficacy of the sterilants at that temperature. Usually the analysis was performed at 20 °C ± 1 °C (e.g., CEN1276, 1997a) or approximately temperature in milieu (18 ± 25 °C) (e.g., CEN13697, 2001). Additional testing is to be performed to understand the activity of the chemical at various temperatures. The potential of hydrogen also influences the efficacy of the disinfectant chemicals (Russell, 2004). At basic pH, the chemicals in non-ionic state establishes the greater efficacy (e.g., phenols, CH_3COOH, C_6H_5COOH), the pH and efficacy in inversely proportional. Similarly at basic pH, the disinfectant showed the maximum efficacy (e.g., cationic biocides, glutaraldehyde).

The components of the formulation of biocides can partially inactivate the antimicrobial formulation. Surface-dynamic mediators, remarkably un-ionized specialists, could influence the movement of microbicidal mixes. When parabens and quarternary ammonium compounds are used as antimicrobials in medical and beautifying materials, the possible halt of un-ionized forms interfere its efficacy. The non-ionic specialist in the carboxy methyl cellulose builds membrane penetrability, yet in addition discharges the biocide to deliver a profoundly dynamic solution.builds membrane penetrability, yet in addition discharges the biocide to deliver a profoundly dynamic solution. Metal particles can likewise influence the antimicrobial action of a biocidal definition, prominently when the detailing contains permeabilizing specialists as particle chelators (e.g., ethylene diamine tetraacetic acid) (Russell, 2004).

4.2 Components Intrinsic to the Microbes

Various sorts of microbes show various degrees of affectability to a known antimicrobial substance. According to vulnerability to disinfectants, endeavors are followed to classify the microbes (Table 3). Generally, such characterization depends upon data on the inherent property of a microorganism; however, it is not intended to offer an certain response to vulnerability of microbes, since it is varied between the same species and strains. Efficacy test of disinfectant conventions for the most part incorporates testing against a scope of fungi and bacteria, which are chosen relying on the normal use of the biocide, for example, food industry, medical clinic

Table 3 Vulnerability of microbes to disinfectants

Type of microbes	Stage of confrontation	Remarks
Prions	Elevated	One of a kind sterilization structures getting heat together with a disinfectant. Exclusive usage is recommended
Bacterial spores	Elevated	Disinfection or raised level purging. Consistently used as characteristic indicators
Mycobacteria	High to intermediate	Elevated level sanitization suggested. Protection from $C_5H_8O_2$ and peroxyacetic acid is accounted for
Small non-enveloped viruses	Transitional	Celiac contaminations might be particularly troublesome when lesser disinfection is used
Fungi	Transitional to low	Generally, less data are accessible on the defenselessness of parasites, and especially contagious spores, to disinfectants. Reasonably less information is open on the weakness of developments, and particularly infectious spores, to disinfectants
Vegetative Gram-negative microbe	Transitional to low	The genus *Pseudomanas* is more resistant
Vegetative Gram-positive microbe	Low	For the most part subtle to sanitization
Large enveloped viruses	Low	The waxy outer covering is particularly fragile to disinfectants

condition, and so forth. However, the quantity of test conventions accessible to assess virucidal and mycobactericidal movement is restricted. Moreover, there is no normalization, and these conventions will in general fluctuate enormously between nations (Fraise et al., 2012) strikingly with the test life forms.

The quantity of microorganisms that ought to be utilized in standard tests has for some time been discussed and contrasts among analysis conventions. It is commonly acknowledged that the degree of contamination of microbes and Problem in purification is directly proportional. The morphology of the bacteria also influences the movement of disinfectants. The factors like physical, chemical, supplement impediment, and aggregation of microbes deliver alternate morphological nature to microbes (Dodd et al., 1997; Holah et al., 2002; Gilbert et al., 2003).

5 Assessment of Antimicrobial Adequacy of Disinfectant

The motivation behind antimicrobial adequacy analysis decides an exceed/flop measure to disinfectants under explicit circumstances. From the outset, analysis seems clear. In any case, in actuality, to acquire suitable and reproducible outcomes, the structure of testing conventions is unpredictable, eminently in the quantity of variables that should be controlled.

5.1 Grouping of Biocides Analysis

Following are the three analysis tests.

1. Essential analysis starts with suspension tests to decide action in opposition to marker bacteria (e.g., *S. aureus* and *P. aeruginosa*).
2. Conceivable research examinations, situations decides if the disinfectant can be dynamic for a given application, that is the states of a specific use are reproduced by choosing fitting test life forms, meddling material, heat and time of contact.
3. Field tests (in loco tests) are exorbitant as well as hard to guarantee a few level of normalization/fidelity (dependability).

CEN TC216 sterilization methods have the following stages. *Stage 1* investigation EN1040 (antibacterial) and EN1275 (antifungal) are standard to all functions. *Stage 2* analysis consists of two parts *stage I*, a progressively included bacterial medium analysis is done, presenting 4 tests living being bacteria (extension to include extra microbes). Factors, for example, hardness of water and meddling materials are contemplated. In *stage II*, viable analysis, for example, “exterior cleansing with no involuntary action” is executed utilizing transporter analysis guideline.

6 Evaluation of Antimicrobial Action

A few elements impact the weakness of microbes to disinfectants. Past investigations are especially productive in indicating development condition to the affectability report of microbes at normal and in dormant states. Nevertheless, the decision of a suitable convention to address each and every issue is befuddling, generally due to the large number of strategies accessible. The national associations like AOAC, 1990, in the USA; DGHM and DVG, AFNOR, in France; and BSI in UK framed the few principles to evaluate the nature of disinfectants.

As specific biocide strength is minimized during storage and expansion of natural issue, its viability need to be analyzed. A few techniques contrast the exhibition and that of phenol though different strategies basically state if the disinfectant is viable or not. There are a few strategies for testing disinfectants, with their own points of benefits and drawbacks. The following tests are used to analyze the effects of biocides: suspension test, carrier test, practical test, field test or in-use test, and capacity test.

6.1 Principles Inherent to the Microorganisms

Carrier Test

Disinfectants and sanitizers are relied upon to have a wide range of action at being used concentration, albeit a few microbes are slightly vulnerable, eminently spores of bacteria and bacteria with mycolic acid or waxy coat in its cell structure. It is the old test in which the carrier substances like thread or sticks were dipped in a grown bacterial culture medium. The carrier was dried and it is allowed to expose with the test biocides to analyze whether the biocide inhibits the growth of microbes or not (Best et al., 1994).

Standards Inherent to the Test Strategies

Extinguishing Antimicrobial Action (Suspension Test)

The utilization of a killing specialist to extinguish the action of biocides or the disposal of biocides from recuperation liquid is basic to decide the deadly movement of biocides/sanitizer. Sadly, these essential advances have been frequently ignored in numerous examinations. The “valid” antimicrobial action of a substance at that point gets hard to decide and to recognize from a lingering bacteriostatic impact in the recuperation medium. Instances of killing operators that extinguish fittingly the movement of explicit biocides are given in Table 4. A few “universal neutralizers” are additionally accessible and contain typically a scope of synthetic compounds. In

Table 4 Instances of neutralizing agents (Maillard, 2005)

Disinfectants	Neutralizers	Remarks
Phenols	Tweens (polysorbate)	Phenolics have a high-fixation type. The movement promptly drops with weakening
Chlorhexidine	Lecithin + tween QACs Lethicin + Lubrol	
Aldehydes Glutaraldehyde Ortho-phthalaldehyde	Sodium sulphite/bisulphite Glycine	Poisonous to certain microbes In extinguishing OPA glycine is useless advanced grouping of $NaHSO_3$ required for OPA
H_2O_2	Catalase or peroxidase Dilution	1 unit leavens the disintegration of 1 mole of H_2O_2/min at 25 °C and at neutral pH

any case, it is indistinct with regard to whether they inactivate the movement of all biocides.

Neutralizing agents are especially significant to disinfectants that interface emphatically toward cell wall of bacteria. Nonetheless, microbes that have endured a specific measure of harm after it is treated with disinfectant probably will not have the option to recuperate in any event, when a neutralizer is included. Moreover, some neutralizers may expand the measure of harm previously continued by the microorganisms. In the event that there is no neutralizer accessible for a specific item, layer straining is utilized as another option. The blend of disinfectant and microbes to be investigated is then separated by a layer channel that is quickly cleaned using flushing fluid. Transfer the layer to a recuperation solution to empower persisters to create provinces following brooding. Filtration helps the decreasing of poisonous nature of neutralizers to the host.

Microbes are tallied by plating in agar medium or by film sieving in the wake of extinguishing/expelling the action of the biocides/sanitizer. The deadly impact of the specialist (ME) is determined as follows:

$$\mathrm{ME} = \log_{10} N_{\mathrm{c}} - \log_{10} N_{\mathrm{D}}$$

Where N_{C} = quantity of CFU in the control(s) before treatment, N_{D} = quantity of CFU checked after introduction of disinfectants.

Capacity Tests

Every time a dirty apparatus is put into a disinfectant urn, a specific amount of grime and microbes is added to the arrangement. The capacity to hold movement within sight of an expanding level is meant as border of the biocides. In a capacity test, the biocides are tested more than once by progressive augmentations of bacteria culture up to the effect of depletion of biocides. It mimics the convenient circumstances of maintenance and apparatus decontamination, for example, Kelsey-Sykes test (Kelsey & Sykes, 1969).

It consists of three kinds of analysis, intended to decide convergences of biocides that is successful in spotless as well as in grimy conditions. Biocides are tested by three progressive augmentations of a bacteria stock throughout the test. The span of analysis assumes control more than half an hour to execute. Grouping of biocides is decreased significantly by expansion of natural issue (sterilized *Saccharomyces*) that develops to last convergence of five-tenth. Contingent upon the sort of biocides, solitary analyzed bacteria is chosen from *Staphylococcus aureus*, *Pseudomonas aeruginosa, Proteus vulgaris*, and *Escherichia. coli*. The strategy is completed below "perfect" or "grimy" circumstances.

Practical Tests

The analysis is executed subsequent to estimating quantitatively the time-fixation connection of biocides. The most popular viable analysis is the exterior sterilization investigation. It evaluates the efficacy of the selected biocides against the microbes of the exterior. The examination is performed by exposing the surface with normalized test microbes, and after drying the test biocides are introduced in that area for a particular point of time, and the presence of microbes were analyzed by exposing the agar medium plates or by a washing method, wherein the transporter is flushed in a diluent, and the quantity of microbes is resolved in the washing liquid. Between a carrier test and a surface disinfectant test, there is a basic distinction: in the former, the transporter is lowered in the biocide arrangement throughout the entire test period, while in latter, the transporter is exposed in the sanitizer for particular test period and from there the transporter keeps on aerated for the duration of introduction.

Surface Time Kill Test

The surface selected for analysis must be sterile, and to that 24 hour culture of bacteria was inoculated as a thin uniform film. The number of organisms present in the inoculated surface was quantified by inoculating the same test organism in the other surface without being subjected to any treatment. At a particular point of time, the surface will be exposed with biocides. The efficacy of the biocides can be identified by the bacteria that are alive in the investigated surface.

In-Use Test

Prince and Ayliffe (1972) portrayed an easy-to-utilize test that can be utilized in emergency clinics and research facilities to distinguish defilement of biocides. About 1 ml of biocides sample was diluted with the inactivator. Few drops of diluted sample were inoculated in the agar plates and incubated. After incubation of 3 consecutive days at room temperature, the growth of organism on the plates demonstrated the infectivity.

7 Manual for the Use of Disinfectants

The accompanying directions are to be viewed as when utilizing the disinfectant:

1. Adhere to producer's directions and guarantee that the right (optimum) dilutions are utilized.
2. Check expiry date of the arrangement. The date ought to be plainly set apart on the compartment.
3. Disinfectant compartments must be cleaned or sanitized before top off between shifts.
4. Disinfectants must not be utilized to clean instruments or equipment (except if indicated in the disinfectant, e.g., endoscopes).
5. Disinfectants ought to be provided, ideally prepared for use from the drug store (new stocks to be provided on receipt of void holders). Try not to dispose of void compartments or use them to store different arrangements. Synthetic compounds can be destructive when utilized in inappropriate circumstances.
6. Open holders of disinfectant ought not to go on without serious consequences in any medicinal services office condition. There is a genuine danger of sullying with multi-resistant bacteria, for example, *S. aureus*, *Pseudomonas* spp., and spores.
7. Where disinfectants are shown for use on surfaces, wipe, Try not to wash, bathe, or floodwash.
8. Decontaminate thoroughly, at that point clean articles before sterilization, that is, expel any substance, for example, dirt and organic materials.
9. The social insurance office drug store ought to guarantee that:
    - The compartments are altogether cleaned, washed, and dried.
    - The compartments are obviously marked with the kind of substance, dilution level, and the expiry date.
    - None of the disinfectants are presented to inactivating substances, for example stopper, elastic tops, or inconsistent cleansers.
10. The disinfectants are weakened by learned work force in sensible amounts, for example, 5 liters or less. This will diminish squander and that incompletely filled holders will not be left on the wards (forestall accumulating).

8 Focal Points and Detriments of Chemical Agents Utilized as Concoction Sterilants or as High-Level Disinfectants

Guthua et al. (2001) analyzed the event of indications owing to exposure to disinfectants among wellbeing work force in clinics. Human service laborers who every now and again presented to glutaraldehyde and hypochlorite have tingling, watery eyes, migraines, sickness, numerous skin inflammation, intense rhinitis, nonproductive cough, wheezing, shortness of breath, and nasal disturbance. Those personnel had an alleviation when they pull back from the area and practice. A few people groups are having a clinical history of hypersensitivity to anti-toxins and dust wood smokes.

Chemical agents can go into the body through three distinct ways presenting danger to wellbeing:

- Through gulping
- Penetration through the skin
- Through inhaling

Wellbeing dangers brought about by the synthetic operators include the following:

Skin – burns, tingle, hypersensitivity, dryness, and swelling.
Eyes – burns, redness, and expanding or visual impairment in genuine cases.
Respiratory – coughing initiated by disturbance; in serious condition, the respiratory tract and lung may be influenced.
Nerve framework – headache, dizziness, and dumbness.
Different organs – liver and kidney capacities may be influenced.

As per the Guidance notes arranged by the Occupational Safety and Health Branch of the Labor Department in 2007 fill in as a source of perspective to encourage clients in recognizing the risks emerging from the utilization of compound disinfectants and taking successful wellbeing measures. The accompanying Table 5 shows a portion of the potential risks brought about by the substance disinfectant to the human service experts.

9 Safe Usage and Storage

The security and wellbeing council in 2003 proposed significant measures to the laborers about the protected utilization of disinfectants just as the crisis estimates when they are uncovered while taking care of.

The accompanying insurance measures ought to be taken when utilizing and putting away the synthetic agents.

- Do not eat, drink, smoke, make up, or store food in the work environment containing synthetics.
- Wash hands, arms, and face following utilizing the synthetics and before taking food after work.
- Keep the floor clean, the way clear, and the work environment very much ventilated.
- Understand the properties of the cleaning operators being utilized.
- Follow the directions and security gauges as suggested by the item producer.
- Containers must be appropriately marked.
- Cover the holder safely.

Table 5 Prospective vulnerability of chemical biocides

Category	Chemical disinfectants	Potential hazards
Alcohols	Ethyl alcohol Isopropyl alcohol	Synthetic concoctions are combustible, could frame hazardous fume/air blends It lyses the materials in the skin and causes dermatitis Inhaling liquor fume causes pulmonary disturbance and focal sensory disturbance
Aldehydes	Formaldehyde Paraformaldehyde Glutaraldehyde Ortho-phthalaldehyde (OPA)	In gas structure, it is incredibly combustible. It structures unstable blends with air Utilized in much ventilated regions Synthetic concoctions are bothering, poisonous to people who expose or inward breath of far above the normal It is a common cancer-causing agent
Chlorine compounds (hypochlorites)	Sodium hypochlorite Calcium hypochlorite	Mixing hypochlorites with solid acids may bring about a severe chemical response that could discharge harmful gases The synthetic compounds respond violently with alkali, amines, or lessening specialists The synthetic compounds may cause skin bothering. Concentrated hypochlorite arrangements can cause synthetic consumes of the dermis
Iodine compounds	Iodine (aqueous solution or tincture) Povidone-iodine	Mixes can aggravate the dermal layer
Oxidizing agents	Hydrogen peroxide Peroxyacetic acid	It is responsive and, touchy Undiluted causes aggravation in eye and dermal layer
Phenols	Cresol Hexachlorophene	Irritation in skin and eye Consuming or exposing is destructive to people
Others	Ethylene oxide	It is exceptionally combustible and dangerous Aggravates skin, pulmonary, and eye infections Efficient cancer-causing agent

- Never blend disinfectants in with other cleaning operators in employments.
- Store the concoction agents in a concealed, cool, dry, and all around ventilated spot.
- Do not place inconsistent materials together.
- Do not discard synthetic specialists inappropriately.
- Use individual defensive hardware appropriately.
- Ask for direction from directors if all fails.
- Understand crisis quantifies completely.
- Inform the specialist of the synthetic operator utilized if feeling unwell.

10 Emergency Measures

If there should arise an occurrence of a crisis when utilizing substance operators, receive the accompanying emergency treatment measures:

Mouth – Rinse the mouth with clean water if the harmed is cognizant.

Inward breath – Rescue staff ought to be secured with all essential defensive gear first. Move the harmed to an area with outside air. Regulate mouth-to-mouth revival if the harmed experiences breathing issues or quits relaxing.

Pocket veil resuscitator is prescribed to use in salvage. It is a mouth-to-mouth revival gadget with single direction valve assists with performing salvage breathing and dispose of direct contact with the harmed's nose and mouth, in this manner keeping him from taking in the acclimated's exhalation.

Skin – Flush the skin with extensive clean water for at any rate 15 minutes and remove the debased garments.

Eyes – Push the eye open and wash with moderate running clean water for at any rate 15 minutes. Abstain from sprinkling the uncontaminated eye with the washings while flushing. Look for clinical help whenever required.

11 Alternatives to Disinfectant

Notwithstanding the antimicrobial opposition danger, specialists of significant economies, including the European Medicines Agency and FDA in the USA, have forced guidelines on antibiotic growth promoters (AGPs) and have attempted to place management anti-infection agents in authentic reconnaissance to diminish microbicidal obstruction throughout decreased utilization of antimicrobial arrangements and compounds. Simultaneously various viable choices have likewise been accounted for; for instance, antimicrobial peptides, which assume different jobs in bacterial end, insusceptible reaction, epithelial fortification, and battling infections like malignant growth (Chu et al., 2015; de la Fuente-Núñez et al., 2017; Ageitos et al., 2017).

Biocidal host safeguard short protein fragment like bacteriocins, L anti-toxins, and chemicals are created by every perplexing living being just as certain microorganisms and have assorted and complex antimicrobial exercises. Overall, these peptides exhibit a wide scope of antiviral and antibacterial exercises and methods of activity, and it is essential to recognize direct microbicidal and roundabout exercises against such microorganisms. The auxiliary prerequisites of peptides for antiviral and antibacterial exercises are assessed considering the differing set of essential and optional structures portrayed for having resistance peptides (Jenssen et al., 2006).

The disinfectant is set up with plant material including self-mend, rhubarb, *Magnolia officinalis*, *Parasitic loranthus*, garlic, neem, solvents like menthol, ethanol, petroleum ether, and distilled water. The plant material removed should be dissolvable, focused, homogenized, and blended to acquire the disinfectant. Terpenoids and fundamental oils, phenolic mixes, alkaloids, lectins and polypeptides, polyacetylenes, and sulfur mixes present in the plant source have the elements of antiphlogosis, disinfection, and calming tingling, and is non-harmful and safe (Pandya et al., 2017).

12 Conclusion

Some disease control practices that require the utilization of synthetic items containing phenols, alcohols, hydrogen peroxide, peracetic acid, and acetic acid may bring about antagonistic wellbeing impacts in uncovered specialists. Health care-associated infections (HAIs) stay a critical danger to understanding wellbeing, and ecological cleaning and sanitization is a key perspective in a far-reaching HAI avoidance plan. Nonetheless, by paying attention to laborer worries about occupational illness and executing controls to lessen presentation to cleaning and purification items, social insurance offices may give a more secure condition to laborers while shielding people from HAIs. This chapter provides the classification of chemical disinfectants, significance of considering disinfectant exposure while assessing human service laborers for occupational ailment, and alternatives to chemical disinfectants. More research is expected to portray the effect of alternative products, its presentation, associated health effects, and control techniques.

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A Review on the Occurrence and Effect of Pharmaceuticals and Personal Care Products on the Environment

Abirami Balakrishnan, I. Athithyan, K. Sri Bala Kameswari, and Chitra Kalyanaraman

Abstract The most crucial challenge of the twenty-first century is water management. In India, only about 38% of the urban population has access to sanitation services. Urban planners are facing dual problems of providing safe drinking water and sanitation facilities. Our existing sewage treatment plants (STPs) are designed for the removal of organic, grit, coarse materials; floating matter; suspended solids; and to some extent, destruction of pathogens in case used for horticulture/agricultural purpose.

Pharmaceuticals and personal care products (PPCPs) or micro-pollutants are classified as emerging contaminants (ECs) because of associated endocrine disruption, chronic toxicity, and the development of resistance to pathogens. The presence of micro-pollutants also endangers the reuse of treated domestic sewage. So far, there is no focus on ECs being either identified or investigated for their removal through conventional wastewater treatment plants. The key sources of PPCPs entering the water environment are excretion, domestic sewage, and direct disposal.

A few studies have been carried out on PPCPs in countries such as Korea, Sweden, the UK, China, Austria, the European Union, Germany, France, Italy, Greece, Switzerland, Spain, the Western Balkan Region, and the USA. In India, knowledge about the load of PPCPs entering into STPs and their removal efficiencies in existing treatment facilities is low.

PPCPs and antibiotics entering water bodies lead to severe ecological damage and potential adverse effects on the existing treatment facilities. Thus, treatment facilities should be concentrated to improve removal efficiencies of antibiotics in STPs. The primary focus of this chapter is to discuss the following in detail: (i) the sources of generation of micro-pollutants or PPCPs, (ii) existing scenario in regard

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to the level of occurrence of PPCPs in STPs, (iii) significant effect of their presence on the environment, and (iv) treatment options proposed/studied so far and additional treatment facilities required to destruct these pollutants, in a form of review to enable the policy makers to address these issues in future.

Keywords Emerging contaminants · Micro-pollutants · Pharmaceuticals and personal care products · Sewage treatment plants

1 Introduction

The most crucial challenge of the twenty-first century is water management. In India, only about 38% of the urban population has access to sanitation services. Pharmaceuticals and personal care products (PPCPs) or micro-pollutants are classified as emerging pollutants because of associated endocrine disruption, chronic toxicity, and the development of resistance to pathogens. The presence of micro-pollutants also threatens reusing treated domestic sewage.

The emerging contaminants (ECs) are unregulated contaminants whose release into the environment has emerged as an approaching crisis. They comprise thousands of chemical substances, such as hormones, flame retardants, PPCPs, pesticides, plasticizers, surfactants, and industrial additives (Ávila & García, 2015). Among the ECs, PPCPs and endocrine disrupting compounds (EDCs) and their transformation products are of great concern for humans and the aquatic environment (Gogoi et al., 2018).

PPCPs include active components of medications prescribed for humans and prescribed by veterinary doctors, diagnostic agents, and nutritional supplements (Kaplan, 2013; Bu et al., 2013). It also includes other consumer products such as disinfectants, sunscreens, fragrance powders, soaps, lotions, toothpaste, and cosmetics. Most of the PPCPs are water soluble in nature and occur in trace levels (Ávila & García, 2015). Owing to the high use of PPCPs along with their transformation by-products all over the world, there has been a considerable increase in the awareness due to their potential threat to human life and aquatic ecosystem (Daughton & Ternes, 1999; Kümmerer, 2001). The environmental distribution of PPCPs in air, water, soil, sediments, and animals is determined by their solubility, polarity, and other properties which may get affected by any small change in their chemical structure (Ávila & García, 2015).

India stands the world's third largest pharmaceutical industry in terms of volume (Patneedi & Prasadu, 2015). The pharmaceutical industry's growth is driven by the huge demand for human medicines required by a large population and veterinary medicines by the huge number of livestock. India will face a severe crisis since most urban areas do not have proper treatment facilities owing to dense population and unfettered use, sale, accessibility, and availability of antibiotics (Mutiyar et al., 2018). The repeated usage of pharmaceuticals by huge number of persons and animals causes a continuous release into the environment, either from untreated or inadequate sewage treatment facilities.

The pharmaceuticals consumed by patients are excreted to the environment through urine and feces (Fang et al., 2012). They are released to the environment through domestic wastewater and a large quantity reaches drinking water, due to poor removal at wastewater treatment plants (WWTPs). In India, sewage generation is higher, but the capacity of municipal sewage treatment plants is lower than the actual amount of generated sewage. A draft bill was published in India on January 23, 2020, mandating limits on the concentration of antibiotics found in the waste discharged by pharmaceutical factories into the surrounding environment. The country is not yet in a position to know the load of PPCPs entering into sewage treatment plants (STPs) and their removal efficiencies in existing treatment facilities. Once these PPCPs enter water bodies, they could lead to ecological damage and potential adverse effects on the existing treatment facilities. Hence, there is a need to study/ review the existing scenario of PPCP occurrence, effect, and treatment. The primary focus of this chapter is to discuss in detail the following:

(i) Sources of generation of micro-pollutants or PPCPs
(ii) Existing scenario in regard to the level of occurrence of PPCPs in STPs
(iii) Significant effect on the environment
(iv) Treatment options proposed/studied so far and additional treatment facilities required to destruct these pollutants

2 Sources and Classification of PPCPs

Balakrishna et al. (2017) identified the possible pathways for entry of PPCPs into the environment. The three main pathways identified were (i) house hold discharge, direct discharge, and excreta; (ii) pharmaceutical industries; and (iii) veterinary discharge. The main possible sources include the following:

(i) Domestic usage of soaps and fragrance talc let out into the sewers by bathing and washing
(ii) Effluents from personal care products manufacturing industry
(iii) Precipitation run-offs that carry soils contaminated with PPCPs and percolating into the ground water or reaching the nearest fresh water body
(iv) Veterinary drugs used in animal husbandry that reach surface water bodies through animal droppings
(v) Chemicals used in aquaculture that reach the fresh water stream directly
(vi) Expired medicines discarded and dumped in solid wastes that dissolve in leachate and contaminate the ground water
(vii) Traces of emerging contaminants (ECs) that are normally not removed in the STPs and released into fresh water streams

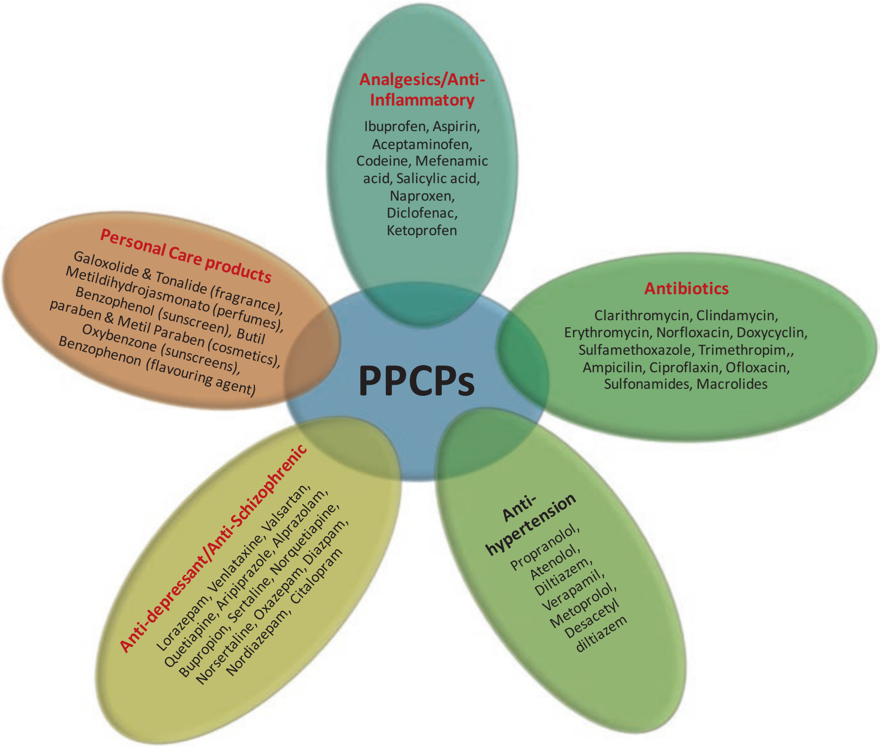

Fig. 1 Classification of PPCPs

The PPCPs are classified into three broad categories, namely, steroids, personal care products, and drugs (Arias et al., 2019). Steroids include estrogens, androgens, progesterone, and veterinary hormones. Personal care products include disinfectants, fragrances, hygiene products, UV protectors, and cosmetics. Drug category includes antibiotics, analgesics, antipyretics, and anti-inflammatory medicines. Figure 1 represents the classification of PPCPs and the list of compounds under each category reported so far.

3 Occurrence of PPCPs

Detection and estimation of PPCPs is dependent on the availability and degree of consumption, geospatial factors, temporal factors, wastewater treatment facilities, economy of the region, and local climatic conditions (Dey et al., 2019). Thus, PPCP levels globally are highly variable in terms of targeted compound and detected concentration level.

Several reviews were available for the occurrence of PPCPs all over the world (Bu et al., 2013; Ying et al., 2013; Kumar et al., 2019). Some of the reported PPCP compounds, present from different sources and regions in the world, are presented in Table 1.

4 Effects of PPCPs

The considerable level of occurrence of PPCPs in the treated wastewater from STPs will have serious effects on water bodies when released into surface water. As a consequence, it possesses an immense threat to the aquatic ecosystem prevailing in such bodies. Treated effluent, when released into land, contaminates the soil and reaches the groundwater, which is not safe in the regions where people depend on groundwater as their drinking water source. Also, these PPCPs, when adhered to the soil particles, may be absorbed by the plant roots, which again when consumed by human beings can be a health menace. The effect depends on the level of occurrence in the treated wastewater. If the levels are in traces, factors such as dilution may help to curb the impact of the effects when released into water bodies. While the PPCPs have no direct effect on human beings, consumption of water or plant that take up PPCPs causes adverse effects.

4.1 Effects on Surface Water

Photolysis and adsorption by sediments are the important environmental processes that PPCPs undergo when they enter the natural surface water bodies. Antimicrobial agents such as triclosan are adsorbed onto sediments and are captured in the pores and reduce the solubility. The process of adsorption is pH dependent (Lin et al., 2011). PPCPs that are adsorbed to sediments can help in reduction, but it may also act as a sink which are released again into the water stream. Liu et al. (2020a) have carried out an environmental risk assessment by screening 33 PPCPs that pose potential risks to aquatic organisms and found that 15 chemicals were categorized to be the priority compounds and 12 compounds posed low to high risk to the aquatic ecosystem.

4.2 Human Exposure

Human beings are directly exposed to PPCPs through routine use of personal care products and dietary intake. Using hair care products, tooth pastes, soaps, body washes, makeup, and skin lotions contribute to 80% of the daily personal care products. As PPCPs have very low volatility, their contribution to atmospheric

Table 1 Concentrations of PPCP compounds reported from different regions in the world

S. No	Compound(s) detected	PPCP category	Reported region	Levels	References
1	Oxybenzone	Sunscreens	Switzerland	69 g per 10,000 people per day	Brausch and Rand (2011)
2	Ibuprofen	Analgesic	Germany	3.5μg/L	Huppert et al. (1998)
3	Sulfamethoxazole, roxithromycin, and erythromycin	Antibiotics	Germany	6μg/L	Hirsch et al. (1999)
4	Clotrimazole	Antifungal medication	United Kingdom	22 ng/L	Thomas and Hilton (2004)
5	Carbamazepine in raw influent samples	Analgesic	England	2336 ng/L	Zhou et al. (2009)
6	Clofibric acid, naproxen, and diclofenac	Anticholesteremic drug and anti-inflammatory	Rio de Janeiro, Brazil	(0.01–0.06μg/L)	Stumpf et al. (1999)
7	Sulfamethoxazole, carbamazepine, and atrazine	Antibiotics	Montano, USA	490 ng/L, 420 ng/L, 130 ng/L	Miller and Meek (2006)
8	Ibuprofen, carbamazepine, paraxanthine, and caffeine	Analgesic and caffeines	North Ohio	2.8, 1.2, 1.8, and 4.2μg/L	Wu et al. (2009)
9	Acetaminophen, naproxen, bisphenol A, carbamazepine, TCS, caffeine, and ibuprofen	Analgesic/ anti-inflammatory	Mississippi, USA	65 ng/L, 135 ng/L, 147 ng/L, 114 ng/L, 26 ng/L, 38 ng/L, 34 ng/L	Zhang et al. (2007)
10	Sulfamethoxazole and carbamazepine	Antibiotics	Cape Cod, Massachusetts, USA	113 and 72 ng/L	Schaider et al. (2014)
11	Diclofenac, ibuprofen, and naproxen	Analgesic	Tula Valley, Mexico	4824 ng/L, 1406 ng/L, 13,589 ng/L	Gibson et al. (2010)
12	Ciprofloxacin	Antibiotic	Hyderabad, India	31 mg/L	Larsson et al. (2007)
13	Ibuprofen, clarithromycin, erythromycin, carbamazepine, and fluconazole	Antibiotic	South Korea	414 ng/L, 443 ng/L, 137 ng/L, 595 ng/L, 111 ng/L	Kim et al. (2009)

(continued)

Table 1 (continued)

S. No	Compound(s) detected	PPCP category	Reported region	Levels	References
14	Estrogenic hormones, ibuprofen, calorific acid salicylic acid	Analgesic/ anti-inflammatory	Pearl River Delta, South China	65 ng/L, 1417 ng/L, 248 ng/L, 2098 ng/L	Peng et al. (2008)
15	Ibuprofen and naproxen	Analgesic	Canada	7800,8600 ng/L	Guerra et al. (2014)
16	Metoprolol and sotalol	Beta blocker	Finland	8350, 1060 ng/L	Vieno et al. (2007)
17	Galaxolide® and Tonalide® (fragrance compounds)	Fragrance compounds	China, Spain	Between 509 and 2337 ng/L, 4750 and 13,399 ng/L	Chen et al. (2013); Pintado-Herrera et al. (2014)
18	Oxybenzone (sunscreen)	Sunscreen	USA	75–1400 ppb	DiNardo and Downs (2018)

environment is negligible. Even though they are less volatile, sometimes they may group with relatively high volatile PPCPs which were prevalent in indoor dusts or air and can be a threat when inhaled. Siloxanes, which are extensively used for personal care, were present in indoor dust samples in considerable concentrations. According to the study, children had higher daily intake from indoor dusts than the adults (Lu et al., 2010). Newborn babies and 3-month-old age group were found to be more prone to human health risks than the other age groups due to their low body weight. Comparatively, carbamazepine and ketoprofen possess great human risk among the other PPCPs.

By different pathways, the PPCPs reach human milk, blood, and urine making it threatening by passing the effect to the next stage. The reason for their occurrence was found out to be related to the daily use of body lotions, hand-cleaning agents, hair dyes, shampoos, and gels (Yin et al., 2012). With the objective of alleviating the agricultural water shortages, reclaimed wastewater is used to irrigate agricultural land. This usage of reclaimed water has raised concerns about soil contamination by PPCPs and the human health risks associated with the crop intake (Liu et al., 2020b).

5 Treatment of PPCPs

As stated earlier, occurrence of PPCPs is widespread in the effluents of WWTPs and poses an adverse effect on the aquatic environment. Even though they are present in trace levels, the existing treatment methods do not remove them completely. Hence, there is a need for specific treatment method in the treatment of PPCP to effectively remove them from the WWTPs.

5.1 AOPs for PPCP Removal

Many studies have reported AOPs for treatment of single compound which provide the basis to understand the degradation pathway and mechanism of degradation of each individual PPCP. Ozonation of diclofenac has been attempted by Qiu et al. (2020), and they observed that most of the degradation products except Oxalaldehyde (P3) and N-(2,6-dichlorophenyl)-2-oxoacetamide (P6) are harmless or less toxic. Ozonation removed 50% of TOC when applied for an anti-inflammatory drug indomethacin by Zhao et al. (2017a) and found that toxicity of indomethacin against *P. phosphoreum* was completely eliminated. Ozonation was attempted for fluoxetine (FX) and norfluoxitine (NFX) and found that the toxicity on *Vibrio fischeri* decreased after ozonation but not eliminated completely due the formation of aldehyde by-products (Zhao et al., 2017b).

Mineralization of about 40% was observed for 60 min of ozonation and 99.5% degradation was obtained for tetracycline (Wang et al., 2020). The best treatment condition of ozonation of nifedipine (NIF) from aqueous solution was obtained at O_3 of 1. 6 mg/L, NIF of 3. 6 mg/L, and pH of 7 (Meiling et al., 2017). Ozonation along with different concentration of NO_3^- was attempted for ketoprofen, and the decomposition kinetics was evaluated (Zeng et al., 2018). Optimum conditions for electro-Fenton process for sodium diclofenac were experimentally determined to achieve 97.21% of COD (Davarnejad & Sabzehei, 2019).

A few studies have reported AOP for PPCP removal from water/wastewater stream. For the total removal of PPCPs from contaminated tap water, ozonation conditions were optimized as PPCP concentration of 1–600μg/L, retention time15–30 min, and pH 6–9 units (Ewadh et al., 2019). A two-staged nanoscale zero valent iron-activated persulfate coupled with Fenton (nZVI-PS-Fenton) oxidation process significantly degraded indomethacin, bisphenol A, tetracycline, norfloxacin, carbamazepine, paracetamol, sulfamethoxazole, sulfamethazine, and phenacetin by 77–100% in water (Wu et al., 2020).

5.2 Adsorption Studies for PPCP Removal

Activated carbon is widely used as an adsorbent and has application for adsorption of PPCPs in wastewater. It has two forms: granular activated carbon (GAC) and powdered activated carbon (PAC). Yu et al. (2008) and Liu et al. (2009) previously reviewed the use of activated carbon in EDC removal. The addition of granular activated carbon directly into the aerated tank caused the enhancement of adhesion of the more PPCPs such as diazepam, diclofenac, and carbamazepine. These PPCPs have higher affinity for activated carbon than musk fragrances (celestolide, tonalide, and galaxolide) and acidic pharmaceuticals (naproxen, ibuprofen) (Serrano et al., 2010).

For removing five PPCPs, chlorophene, 1-H-benzotriazole, nortriptyline-HCl, and 3-methylindole from wastewater, powdered activated carbon/ultrafiltration (PAC/UF) process was investigated and reported that the adsorption capacity of activated carbon was in concurrence with hydrophobicity of PPCPs (Rodriguez et al., 2016). Even though activated carbon has the capability of removing EDCs, it has two problems, namely, decrease of adsorption capacity and deterioration of activated carbon, which requires further studies to improve the performance (Mailler et al., 2015; Meinel et al., 2015). The charge of the PPCPs and hydrophobicity are the two main factors which decide the adsorption capacity of activated carbon to PPCPs. The main factors that affect the efficiency of activated carbon for the removal of PPCPs are pH, structure (Mestre et al., 2007), and contact time (Nam et al., 2014).

5.3 Biological Treatment Studies for PPCP Removal

Several studies have been conducted by using pure isolates obtained from activated sludge to remove the reported PPCPs, such as iopromide (Liu & Wang, 2013), carbamazepine (Santosa et al., 2012), ibuprofen (Almeida et al., 2013), paracetamol (Zhang et al., 2013), sulfamethoxazole (Jiang et al., 2014; Reis et al., 2014), triclosan (Zhou et al., 2014; Roh et al., 2009), and diclofenac (Hata et al., 2010). On the contrary, tetracycline, ciprofloxacin, and trimethoprim are not capable of inducing the required enzyme production by the microbes and make them difficult to biodegrade (Wang & Wang, 2016).

The use of plant-bacteria partnerships was studied to emphasis on phytoremediation of PPCPs. The bacteria improve the bioavailability of intricate nutrients and help the host plant to gain biomass with plant growth–promoting hormones. The study suggests that plant-bacteria partnerships have synergetic effect yet requires efforts to organize relations between specific plant species, type of microbes, and target pollutants (Nguyen et al., 2019). In the lab-scale constructed wetland (CW) – stabilization tank (ST) – GAC slow sand filtration system, Proteo-bacteria were the most dominant phylum among 47 phyla that were detected. The diversity of microbial community was decreased potentially because of the influence of exposure to the increased PPCP compounds (Li et al., 2019).

5.4 Combined Treatment Methods for PPCP Removal

As discussed above, PPCPs are highly recalcitrant and toxic to microorganisms. Thus, complete degradation of PPCPs is not achieved by adopting one method. In such a scenario, combined methods such as series of AOPs or biological degradation are needed (He et al., 2014).

Activated sludge followed by ultrafiltration, MBR reverse osmosis/ ultrafiltration/ microfiltration/ ozonation, ozonation followed by biological activated carbon, MBR followed by RO, and ozonation followed by biological activated carbon are some of the combination of biological and chemical treatments to degrade PPCPs. Salicylic acid, beta blockers, salbutamol, and sotalol were degraded efficiently in MBR-reverse osmosis hybrid system (Ahmed et al., 2017).

For tetracycline, single-step biodegradation was not sufficient to degrade and eliminate toxicity. Thus, an integrated process was developed and completed with 10 min of ozonation (Gómez-Pacheco et al., 2011). A method of UV/H_2O_2 followed by a bacterial consortium was employed to mineralize carbamazepine (Keen et al., 2012).

Electro-Fenton was applied for cephalexin (Estrada et al., 2012), furosemide, and ranitidine (Vargas, 2014). The toxicity can be reduced further by subjecting to an aerobic system. Hence the combination of chemical pretreatment followed by aerobic biological treatment is a better choice, compared to a single treatment. From the review, it is clearly understood that more studies are required to conclude the optimum parameters for each method even though combined systems degrade the PPCPs and contribute to reduction of toxicity.

6 Conclusion

From the review of literature, it is evident that the levels of PPCPs from various sources are increasing in surface water, groundwater, and plant uptake. Even though the increasing levels of PPCPs in different environments are not alarming at present, the rate suggests that these PPCPs can pose a threat in the near future. Due to the recalcitrant nature of PPCPs, the conventional biological treatment adopted in STPs is not efficient in PPCP removal. Since, either a biological or a chemical treatment of PPCPs is not efficient in degrading them, a combination of biological and chemical treatments, which show fair results in degrading the PPCPs, should be opted. Adsorption studies showed mixed results and suggest that adsorption depends on various factors like hydrophobicity of PPCPs, binding sites, and deterioration of activated carbon. PPCPs in soil strata and groundwater can be treated by plant-bacteria's synergism and using some of micro-algal degradation. More studies are needed to establish the relationship between specific plant species, type of microbes, and target pollutants.

The effect of PPCPs on humans depends on the daily intake or exposure to the PPCPs. Practices like responsible disposal of drugs, product stewardship, and recycling and improving the sewage treatment infrastructure by equipping new technologies to remove PPCPs can curb the effects. Hence, more research has to be focused to fix a desirable or acceptable limit of intake or exposure levels of different compounds, based on their toxicity, in order to guide or design a working model to manage or treat them effectively.

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DNA Damage and Effects of Antioxidant Enzymes in Earthworm (*Eudrilus Eugeniae*) Exposed to Contaminated Soil with Organic Environmental Pollutant: Triclosan

V. Swabna and M. Vasanthy

Abstract Triclosan is a nonionic, phenolic, antimicrobial compound that is used all over the world, as a key ingredient in pharmaceutical and personal care products (PPCPs) such as disinfectants, soap, detergent, toothpaste, mouthwash, fabric, deodorant, shampoo, and plastic additives. It causes a range of adverse effects in animals and has a great impact on environment also. This chapter investigates the effect of triclosan in varying concentrations and triclosan-contaminated soil by using earthworms as bioindicators. The effects were calculated by analyzing their antioxidative enzymes and DNA damages. The antioxidant enzymes were estimated by analyzing the antioxidant properties of earthworm which include glutathione peroxidase and catalase. Comet assay was done to monitor the DNA damage of the earthworms with regard to triclosan toxicity. The investigation proves that when the concentration of triclosan increases, the effects in the earthworms were also radical. This study thus denotes that triclosan induces adverse consequences on earthworms which sever the antioxidant enzyme mechanisms and DNA damage.

Keywords Triclosan · Earthworm · Antioxidant enzymes · DNA damage · PPCPs

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1 Introduction

Organic contamination is briefly visualized as the exploitation of water resources by organic compounds from various sources by anthropogenic sources. Contamination occurs in varied ways that are persistent in nature which may conclude in a major concern that may lead to a great impact on the environment. Organic pollutants that may enter the fresh water resources increase day by day due to manmade activities, and these pollutants degrade naturally to less toxic or nontoxic forms (Focazio et al., 2008). However, these pollutants get accumulated or biomagnified in organisms through food chain which might alter the diversity (Thornton et al., 2001). Among the organic pollutants, the presence of pharmaceutical and personal care products (PPCPs) causes inimical effects toward the aquatic and terrestrial organisms. The major anthropogenic sources of pharmaceutical and personal care products (PPCPs) include communal waste and byproducts of fertilizers from farmlands. PCPs such as diclofenac, iopamidol, carbamazepine, ibuprofen, clofibric acid, triclosan, phthalates, and bisphenol A were classified as the major entrants that can cause detrimental effects (Ellis, 2008).

5-Chloro-2-(2, 4-dichlorophenoxy) phenol, commonly known as triclosan, is a synthetic antimicrobial, antifungal agent that has some antibiotic properties (Singer et al., 2002). It is an aromatic halogenated compound containing phenolic, diphenyl ether, and polychlorinated biphenyls (PCBs) as supporting structures. The chief mode of triclosan discharge into the environment is through pharmaceutical and personal care products (PPCPs) that are used by humans, such as toothpastes, shampoos, detergents, and cosmetics (McBain et al., 2002). Presently, triclosan and its by-products have settled all over the environment and even found in human breast milk. The health issues concerned with triclosan and its by-products include antibiotic resistance, dermal irritations and allergies, endocrine disruption, altered metabolism, and development of tumors (Latch et al., 2003).

Earthworms are considered as bioindicators for testing the contaminants and to check the toxicity of the soil. The toxic tests which are used to identify the toxic contaminants are quantified by the earthworm's survival and reproductive rates, biomass index, and behavioral changes. This assessment gives us knowledge about the contaminant uptake, its metabolism, and the by-product elimination which in other words is called as toxicokinetics. Earthworms are present in various types of soils ranging from temperate to tropical regions. Hence, they are aforethought to be decisive in food chains as these earthworms are contemplated as a prime source of food for many organisms including birds and mammals which have turned out to be the dominant impetus for ecologists and ecotoxicologists to explore the whereabouts of the earthworms (Lokke & Van Gestel, 1998). This is the major reason for which earthworms are habitually used as experimental organisms to analyze the chemicals deposited in the soil and also to find out the nature and characteristics of the chemicals (Oste et al., 2001).

The effect of triclosan in varying concentrations and PPCP-contaminated soil was analyzed by using earthworms as knockoff organism. This was done by estimating their changes in antioxidative enzymes and DNA damages. The estimation of antioxidative enzymes and protein was done to perceive the antioxidant properties of the earthworm after introducing into the triclosan-contaminated soil. The antioxidant enzymes were analyzed for estimating the antioxidant properties of earthworm which include gluthothione peroxidase and catalase. Comet assay was also done to check the DNA damage of the earthworms with respect to triclosan toxicity.

2 Materials and Methods

2.1 Earthworm Exposures

Earthworms used in this assay (*Eudrilus eugeniae)* were purchased from an earthworm culturing farm at ICAR-Krishi Vigyan Kendra (KVK) in Karur District, which were introduced into the artificial soil, which is composed of 10% kaolin clay, 20% of coir pith, and 70% of industrial soil. Triclosan was added to the soil in the concentration of 0 (control), 0.25 mg, 0.50 mg, 0.75 mg, 1.00 mg, and one bowl with PCP-contaminated soil obtained from river beds of Kaveri. For each concentration bowl, 15 earthworms were inoculated.

2.2 Enzyme Extraction

Earthworms were killed by introducing into the formaldehyde solution for a minute and placed in a dissection tray. It was dissected vertically, its gut was cleared, then placed into a prechilled mortar and pestle, and crushed under ice-cold condition with 0.5 M Phosphate buffer (pH 7.0). The homogenate was centrifuged at 8000 rpm at 4 °C for 30 min (Song et al., 2009).

2.3 Protein Estimation by Bradford Assay

Measurement of protein content was necessary to calculate enzymatic activities. The protein content was determined using the Bradford method (Bradford, 1976). It is widely used and more reliable for detecting 20-400 μg. To the clean test tubes, 2.50 ml of Bradford reagent was added. To the reagent, 10-20 μl of earthworm extract is added which produces a blue color by reaction. Its absorbance is measured at 595 nm.

2.4 *Enzyme Assays*

Catalase

Catalase (CAT) activity was determined as described by Jingbo et al. (1997). 1.5 ml of phosphate buffer is added into the test tube. 0.5 ml of hydrogen peroxide is added to the buffer. To the mixture, 100 µl of earthworm extract is added. At this stage to the reaction mixture, 250 µl of potassium dichromate is added which when added arrests the reaction at different time intervals. Then the whole set is kept in boiling water bath for 10 minutes. After 10 minutes, the reaction mixture develops a green color to which the absorbance is measured at 570 nm.

Glutathione Peroxidase

Glutathione peroxidase activities were assayed according to the method of Saint Denis et al. (1998). 200 µl of EDTA is added to the centrifuge tubes. To that 100 µl of sodium azide is added along with that 100 µl of hydrogen peroxide was added. To the reaction mixture, reduced glutathione was mixed. 400 µl of phosphate buffer is added simultaneously. To that, earthworm extract is added followed by an incubation of 37 °C for 10 minutes. Then the reaction is arrested by adding 500 µl of 10% TCA. Subsequently the whole mixture is centrifuged at 3000 rpm for 3 minutes. The supernatant is transferred to a test tube and 3 ml of disodium hydrogen phosphate is added. Then 1 ml of DTNB was added which develops a yellow color. Absorbance is measured for the reaction mixture at 412 nm.

2.5 *Comet Assay*

The comet assay was performed by the method described by Eyambe et al. (1991). The earthworm cells were collected by trypsinization from the six tissue samples. The microscopic slides were sequentially coated with 200 µL of 0.75% normal melting agarose as the first layer and 100 µL of 0.5% low melting agarose as the second layer. Then 20 µL of each cell suspension was added to 60 µL of 0.5% low melting agarose, which was distributed on the slides as a third layer. Then the slides were incubated in cell lysis buffer (2.5 M NaCl, 0.2 M NaOH, 100 mM Na_2EDTA, 10 mMTris–HCl, 1% Triton X-100, and 10% dimethyl sulfoxide, pH =10.0) for overnight at 4 °C. After that, the slides were immersed in double distilled water for three times followed by 20 min incubation of unwinding solution (3 M NaOH). Subsequently, the slides were placed in a horizontal gel electrophoresis tank containing electrophoresis solution (1 mM Na_2EDTA and 300 mM NaOH, pH =13). The electrophoresis was conducted at 25 V (1 V/cm, 300 mA) for 25 min. Then the slides were incubated in neutralization buffer (0.4 M Tris–HCl, pH =7.5) for 10 min followed by immersion in ultrapure water for three times and air-dry. The cells were stained with 50 μL of ethidium bromide (5 mg/L) and observed under fluorescent microscope. All steps were carried out under dim light to minimize extra DNA damage.

3 Results and Discussion

3.1 Mortality Table

The mortality of the earthworms was observed throughout the study period (Table 1). The mortality of the earthworms significantly increased with increase in the concentration of the triclosan. This signifies that triclosan induces mortality in the earthworms.

3.2 Effect of Triclosan on Protein Content

The total protein content was subsequently increased in the second week and decreased throughout the week in the control. There was a decrease in the protein levels (0.25, 0.50, 0.75, 1.00 mg kg^{-1}) from the first week to the fourth week. Decreased levels of protein content have also been noted in the PCP-contaminated

Fig. 1 Experimental setup of earthworms with different concentrations of triclosan. A - Control, B – 0.25 mg, C – 0.50 mg, D – 0.75 mg, E – 1.00 mg, F – contaminated soil

Fig. 2 Different stages of earthworm in 4 weeks (control)

Fig. 3 Different stages of earthworm in 4 weeks (contaminated soil)

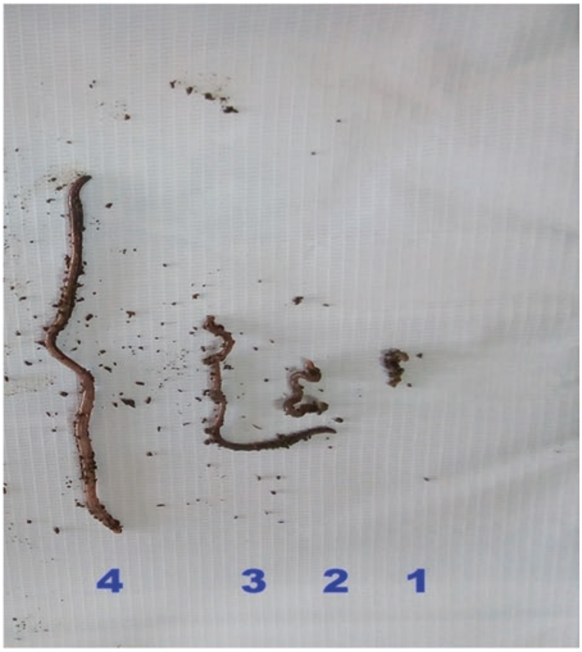


Table 1 Mortality of earthworms

Sl.. no	Concentrations	Number of earthworms introduced	First week	Second week	Third week	Fourth week
1	Contaminated soil	15	15	12	10	7
2	Control	15	15	14	14	13
3	0.25 mg	15	15	14	13	12
4	0.50 mg	15	15	13	13	12
5	0.75 mg	15	15	13	12	10
6	1.00 mg	15	15	13	11	9

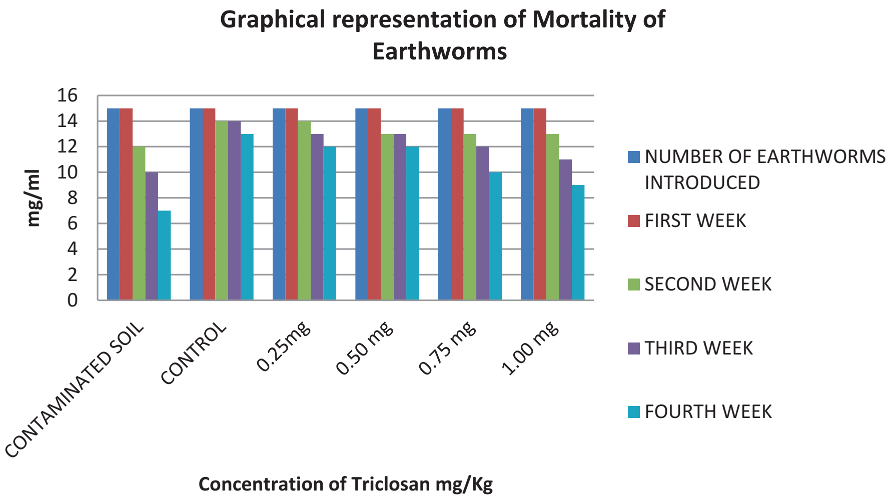


Fig. 4 Mortality of earthworms

soil. This could be due to the fact that triclosan may have induced and enhanced the gene transcription and expression of mRNA (Lescoat et al., 2000) (Table 2).

3.3 *Enzyme Assays*

Effect of Triclosan on Catalase Concentration

The catalase activity of the control has been increasing from the seventh day onward and increased weekly. But there is a marked increase in the other concentrations of soil with triclosan (0.25 mg, 0.50 mg, 0.75 mg, and 1 mg) concentration throughout the 4 weeks. The catalase activity tended to increase in the tissues of the earthworm at the start of the treatment and then they have been increased till the fourth week. Compared to the concentration, the catalase activity tends to be more effective in the

Table 2 Estimation of protein concentration of earthworm sample

Concentrations	First week	Second week	Third week	Fourth week
Control	0.1234	0.1453	0.1335	0.1136
0.25 mg	0.0934	0.0734	0.0686	0.0499
0.50 mg	0.0789	0.0519	0.0491	0.0358
0.75 mg	0.0654	0.0413	0.0354	0.0255
1.00 mg	0.0529	0.0347	0.0281	0.0137
Contaminated soil	0.0401	0.0235	0.0194	0.0091

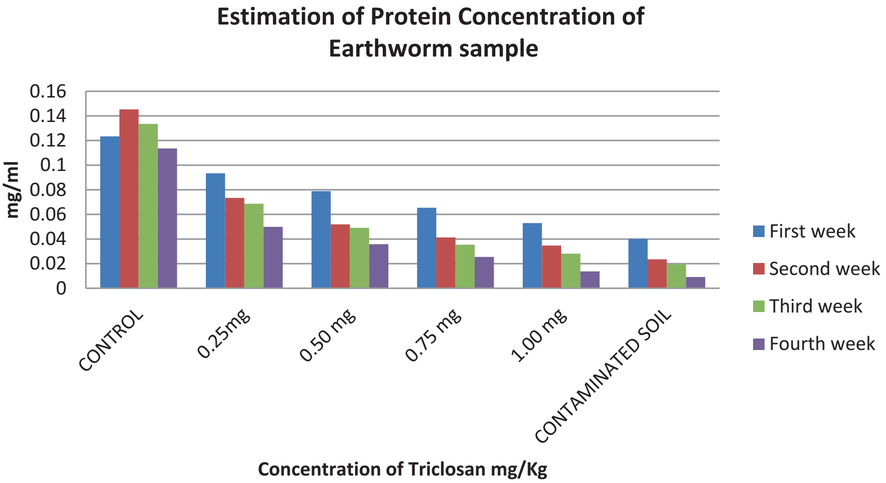


Fig. 5 Graphical representation of estimation of protein concentration of earthworm sample

contaminated soil. The highest catalase activity was observed in the triclosan-contaminated soil in the fourth week which is denoted with 1.996 IU/ml (Table 3 and Fig. 6).

The catalase activity may be induced in the cells that were exposed to PCPs. The escalation and deterioration of catalase activity is regulated at the mRNA level of the earthworms (Mutoh & Hayashi, 1988).

Effect of Triclosan on Glutathione Peroxidase Concentration

There was significant increase in the GPx activity in all the four concentrations of triclosan (0.25, 0.50, 0.75, 1.00 μg kg^{-1}) and the contaminated soil when compared to the control (Table 4 and Fig. 7). The highest Gpx activity was signified in the earthworms present in the contaminated soil samples with the highest value of 2.108 IU/ml in the fourth week.

Table 3 Estimation of catalase concentration of earthworm sample

Concentrations	First week	Second week	Third week	Fourth week
Control	0.4618	0.8625	1.2797	1.4645
0.25 mg	0.503	0.8921	1.3705	1.3133
0.50 mg	0.7111	0.9333	1.5748	1.4954
0.75 mg	0.8218	0.9581	1.7524	1.0254
1.00 mg	0.8725	0.9639	1.8001	1.8408
Contaminated soil	1.1021	1.312	1.797	1.996

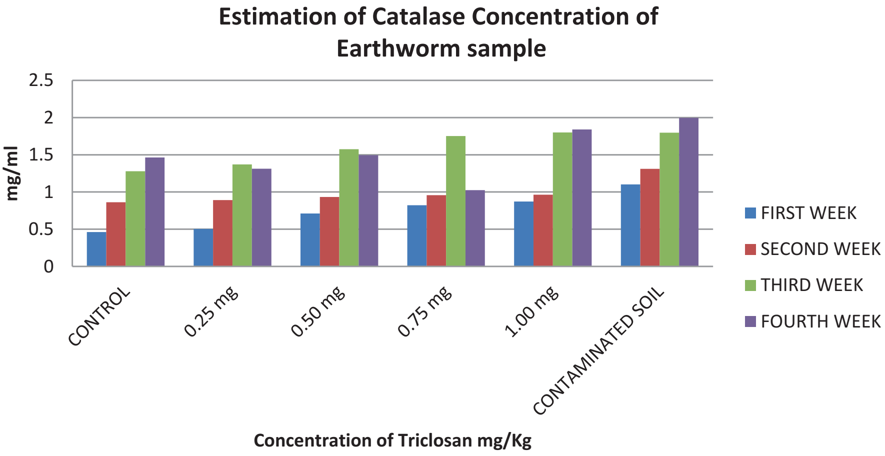


Fig. 6 Graphical representation of estimation of catalase concentration of earthworm sample

Table 4 Estimation of glutathione peroxidase concentration of earthworm sample

Concentration	First week	Second week	Third week	Fourth week
Control	0.6646	0.6975	0.8426	0.9462
0.25 mg	0.6961	0.7234	0.9243	1.2129
0.50 mg	0.7321	0.8189	1.008	1.6498
0.75 mg	0.7871	0.9461	1.3515	1.8593
1.00 mg	0.8692	1.1234	1.6352	1.9961
Contaminated soil	0.9971	1.2254	1.7651	2.1098

The GPx activity increased from the first day and then throughout of the experiment period in all the groups prompting that antioxidant defense is overwhelmed by the reactive oxygen species. Glutathione has the ability to control the levels of peroxides in the body. Predominantly in a system, there should be a balance between the GPx production and peroxide level. In the earthworms, the system has lost its critical balance of redox states compared to control animals (Song et al., 2009).

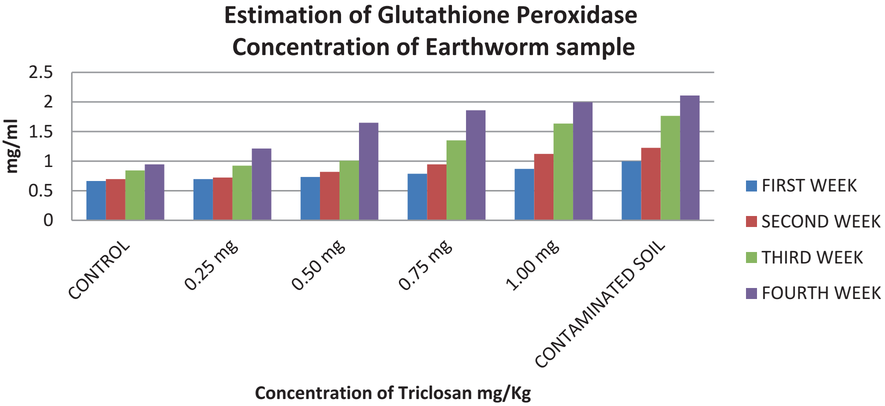


Fig. 7 Graphical representation of estimation of glutathione peroxidase concentration of earthworm sample

3.4 *Comet Assay*

Comet assay of the earthworm coelomocytes were tested on the seventh, 14th, 21st, and 28th day after treatment with different doses of triclosan. In the control group (Figs. 8, 9, 10, 11, 12, and 13), cells with intact DNA and few comets with very short tail length were seen. The extent of DNA damage along with number of comets was increased with increased doses of triclosan (control, contaminated soil, 0.25 mg, 0.50 mg, 0.75 mg, 1.00 mg) and triclosan-contaminated soil. These were significantly higher than those of the controls due to DNA fragmentation; therefore, DNA damage increased as triclosan concentration increased.

Oxidative stress induces many types of negative effects such as membrane peroxidation, loss of ions, protein cleavage, and DNA strand breakages, which could lead to cancer in humans or animals (Collins & Harrington, 2002). In this chapter, the induction of the DNA damage was majorly due to oxidative stress, which indicates that ROS accumulation in the earthworm tissues which may have caused subsequent DNA damage, or due to the activation of DNA repair mechanisms inducted by triclosan in earthworm coelomocytes.

Numerous studies show that reactive oxygen species is the major reason for DNA damage which cause strand breaks, nucleotide removal, and modifications in the nucleotide bases. A1lthough the cells had developed repair mechanisms to correct naturally occurring errors in DNA, enormous ROS can lead to a permanent error or damage of DNA (Mittler, 2002).

1. *Control*

2. *Contaminated soil*

3. *Earthworm (0.25 mg)*

Fig. 8 Comet assay – control

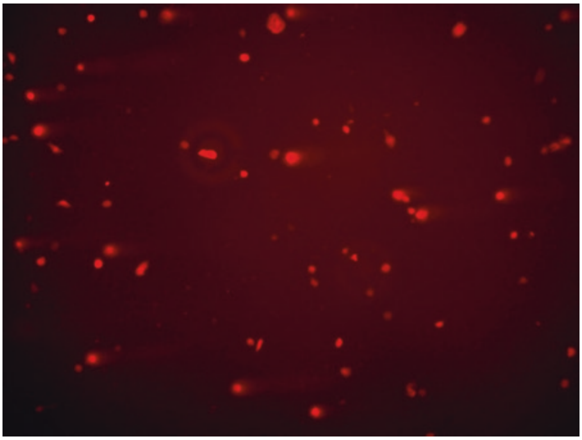


Fig. 9 Comet assay – contaminated soil

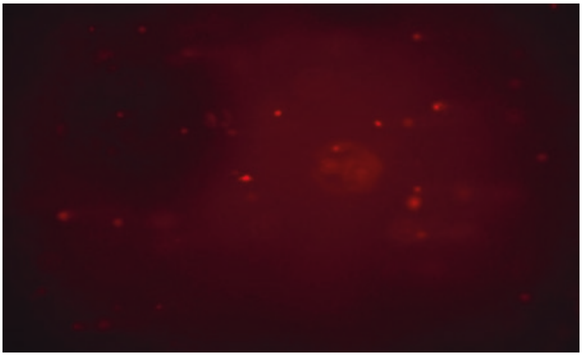
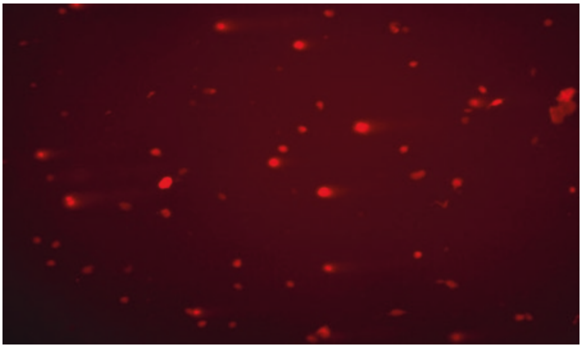


Fig. 10 Comet assay – 0.25 mg



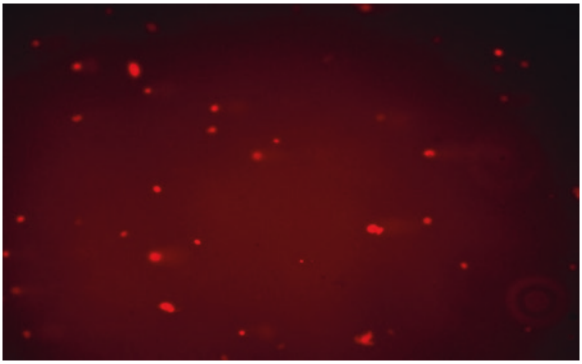


Fig. 11 Comet assay – 0.50 mg

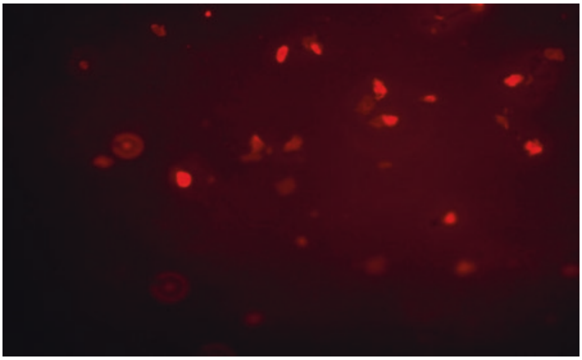


Fig. 12 Comet assay – 0.75 mg

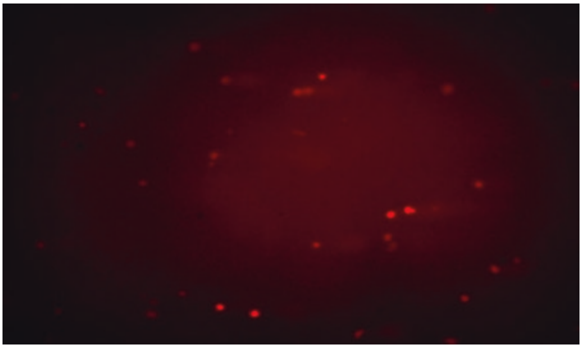


Fig. 13 Comet assay – 1.00 mg

4. *Earthworm (0.50 mg)*
5. *Earthworm (0.75 mg)*
6. *Earth worm (1.00 mg)*

4 Summary and Conclusion

Earthworms are the most suitable animal for testing the contaminants and to check the toxicity of the contaminated soil. Acute and chronic toxicity tests have been used traditionally to assess the toxicity of contaminants, with mortality and changes in biomass, reproduction rates, and behavioral responses representing endpoints. The uptake, accumulation, and elimination properties of metals by earthworm are the major part of toxicology, which is called toxicokinetics. Triclosan in the form of pharmaceutical and personal care products (PPCPs) is widely distributed in the environment, and it causes a range of adverse effects in animals. It has been shown to inhibit enzymes and alter biological membranes related to the formation of lipid peroxides.

The effect of triclosan in varying concentrations and triclosan-contaminated soil was analyzed by using earthworms as model organisms. This was done by estimating their antioxidative enzymes and DNA damages. The estimation of antioxidative enzymes and protein was done to perceive the antioxidant properties of the earthworm after introducing into the triclosan-contaminated soil. The antioxidant enzymes were analyzed for estimating the antioxidant properties of earthworm which include glutathione peroxidase and catalase. Comet assay was also done to check the DNA damage of the earthworms with regard to triclosan toxicity.

The investigation concludes that when concentration increases, the effects in the earthworms are also drastic. This shows that triclosan induces an adverse effect on earthworms which amputate the antioxidant enzyme mechanisms and DNA damage.

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Pharmaceutical Pollutants in Water: Origin, Toxicity Hazards, and Treatment

Ravikumar Dhanalakshmi, Ponmudi Priya, and Vajiravelu Sivamurugan

Abstract Medicines are immensely playing an essential role in protecting human and animal health. Pharmaceuticals are categorized into myriad therapeutic divisions, including anti-inflammatories, antibiotics, antipsychotics, antihypertensives, antidiabetics, antihistamines, lipid regulators, anticonvulsant, β-blockers, stimulants and statins. This chapter is aimed to offer a brief overview on the origin of pollutants of antibiotic and anti-inflammatory medicines and their brief toxicity hazards to human and aquatic life. Due to the high prevalence of infectious diseases, antibiotics and related by-products are one of the major pharmaceutical pollutants. Non-steroidal anti-inflammatory drugs (NSAIDs) are customarily being used and consequently are perceived in effluent and wetland water and may be found in groundwater systems. There are growing environmental concerns and excessive usage of medicines emerging as contaminants when their residues enter freshwater systems. Overwhelmed use of pharmaceuticals showed impact on aquatic and terrestrial living beings as well as the environment.

Keywords Antibiotics · Pharmaceuticals · Pesticides · Xenobiotic

Abbreviations

AC	Activated carbon
AMWPE	Average molecular weight medium density polyethylene
AOP	Advanced oxidation process
API	Active pharmaceutical ingredient
BIS	Bureau of Indian Standards

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BOD	Biological oxygen demand
CL	Castor leaves
COD	Chemical oxygen demand
COF	Carbon organic frameworks
CPCB	Central Pollution Control Board
DCF	Diclofenac
GnO	Graphene oxide
GWRC	Global Water Research Coalition
HQ	Hazard quotient
IBU	Ibuprofen
ICMR	Indian Council of Medical Research
ICNP	Iron composite nanoparticles
KTP	Ketoprofen
LF	Luffa cylindrical
MeIM	Methylimidazole
MOF	Metal organic framework
NPX	Naproxen
NSAID	Non-steroidal anti-inflammatory drug
POP	Pseudo-persistent pollutant
PP	Polypropylene
PXRD	Powder X-ray diffraction
RH	Rice husk
SB	Sugarcane bagasse
SIL	Silica modified with ionic liquids
UHMWPE	Ultra high molecular weight polyethylene
WHO	World Health Organization
ZIF-8@NiAl-LDHs	Zeolitic imidazolate framework @ layered double hydroxides

1 Introduction

1.1 What Are Organic Pollutants?

Organic pollutants are defined as any kind of organic molecules which persist in the environment and contaminate soil and water. Various sources of organic contaminants cause penetration in soil and pollute groundwater. It will reduce the penetration of light into the water (Verma et al. 1984). So, automatically the quality of the surface water is damaged and becomes hazardous to humans also called wastewater (Gupta et al. 2017). Removal of organic hazardous waste have become the highly rewarding environmental topic for discussion besides heavy metals which are contaminated with water, because they are intractable and purposeful. These pollutants contain medicinal products, skin care and hygiene products, insecticides, detergents, organic mordants, and habitual industrial organic chemicals such as phenolic, halogens, and aromatics (Lu and Astruc 2020; Nouri et al. 2020). These organic pollutants are classified into two types, namely, oxygen demanding waste and synthetic organic pollutants. The first type of oxygen demanding waste are degraded by bacterial activities, but the second type of organic pollutants cannot be degraded, and it can be dissolved, contaminated with water, and turned to harmful for the aquatic environment.

1.2 Pollution from Pharmaceutical Sources

Water plays a vibrant role in the human body, and it is a key component of all the existing things. Due to various reasons such as population, extra usage of water in industries, and wastage of water, 0.01% of freshwater is under serious problem at present. Pollutant in water is an important topic to discuss because it is directly linked with the ecosystem with all living and non-living things. The disposal of water from various sources, such as industrial activities of food, textile, paper, rubber, leather, plastics, coal, petrochemical, pharmaceutical, and others; personal care products such as painkillers, tranquilizers, antibiotics, skin care products, and hair styling agents; household utilization, chemical laboratories throughout the world, exhibits pollutants (Elhalil et al. 2018).

The quality of water according to WHO, CPCB, BIS, and ICMR estimate that 70% was seriously affected by the contamination from various pollutants (Ramakrishnaiah et al. 2009; Jindal and Sharma, 2010) in India, and it is not potable for human consumption (Gupta et al. 2017). Environmental issues created by the pharmaceutical pollutants were initially brought to widespread notice in the 1990s when some of the pharmaceutical sediments were detected in drinking water across Europe (Yang et al. 2020). In today's world, the pharmaceutical industry is one of the most illustrious fields. It can be classified as an extraction pharmacy, biopharmacy, and chemical pharmacy. In association with chemicals used in the pharmaceutical industries, which also produce many types of harmful contaminants to the environment and on account of their structural firmness and non-biodegradation, they persist in the environment (Li and Yang, 2018).

The chemical contaminants originated from various pharmaceutical processes such as synthesis, separation, and purification not only affect the surface but also groundwater due to its persistent nature (Fig. 1). Pollutants may also be created in pool water for various reasons such as source and continuous release of organic matter by bathers (Fantuzzi et al. 2018). All the pollutants were not completely removed by chlorination or any other means of disinfection, and it will again pose serious problems for humans (Teo et al. 2015). In Australia, an investigation showed daily variability of about 30 different pharmaceuticals detected in pool water. Ibuprofen is one of the most used NSAIDs with a concentration of 16–83 ng L^{-1}. In Spain, 32 pharmaceuticals were evaluated with concentrations lower than 100 ng L^{-1} (Ekowati et al. 2016).

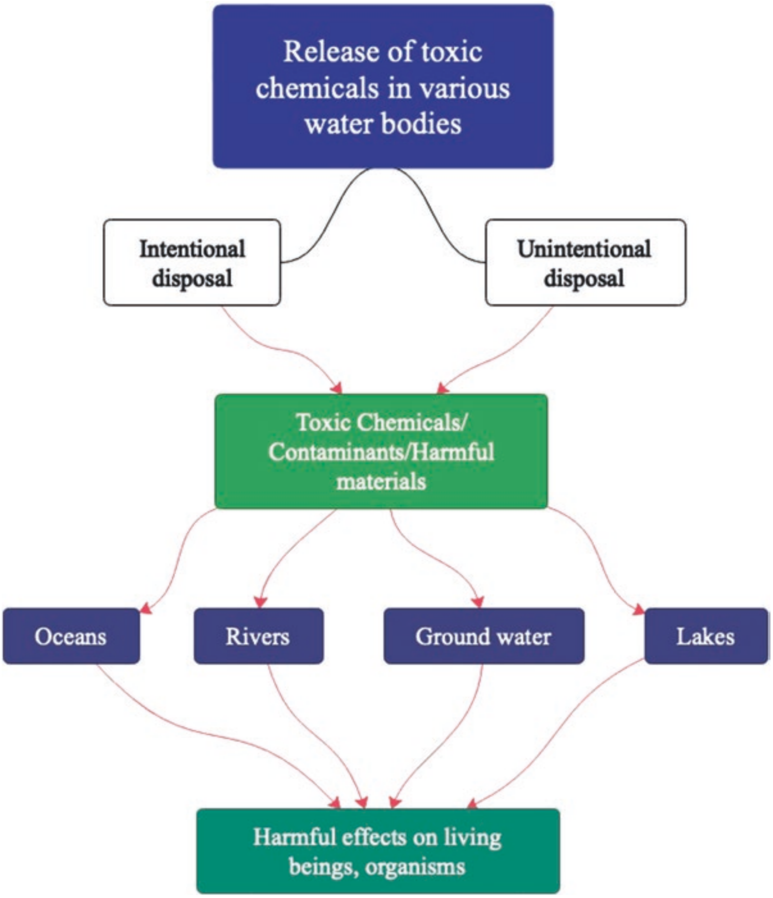


Fig. 1 Release of toxic chemicals in various water bodies

Anti-inflammatory drugs are more long established as pharmaceuticals for the treatment of animal and human diseases. AIDs are high aqua stable, high hydrophilicity (Fu et al. 2019). NSAIDs are spreading widely as metropolitan garbage water contaminants, of which several are protecting shield for the biological and chemical degeneration in traditional sewerage treatment, and represent a significant environmental health threat pandemic (Sarker et al. 2018). Prolific investigations have explored that these pollutants cannot be completely eradicated during treatment in wastewater treatment plants. For the domestic microbial wastewater treatment with operational parameters such as cathode, medium pH, applied voltage, air flow, concentration of NSAIDs, iron(II) concentration, and contact juncture are considered. For this purpose, EAOP is a suitable method to remove degradable pollutants (Nadais et al. 2018). A wide spectrum of chemical degradation methods are developed, regrettably most of these techniques have to overcome the disadvantages, as well as diminished confiscation proficiently, formation of noxious effluent by-products, excess capital, and labor costs. To compete with these problems, metal organic frameworks such as UiO-66, MOF-802, and MOF-808 are used as effective adsorbents for pollutants (Lin et al. 2018). NSAIDs are the most well-known pharmaceutical drugs, and ibuprofen is administered orally as racemate mixture (Ma et al. 2019). This enantioselective existence of NSAIDs in Beijing, China, is the first time reported process of degradation. Waste-water-treatment plants depend on various factors such as sludge retention time, hydraulic detainment time, and temperature (Kebede et al. 2018). The human body, aquatic environment, and other biological environments may not be able to completely metabolize the pharmaceuticals and intermediates.

Organic supports such as water-soluble *Moringa Stenoptala* seed protein could be used as an efficient biomaterial for the removal of pollutants in water. Pharmaceuticals in water are generally discovered at lower concentrations, ranging from few ng L^{-1} to several µg L^{-1}, even at ppm level their biological activity can still make them toxic to organisms in the chronic exposure. Carbon-based materials have good properties of hydrophobicity and as surface modifiers, but they have a high production cost. Due to this disadvantage, magnetic nanoparticles are used as attractive adsorbents (Springer et al. 2018). Carbonaceous activated carbon material acts as an adsorbent to remove various pollutants. But this kind of material is widely used on a large industrial scale. To overcome this problem, activated carbon derived from orange peel is used (Tomul et al. 2019). Plastics are disposed of in uncontrolled rates in the environment due its low price and high accessibility (Elizalde-Velázquez et al. 2020).

Adsorption studies of NSAIDs onto micro plastics such as polystyrene (PS), ultra-high molecular density polyethylene (UHMWPE), average molecular weight medium density polyethylene (AMWPE), and polypropylene (PP) are used to investigate via sorption mechanism, pH, and salinity. Multitude explorations have proved the perception of pharmaceutical compounds in numerous water sources of the UK, China, India, Italy, Mexico, USA, Canada, etc. The investigations show that spoilation of water with pharmaceuticals is a worldwide issue that requires immediate recognition to preclude the upcoming sequences, and it is needful to eliminate the present contaminants in waters from pharmaceutical impurity. For this purpose, many researchers have found various methods to remove pollutants. But many of the methods have limitations within their lower-scale or high-cost or applied on an industrial scale, etc. So, for these unavoidable limiting parameters, the Luff Cylindrica (LF) plant was used (Khadir et al. 2020). The ultra-performance liquid chromatography-tandem mass spectrometry method was used to degrade NSAIDs such as indoprofen, sulindac, naproxen, diclofenac and ibuprofen (Ganesan et al. 2020).

1.3 Impact of Pollution

In the polar region like Antarctica, lower ocean temperature between 0.35 and 1.9 °C, full ice cover in water, and long periods of darkness can reduce the process of degradation. These extinct conditions such as temperature and saline nature differ from other environments and its equilibrium (González-Alonso et al. 2017).

From 2012 to 2016 as per the data reported, in African continents such as Zimbabwe, Mali, and Lesotho, including 54 other countries, they are facing troubles in the implementation of sanitation processes. The organic compounds present in the soil and groundwater are monitored by HPLC and gas chromatography techniques for non-volatile compounds, and UV-Vis and photodiode array detectors are used to detect sensitivity of the sample (Madikizela et al. 2018).

The creation of unwanted by-products from pharmaceutical products has reached greater than 20 million tons (Hiew et al. 2019). From this estimation, approximately 30–90% of the drugs were used by human and animal bodies, but the rest of the percentage of the chemical compounds remained as pollutants to the environment (Rivera-Utrilla et al. 2013; Wang et al. 2016).

1.4 The Environmental Effects of Over Consumption of Anti-Inflammatory Drugs

There is a general opinion that we hold is to assess an initial point of the need for environmental monitoring in the water system (González-Alonso et al. 2017). In Antarctic areas, day-by-day visitors increased and tourists flock, thereby causing pollution through their human excreta. With the help of several detection methods, analytical tools, treatment processes, and various NSAIDs, drugs have been detected in groundwater, sediments, river water, marine water, industrial waste, household waste, drinking water, sediment, soil, sludge, and surface water. Due to these inferences, NSAIDs as environmental pollutants depend on various factors such as population, local disease, lifestyle of people and environment, natural conditions and industrial process.

Based on various research statements, the Spanish government reported that about 20 molecules have been identified for 83% of the main pharmaceutical pollutants in city sewage treatment plants, including diclofenac, ibuprofen, and naproxen. In Japan, 259.7 ng/L of diclofenac, 162.9 ng/L of ibuprofen, and 11.8 ng/L of naproxen are found in domestic wastewater. Based on all the detectable reports from various countries, NSAIDs especially diclofenac and ibuprofen, naproxen, and ketoprofen are enormously reported in many studies and they are among the very high marked organic pollutants (He et al. 2017).

Pharmaceutical wastewater could be characterized as follows:

(i) High concentration of suspended solids and salinity.
(ii) High BOD and COD values and highly variable between BOD and COD values.
(iii) High NH_3-N concentrations (Li and Yang, 2018).

Toxicity and its concentration of pharmaceutical residues need to be reduced to control toxic levels and wastewater.

2 Origin of Toxicants

2.1 Types of Pharmaceutical Products

Pharmaceuticals are ranging from very simple to complex molecules that can be estimated in the environment and most of them non-susceptible to traditional treatment of wastewater (Fig. 2). Pharmaceutical compounds are commodious tools for humans and animals including agriculture and aquaculture also. These are planned to have discrete modes of action, targeting the action of organs and metabolic pathways to attune physiological functions. Globally, people blindly believe pharmaceutical drugs will cure all the problems. Based on this popular belief, tons and tons of compounds were prepared and synthesized on a day-by-day basis. At the same time, adopting improper waste treatment can also be experienced to cause pollution (Parolini, 2020). In the Contaminant Candidate List, pharmaceutical compounds have also been added due to the requirement for upcoming directives depending on their occurrence, potential health effects, and the nature of ecological toxicity.

Ibuprofen (IBU; ((+/−)-2-(p-isobutylphenyl) propionic acid containing both the isomers) is one of the very largest repeatedly utilized active pharmaceutical ingredients (API) worldwide, which is the second most consistently found in drinking water with the properties of slight water solubility and high mobility, with high concentrations of range of >1 ppb (Mellah et al. 2018). With various 47 countries, IBU was detected between 0.108 $\mu g\ L^{-1}$ and 303 $\mu g\ L^{-1}$, and these are the common relieving agents for arthritis, rheumatic disorders, pain and fever (Parolini, 2020).

Acetaminophen (also called paracetamol) has the highest concentration and is the highly cited pollutant with effluent along the Lis River in Portugal (Quesada et al. 2019). The concentration of acetaminophen in water is 48.74 mg L^{-1} and 25 ng L^{-1} in surface water. Contamination of hospital effluent levels ranged between 500 and 2900 ng L^{-1} in Spain and 36.95 mg L^{-1} in Taiwan (Gonzalez-Alonso et al. 2017).

Diclofenac (DCF; 2-[(2,6-dichlorophenyl)amino] phenylacetic acid) is a derivative of phenylacetic acid moiety containing two aromatic chlorine substituents. It is used to reduce arthritis, osteoarthritis, rheumatoid arthritis, and ankylosing spondylitis (Parolini, 2020). In India and Pakistan, environmental imbalances caused by vulture populations shrink owing to diclofenac surplus in dead animals (Kaur et al.

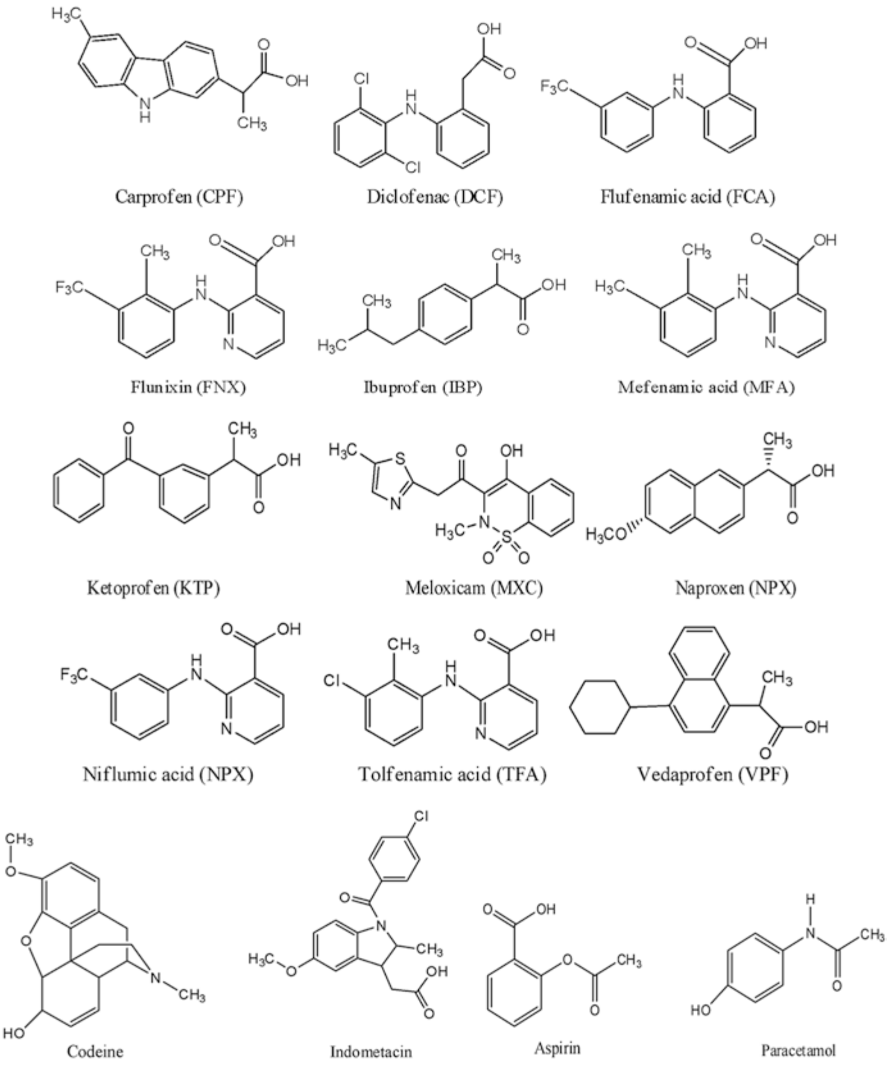


Fig. 2 Chemical structure of NSAIDs

2016; Ali et al. 2019). With the data of various 50 countries worldwide, average concentrations of 0.032 μg/L and 18.74 μg/L were detected (Parolini, 2020; Chi-Yu et al., 2018).

Naproxen (NPX; (S) 6-methoxy-α-methyl-2-naphthalene acetic acid) is a 2-napthyl propionic acid group. It is used for muscle pains, fever and inflammation, migraine, rheumatoid arthritis, and osteoarthritis. According to the data received from various 45 countries worldwide, average concentrations between 0.050 μg/L and 32 μg/L were detected in fresh water (Parolini, 2020).

Aspirin (or) acetyl salicylic acid is known for more than 9 decades and mostly used as an analgesic drug for the medication of pain, arthritis, and fever. Aspirin plays a momentous role in avoiding heart attacks and strokes, to avoid the generation of blood clots inside the arteries (Kaur et al. 2016). According to the investigation and with the support of data from various 15 countries worldwide, average concentrations of 0.922 and 20.96 μg/L were detected in freshwater sources (Parolini, 2020).

Paracetamol (PCM; N-(4-hydroxyphenyl)acetamide), also called as acetaminophen, is an analgesic and antipyretic drug. Actually, it is not an NSAID type of drug but the mechanism and action are similar. With the data of various 29 countries worldwide, average concentrations of 0.161 and 0.161 μg/L were detected (Parolini, 2020).

2.2 Toxicology Profile

Pharmaceutical pollutants differ from other contaminants due to following factors (Kumar et al. 2019):

- Based on the properties, structure, molecular weight, etc., pharmaceuticals can form countless complex molecules.
- Oral administration of their receptors enters into the human body, causing disturbances and structural changes during metabolism.
- Generally polar with various groups, behaves with different pH medium.
- Moderately soluble in aquatic medium.

Based on several factors such as population growth, discovery of new properties of already existing drugs, and low price of drug, NSAIDs are turned as a common pollutant in today’s world. Their highly aqueous stability nature and polar nature could result in obscurity in their degradation behavior in treatment plants. Usage of NSAIDs with heavy dosage for longer periods may result in impeding the body’s endocrine system leading to toxicity (Mlunguza et al. 2019).

More consumption of micropollutants causes many health impairments for humans as well as wildlife. It is estimated that the about 940 tons per annum of DCF is globally consumed (Tomul et al. 2019). In Germany, the production of acetyl salicylic acid (Aspirin) estimated to be 836 tons, paracetamol is about 622 tons and ibuprofen about 345 tons. Generally, pharmaceutical products are designed with a single pharmacodynamics mechanism with non-target receptors. But unexpected side effects resulted due to structural instability or other biological circumstances (Quesada et al. 2019).

Diclofenac has an annual global consumption of about 1443 tons. Diclofenac was found in the marine environment, with the concentrations up to 15 mg. L^{-1}. In marine bivalves, 0.5 ng.g^{-1} was collected at the Portuguese Atlantic Coast (Almeida et al. 2020). In Italy, a coastal lagoon in Ravenna was collected between 2.1 and 4.6 ng. g^{-1}. Diclofenac is considered as a “pseudo-persistent pollutant (POP).” In 2015, around 156 publications reported that diclofenac produced many harmful effects, with a concentration range of 77 ng. L^{-1} to 15.09 mg/L^{-1}. DCF causes renal lesion and gill alterations to rainbow trout at 1 mg.L^{-1} and dreadful effects to the wildlife and animals population (González-Alonso et al. 2017). According to a 2018 report, European DCF concentrations are 49.5 ng.L^{-1} and consumption doses up to 1033 mg per inhabitant per year in Germany (Pierattini et al. 2018).

With respect to WHO report, health-based values, which show preventive health effects, are exposed to sodium bentazon at 0.5 ppm. Bisphenol A is a phenolic compound, a most common pollutant found in water treatment plants and the concentration is ppt to ppb level. The worldwide known banned product of infant feeding bottles is Bisphenol A. European Food Safety Authority (EFSA) reported that daily intake for 50 μg/kg of body weight. In Switzerland, Lake Greifensee was estimated to be contaminated with 6.07 g of Ibuprofen per day (Peydayesh et al. 2020).

3 Removal of Organic Pollutants

The above results showed that continuous release of NSAIDs in water systems causes severe toxic effects to the humans, environment, and wildlife. So in order to minimize these toxic conditions and improve the regulation of the ecosystem, we need methods or solutions to encounter the problem safely (Fig. 3).

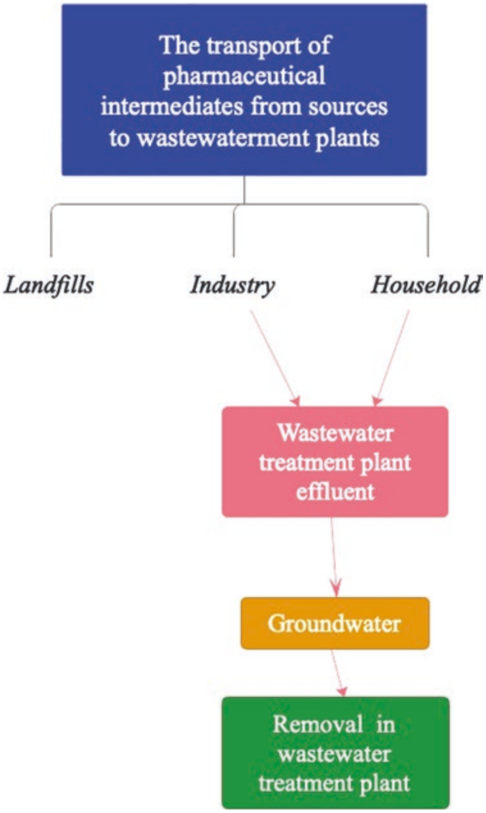


Fig. 3 The transport of precursors from sources to waste treatment plants

Adsorption is one of the best processes that has the ability to remove various organic pollutants with the removal of compounds. For example, the removal of adsorbates or pollutants from an aquatic environment with ligninolytic enzymes, activated carbon, molecularly imprinted polymers, graphene-based adsorbents, electrochemical degradation, photocatalytic degradation, sonochemical process, electrochemical advanced oxidation process, graphene-based adsorbents (Mlunguza et al. 2019). In addition, membrane filtration, oxidation, extraction, chemical precipitation, ion exchange, reverse osmosis, complexation and solvent extraction can also be used for the elimination of polluting chemicals from the wastewater (Flores-Céspedes et al. 2020) (Fig. 4).

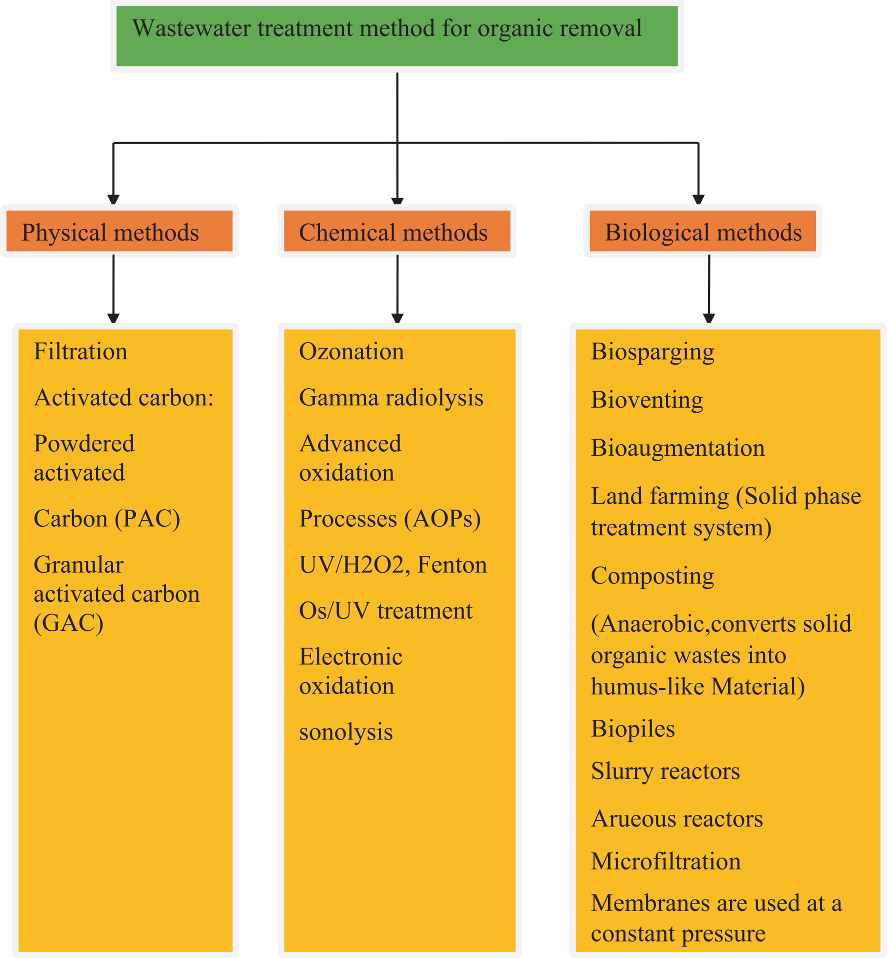


Fig. 4 Methods of pollutant removal from wastewater

3.1 UV Photolytic Process (or) Photo Degradation of Pollutants

Relatively, light sensitized degradation process is a clean and eco-friendly process as compared to other methods. During UV-Vis-mediated or photosensitive degradation process, when persulfate is irradiated by UV, the hydroxide radicals are generated and the radicals play an overriding role in NSAID degradation with an evidence on the degradation of the 92% of DCF, 28% of IBP, and 52% of NPX were removed, which showed the importance of UV photolysis system (Fu et al. 2019). For the first time, the seawater samples collected from Red Sea coastal water in Jeddah, Saudi Arabia, DCF and its two by-products were determined simultaneously (Ali et al. 2019). Diaryl amine component of DCF, with its activation of such compounds under photochemical conditions, required the unpaired electrons present on the nitrogen atom. Photo oxidation of DCF is strongly associated with solution pH. LC combined with ESI-MS/MS method was used for the appraisement of DCF with 180 and 214 m/z values (ng.ml^{-1}).

The direct photolysis system is used for degradation of chemical compounds, but at the same time not all the compounds are degraded (Fu et al. 2019). For this inconvenience, UV/PS systems are used to degrade pollutants such as DCF, IBF, and NPX and evaluated to find the water quality by estimating HCO_3^-, Cl^-, and NO_3^-. The reaction in the pH value in wastewater was adjusted to 7, but for pure water it was unadjusted. The UV-Vis absorption spectra with 2500 μW. cm^{-2} shows that the radiation intensity of solar light is much higher than UV lamps. By harnessing the solar light efficiently, this solar-radiated photocatalytic process is more remunerative with significantly reduced energy and would be more economical (Villanueva-Rodríguez et al. 2018).

3.2 Pollutant Removal by Adsorption Process (AP)

Adsorption is a physical phenomenon, which can be used to attract the polar and non-polar pollutants by suitably functionalizing the surface of the adsorbent. Most of the adsorption process is enhanced by porous materials because of its high surface area. Based on the properties of simple synthesis, porous in nature, potential applications, purification of water and fuel using MOFs including carbonaceous materials are selected as adsorbents for the elimination of AIDs. On the basis of numerous processes such as photo transformation, oxidation, and ozonation processes, adsorption is the most promising method for the withdrawal of pharmaceuticals, especially naproxen (NAP) as well as ketoprofen (KTP). In addition, the organic pollutants generated by using personal care products can also be due to simple operation, inexpensive, and the absence of any other secondary pollutants generated in water.

Based on the various adsorbents in particular soil, clay, carbon materials such as animal charcoal, mesoporous carbon, bone black, and porous aluminosilicate and silicate materials, the type of adsorbent can be designed for the effective adsorption of the pollutants. Metal Organic Frameworks (MOFs) are applied successfully for the adsorption of pollutant from aquatic environments. MOFs are used as best adsorbents on account of their properties, namely, high porosities, high surface area, and good thermal stabilities (Sarker et al. 2018).

Sheet-like graphene is containing sp^2 hybridized carbon atoms, structured in a honeycomb – hexagonal-like structure with a thickness corresponding to the diameter of an atom (Hiew et al. 2019). When the amount of GnO increases, the nature of hydrophilicity decreases. On easily achieved synthesis, excellent reusability, remarkable adsorption efficiency, excellent reusability, tenable hydrogen bonding, and adsorption mechanism owing to the presence of adequate surface functional moieties on GnO shows promising adsorbents for removal of AIDs from water (Sarker et al. 2018). Based on the results, the graphene-based adsorbents can absorb plenty of pollutants at once due to extracting more compounds and are not easily saturated by pollutants. This means graphene oxide is a good adsorbent for micropollutants (Mlunguza et al. 2019).

The first time reported GnO/MOF compound (GnO/MIL-101) was pertained as an effective adsorbent for the elimination of NAP and KTP from wastewater. The major products of NSAIDs were further decomposed to aliphatic acids, and the increase of aliphatic acids during the decomposition reduced the harmful nature (Fu et al. 2019). Adsorption of atenolol (ATL), carbamazepine (CBZ), ciprofloxacin (CIP), gemfibrozil (GEM), ibuprofen (IBU) as well as diclofenac (DCF) with highly hydrophobic surface of graphene nano-adsorbent is an another method of advantage from wastewater (Khalil et al. 2020).

The state of significance of high adsorption value and large MOF holes are the reasons for efficacious adsorption with the removal of NSAIDs such as ketoprofen, ibuprofen, naproxen, indomethacin, salicylic acid, and furosemide. MOFs with regulatable crystalline arrangements with extremely high porosity in nature and extensive internal surfaces can be depicted. MOFs can further promote adsorptive removal on account of their solitary attributes of internal copious and abundant ligands with functional sites for adsorption (Lin et al. 2018).

Consider the case of $ZrCl_4$ (0.125 g, 0.54 mmol) dissolved with BDC (0.123 g, 0.75 mmol) in a 60 mL mixed solvent of DMF/conc. HCl. The mixture reacted for 24 hrs at 120 °C, yielding a white precipitate of UIO-66$[Zr_6)_4(OH)_4(BDC)_5]$. FE-SEM explained their nanosize is about 100 nm. $ZrOCl_2.8H_2O$ (0.160 g, 0.50 mmol) dissolved with BDC (0.110 g, 0.50 mmol) in DMF/formic acid (20 ml) then reacted with 150 °C yield MOF-808$[Zr_6O_4(OH)_4(BTC)_2]$. FE-SEM explained their nanosize is about 300 nm. $ZrOCl_2.8H_2O$ (0.20 g, 0.65 mmol) dissolved with PZDC (0.135 g, 0.75 mmol) in DMF/formic acid (20 ml) then reacted with 150 °C yield MOF-802$[Zr_6O_4(OH)_4(PZDC)_5]$. FE-SEM explained their nanosize is about 500 nm (Lin et al. 2018).

Based on PXRD patterns and inductively coupled plasma-optical emission spectroscopy data, MOFs were also stable in aqueous solutions with high pH ranges. Comparatively, MOF-802 has smaller pores and less diffusion of pharmaceutical pollutants due to its smaller porosity and confined inner pore dimension. Other MOR-808 and UIO-66 have large effective adsorption and removal capabilities.

Activated carbon is a highly microporous material with large pore volumes, internal surface region, and excellent adsorptive capacity like other inorganic porous materials. By using several techniques to detect NSAIDs, adsorption using activated carbon (AC) is an efficient process for being low cost. These ACs have more stable properties than some others such as clays, polymers, zeolites, and GnO. Generally, the amount of concentration of drugs in wastewater is very low, and it is not an environmental risk but the continuous release of these chemicals causes pollution as an environmental problem (Ahmed, 2017). The carbonized ancestor or char produced by pyrolytic decomposition from 400 to 800 °C is a remarkable step. For its praising porosity and surface area of activation, carbon dioxide is preferred due to clean, flexible use than steam and air at 600–900 °C. On chemical activation of char with potassium carbonate, $ZnCl_2$, H_3PO_4, and NaOH were used in 300–500 °C to develop porosity. Comparatively chemical AC has higher porosity and surface than the other. The favorable nature of this method was confirmed by a pseudo-second-order replica which confirmed chemisorption behavior. Spontaneous nature and high drug adsorption with low temperature furthermore favor this method (Ahmed, 2017).

3.3 *Layered Double Hydroxides (LDH) Micro-Flowers*

The viable way of design and construction of water purification and detection of contaminants using layered double hydroxides was better explained by adsorption technique using ZIF-8@NiAl-LDHs. These LDH surfaces can be awarded π-conjugated abilities by inserting organic materials into LDHs, thus can also be used to improve adsorption capacity of organic contaminants. Compared with 2D, 3D structures have high absorption capacity and sorption active sites. 0.2 g of solvo thermally prepared Ni-Al-LDH with 2-methylimidazole (H-MeIM) in 50 ml of methanol solution was added, agitated for 2 h at 120 °C followed by the addition of 12 mmol of $Zn(NO_3)_2.6H_2O$ under constant stirring with optimized conditions. After 6 h of reaction, zeolitic imidazolate scaffolding on layered double hydroxides was collected. These sandwich-type structure 3D ZIF-8@NiAl-LDHs were used to remove NSAIDs such as indomethacin, ketoprofen, flurbiprofen and ibuprofen; anionic dyes such as Congo red and orange G; and cationic dyes such as methylene blue and rhodamine B (Yang et al. 2020).

3.4 Carbon Organic Framework–Based Adsorbent

The first report on new fluorine-bearing COF, which can adsorb ibuprofen as a pollutant, is frequently detected in wastewater from various sources in both neutral and acidic pH. Tp-series of COFs, such as TpBD-$(CF_3)_2$ (triformylphloroglucinol 3,3′-bis (trifluoromethyl)benzidine), are reported for targeting lipophilic pharmaceutical contaminant. These COFs, fluorine-containing compounds, are used with the properties of high electronegativity, low polarizability, high water stability, enhanced light and air stability, and low surface tension (Mellah et al. 2018).

1.0 mmol of Tp and 1.6 mmol of 3,3′-bis(trifluoromethyl)benzidine in dioxane solvent and 4.0 mL of mesitylene in 5.0 mmol of aqueous acetic acid were added at 120 °C and stirred for about 72 h and an yellow-colored solid product of TpBD-$(CF_3)_2$ was obtained (Mellah et al. 2018). TpBD-$(CF_3)_2$ has high water stability in both acidic and basic conditions. These fluorine-containing compounds result in different properties of the resulting material due to their stability and low surface tension. This is the first time it has been reported that fluorine-bearing COFs can absorb higher efficiency of NSAIDs and ibuprofen than other lipophilic pharmaceuticals. Hydrophobic interaction is a key role in the adsorption process with high efficiency.

3.5 Amyloid Fibrils Aerogel as Adsorbents

The amyloid fibril aerogel is an inexpensive, eco-friendly, biocompatible, sustainable adsorbent for organic removal from water (Peydayesh et al. 2020). These aerogels are good adsorbents because of the advantages of lower density, huge porosity, high surface area, and stability in aqueous, mechanical, and thermal conditions. The adsorption capacity with amyloid fibrils aerogel was used to remove pollutants of ibuprofen, bisphenol A, and bentazone with 98%, 78%, and 92% from water with the quantification of 25, 216, and 216 ppb, respectively. Adsorption efficiency of bentazone and ibuprofen is higher compared to bisphenol A. It was evidenced by adsorption equilibrium with saturation limiting amounts of ibuprofen of 446×10^{-6} m with the binding constant of 9.44×10^{3} m^{-1}, bentazone amounting of 502×10^{-6} m with the binding constant of 7.60×10^{3} m^{-1}, and bisphenol A amounting of 26×10^{-6} m with the binding constant of 4.09×10^{4} m^{-1}. Compared to activated carbon, this method reveals a superior role in the energy and recycling process.

Adsorption efficiency of amyloid fibers depends on molecular size, pKa, solubility in water, aromatic substituents present on molecules, and electrostatic forces between organic compounds and aerogel. The lifespan and reusability of aerogels was up to three cycles, and this economically feasible regeneration process is an important criterion for adsorption performance.

According to the Global Water Research Coalition (GWRC), some NSAIDs are the main constituents of the list of top 10 resolute pollutants. Researchers are aiming to identify a solution to rectify this problem. One such work (Almeida et al. 2020) addresses silica modified with ionic liquids (SILs) as an alternative adsorbent to remove one of the NSAIDs, diclofenac, in aquatic systems. Modified silica-based materials encompassing 1-methyl-3-propylimidazolium cation combined with six anions were prepared. Like adsorption based on activated carbon and carbon nanotubes, this method is also responsible for adsorbent. This physical adsorption involves the removal of sodium diclofenac from an aqueous solution that could be confirmed by their chemical structure, π-π, non-covalent interaction, and absence of anion exchange.

3.6 Electrochemical Degradation Using Advanced Oxidation Process (EAOP)

Fenton process or electro-oxidation process (E-Fenton) is a kind of oxidation process involving electrochemical reactions. Based on the several articles and that data, which may bring about the elimination of these toxic wastes from urban, sanatorium, and factory sewerage waters, EAOPs are being economical, simple and efficient process to oxidize various types of functional groups present in organic compounds that are resistant to microbial treatment. This oxidation process is efficient in terms of degrading the pollutants as compared to the other oxidation process due to Fenton reagent. This process is dependent on the electrochemical production of H_2O_2 in the cathode via reduction of oxygen involving 2 electrons. Due to higher conductivity and chemical resistance, carbon cathode is highly preferable for designing EAOPs. In addition, the carbon cathods having higher overpotential for H_2 production and lower catalytic activity for H_2O_2 decomposition with lesser toxicity (Nadais et al. 2018).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH - + OH^{\cdot} OHOH *$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

According to the results, adsorbents based on graphene can absorb plenty of pollutants at once due to extracting more compounds and are not easily saturated by pollutants. This means graphene oxide is a good adsorbent for micro pollutants. The adsorption process follows first-order kinetic studies, and removal efficiencies with various parameters showed the low concentrations of non-compliant pollutants containing wastewater treatment. For example, in 5 h, efficiency of pollutant removal was found to be for ketoprofen, diclofenac, ibuprofen, and naproxen in 59–61, 87–97, 80–86, and 75–81%, respectively (Nadais et al. 2018).

This study exhibits the heterogeneous Fenton reactions initiated by Cu or Fe catalyst, which can be lucrative when used in the treatment of ibuprofen from wastewater. Removal of organic pollutants by the heterogeneous Fenton process is a novel method that is primarily based on recovery and reusability of the catalyst, requiring temperatures around 60–80 °C, various catalytic loadings, pH, and oxidant doses. The heterogeneous Fenton process is superior to the homogenous Fenton process. Based on overall evaluation and comparative studies, homogeneous types had some limitations such as low pH (around 3), cost expensive, and difficult steps to recycle. Copper and iron catalysts supporting zirconia were prepared to investigate IBP (Wang et al. 2016; Hussain et al. 2020).

3.7 Magnetic Nanoparticle–Mediated Adsorption

High surface area, easy recoverable nickel ferrite nanoparticles could be utilized for the elimination of organic as well as inorganic pollutants from wastewater samples (Springer et al. 2018). The method of preparing magnetic nanoparticles is very similar to co-precipitation method with particle size distribution and low cost, and it is suitable for removal of dipyrone (DIP) and diclofenac (DC). At the pH value of 5.8 ± 0.2, they can act as excellent ligands to bind Fe^{3+} as well as Ni^{2+} at the periphery; 40–60% of DIP has been effectively removed from aqueous solutions using magnetic nickel ferrite nanoparticles than DC of about 30–42%. Based on its magnetic properties, these are very easy to synthesize and recover by applying magnetism. Adsorptive characteristics of these nanoparticles are economically favorable processes for DIP and DC NSAIDs.

Iron composite nanoparticles (ICNPs) using chitosan were used to eliminate DCF sodium pollutant (upto 85%), and it was evaluated in terms of pH of solution, dose of ICNPs, optimization time, and temperature (Alothman et al. 2020). ICNP can be obtained adding epichlorohydrin (2.5 ml) and respective nanoparticles (2.50 g) blended with 25 ml of 25% acetic acid were agitated for 24 hrs. Then 2 g of chitosan was added, the mixture was continuously agitated for another 15 minutes, and after 24 hrs, composite nanoparticles were derived. This sorption method was spontaneous and exothermic.

3.8 Sorption Studies Using Microplastics as Adsorbents

Sorption capacity increases with decreasing particle size of the plastics. This is the reason for microplastics could act as adsorbent via particle size and surface area (Elizalde-Velázquez et al. 2020). However, different environments and their factors will not be favored by the above reported parameters. These pollutants and microplastics were under fresh water at pH 6.90 and artificial seawater at pH:8.10, and basic conditions at pH 10.00 were studied. Under these conditions, pH 2 showed highly hydrophobic interaction and in acidic conditions. But WHO, ICMR, CPCB, and BIS reported pH less than 6.50 breaks off the making of vitamins and minerals from the human embodiment. pH greater than 8.50 shows salty taste in water. pH

>11 creates skin disorder and eye irritation in the body. pH 3.5–4.5 for aquatic life and pH 5.50–6.00 are not harmful (Gupta et al. 2017). In the first study, degradation of Piroxicam (PIR) by iron-activated persulfate with parameters such as pH, oxidant, concentration, and water matrix was examined.

4 Biological Process

Biological treatment of wastewater or biological remediation is an environmentally sound and potential method used for the destruction of organic pollutants for the removal of toxicants with cost-efficiency. This is one of the low-cost treatment methods than the others and required only milder treatment conditions. Mechanism of biological absorption process is applied on ion exchange, surface complexation, absorption, adsorption, and precipitation. This non-living biomass does not have need of any attentive storage process. Reacting groups in particular $-NH_2$, –OH, and –COOH produce spontaneous interaction with biosorbent to bind with polar groups present in the organic pollutant that positively facilitate the adsorption mechanism.

Similar to inorganic adsorbents such as zeolite, silica, alumina, and SBA-15, all organic bioadsorbents derived from agricultural biomass have their unique fruitful properties and most of them are locally available and replacements as a low-cost adsorbents (Kebede et al. 2018). From this biological point of view, *Moringa stenopetala* was selected. The seeds of this plant are used as a good purifier, the leaves of this plant are used as a hypertensive agent, while the roots are abortifacient, the seeds of this plant are a source for vegetable oil. *Moringa stenopetala* is the first time reported as a water-soluble protein that is used as wastewater treatment material to remove heavy metals and effectiveness toward the adsorption of ketoprofen, fenoprofen, diclofenac, ibuprofen, and carbamazepine. The data perceived from FT-IR and the appropriate vibration frequencies confirm the interaction between reported water-soluble protein molecule that contains amino, amide, and alcoholic functional groups interact with the functional groups of pollutants though H-bonding for the removal of NSAID pharmaceutical drugs. Removal of the analyte was pH dependent and affected by zeta potential via hydrogen and peptide bond. This cost-effective, easily acceptable method from *Moringa stenoptala* seeds is useful to the society (Kebede et al. 2018).

Fibrous materials collected from agricultural-cum-industrial biowaste such as rice husk (RH), sugarcane bagasse (SB) and castor leaves (CL) have been selected to deliver biosorbents, and these biosorbents played an adsorption role for heavy metal ions such Pb^{2+} and Ni^{2+} (Saxena et al. 2017; Bhardwaj et al. 2017; ElSayed, 2018). FT-IR spectral data confirm the interaction with biosorbent with presented organic pollutants via carboxylic, hydroxyl, and amide functional groups with approximately 1600 cm^{-1} for C = O and 3400–3300 cm^{-1} for –OH and NH_2 regions. Based on Langmuir adsorption isotherm mechanism,

$$Q = \frac{x}{m}\frac{KbC}{1+KC}$$

Efficiency of biosorption is in order as CL > RH > SB and study showed CL has better adsorption capacity with 1180 mmol per Kg of Pb(II).

This is the first time, lignocellulosic material combined with polypyrrole (LF/ppy) was reported as an economically favorable cost-effective adsorbent for the removal of ibuprofen. Lignocellulosic material of LF contains 60% cellulose, 30% hemicellulose, and 10% lignin. Based on BET surface analysis and SEM results, LF/ppy is an effective biosorbent due to their porous nature and spherical shape. At the equilibrium state with 90 minutes of contact time, 61.81% of 18.11 mg.g^{-1} of 100 ppm solution of ibuprofen was adsorbed (Khadir et al. 2020). Non-toxicity, high efficiency, low-cost, high removal of contaminants, and elementary synthesis are the main advantages of this material. And this work ascertained that the LF/ppy composite could be a propitious material for the elimination of ibuprofen from hydrophytic system (Khadir et al. 2020).

5 Analytical Methods for the Determination of NSAIDs in Wastewater

Many synthetic methods such as direct synthesis and chemical vapor deposition (CBD), carbonization, sugar blowing, plasma-enhanced CVD, solution-based synthesis such as template-assisted freeze drying, template-assisted hydrothermal, reduction, and cross-linking that are used for synthesis are reviewed (Hiew et al. 2019). The presence of various kinds of drug pollutants are determined by several analytical methods. Ultra-performance LC-MS/MS method along with microextraction method is used for the quantification of NSAIDs (Ganesan et al. 2020).

5.1 Chiral LC-MS Method

Based on the chiral inversion, S(+)-ibuprofen degraded faster during sewage treatment than R-ibuprofen, and it could be monitored by using chiral LC-MS for detection and quantification (Ma et al. 2019). Environmental surveys have revealed that this quick, simple, sensitive analytical method showed ibuprofen is the most abundant. The first time reported simultaneous enantio-separation of the method was reported by HPLC. The method was proven to be expeditious, uncomplicated, and tactful. The S-enantiomer of ibuprofen was removed in appreciably at higher concentration as compared to R-enantiomer, and it is decomposed quickly (Dogan et al.

2020). The retention and relative abundance of molecular ion peaks and fragmentation of GC-MS were used to identify and separate pollutants efficiently (Gumbi et al. 2017).

5.2 *Thermal Degradation*

The prepared activated carbon using orange peel as a biosorbent is used to remove diclofenac from water. $FeCl_3$ is an effective reagent to prepare AC with high competency to remove DCF (Tomul et al. 2019). For making activated carbon with high surface area such as potassium hydroxide, potassium carbonate, zinc chloride, hydrogen sulphate, and iron chloride salts such as $FeCl_2$, $FeCl_3$, mixture of $FeCl_3$ with $ZnCl_2$ were also used as chemical agents to remove pollutant (Tomul et al. 2019). Langmuir adsorption with the criterion for instance Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Van't Hoff equation shows the diclofenac removal process using activated carbon. Based on these adsorption studies, DCF shows adsorption is endothermic with respect to $\Delta H° > 0$ and $\Delta S° > 0$, iron (III) chloride confirmed as an optimistic activating agent for purification and reported emergent organic pollutants in aquatic ecosystems. Another study reported the thermal studies on adsorption of bichor, a paracetamol from pure glucose, as well as pomelo peel waste (Tran et al., 2020).

The formation and surface properties of core shell polyaniline/polyacrylonitrile (PANI/Pan) nanofibers were prepared and used for adsorption of NSAIDs, and it is confirmed by FT-IR, TEM, and SEM. The negative ΔG values show the adsorption is spontaneous in nature and fall in ΔG value with a rise in temperature, which will favor the adsorption process. The positive ΔH values show endothermic process and with positive ΔS shows more randomness during adsorption of solid-liquid interface medium (Jian et al. 2019).

5.3 *Hazard Quotient (HQ) Method*

On an island near the Marambio Station, AID samples were collected. Research studies have reported that there is a relationship of population density with the pharmaceuticals present in the environment. The Antarctic Peninsula region ranges between 1000 and 4500 people. But tourist visits showed greater factors for pharmaceutical pollution in the wastewater environment. To rectify this environmental risk, hazard quotient (HQ) calculation was used to identify acetaminophen, diclofenac, and ibuprofen. This HQ method is used to standardize the measure of risk by comparing different compounds with toxicities. Toxicity values between 1.0 and 10 pose a low risk, and if HQ values exceed 10, they pose a high risk (González-Alonso et al. 2017).

5.4 *Chitosan Microsphere Method*

Chitosan is the most abundantly available natural biopolymer, and it has been used as a adsorbent for oxycam and NSAID pollutants because it contains amine functional groups that interact as mediators between chitosan and organic contaminants in aqueous medium. This medium was used to remove oxycam pollutants with a low-cost budget (Braga et al. 2017).

The heterogeneous fibrous structure of chitosan and microsphere particles with a diameter below 500 μm on scanning electron microscopy confirms the surface area. The ^{1}H-NMR spectrum showed peaks corresponding to C-2,3,4,5 and 6 of glycosidic ring, at the region between 1 and 4 ppm with 83.5% and FTIR analysis showed that, 1630–1740 cm^{-1}, 1370 and 1220 cm^{-1} predicts the interaction with oxycam-anti-inflammatories with biopolymer. Thermal studies interactions with microsphere (microsphere) particles of meloxicam, tenoxicam, and piroxicam are enthalpically ($\Delta H < 0$) favored but entropically ($\Delta S < 0$) unfavored.

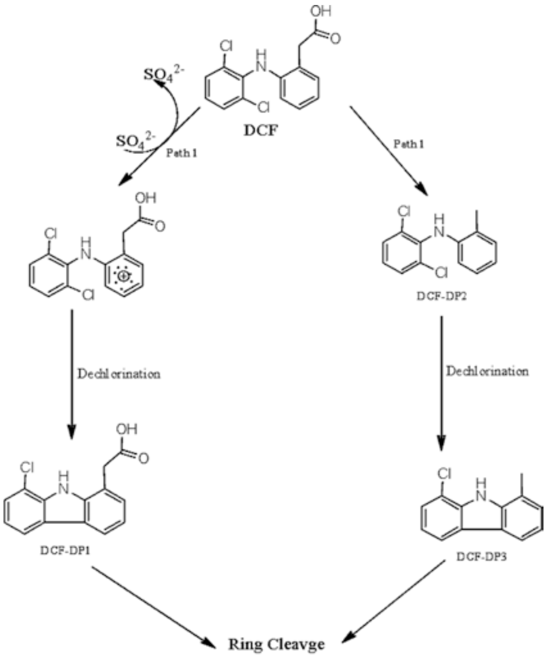
5.5 *Mass Spectroscopy*

To find the IBP degradation and its mechanism, Orbitrap Liquid Chromatography coupled with Mass Spectrometry (LC-MS) (ARPS, Udine, Italy) have been used (Fu et al. 2019) (Fig. 5). This method is used to degrade toxic metabolites in the course of the oxidation process. Supported catalyst used to degrade IBP to secondary compounds. The LC-MS analysis used to predict left-over products of IBP is more toxic than dihydroxy ibuprofen, IBP, 1-(4-Isobutylphenyl)-1-ethanol, and 4-isobutylacetophenone. With catalysts, lower than 90% and 25–40% of degradation and mineralization of organic pollutant activities were monitored (Adityosulindro et al. 2018; Wang et al. 2016; Hussain et al. 2020).

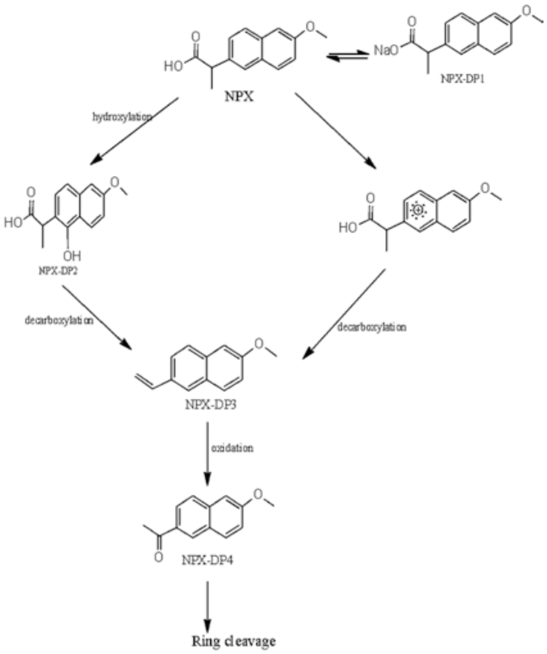
6 Summary

Many investigations reported on the detection of pharmaceutical compounds in the UK, China, India, Mexico, the USA, Canada, etc., denote contamination of aquatic systems with pharmaceuticals will be a global issue. Switching off these problems with water pollutants, an environmental assessment is needed with a rigorous analysis and strict implementation of regulations. Environmental contamination was gradually enhanced by hospitals, pharmacies, improper disposal methods of industries, and unawareness of people with residential wastages. Toxicity of water with pharmaceutical pollutants is a global problem that requires further scrutiny to avert the forthcoming sequences.

Decomposition of NSAIDs by UV/PS method is comparatively better than UV based on their hydroxylation, decarboxylation, electron transfer, and dechlorination



Degradation pathways of Diclofenac



Degradation pathways of Naproxen

Fig. 5 Degradation pathway of NSAIDs (Credit: Fu et al. 2019, Permission granted)

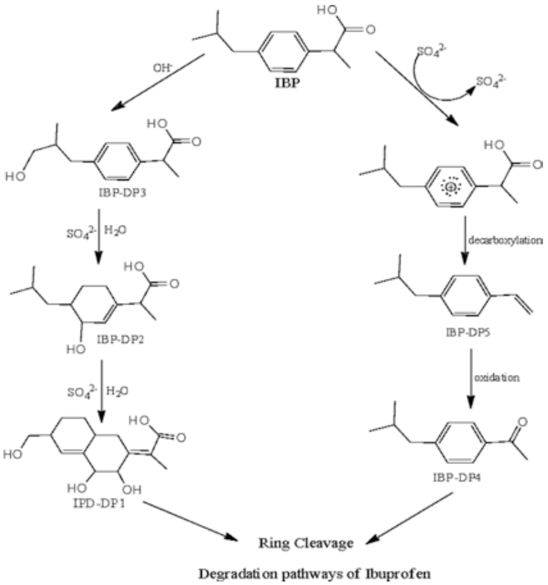


Fig. 5 (continued)

pathways. But the degradation efficiency of UV/PS is much lower for obtaining pure water. It takes a longer duration of degradation. Based on the merits and demerits, this method needs to be further advanced in the future.

Adsorption is one of the replacement methods of degradation of drugs or it can be used as a combination with other methods, but this method has certain limitations for poorly adsorbing drugs. For this, carbon adsorbent having a high inclination to absorb pharmaceutical toxicants should be used, but the separation of spent carbon from wastewater is a challenging goal. Activated carbon methods of adsorption are not considered sustainable for a longer period. Because 1000 g of carbon material needs for about 97 MJ of energy and generate 6600 g of CO_2 equivalent emission in the atmosphere. Hence, the necessity arises to fabricate low-cost methodology to remove organic pollutants from aquatic systems. Although there are an increasing number of studies that should have to include activated carbon from agro-industrial waste such as implementation of composite adsorbents, treatment of real effluents, binary and multi-component adsorption, modification of adsorbent, and regeneration steps. Treatment with economically sustainable amyloid fibril aerogels is a widely important tool for the removal of organic compounds. Several studies need to be conducted for future applications.

Biological process is an eco-friendly and economical adsorption method, but it may not be applicable to remove all pharmaceuticals, and it has restrictions with parameters namely, temperature, pH, and toxic nature of pollutants. Emerging contaminants of pollution increase at the same time and water scarcity also increases alongside it, which is mainly related to agriculture and industrial development. The solar-mediated advanced oxidation process is a better method to remove pollutants for this particular concern. The heterogeneous photocatalytic process using AOP sunlight/H_2O_2 evaluates carbamazepine and diclofenac-like drugs. But it is better to try to study for a higher number of drug studies.

Based on the polarizability and ionizability nature, inorganic porous materials could be used as good adsorbents to remove pollutants such as carbamazepine. During the efficient removal process, unexpected by-products also occurred. This statement confirms that removal rates strongly depend on the concentration of compound/ pollutant. This use of limited material should be highly concentrated in the future. Functionalized mesoporous silicas with their surface morphology and porosity nature, can act as a good sorbent for the application of eliminating organic pollutants such as diclofenac, ibuprofen, and penicillin G.

Undoubtedly, nanomaterials have proven to have potential application as a remedy for emerging organic contaminants due to their adsorption capacity, efficiency, selectivity, preparative techniques, and stability. However, the more advanced development of some automated methods required for nano sorbents. With the advanced method of nanotechnology-based materials, nano sensors could detect contaminants and rapid degradation of pollutants.

In our current scenario, new contaminants are entering wastewater every day and it also leads to the detection of contaminants. It is necessary to improve the technologies and treatment methods to detect pollutants by easy and automatic methods.

7 Future Perspectives

The evolution of novel methods for the determination, quantification, and removal of NSAIDs with elucidation of proper degradation mechanisms of pharmaceutical pollutants such as anti-inflammatory drugs in natural environments with their biological activities is taking place around the globe.

Scientists from various areas with greater effort are attempting to find emerging contaminants by generating new data. In addition, it is a bigger task to find the mechanism of soil-water contamination and remedial action. This is the major problem not only for today’s world, but will be reflected to future generations also. Many reports said, our carelessness causes dramatic water problems and will be reflected in 2025. Water is highly superior to gems, and it is a treasure from earth. Hence the public needs some increased awareness to make some changes in their lifestyle. For this current status, additional new methods need to be invented by the researchers to control and avoid the pollutants in water. We need strong cooperation among all the public, farmers, governments, industries, and researchers and we need to have a very strong water users association to be able to uphold this scheme.

Save Water! Save Nature!

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Chemical and Biological Remediation Technologies for the Effluents' Mineralization and Toxicological Effects of Nanocatalysts: An Overview

P. Sathishkumar, N. Pugazhenthiran, and S. Anandan

Abstract As a consequence of industrial development, effluents from various industrial practices augmented the concentration of environmental contaminants on the earth's surface. Therefore, the materials adopted for decontamination of these environmental contaminants must be environmentally safe and could not produce any toxic side effects to any component of the living organism. In reality, nanoscience and nanotechnology offered the greatest efficiency for the removal of perilous environmental contaminants, and toxicological effects resulted due to the unsafe disposal of these nanoparticles, nanomaterials, and nanocomposites. Herein, we discuss biological and chemical treatment technologies for the mineralization of various environmental contaminants and nanocatalysts' efficiency toward their complete removal. The second part of this chapter essentially concentrated on toxicological effects generated by the unsafe disposal of nanomaterials/nanocatalysts to the environment. Two noteworthy components of the food cycle are plants and fishes; accumulation, translocation, and biotransformation of nanoparticles/metals/semiconductor nanocomposites in the food cycle are discussed for a better understanding of the underlying relation between catalytic and toxicological effects of nanomaterials.

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Keywords Nanomaterials · AOPs · Chemical and biological treatment processes · Cytotoxicity and toxicological studies

1 Introduction

Various industrial developments constitute aesthetic pollutions of the total environment. The quantity of water utilized in various industries is of paramount importance since the release of aquatic effluents is a great hazard to the ecosystem, carcinogenic and mutagenic (Mon et al., 2018; Muralikrishna & Manickam, 2017; Sathishkumar, Mangalaraja, & Anandan, 2016a). Untreated aquatic effluents significantly contribute to surface and groundwater contamination and a continuous increase in the concentration of environmental contaminants was noticed during recent years (Khatri & Tyagi, 2015; Sathishkumar, Mangalaraja, Rozas, et al., 2016; Sharma & Bhattacharya, 2017). Environmental contaminants released near agricultural lands accumulate in food crops and vegetable products which lead to chronic effects on consumers (Isla & Aragüés, 2010; Ke et al., 2007; Kinnersley & Scott, 2001). For example, numerous chemicals, stabilizers, and bleaching agents were utilized in textile industries, approximately 1.6 million liters of water has been applied in average-sized textile mills (Kant, 2012). Among various agents practiced in textile industries, Kant (2012) reported regular consumption of chemicals per month which is reprinted in Table 1 (Kant, 2012). Consumption of these chemicals enhances every year and leads to increased negative effects on the total environment.

On the other hand, the global need for drinking water increases along with increased population, which creates a threat for all the living organisms on the earth's surface. Wretchedly contaminated water has been consumed by the people to save their lives and even they are not aware of various types of adulteration in drinking water. To manage and distribute the rarely available natural resources to all living organisms, the water discharged with industrial effluents needs to be recycled which will solve the issues associated with water shortage. Freshwater utilization in the industrial sector can be reduced with recovered water from aquatic effluents. However, recycled water cannot be used for the purpose of drinking directly, but it will solve the needs of domestic requirements of living organisms besides recycled water can be used in agricultural lands. The release of recycled water into the environment could be further purified by naturally available various layers of sand filters. Thus, it enhances the availability of groundwater, and naturally purified water can be further used for the drinking purpose.

To recycle the aquatic effluents and to mineralize various environmental contaminants released from the industrial sectors, various methodologies are proposed, developed, and practiced for the betterment of living organisms (Deng & Zhao, 2015; Kehrein et al., 2020; Paździor et al., 2019; Sathishkumar, Mangalaraja, & Anandan, 2016c; Yasar et al., 2006). There are various drawbacks associated with

Table 1 Approximate chemical consumption in the average-sized textile industry

S No.	Chemical	Quantity Kg/month
1	Acetic acid	1611
2	Ammonium sulphate	858
3	P V acetate	954
4	Wetting agent	125
5	Caustic soda	6212
6	Softener	856
7	Organic solvent	247
8	Organic resin	5115
9	Formic acid	1227
10	Soap	154
11	Hydrosulphites	6563
12	Hydrochloric acid	309
13	Hydrogen peroxide	1038
14	Leveling and dispersing agent	547
15	Solvent 1425	321
16	Oxalic acid	471
17	Polyesthylene emulsion	1174
18	Sulphuric acid	678
19	Disperse dyes (polyester)	1500
20	Vat dyes (viscose)	900
21	Sulphur dyes	300
22	Reactive dyes	45

Reproduced from Kant (2012)

the expansion such technologies in a large scale. To evade the disadvantages of every invention, subsequent research has been developed for improved efficiency. Nevertheless, the pursuit of researchers continues till finding a suitable, eco-friendly, and economically viable technology(ies) for the treatment of industrial effluents into zero-carbon release to the environment. In this chapter various environmental remediation technologies, nanotoxicity of nanoparticles, and nanocomposites were discussed to give ample information on recent investigations.

2 Chemical and Biological Remediation Technologies

Remediation technologies for the degradation of various contaminants can be classified into chemical and biological techniques. The operation of chemical technologies was based on photochemical and non-photochemical processes. In both processes, the generation and quantity of hydroxyl radicals are the rate-determining factors for the degradation techniques. However, chemical and biological technologies for the degradation of various azo dyes have both advantages and disadvantages, and the maximum degradation efficiency can be attained under particular environmental conditions as cited in reference (Katheresan et al., 2018). Besides, Mishra et al., (Mishra et al., 2020) reported the preparatory flowchart for carrying out the biocatalytic degradation of various hazardous pollutants (Fig. 1). The flowchart might be useful for the young researcher to design their biocatalytic degradation experiment before starting the laboratory studies. The initial screening is very essential to improve the efficiency of biocatalytic processes. Moreover, according to Mishra et al. (Mishra et al., 2020), xenobiotic mixed reactive dyes discharged from the textile industry without any treatment or partially treated have much influence on the ecosystem. The authors proposed a biocatalytic degradation of mixed dyes (reactive red 121 (RR121) and reactive orange 121 (RO121)) in the presence of *Pseudomonas aeruginosa* 23 N1. The progress of the degradation process was monitored using ADMI (American dyes manufactures institutes) index by monitoring the UV-visible spectrum and achieved ~87% of initially mixed dye degradation (Fig. 2). The bacteria involved in biocatalytic degradation have significantly demonstrated the degradation of mixed reactive dyes.

Moreover, the degradation intermediates of reactive orange 16 (RO 16) were investigated by Sultana et al. (Sultana et al., 2015) using a combined anaerobic-aerobic process involving a single-chambered microbial fuel cell (SMFC) followed

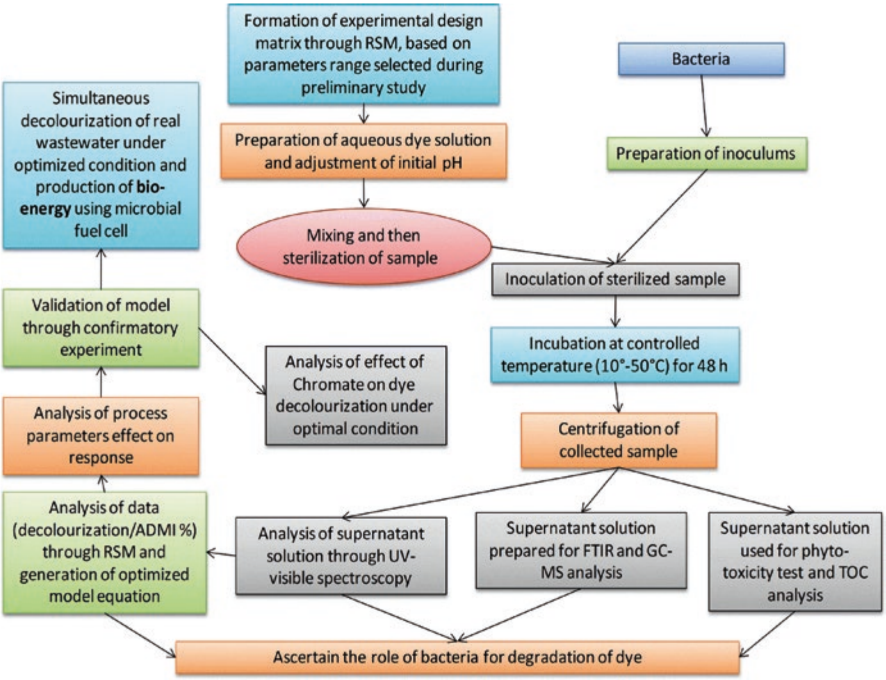

Fig. 1 Schematic representation of flow diagram of the biocatalytic experimental procedure. (Reprinted with permission from Mishra et al. (2020). Copyright 2020, Springer Nature Switzerland)

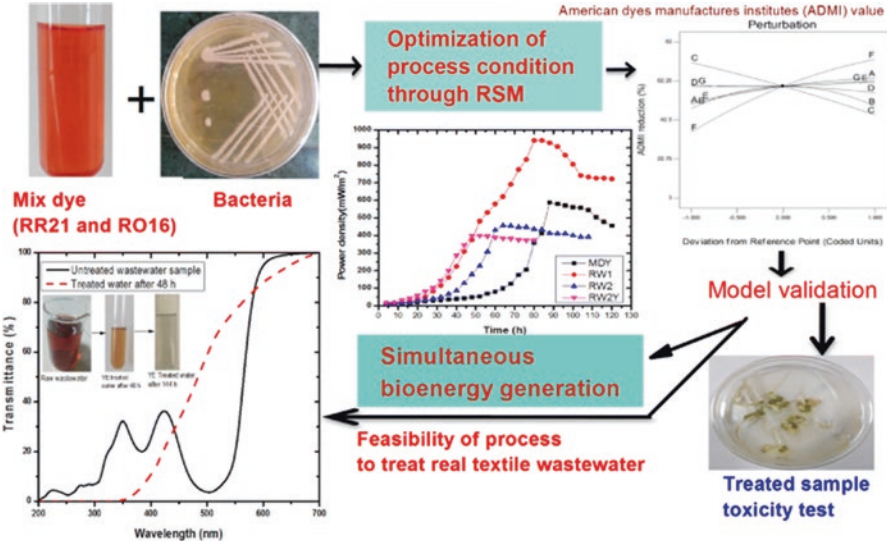

Fig. 2 Graphical representation of biocatalytic degradation of mixed reactive dyes (RR120 and RO 121) and the various characteristic analysis for monitoring the progress of degradation. (Reprinted with permission from Mishra et al. (2020). Copyright 2020, Springer Nature Switzerland)

by an aerobic downstream treatment process. There are various intermediates possible during RO 16 degradation by the SMFC-assisted biocatalytic degradation. Generally, the cleavage of the azo link tends to produce the corresponding aromatic amines, during the reaction, where aromatic amines are converted into various small molecular products. The mechanistic pathway of RO 16 biocatalytic degradation was reproduced here in Fig. 3 (Sultana et al., 2015) to understand the various intermediates produced during the SMFC-assisted biocatalytic degradation. The gas chromatography coupled with the mass spectroscopy (GC/MS) technique was adopted for the analysis of various intermediates produced during the degradation of RO 16.

The degradation pathway demonstrated that the formation of aromatic amines is the preliminary step involved in the degradation of RO 16 followed by the formation of phthalic acid, and subsequent intermediate analysis confirms the origination of benzoic acid. This confirms the efficient degradation of RO 16 by SMFC-assisted biocatalytic degradation along with energy production.

Furthermore, photocatalytic degradation of ternary dyestuff was reported by Sathishkumar et al. (Sathishkumar et al., 2013) in the presence of gold nanoparticles loaded amino and mercapto functionalized TiMCM-41 nanocatalysts in the presence of visible light. The authors prepared the ternary dyestuff using methyl orange (MO), acid orange 10 (AO 10), and acid red 88 (AR88) that was analyzed with the assistance of UV-visible spectroscopy which is represented here in Fig. 4a. The artificial dyeing process was carried out to prepare the effluent to study the

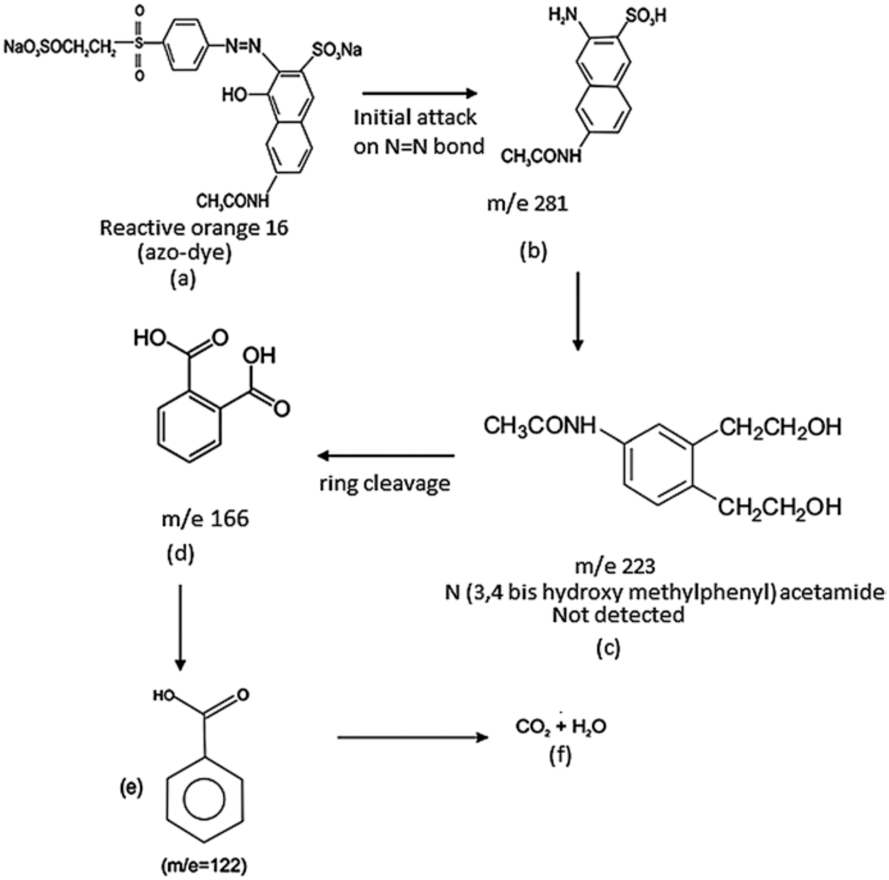

Fig. 3 Proposed scheme for the biodegradation of reactive orange 16. (Reprinted with permission from Sultana et al. (2015) The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015)

degradation of ternary dyestuffs. However, the efficiency of photocatalytic degradation was found to be low when compared with the kinetic degradation of individual azo dyes. The introduction of various chemicals such as sodium chloride and formic acid while preparing the artificial dyebath tends to attribute the slow degradation of ternary dyestuffs in the presence of the prepared hybrid inorganic photocatalysts.

The photocatalytic degradation of ternary dyestuffs was further improved in the presence of electron acceptors along with amino and mercapto functionalized hybrid inorganic nanophotocatalysts. However, the addition of sodium chloride and formic acid during the preparation of dyebath influenced the kinetics of ternary dyestuff degradation due to the presence of foreign substances, which significantly increased the optical density and reduced the population of hydroxyl radicals (Fig. 4b). Also, the adsorption/desorption properties of the mixture of dyestuffs

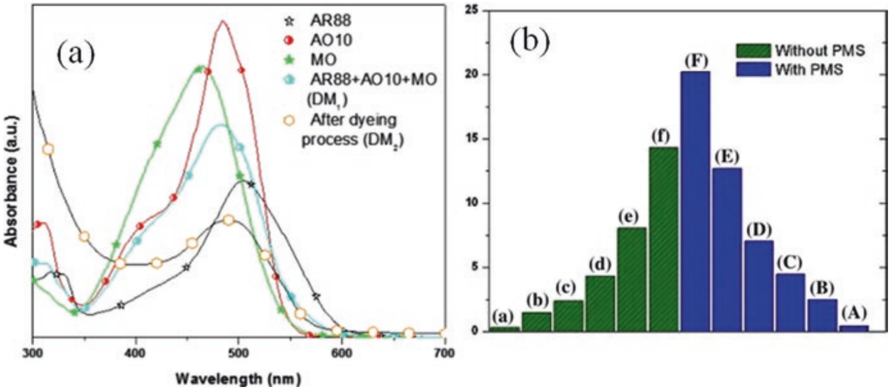

Fig. 4 (**a**) UV-Vis spectral analysis of various dyestuffs. (**b**) Comparison of photocatalyzed decolorization rate (1 h) of DM$_2$ (100 ml) solution in the presence of (A) NM, (B) SM, (C) NTM, (D) STM, (E) ANTM, (F) ASTM nanocatalysts [1 g/l] in the presence of PMS (0.08 mM); (a) NM, (b) SM, (c) NTM, (d) STM, (e) ANTM, (f) ASTM nanocatalysts [1 g/l] in the absence of PMS. (Reprinted with permission from Sathishkumar et al. (2013). Copyright 2013, Elsevier Publications)

(methyl orange (MO), acid orange 10 (AO 10), and acid red 88 (AR88)) are found improved in the microphotocatalytic environment since adhering of dyestuffs significantly ensures the availability of reactants near to the surface of nanophotocatalysts. The immediate reaction of sulphate ($SO_4^{\bullet -}$) and hydroxyl radicals ($^{\bullet}OH$) from the peroxomonosulphate was effectively utilized for the improved quantum efficiency of photocatalytic degradation of ternary dyestuffs.

Pugazhenthiran et al. (2013) reported the photocatalytic degradation of ternary dyestuffs in the presence of heteropoly tungstic acid (HPA)-loaded amine and mercapto functionalized MCM-41 hybrid inorganic nanophotocatalysts. The schematic representation of the interaction of HPA with the inorganic hybrid nanophotocatalysts was shown in Fig. 5. The binding of HPA over the framework of nanoporous catalysts augmented the generation of hydroxyl radicals ($^{\bullet}OH$) during the photocatalytic degradation of ternary dyestuff after the artificial dyeing processes. In addition, the authors demonstrated the reuse and recyclability of inorganic hybrid nanophotocatalysts which significantly prevented the leaching of HPA. The loading of HPA essentially improved the visible-light-driven characteristics of the resulting nanophotocatalysts. Thus, the reports demonstrated by Sathishkumar et al. (Sathishkumar et al., 2013) and Pugazhenthiran et al. (Pugazhenthiran et al., 2013) indicate the synthesis of novel inorganic hybrid nanophotocatalysts enhanced the possibility of degradation of ternary dyestuff after the dyeing processes in the presence of solar light irradiation.

In addition to dyestuffs, various industrial contaminants are perilous to the environment. Diclofenac is a non-steroidal anti-inflammatory painkiller prescribed for the treatment of aching in various parts of living organisms. The release of diclofenac to the environment from the production area, excretion from animal and human,

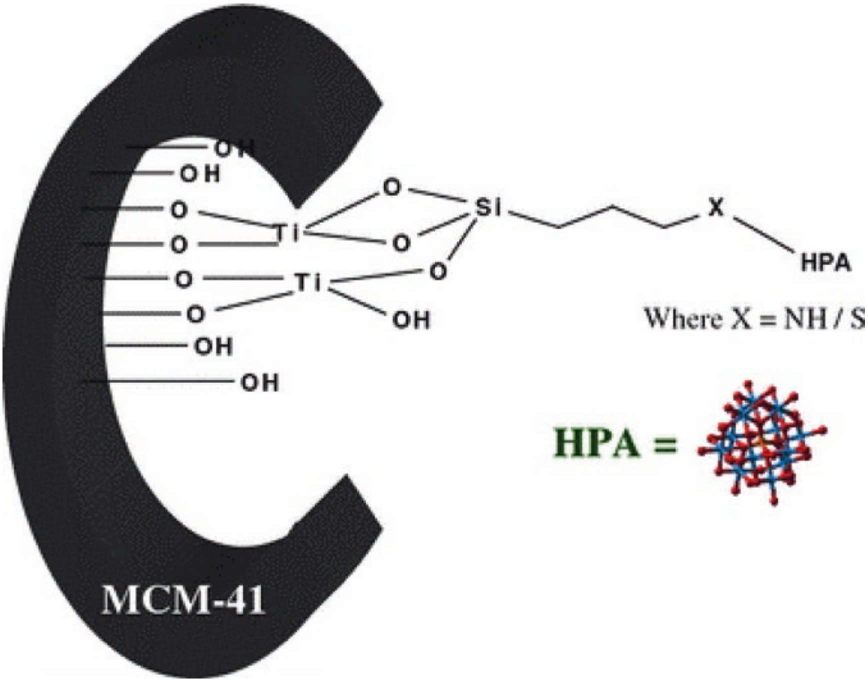

Fig. 5 Schematic illustration indicates the interaction between functionalized TiMCM-41 and HPA. (Reprinted with permission from Pugazhenthiran et al. (2013) Copyright 2013, Springer Nature Switzerland)

expired medicine from hospitals and medical centers (Ebele et al., 2017; Madhavan, Kumar, et al., 2010) augmented the concentration of diclofenac and enters the humans globally through drinking water and creates various side effects (Fu et al., 2020). Similarly, bisphenols are utilized as starting material for the production of various commercial products. The use of bisphenols in the production of feeding bottles was found to affect the brain growth of infants (Inadera, 2015; Palanza et al., 2008). Various industrially and economically significant materials were antagonistic to the common people. Hence, the complete mineralization of these contaminants essentially required before discharging them into the environment. Numerous techniques have been reported elsewhere for the degradation of various industrial effluents and are directed for further studies (Deng & Zhao, 2015; Kehrein et al., 2020; Paździor et al., 2019; Sathishkumar, Mangalaraja, & Anandan, 2016c; Yasar et al., 2006). In addition, biocatalytic degradation of commercially and economically significant chemicals are reproduced here in Table 2 (Sharma et al., 2018). The biocatalysts tend to eliminate and/or induce biotransformation of environmental industrial pollutants.

Table 2 The removal efficiency of contaminants by biocatalyst

#	Contaminants	Biocatalyst	Removal efficiency (%)
1	Diclofenac	Free laccase	27
2	Oxybenzone	Trametes versicolor laccase	Total elimination
3	Carbamazepine	Laccase with mediators p-coumaric acid, syringaldehyde, and acetosyringone	60
4	Sulfamethoxazole and Isoproturon	Laccase with mediators acetosyringone, ABTS, and syringaldehyde,	Complete removal
5	Diclofenac	Laccase with 1-hydroxybenzotriazole	Almost total biotransformation
6	Diclofenac	Laccase with syringaldehyde and violuric acid (VA)	Almost total biotransformation
7	Triclosan	Laccase immobilized on copper alginate	89
8	Bisphenol A	Immobilized laccases on the surface of yeast cells	46
9	Triclosan	Soybean and horseradish peroxidases	98
10	2,4-Dichlorophenol	Potato pulp peroxidase	98
11	Carbamazepine	Immobilized laccase on functionalized nanobiochar	83
12	Orange I, orange II, and methyl orange	Soybean peroxidase as free and immobilized on silica monoliths	Complete removal

Reproduced from Sharma et al. (2018) and further references are cited therein

2.1 *Mechanistic Investigation of Environmental Contaminants Degradation*

Maximum efficiency could be achieved by various advanced oxidation technologies for the complete removal of numerous environmental pollutants as discussed in Tables 2 and 3; however, the study of the mechanistic investigation of environmental contaminants essentially provides the knowledge and understanding about the chemical reaction occurring in the microenvironment. For example, Hapeshi et al. (Hapeshi et al., 2013) identified the formation of more than 20 intermediates during the degradation of ofloxacin which gives the idea about the toxicity and toxic intermediates produced during the mineralization. The proposed mechanistic pathway for ofloxacin degradation was represented in Fig. 6.

Hapeshi et al. (2013) further reported that the toxicity assessment of ofloxacin not only depends on the parent compound but also depends on the concentration of transformation products, besides dissolved organic matter plays a vital role in the degradation processes. The spirit of ofloxacin mineralization suggests that complete mineralization is required before effluents discharge into the environment since the complex kinetic degradation of ofloxacin tends to the formation of multiple intermediates. Moreover, Sathishkumar, Mangalaraja, Rozas, et al. (2016) reported various intermediates produced during the mineralization of Norflurazon. Norflurazon is a preemergence, bleaching herbicide utilized in agriculture and a long-standing

Table 3 Cytotoxicity mechanism of various nanomaterials and their combination

Nanomaterials	Composition	Mechanism of toxicity
Metallic	Gold	Size-dependent cytotoxicity. Larger, anisotropic AuNPs have more exposed surface available for oxidation and are cytotoxic than the smaller ones. Associated cationic side chains, surface-coated ligands, and stabilizers used with AuNPs also increase its cytotoxic effects. Higher surface area-to-volume ratio provides higher surface activity
	Silver	Accumulation of a significant amount of AgNPs exhibits toxicity through oxidation. These particles then degrade the antioxidant cells in our body. ROS generation is also higher from AgNP compared to bulk silver. Size and coatings provided over AgNPs also produce cytotoxic effects
Metallic oxide	Aluminum oxide (Al_2O_3)	Al_2O_3 NPs have the ability to oxidize cells and inhibit respiration and permeability of cells leading to cell death
	Copper oxide (CuO)	CuO NPs reduce glutathione and increase lipid peroxidase, catalyze, and superoxide dismutase in the epidermal cells of humans
	Zinc oxide (ZnO)	Generates reactive oxygen species and helps in the disintegration of the cell membrane which reduces cellular viability. It alters the cell cycle with micronuclei production, phosphorylates the H2AX molecules, and produces DNA damage
	Iron oxide (Fe_2O_3, Fe_3O_4)	Higher concentration of iron oxide accumulation can result in imbalance in its homeostasis and can cause aberrant cellular responses including cytotoxicity, DNA damage, oxidative stress, epigenetic events, and inflammatory processes
	Titanium oxide (TiO_2)	The mechanism is not yet clear. These nanoparticles do not release metallic ions, but they interact with different biomolecules present inside through surface to surface interaction. This leads to the generation of ROS, mitochondrial depolarization, plasma membrane leakage, intracellular calcium influx, and cytokine release. They also possess photocytotoxicity
Non-metallic	Carbon nanotubes	Multiwalled carbon nanotubes are able to stimulate the release of cytokines, IL-1β, TNF-α, IL-6, and IL-8 from mesothelial cells and macrophages. They induce ROS generation in the several cell lines and activate different ROS-associated intracellular signaling pathways such as mitogen-activated protein kinase (MAPK), activator protein-1 (AP-1), and nuclear factor kappa-light-chain enhancer of activated B cells (NF-κB) in mesothelial cells
	Quantum dots	The Cd^{2+} ions present in QD structures are often found to interfere with the DNA repair process. It even substitutes the physiological Zn content. Cd^{2+} readily helps in the oxidation of CdSe- and CdTe-derived QDs and achieves photoactivation on exposure to UV or visible light

(continued)

Table 3 (continued)

Nanomaterials	Composition	Mechanism of toxicity
	Silica	Induces cell death with long-term exposure and the lethal dose applied. Enhances immunotoxicity with the gene expression activation and release of interleukins IL6 and IL8. Activates reactive oxygen species. Increases malondialdehyde levels and upregulates pro-apoptotic genes.

Reproduced from Sarkar et al. (2019) and further references are cited therein

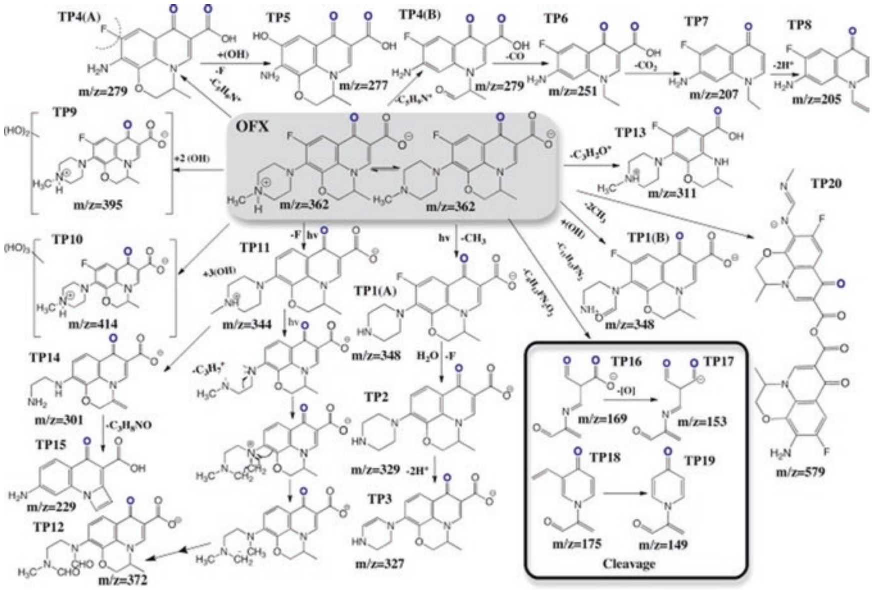

Fig. 6 Proposed mechanistic pathway for the degradation of ofloxacin. (Reprinted with permission from Hapeshi et al. (2013). Copyright 2013, Elsevier Publications)

pollutant in the soil which will not undergo the natural decomposition. The typical practice of the farmers tends to increase the concentration of Norflurazon in the water resources since the maximum solubility of Norflurazon was >16 ppm. Besides, the improved concentration of Norflurazon in the ecosystem mainly affects chlorophyll present in the producers of the ecosystem. Various intermediates produced during the degradation of Norflurazon and pseudo molecular ions identified during the ultra-high-performance liquid chromatography diode array detector electrospray ionization tandem mass spectrometry (UHPLC-DAD-ESI) analysis was reproduced in Fig. 7 which suggests the various degradation pathways available for the Norflurazon degradation. The continuous irradiation greater than 5 hours tends to produce the mineralized products of Norflurazon which gave the idea for the complete removal of Norflurazon from the aquatic as well as from the agricultural lands since it reduces the fertility of the agricultural lands.

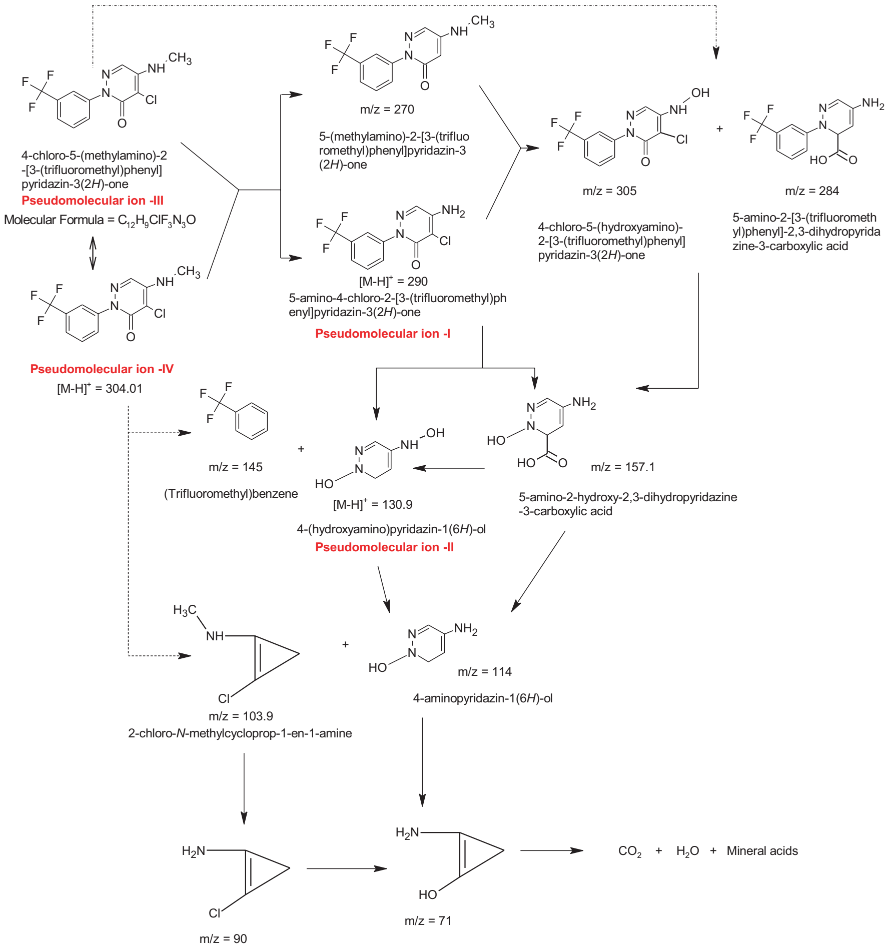

Fig. 7 Proposed mechanistic pathway for the mineralization of Norflurazon and its intermediates. (Reprinted with permission from Sathishkumar, Mangalaraja, Rozas, et al. (2016). Copyright 2016, Elsevier Publications)

Similarly, Madhavan, Sathishkumar, et al. (2010) reported the kinetic degradation of Acid Red 88 and the plausible intermediates during the mineralization of Acid Red 88. The schematic pathway for the degradation of Acid Red 88 was reproduced in Fig. 8. Apart from the class of pharmaceutical and agrochemical pollutants, azo dyes are heavily hazardous to the environment when their concentration in the environment increases above the permissible quantity since it is being utilized in various industrial sectors. About 1–20% of the untreated dye is discharged into the environment which is a significant threat to the ecosystem. Various possible intermediates produced during the degradation of Acid Red 88 was represented in Fig. 8 to understand the degradation pathway of Acid Red 88.

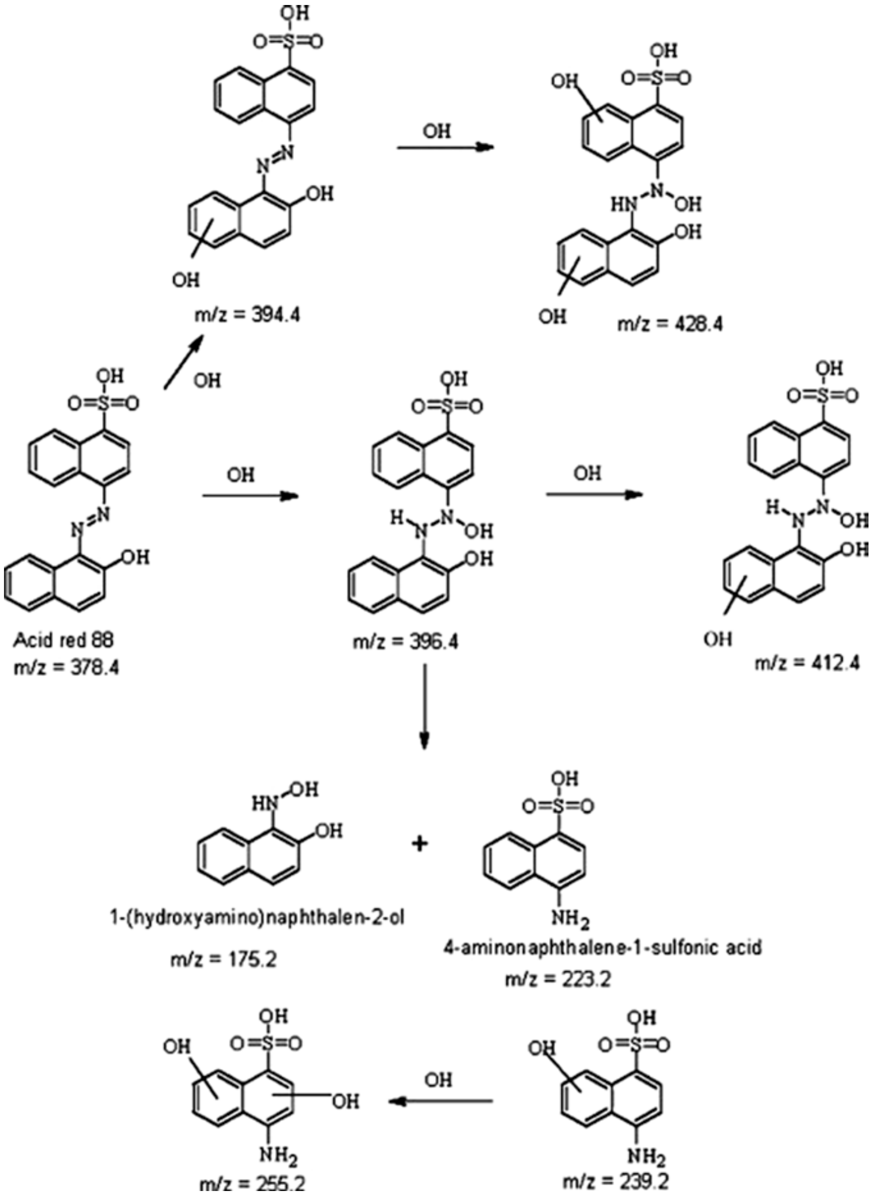

Fig. 8 Degradation pathway for the Acid Red 88 mineralization. (Reprinted with permission from Madhavan, Sathishkumar, et al. (2010). Copyright 2016, Elsevier Publications)

3 Nanotoxicity

Numerous applications of nanoparticles resulted due to the growth of nanoscience and nanotechnology. Nanoparticles have been applied to improve the commercial applications starting from medicine to industry (Armstead & Li, 2016; Hansen et al., 2008; Silva, 2007; Stamm et al., 2012; Wang et al., 2013; Wang et al., 2016). Utilization of nanomaterials in various sectors tends to unsafe disposal of nanomaterials which creates nanotoxicity and received huge attention from various research communities. Perilous disposal of nanocatalysts enters the food chain through accumulation in plants and fishes, since the metal uptake by these species is high and the nanomaterials can be accumulated in various parts of living organisms. Armstead and Li (Armstead & Li, 2016) presented various possibilities of nanoparticle entry into the environment and their primary and secondary toxic effects on the living organisms (Fig. 9). In addition to the external disposal of nanoparticles, internal disposal significantly augments the nanoparticle concentration in the total environment which leads to potential toxic effects (Fig. 9).

Rico et al. (2011) reported the level of metal uptake from earth to various parts of the plant and migration of nanomaterials from root to tissue level. Schematic illustration of metal uptake by various parts of the plant was reprinted in Fig. 10a. According to Rico et al. (2011) accumulation of nanoparticles is contingent on the nature of plant species. Translocation and biotransformation of nanoparticles at various parts of the plant significantly enhanced the knowledge of toxicological effects that transpired to a living organism. However, the transverse root examination indicates the penetration of nanoparticles into various zones which is alarming the inhabitants of the earth to keep the environment clean and green (Fig. 10b). In other words, the unsafe disposal of nanomaterials will enter the food chain through various natural progressions. Rico et al. (2011) further explored the possibilities of

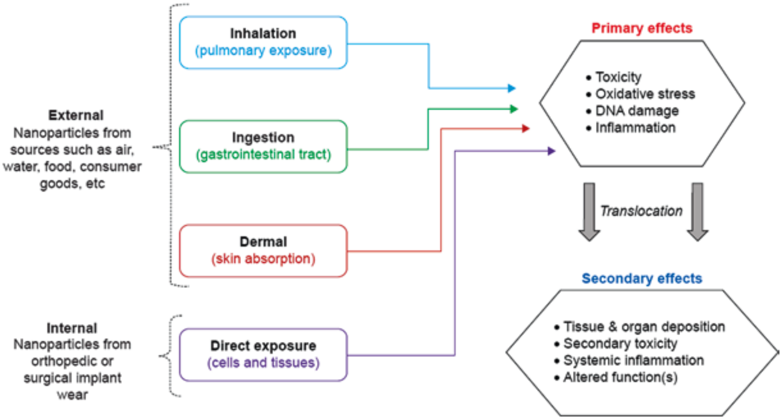

Fig. 9 Various paths for the entry of nanoparticles into the environment and their toxic effects. (Reprinted with permission from Armstead and Li (2016). Copyright 2020, Dove Press Limited)

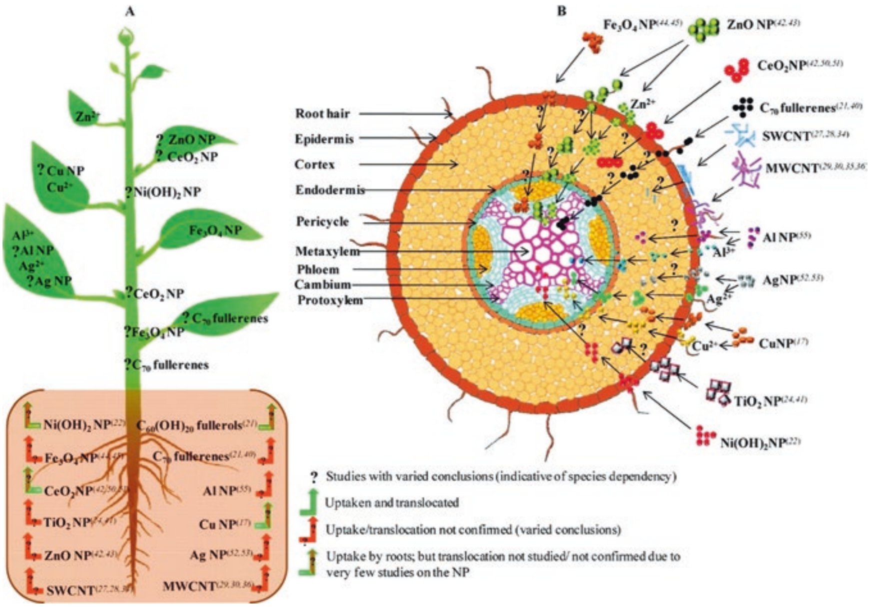

Fig. 10 Migration of nanoparticles into various parts of the plant species. (**a**) Selective uptake and translocation of nanoparticles. (**b**) Transverse cross section of the root absorption zone showing the differential nanoparticle interaction on exposure. (Reprinted with permission from Rico et al. (2011). Copyright 2011, American Chemical Society)

future research about the toxicological effects of nanoparticles accumulated in various parts of plant species. However, there are wide opportunities for young researchers to investigate the various perilous effects associated with the accumulation of numerous nanoparticles and their critical concertation. Accumulation of nano-sized metal nanoparticles augments the adverse effects to consumers; hence, a detailed analysis is required in the future to understand the toxicity of metal and its associated substances.

Instantaneously, noble metal nanoparticles play a vital role in maximum research fields due to their novel physicochemical properties, and the extended application of noble metal nanoparticles fetches enhanced disposal of nanomaterials and accumulates in the environment. The transformation of noble metal nanoparticles not only occurs through plant species but also via fishes. Lee et al. (2007, 2012) selected zebra fishes as the model to demonstrate the nanotoxicity of noble metal nanoparticles. Zebra fishes are well-understood biological species, exhibit fast and transparent embryonic development (Bakshi, 2020; Plantie et al., 2015), and hence nanometallic toxicity can be studied at various levels of transparent embryonic development. The characteristic surface plasmon resonance (SPR) was employed as a tool to investigate the cytotoxicity of noble metal nanoparticles against zebra fishes.

Herein, we reproduced Fig. 11 from Lee et al.'s analysis regarding the cytotoxicity of silver nanoparticles during the embryonic development of zebra fishes (Lee

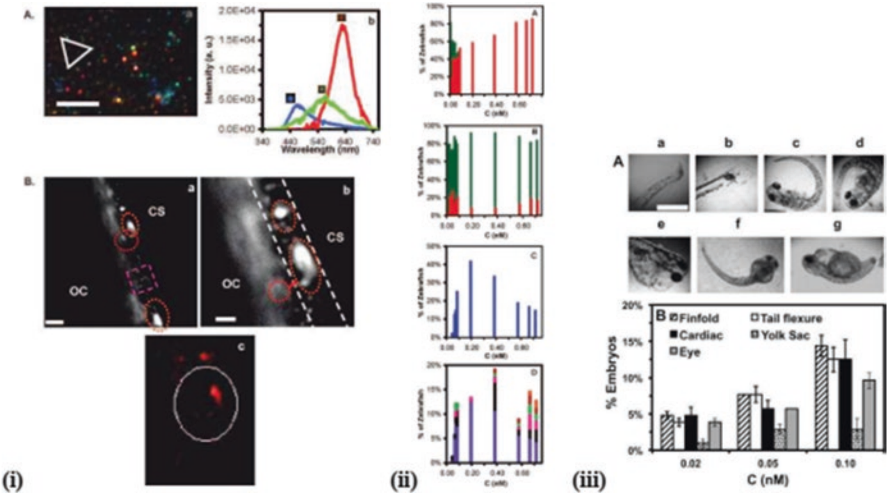

Fig. 11 (**i**) Characterization of Ag NPs embedded in embryos. (A) Representative (a) color image and (b) localized surface plasmon resonance (LSPR) spectra of single Ag NPs embedded in chorion layers. (B) Representative images of individual Ag NPs embedded in the chorion layers, illustrating those Ag nanoparticles (as indicated by a circle) trapped in the chorion pore canals, outlined by ellipses. (**ii**). Histograms of the distribution of normally developed (green) and dead (red) zebrafish, (A) versus concentration of Ag NPs and (B) versus concentration of supernatants resulting from washing Ag NPs (negative control). (C) Histogram of distribution of deformed zebrafish (120 hpf) versus concentration of Ag NPs. (D) Histogram of distribution of five representative types of deformities of the zebrafish versus concentration of Ag nanoparticles. (**iii**). Dependence of types of deformed zebrafish on Ag NP concentration. (A) Optical images of deformed zebrafish show (a,b) fin fold abnormalities; (c,d) tail/spinal cord flexure; (e) cardiac malformation and yolk sac edema; and (f,g) eye abnormality. (B) Histograms of distributions of embryos that developed into deformed zebrafish with five distinctive types of deformities at NP concentrations of 0.02, 0.05, and 0.10 nM. The scale bar is 500μm for all images in A. (Reprinted with permission from Bakshi (2020). Copyright 2020, Elsevier Publications)

et al., 2007, 2012). Initially, Ag nanoparticles were prevented by the chorion layers, whereas the nano-sized Ag nanoparticles act as the center for nucleation and growth of Ag nanoparticles which further diffused into embryos. The critical concentration of Ag nanoparticles was higher than 0.19 nm which was the essential finding from Lee et al. (2007, 2012) since above the critical concentration of Ag nanoparticles led to the death of embryos. Further accumulated Ag nanoparticles inside the embryos significantly alter diffusion, charge, and biomolecular-level interaction which misleads the research. Joshi et al. (2015) exposed the living bioreceptor cells to the Ag nanoparticles and found that the mortality rate of bioreceptor cells was very high even at the low concentration of Ag ions which indicates the nanotoxicity of Ag nanoparticles is very high (Fig. 12).

Meng et al. (2008) investigated the toxicity of ionic, micro, and nano-sized copper nanoparticles against the male ICR mice aged 8 weeks and weight of 25 ± 1 g. Digital photographs reprinted in Fig. 13 demonstrate the morphological changes that occurred after single oral gavage for one day. The stomachs exposed to the

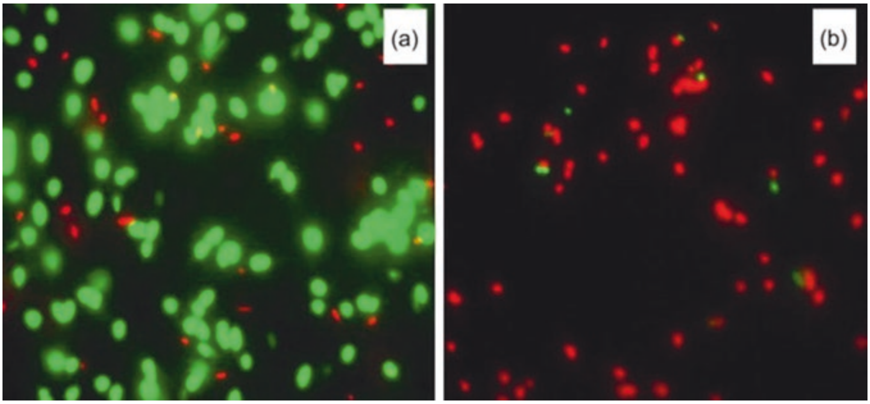

Fig. 12 Live dead images of the bioreporter cells before (**a**) and after treatment with silver nanoparticles (**b**). The high mortality rate upon exposure to nanoparticles occurs despite low ionic silver concentrations in nanoparticle supernatants, suggesting that lack of bioreporter response is due to cell mortality and further that ionic silver is not the only nanotoxicity mechanism. (Reprinted with permission from Joshi et al. (2015). Copyright 2020, Elsevier Publications)

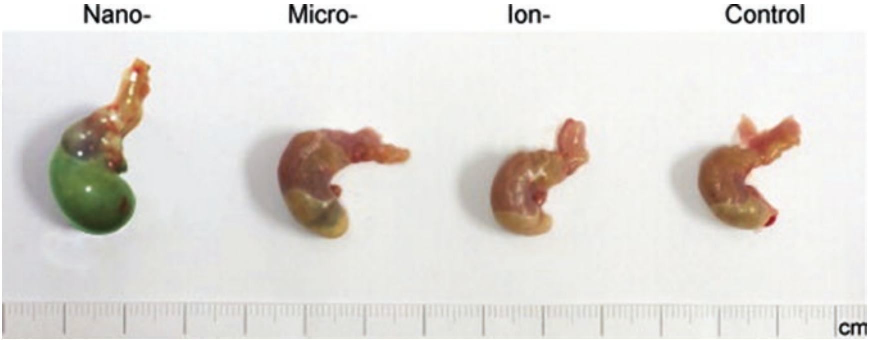

Fig. 13 The appearance of mice's stomach after single oral gavage for 24 h. The stomach is swelling up after nano-copper treatment and appearing significant color changes. (Reprinted with permission from Meng et al. (2008). Copyright 2020, Elsevier Publications)

control, ionic, and micro-level copper (Cu^{2+}) proficiently exhibit the same or minimum level of toxicity, whereas the stomach exposed to the nano-level copper experienced steeply increased toxicity and the color essentially changed to cyan. Thus, it confirms that the nanosized copper will retain in the stomach for a long time followed by the subsequent damages that will be created by copper nanoparticles. In other words, the cytotoxicity of copper nanoparticles is very high when compared to the ionic and micro-sized copper particles.

In addition to that, Sarkar et al. (2019) tabulated various toxic effects of semiconductors and metal nanoparticles, and the authors discussed the mechanism of toxicity which was reprinted in Table 3. According to Sarkar et al., (2019) the release of metal ions from nanoparticles/nanocomposites predominantly enhanced the toxicity level. The second essential factor is the penetration of metal nanoparticles through cell membranes. Moreover, reactive oxygen species (ROS) generated various free radicals during redox reactions carried forward by the nanoparticles, which dramatically increased the toxicological effects associated with the unsafe disposal of semiconductor/metal nanoparticles and/or nanocomposites. The cytotoxicity of metal nanoparticles can be accounted for the redox reactions, catalysts, and radical intermediates.

4 Conclusion

The efficiency of nanocatalysts/nanomaterials was found to enhance by multifold when compared to their bulk or micro counterparts. Thus, extensive applications were developed in diverse research fields and various products based on nanotechnology are available in the market with increasing demand due to their enhanced efficiency. At the same time, bulk titanium, gold, silver, and aluminum are known as the most stable and biologically inert materials; however, nanoparticles of these metals demonstrated the heightened cytotoxic nature and bioaccumulation make the situation most horrible. The perilous disposal of nanomaterials into the environment becomes problematic to the total environment, for example, the bactericidal efficiency of nanomaterials hinders the naturally available soil ecosystem. Accumulation of nanomaterials from lowest to highest trophic level organisms exhibits the various toxicological effects associated with the critical concentration of nanomaterials exposed to various organisms. Moreover, diffusion of nanomaterials through the food chain fetches innumerable health hazards to the living organisms. The origin of the toxicity of nanomaterials starts with unsafe disposal either in indirect form and/or disposal after specific application leads to contamination of the total environment. Therefore, during the synthesis and application of nanomaterials, cytotoxicity should also to be taken into consideration for a better environment for the present and future generations of the globe. One of the finest techniques available in modern research is to modify the surface of the nanomaterial with biocompatible materials as these substances essentially decreased nanotoxicity. However further research to protect the total environment from contamination of environmental pollutants will explore numerous materials and/or techniques to protect and maintain a clean and green environment.

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Retrospective and Prospective Bioremediation Technologies for Industrial Effluent Treatment

Rajesh Kanna Gopal, Gaurav Joshi, and Roshan Kumar

Abstract Bioremediation is an alternative, sustainable, renewable, cost-effective, and ecofriendly process for industrial effluent treatment rather than unsustainable, non-renewable, costlier, and non-eco-friendly conventional methods of effluent treatment. Therefore, bioremediation is a boon to all the industries to control the pollutant levels in effluents after treatment and before discharge to the environment. Some of the significant effluent-producing industrial sectors are petrochemical, agrochemical, food, tannery, domestic sewage, and nuclear power. Among different types of bioremediation, phycoremediation has evolved to commercial scale, industrial bioremediation plant and ensures potential in removing pollutants and simultaneously serves in clean energy technology. Phytoremediation using terrestrial green plants is familiar and favorable for mass-scale in situ bioremediation strategy. Bioaugmentation and biostimulation are the most critical processes for selecting an indigenous or consortium of microbes and providing favorable nutrients, respectively, to enhance and evolve microbial bioremediation. Bioengineering is a powerful tool for the synthesis of efficient biocomponent with desired traits to enhance bioremediation. Designing bioreactors for indigenous microbes or consortium of a microbial system is fruitful in bioremediation strategy. For example, tubular photobioreactors are designed especially for the microalgal system for efficient bioremediation strategy in industries followed by the production of value-added by-products. However, an integrated bioremediation strategy will be efficient in the future by

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coupling anaerobic, aerobic, photoautotrophic, followed by terrestrial and aquatic green plants in a series of wastewater treatment measures to efficiently reduce pollutants in all the stages.

Keywords Phyco-remediation · Microbes · Industrial effluents · Integrated strategy

1 Introduction

Water is the most essential resource gifted by our mother nature, on which every living 'dwells. Our Earth constitutes of one-third of the freshwater resource. Therefore, it is every global citizen's duty to save and utilize water properly to defend water scarcity. Innovation, technology, and industrial development are the major components of a developing country to build and improve its economy. However, even though there are several positive effects on the industrial revolution, there are some adverse effects, in which the central problem is the excessive generation of industrial effluents, its treatment, and disposal. Population explosion is also a factor that enhances the production rate in industries and, as a result, generates a high volume of industrial effluent. Industrial effluents are completely different with respect to the products they produce, which includes agrochemicals, pharmaceutical waste, petrochemical waste, tannery waste, electric battery waste, food industry waste, nuclear industry waste, heavy metal waste, hydrocarbon, and sewage. Hence, every industry needs its own kind of effluent treatment methods. Conventional methods of effluent treatment are common and effective, but costlier nor eco-friendly than bioremediation.

Bioremediation is defined as a remedy or a solution for any contaminated environments by the use of natural biodegradation processes with microbial cultures or its enzyme additives (OTA, 1991; Nichols, 2001). Bioremediation is further classified into in situ and ex situ bioremediation, where the former involves biodegradation processes at the site, and the latter involves excavation from the site and treated elsewhere. However, the latter is considered more expensive than the former, including excavation and transport. Henceforth, in situ bioremediation is impossible or ineffective in some of the polluted sites, where installation of equipment and monitoring may not be possible. Therefore, the selection of an affordable technique will be useful in reducing the concentration of the pollutant in an eco-friendly manner (Azubuike et al., 2016). For a proper selection of a bioremediation technique, some of the selective criteria to be given importance include nature of the pollutant, degree of pollution, type of ecosystem, cost and location, and environmental policies of the government (Frutos et al., 2012; Smith et al., 2015).

Intriguingly, the microbes proliferate in the polluted ecosystem and have the solution to solve the challenges within biodegradation-based bioremediation (Verma & Jaiswal, 2016), where these autochthonous microbes have had adapted to the existing polluted environments. Some of the molecular biology techniques, namely, genomics, metabolomics, proteomics, and transcriptomics, have had provided deep insight in understanding the microbial functions, catabolic and metabolic pathways, and its community diversity to overcome limitations associated with microbial degradation (Azubuike et al., 2016). In most of the cases, the microbial consortium was found effective in bioremediation than pure isolate treatment methods (Silva-Castro et al., 2012). For heavy metal removal, some anaerobic microbes can utilize water-soluble uranium U^{6+} as an electron acceptor and reduce it into insoluble U^{4+}, which was further precipitated and segregated from water (National Research Council, 1993). However, this chapter deals with bioremediation technologies for future challenges in industrial development.

2 Types of Bioremediation

The most common bioremediation types are microbial bioremediation (bacteria), phytoremediation (plants), mycoremediation (fungi), and phycoremediation (algae).

2.1 Microbial Bioremediation

Microbial bioremediation refers to the involvement of bacteria in the biodegradation of pollutants. A practical method of microbial bioremediation is using the native microbial communities which dwell in the same polluted environment and is termed as biostimulation. In addition to this, providing favorable edaphic factors and nutrients to such microbes yield highly efficient bioremediation. Bioaugmentation is another strategy contrast to biostimulation, where selective and potential microbial strains were introduced to a polluted site for bioremediation (Sylvia et al., 2005). Solvents, fuels, and pesticides are the most common source of organic pollutants polluting the environment through anthropogenic activities (Kang, 2014). Microbial metabolism is the crucial factor for biodegradation, which can consume pollutants as carbon or energy source (Vidali, 2001). Bacteria are the best key players in biodegradation-based bioremediation while providing an appropriate substrate and favorable edaphic factors.

For example, *Pseudomonas putida* (Gram-negative), a soil bacterium found efficient in bioremediation of toluene (paint thinner), is also potent in naphthalene biodegradation in polluted soils (Nitrification and Denitrification Wastewater Treatment, 1996). Similarly, *Dechloromonas aromatica* was found efficient in anaerobically oxidizing aromatic pollutants such as toluene, chlorobenzoate, and benzoate coupled with the reduction of chlorate or nitrate and oxygen. Nitrifiers and denitrifiers play a significant role in the removal of eutrophicated nitrogen compounds such as nitrate, nitrite, and ammonia. The former (*Nitrosomonas* sp.) oxidizes ammonia into nitrite and latter (*Nitrobacter* sp.) further oxidize nitrite into nitrate. However, anaerobic bacterium, such as *Paracoccus denitrificans* utilizes nitrate as an electron acceptor during oxidation and releases resultant nitrogen (N_2) gas (Nitrification and Denitrification Wastewater Treatment, 1996). Likewise, the eutrophicated nitrogen wastes in waterways would be remediated biologically. In the marine environment, a rod-shaped bacterium found proliferating on oil spills named *Alcanivorax borkumensis* was reportedly potent in utilizing oil spills as a carbon source and generates carbon dioxide. Moreover, it was reported that it cleanses 830,000 gallons of oil from the Deepwater Horizon oil spill in the Gulf of Mexico (Biello, 2010). *Methylibium petroleiphilum* is another bacterium that utilizes methyl tert-butyl ether (MTBE) (a significant pollutant) as a sole carbon source and thereby scavenges it from the effluent (Jessica et al., 1999). Intriguingly, a genetically engineered extremophilic bacterium *Deinococcus radiodurans* was efficient in the bioremediation of heavy metals, and solvents include mercury and toluene, respectively (McFarlan et al., 2000).

2.2 Phytoremediation

Heavy metal toxicity is a significant problem in industrial effluents contaminating freshwater resources, including groundwater. Land plants have channel proteins specifically for the transport and uptake of the metal ion into the plant system. The iron (Fe) regulated transporter (IRT1) is a channel protein specific for the uptake of Fe into plant cells, which may take other metals when Fe at low concentrations. In other words, uptake of nonessential metals also may take place via membrane transporters. A good example is a phosphorous transporter protein utilized to uptake arsenic (As) as AsO_3. However, organic compounds flow into roots by simple diffusion. This technology would be efficient for acceptable levels of pollutants in the ecosystem, hence limited to the root zones of plants and higher concentrations of toxic elements to plants. Phytoremediation technology involves different processes and include phytostabilization, phytodegradation, phytovolatilization, and phytoextraction (Fig. 1).

Phytostabilization

It is one among the process of phytoremediation to prevent the dispersal of pollutants and hence retained around the rhizosphere of plants (Fig. 1). This kind of phytoremediation is practiced in mine tailings to prevent the dispersal of heavy metals. Metal resistance and sequestration in plants are enhanced by the symbiotic association of rhizosphere-colonizing arbuscular mycorrhizal fungi. Some of the metal resistance grass varieties are *Festuca rubra* cv. Merlin and *Agrostis tenuis* cv. Goginan and cv Parys. Natural chelators synthesized by plant roots, sequester metals in the rhizosphere, which are organic acids, phenolic compounds, and siderophores. Plants also convert the toxic pollutants into less toxic forms by enzymatic bioconversion method or decrease their bioavailability. For example, highly toxic

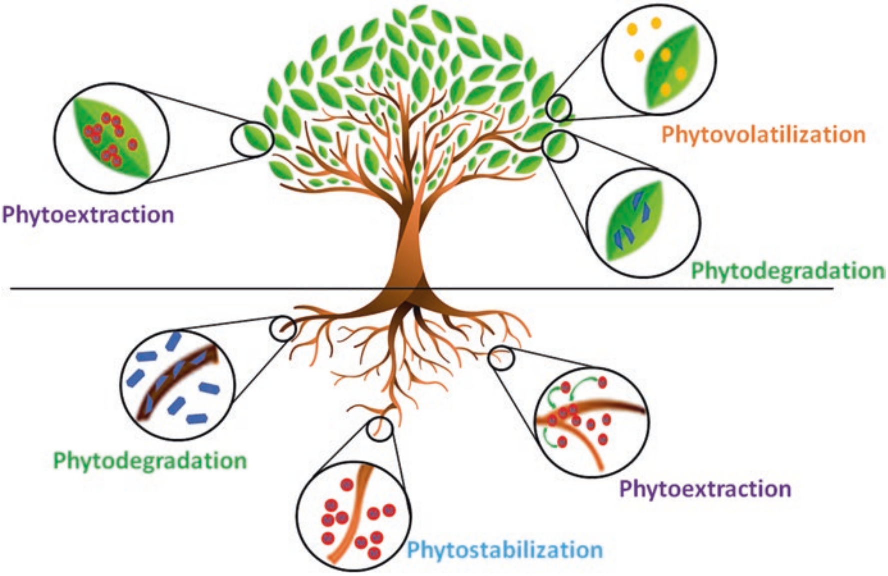


Fig. 1 Processes involved in phytoremediation of environmental pollutants

chromium Cr (III) can be converted into much less toxic form Cr (VI) by plants. Rhizofiltration is one of the process of phytostabilized phytoremediation, where metals are precipitated as metal plaques around the rhizosphere, while the released water is free from toxic metals.

Phytodegradation

This involves the biodegradation of organic pollutants directly through plant metabolism, mainly by the role of several enzymatic pathways (Fig. 1). The toxic recalcitrant organic compounds can be successfully detoxicated by the phytodegradation of a tree named *Populus* spp. Phytodegradation takes place in the rhizosphere of trees; bacterial microbiota also involves in this process to enhance the process through symbiotic association with trees.

Phytovolatilization

The most successful process of phytovolatilization takes place by the process of plant's evapotranspiration (Fig. 1). Plants uptake pollutants through its root system, transforms it into a gaseous state, and liberates into the atmosphere. Volatile organic compounds (VOCs) are the primary targets, for example, volatile trichloroethylene (TCE) can be converted into chlorinated acetates and CO2 by Populus trees. Even though metals such as Selenium (Se) can be volatilized into dimethyl selenide. Hybrid plants obtained through genetic engineering were found fruitful to volatilize methyl-mercury (Hg) from the soil into the atmosphere through evapotranspiration by inserting modified mercuric ion reductase gene (*merA*) into plants through *E. coli* bacteria.

Phytoextraction

Plant metabolism that has the ability to consume the pollutants from the soil and accumulate into harvestable biomass is termed as phytoextraction (Fig. 1). However, this can be enhanced by repeated harvesting of plant biomass in order to reduce the pollutants in the soil. Therefore, through continuous phytoextraction, heavy metal pollutants can be gradually decreased in the soil and accumulated in the plant biomass. It has been reported that about 400 different types of plant species can hyperaccumulate various metal ions up to an average of 1% of their dry biomass. Nearly 4% of nickel (Ni) ions were phytoextracted by the plant *Berkheya codii* from the polluted grounds and successfully extracted from the harvested biomass by phytomining. The transporter proteins are significant carriers of metal ions into the plant system, which are Cu-transporter (COPT1) and Zn-transporter (ZNT1). Some studies state that the application of chelators include EDTA, which enhances the phytoextraction ability of plants.

2.3 *Mycoremediation*

Bioremediation through fungi is termed as mycoremediation, which can be economically and eco-friendly effective to remediate soil and industrial effluents. Fungi are fast-growing organisms with the vast hyphal network with its ability to resist heavy metals, temperature, pH, and adapt adverse environmental conditions that made it a successful candidate for the remediation of industrial effluents (Singh et al., 2015; Kapahi & Sachdeva, 2017; Khan et al., 2019). Mycoremediation can be employed in terms of in situ remediation of various industrial effluents including herbicides, dyes, and pharmaceutical drugs. Ligninolytic enzymes are the principal weapon of several fungi for the removal of polyaromatic hydrocarbons. It is considered as a cost-effective and eco-friendly bioremediation technology than any other conventional methods (Rodarte-Morales et al., 2012; Bhattacharya et al., 2014). Some of the reported ligninolytic enzymes from fungi are lignin peroxidase, laccase, and manganese peroxidase (Pozdnyakova, 2012). In addition, cytochrome P450 monooxygenase also reported metabolizing PAHs (Bhattacharya et al., 2013). The fungus *Dentipellis* sp. KUC8613 has several enzymatic mechanisms including cytochrome P450, dehydrogenase, dioxygenase, glutathione transferase, FAD-dependent monooxygenases, and epoxide hydrolase for PAH degradation into quinones (Pozdnyakova, 2012; Park et al., 2019; Hammel et al., 1991).

Oyster mushroom *Pleurotus ostreatus* has the capability to tolerate and remove a wide range of heavy metals such as copper, nickel, cobalt, zinc, chromium, and lead present in the coal washery industrial effluents. The primary defense mechanism for its toxic metal resistance is the biosynthesis of several antioxidant enzymes in fungal metabolism (Vaseem et al., 2017). It is also reported to scavenge manganese from industrial effluents by the supplementation of surfactants. The surfactants enable high surface area and binding sites on the fungal hyphae for high bioaccumulation of manganese from the effluent (Wu et al., 2016). Fungi include *Rhizopus microsporus*, *Fomitopsis meliae*, *Trichoderma ghanense*, *Absidia cylindroslora*, *Trichoderma harzianum*, and *Trametes maxima*, and *Paecilonyces carneus* have been reported to resist heavy metals such as arsenic lead, copper, iron, cadmium, silver, and atrazine, respectively (Oladipo et al., 2018; Albert et al., 2018; Cecchi et al., 2017; Chan-Cupul et al., 2016). Xenobiotic compounds, especially glyphosphates were effectively degraded biologically by fungi such as *Aspergillus flavus*, *Penicillium verruculosum*, and *P. spiculisporus* isolated from herbicide polluted farms (Eman et al., 2013) (Fig. 2).

Fungi such as *Trichoderma citrinoviride*, and *Trametes versicolor* were found to inhibit the growth of microalgae and show algicidal activity (Mohamed et al., 2014; Gao et al., 2017). Then it has been proved that the ligninolytic enzymes including hydrolase, protease, cellulase, laccase, and manganese peroxidase play a major role in the inhibition of algal bloom formation and biodegradation of cyanotoxins they

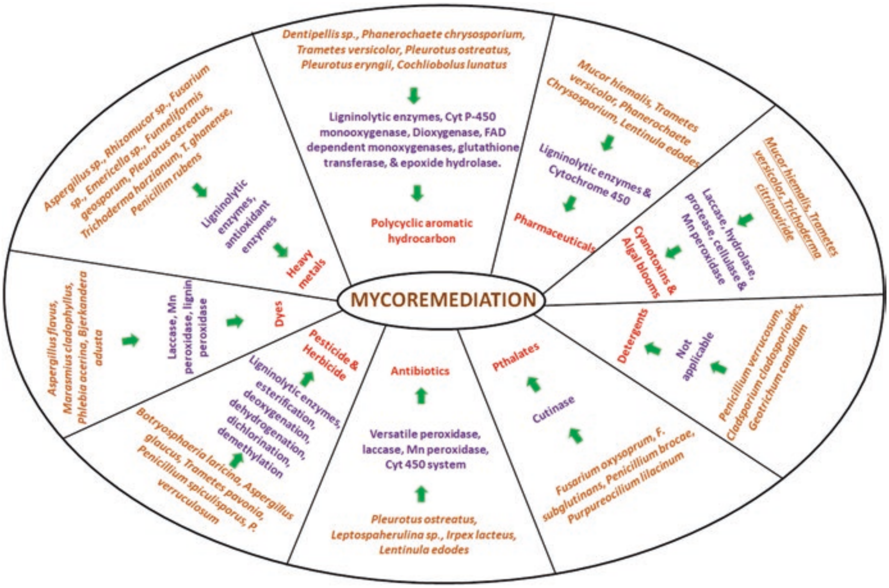


Fig. 2 The illustration of mycoremediation technology by fungi on different pollutants and its degradation. (Akhtar & Mannan, 2020)

produce (Dai et al., 2018; Gao et al., 2017; Du et al., 2015). Antibiotics such as fluoroquinolone, oxacillin, sulfonamides, oxytetracycline, clotrimazole, and bifonazole can mycoremediate through various types of fungi (Gothwal & Shashidhar, 2015; Copete-Pertuz et al., 2018; Migliore et al., 2012; Kryczyk-Poprawa et al., 2019). Intriguingly, cutinase and esterase are additional enzymes in plant pathogenic fungus *Fusarium oxysporum* which have the capability to degrade especially phthalates including dipentyl phthalate, butyl benzyl phthalate, dipropyl phthalate, di-hexyl phthalate, and di-2-ethylhexyl phthalate without any yield of toxic substances (Kim et al., 2007; Kim et al., 2005; Kim et al., 2002; Kim et al., 2003; Ahn et al., 2006) (Fig. 2).

2.4 Phycoremediation

Employing photoautotrophic algae for bioremediation is termed as phycoremediation, and it is a green technology due to its vast eco-friendly benefits. In the past two decades, phycoremediation has mainly evolved in treating various types of industrial effluents, including food industrial effluents, domestic sewage effluent, paper, and pulp industrial effluents, algal biofuel cells, and mitigate flue gas. Several algal species have been implemented in high-rated algal ponds, tubular photobioreactors, and airlift photobioreactors to treat different types of industrial effluents varying in nutrients and organic loads (Gupta et al., 2016; Shriwastav et al., 2014). The significant advantage of phycoremediation is devoid of any additional organic carbon source, since, algae are photoautotrophs that mitigate CO_2 as its sole carbon source. Unicellular microalgae *Scenedesmus* sp. and *Chlorella* sp. are the common algae most probably implemented for industrial effluent treatment, due to their fast growth rate, feasibly adaptable ability, and high-efficient nutrient removal capabilities.

Microalgae are successful mitigators of nitrate and phosphate eutrophicated industrial effluents (De la Noüe & Pruix, 1988; Oswald, 1988; Nagase et al., 2001; Thomas et al., 2016; Ghosh, 2018). Through phycoremediation, microalgae can assimilate nitrogen and phosphorous for the synthesis of its proteins (50–60%), nucleic acids, and phospholipids (Oswald, 2003). Some microalgae are facultative heterotrophs which are employed in high levels of organic carbon eutrophicated industrial effluents (Li et al., 2011). Therefore, the efficiency of phycoremediation enhances under aerobic, heterotrophic, and mixotrophic conditions for treating domestic, agricultural, and industrial effluents (Zhou et al., 2013). In another study, reduction of biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) of about 82% and 75% each, respectively, were reported in treating pulp and paper mill effluent by phycoremediation (Usha et al., 2016). Similarly, the metal-resistant cyanobacteria reported scavenging about 85% of manganese and 96% of Zinc (Bender et al., 1994). Phycoremediation removes about 92% of sulfate ions in tannery effluents (Ballén-Segura et al., 2016).

Microalgae are natural pH regulators, enhance the alkalinity of the medium by accumulating inorganic carbon, and thereby generating hydroxides. Therefore, these microalgae are efficiently employed in treating acidic industrial effluents. In contrast, microalgae can control acidity by reducing metals by acid mine drainage (Casiot et al., 2004). A cyanobacterium *Chrococcus turgidus* is used to neutralize highly acidic industrial effluent by continuous operation mode since 2006. Microalgae also have the ability to synthesize metal chelators, exopolysaccharides, or biosurfactants for biosorption of heavy metals in industrial effluents. Additionally, microalgae increase the pH of industrial effluents, which paves the way for enhancement of heavy metal precipitation (Chojnacka et al., 2005). Microalgae such as *Scenedesmus* sp., *Nostoc muscorum*, *Plectonema* sp., *Oscillatoria* sp., *Anabaena variabilis*, *Phormidium* sp., *Spirulina* sp., *Euglena* sp., *Chlorella* sp., *Chlorella vulgaris*, *Botryococcus braunii*, *Micratinium* sp., *Desmodesmus* sp., *Scenedesmus acutus*, and *S. obliquus* were found suitable for domestic wastewater treatment (Gani et al., 2016; Abdel-Raouf et al., 2012; Dewangan, 2016; Arone Soul Raj et al., 2016).

Microalgae have high efficiency in degrading textile dye effluents, and about 30 different azo dye compounds were reported to biodegrade and decolorized by microalgae *Chlorella vulgaris*, *C. pyrenoidosa*, and *Oscillatoria tenuis* into a simple form of aromatic amines (Yan & Pan, 2004). The most intriguing factor in phycoremediation is the biomass of microalgae with value-added by-products such as biofuel, cattle or pet feed, and aqua-feed (Tang et al., 1997; Elumalai et al., 2014). *Spirulina* was found useful in the reduction of 73% and 70% of BOD and COD, respectively, in pharmaceutical industrial effluents (Kshirsagar, 2010). Facultative heterotrophic microalga *Prototheca zopfii* was reported to degrade petroleum hydrocarbons and engine oils (Walker et al., 1975). Marine microalgae have high tolerance on high concentrations of crude oil, and some marine cyanobacteria have the ability to sequester hydrocarbons and accumulated in inter-thylakoid spaces (Al-Hasan et al., 2001). Figure 3 represents the potential efficiency of phycoremediation technology on various pollutants and its sequestration by microalgae.

3 Advanced Technologies in Bioremediation

3.1 Biosorption

Biosorption in bioremediation refers to the physiochemical process of absorption or adsorption of pollutants by a biological organism. Adsorption is defined as a surface adherence, or bonding of molecules or ions with biological material, whereas absorption is uptake of pollutants as precursors for its metabolism. Hence, biosorption takes place through live or dead biomass by metabolism-dependent (bioaccumulation) or metabolism-independent manner (biosorption) (Anjana et al., 2007; Avery et al., 1993; Garnham et al., 1993a) (Fig. 4). Therefore, bioaccumulation is an active process through membrane transport proteins into the cells (Garnham et al., 1993b). However, the passive process of bioaccumulation is faster. One of the passive processes is the transportation of pollutants through the cell membrane.

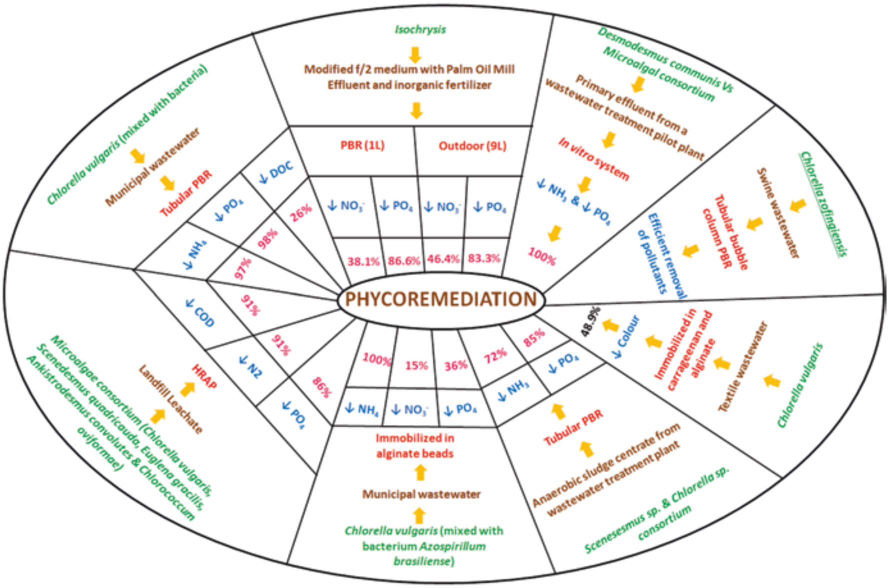


Fig. 3 The illustration of phycoremediation by microalgae on various pollutants and its removal. (Hanumantha Rao et al., 2019)

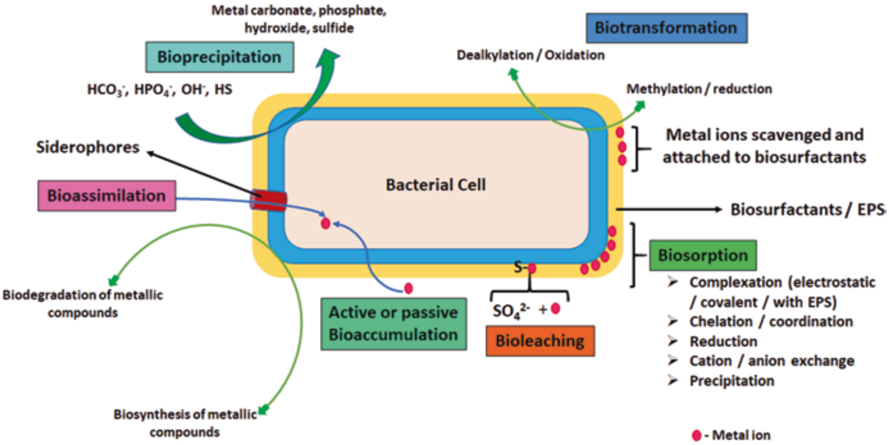


Fig. 4 Pictographic representation of various biosorption technologies carried out by bacteria in bioremediation of different pollutants, including heavy metals. (Ilyas et al., 2020)

This mechanism does not require metabolic activity, and which has two steps that include binding of metals to cell walls and uptake of metals into cells through the cell membrane (Huang et al., 1990; Costa & Leite, 1991; Nourbakhsh et al., 1994). Physical adsorption is a kind of biosorption, where dead biomass of fungi, algae, and yeasts was utilized to sequester metals such as cadmium, copper, cobalt, zinc, and uranium from industrial effluents through Van der Waals forces, and electrostatic interactions between the biomass and metal ions. For example, fungi such as *Ganoderma lucidum* and *Aspergillus niger* were reported to scavenge chromium by electrostatic interaction-based biosorption. Similarly, a green microalga *Chlorella vulgaris* and a bacterium *Zoogloea ramigera* are reported to sequester copper by biosorption through electrostatic interaction (Asku, 1992) (Fig. 4).

Ion exchange is another mode of biosorption, where the polysaccharides of macroalgae serve as ion exchangers with heavy metal ions to scavenge them from industrial effluents. An excellent example is the alginate of macroalgae, which have ionized salts such as Mg_2^+, Na^+, K^+, and Ca_2^+ interact and exchange ions with Cd_2^+, Cu_2^+, Co_2^+, and Zn_2^+ and indirectly uptake heavy metals and sequester from wastewater (Kuyucak & Volesky, 1988). Copper biosorption through the ion-exchange mechanism was proven in fungi *Ganoderma lucidium* and *Aspergillus niger* (Muraleedharan & Venkobachar, 1990). Metal-chelating agents are polymers synthesized or excreted by microbes such as biosurfactants, exopolysaccharides, proteins, and nucleic acid that react electrostatically with heavy metals by biosorption is termed as complexation. These metal chelators have electrons, neutralize with metal ions, and form a complex (Veglio & Beolchini, 1997; Davis et al., 2003).

Metal precipitation is based on cellular metabolism or metabolism-independent mechanism of biosorption, in which, chemical interactions between the heavy metal and cell surface play a significant role in precipitation. Siderophores are specialized low molecular weight transport proteins specifically for iron (Fe), in iron-deficient culture medium. It is termed as an iron chelator and plays a vital role in scavenging toxic metals and radionuclides by enhancing their solubility. Soil bacteria such as *Azotobacter*, *Actinomycetes*, and *Pseudomonas* sequester iron for their metabolism (Pattus & Abdallah, 2000; Gazsó, 2001). Biosurfactants are by-products synthesized by algae, bacteria, and fungi excreted into the culture medium. Biosurfactants consist of hydrophilic part constitutes of peptides, saccharides, or amino acids, and hydrophobic part constitutes of unsaturated or saturated fatty acids (Champion et al., 1995; Li & Li, 2011; Mulligan, 2005). Rhamnolipids are one such biosurfactant used in bioremediation and are biologically synthesized by *Pseudomonas aeruginosa* (Champion et al., 1995; Bognolo, 1999; Zhang et al., 2005; Mulligan, 2005; Tabak et al., 2005).

Prokaryotic bacteria have the capability of reducing metals such as SeO_4^{2-}, AsO_4^{2-}, Mn^{4+}, Fe^{3+}, and Co_3^+ or oxidize metals such as Fe_2^+, Cu, AsO_2^-, SeO_3^{2-}, Mn^{2+}, and Co^{2+} to obtain energy through redox reactions (Gavrilescu, 2004). Microbes tend to convert toxic metal ions to fewer toxic forms by the addition of methyl group (CH_3) to the metal ions, and the process is termed as biomethylation. Bacteria, filamentous fungi, and even microalgae can methylate metal ions such as Te, Pb, Sn, Se, Cd, Hg, and As by enzymatic mechanism in both aerobic and anaerobic conditions, where, the nature of metal ions such as volatility, toxicity, and solubility varies after biomethylation (Roane & Pepper, 2001; Gadd, 2004). Metallothioneins are cysteine-rich proteins dispersed in all the organisms, act as antioxidants when cell reacts with toxic metals. The thiol groups (SH) of metallothioneins sequester toxic metal ions including Zn^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+}, and Cu^{2+}

(Cobbett & Goldsbrough, 2002; Thirumoorthy et al., 2007) (Fig. 4). The metallothioneins play a dual role as scavengers of toxic metals and antioxidant protection against reactive oxygen species (ROS).

The biomass of brown algae, *Laminaria digitata*, constitutes a large number of polysaccharides, including alginic acid, and cellulose reported to sequester Strontium Sr^{2+} through biosorption and ion-exchange mechanisms (Sheng et al., 2005). Furthermore, it also sequesters radionuclides such as ^{85}Sr and ^{226}Ra (Pohl & Schimmack, 2006). Orange peels pretreated with NaOH and KOH have shown better biosorption of Sr^{2+} (Abdelkreem & Husein, 2012). Similarly, live and dead cells of a bacterium *Bacillus polymyxa* have shown biosorption of Sr^{2+} in the absence of Ca^{2+} ions as its competitor (Khani et al., 2012).

3.2 Bioleaching

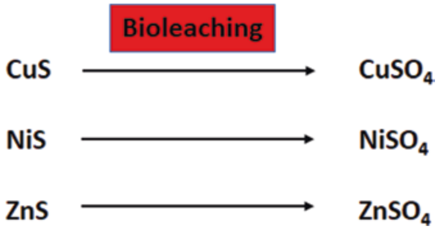
The biological conversion of the insoluble form of metals into soluble form is termed as bioleaching (Fig. 5).

The solubilized metal in aqueous solution can be easily segregated. Bioleaching is applied commercially for the extraction of copper and uranium from low-grade ores. This technology is applied for remediation of sewage effluents contaminated with heavy metals (Murali & Mathur, 2002; Samanta et al., 1992; Krishna et al., 2004). Most probably, the bioleaching bacteria are chemolithoautotrophic or acidophilic, or iron-sulfur bacteria such as *Acidothiobacillus*, *Thermithiobacillus*, *Sulfolobus*, and *Halothiobacillus*. *Acidothiobacillus ferrooxidans*, and *A. thiooxidans* are chemolithoautotrophs that oxidize element form of sulfur and reduce it into sulfuric acid (Favre-Réguillon et al., 2001) (Fig. 5).

3.3 Bioreactor

Bioreactors are a closed system, favorable for controlled microorganism cultivation via bioremediation. Most commonly, enzymes were employed to degrade environmental pollutants along with microbes to enhance bioremediation efficiency (Kumar et al., 2011; Sharma, 2012). Well-equipped bioreactors ensure right optimal

Fig. 5 The biological conversion of toxic insoluble heavy metals in wastewater into non-toxic soluble form through bioleaching

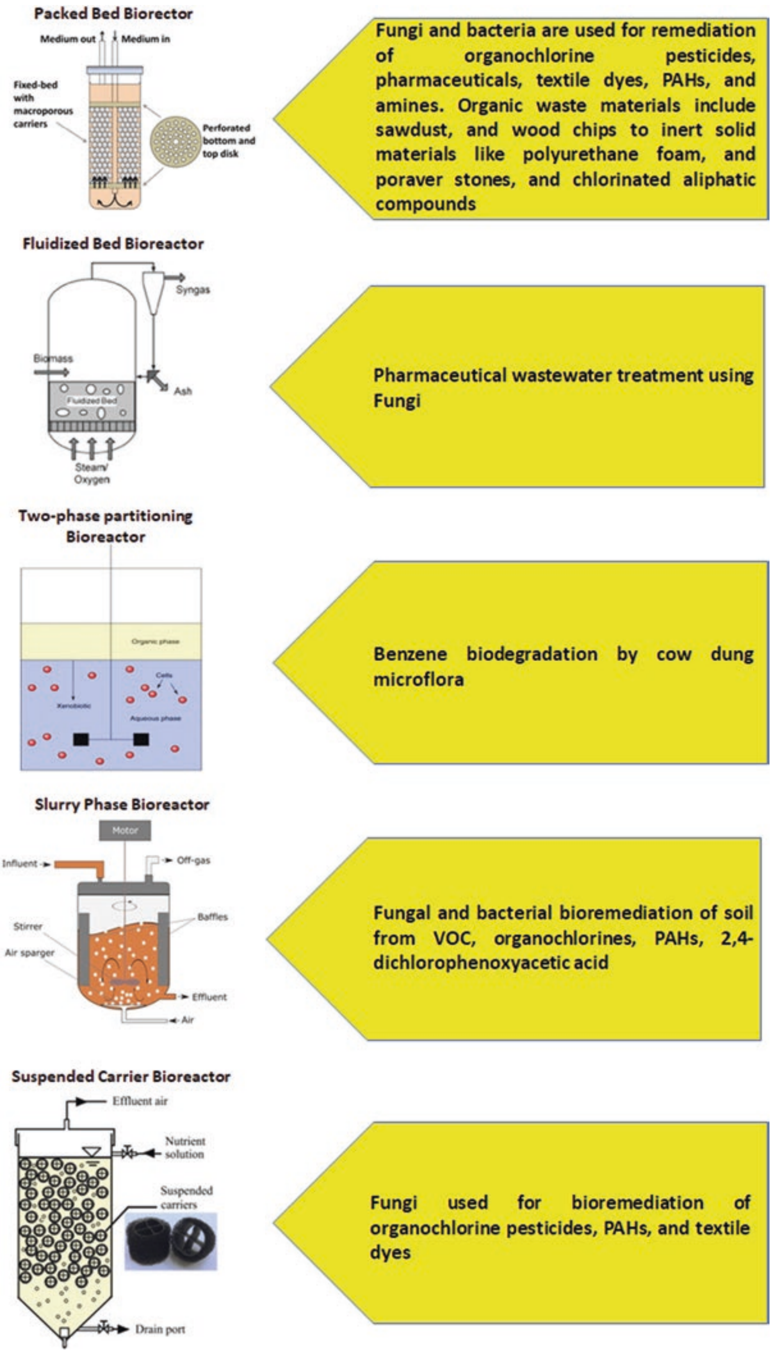


conditions for the microbes in a controlled environment that is necessary for bioremediation (Jeon & Madsen, 2013; Quintero et al., 2007; US EPA, 2003). Membrane bioreactors, up-flow anaerobic sludge blanket bioreactors (USAB), trickling bioreactors, and slurry bioreactors are some of the well-equipped bioreactors designed for industrial effluent treatment (Fig. 6).

The slurry bioreactor is an ex situ method of bioremediation most commonly used to retrieve tars, herbicides, pesticides, explosives, petrochemical hydrocarbons, creosotes, and chlorinated solvents from a solid substrate (Quintero et al., 2007; Plangklang & Reungsang, 2010; Robles-González et al., 2008; Pino-Herrera et al., 2017). The application of two different phases, such as organic solvent phase and aqueous phase, was employed in partitioning bioreactors to segregate water-insoluble compounds from industrial effluents (Singh & Fulekar, 2010; Daugulis, 2001). These bioreactors were used in bioremediation of toxic compounds in petrochemical industries such as volatile organic compounds (Dorado et al., 2015; Muñoz et al., 2012). Continuous two-phase partitioning bioreactor was studied and found useful for treating tannery industrial effluents (Angelucci et al., 2017). However, stirred tank bioreactors were designed for immersed microbial cultures which are mechanically agitated by sparging air into the bioreactor for practical bioremediation. By using continuous stirred tank bioreactor, the total petroleum hydrocarbon (TPH) was found reduced from 320 to 8 mg of TPH per liter by a microbial consortium of hydrocarbon-rich industrial effluents (Gargouri et al., 2011). Hence, it is successfully employed in the bioremediation of organic solvents such as benzyl alcohol, ethanol, and toluene by *Pseudomonas putida* (Bi, 2005) (Fig. 6).

Biofilters are the oldest bioremediation techniques where composted yard waste, bark, coarse soil, plastic shapes, gravel, and peat were used as a bed (Schmidt & Anderson, 2017; Lebrero et al., 2014; Rabbani et al., 2016). Biotrickling filters are used in the treatment of industrial effluents, which are cylindrical tank filled with ceramic or plastic media (Schmidt & Anderson, 2017). Microbes are allowed to grow on the materials by forming a biofilm and are allowed to degrade pollutants from the effluent. Biotrickling filters were found thriving in the efficient removal of butanol at a maximum removal efficiency of 100 gm^{-3} per hour (Schmidt & Anderson, 2017). Packed bed bioreactors are designed for high substrate flow, in the presence of live microbes (Bisping & Rehm, 1988), which was used to remediate textile dyes, polycyclic aromatic hydrocarbons, and amines. The packing materials used are polyurethane foam, sintered glass, porous ceramics, propylene agarose, and agar gel beads, silicone tubing, stainless steel, and nylon web for their respective industrial effluent used (Talha et al., 2018; Geed et al., 2017; Torres-Farradá et al., 2018). This type of bioreactor is favorable for fungal hyphal growth and facilitates mycoremediation (Fig. 6).

The airlift bioreactors are dependent of the sparging of air into liquid effluent and facilitates complete circulation and mixing. About 100% of phenol was removed by using airlift bioreactor and bacterium *Pseudomonas putida* (Nikakhtari & Hill, 2005). However, membrane bioreactors (MBRs) are designed with the use of a membrane that mediates the filtration system. The membrane serves as a barrier wall and segregates solid and liquid phases to maintain the quality of the effluent.



Fungi and bacteria are used for remediation of organochlorine pesticides, pharmaceuticals, textile dyes, PAHs, and amines. Organic waste materials include sawdust, and wood chips to inert solid materials like polyurethane foam, and poraver stones, and chlorinated aliphatic compounds

Pharmaceutical wastewater treatment using Fungi

Benzene biodegradation by cow dung microflora

Fungal and bacterial bioremediation of soil from VOC, organochlorines, PAHs, 2,4-dichlorophenoxyacetic acid

Fungi used for bioremediation of organochlorine pesticides, PAHs, and textile dyes

Fig. 6 Different types of bioreactors designed for the bioremediation of specific pollutants (Tekere, 2019)

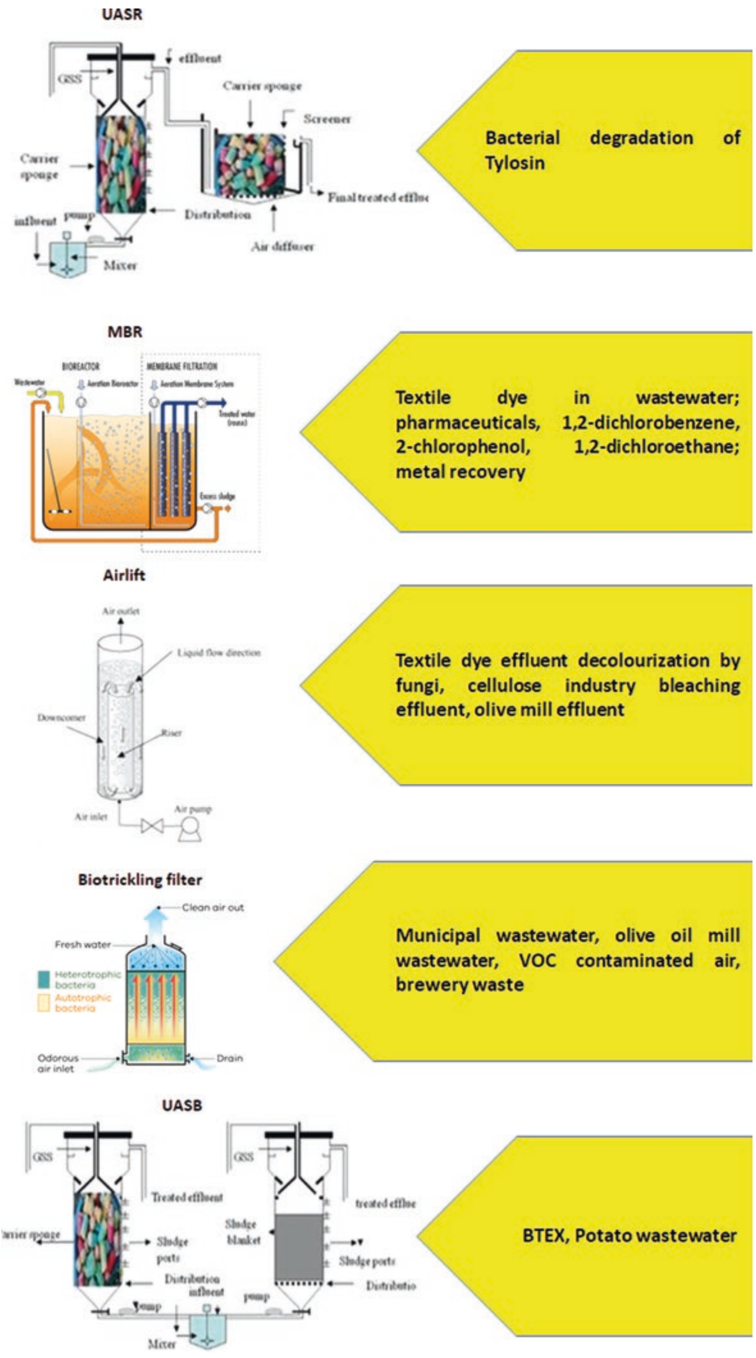


Fig. 6 (continued)

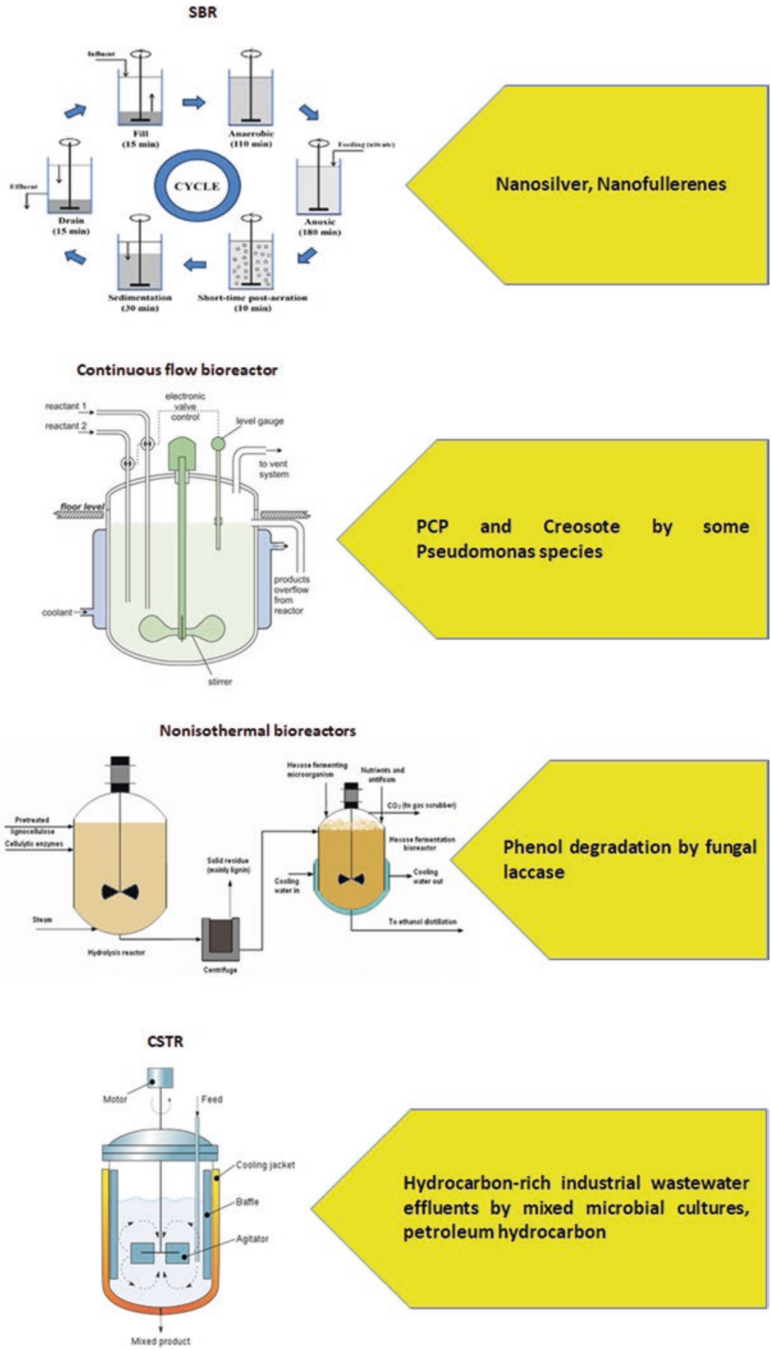


Fig. 6 (continued)

Hence, the treated effluent will be of high quality than other methods of bioremediation (Meng et al., 2009; Visvanathan et al., 2005). Domestic wastewater, industrial effluent, and textile wastewater are the best choice of bioremediation treatment with MBR (Hossain & Ismail, 2015). Bioremediation of 1,2-dichlorobenzene, 2-chlorophenol, 1,2-dichloroethane, and pentachlorophenol was carried out successfully in MBR (Visvanathan et al., 2005; Carucci et al., 2007) (Fig. 6).

3.4 High Rate Algal Ponds (HRAPs)

High rate algal ponds are huge raceway ponds constructed for the cultivation of microalgae for industrial wastewater treatment (Fig. 7). This technology is explicitly developed for phycoremediation, applied worldwide by many enterprises such as Aquonos Energy Ltd., Israel; Algae Systems and Sundine Enterprises, Inc., United States of America, and I-PHYC, United Kingdom (Wollmann et al., 2019; Herrador, 2016). Based on this technology, microalgae had efficiently reduced 80% of nitrogen and 70% of phosphorous from industrial effluent (Gentili & Fick, 2016). Similarly, another study on a microalga *Tetradesmus dimorphus* grown in HRAP with pharmaceutical wastewater, intriguingly depletes 90% of pharmaceuticals such as bupropion, diltiazem, bisoprolol, atracurium, metoprolol, atenolol, and citalopram (Sutherland & Ralph, 2019; Asselborn et al., 2015). HRAP system with microalgae was found 10 times greater in the removal of copper than the waste

Fig. 7 Photographic image of high rate algal ponds (HRAPs) built for phycoremediation of industrial effluents

stabilization pond system (Toumi et al., 2000). However, in another study, the heavy metals were found precipitated with high pH when the effluent is treated with HRAP (Perales-Vela et al., 2006). Highly efficient removal of heavy metals including iron (Fe), zinc (Zn), copper (Cu), and lead (Pb) was achieved at 100%, 98%, 76%, and 78%, respectively, when *Spirulina* sp. was allowed to treat industrial effluent in HRAP (Rose et al., 1998). The mixed algal population reduced 57% of sulphates, and 52% of COD by treating in HRAP (Molwantwa et al., 2000).

3.5 Composting

Composting is also a method of bioremediation to scavenge and breakdown pollutants in industrial effluents with the support of microbes in the soil. These microbes consume pollutants from water and metabolize or transform it into inert by-products such as water, CO_2, and mineral salts. This is a conclusively proven method of bioremediation in degrading a wide range of pollutants such as wood-preserving chemicals, heavy metals, pesticides, herbicides, explosives, petroleum products, solvents, and chlorinated and non-chlorinated hydrocarbons. Unique composts are designed for specific pollutants at specific sites, though they are termed as tailored composts. For example, tree leaf compost was designed for stormwater filtration and bioremediation. This method was found useful in the removal of 85% of grease and oil and 98% of heavy metals from stormwater runoff.

3.6 Bioaugmentation

Bioaugmentation is termed as the use of potential and selective microbial isolates for specific industrial effluent treatment. For example, a consortium of microbes (*Comamonas* B-9 and *Pandoraea* B-6 (bacteria), and *Aspergillus* F-1 (fungus)) isolated from lignocellulose from the activated sludge from a sequencing batch reactor (SBR) were found effective in biodegrading lignin greater than 50% than other methods (Zheng et al., 2013; Chai et al., 2010). Similarly, quinoline and pyridine biodegradation was improved further by using *Bacillus* sp., *Burkholeria pickettii*, *Paracoccus* sp., and *Pseudomonas* sp. isolated near a reactor filled with petrochemical effluents (Tuo et al., 2012; Jianlong et al., 2002; Bai et al., 2009). Bioaugmentation was applied in the biodegradation of cyanides from coke waste effluent using cyanide-degrading yeast *Cryptococcus humicolus* (Talhout et al., 2011) and a consortium of *Paracoccus denitrificans* and five different species of *Pseudomonas* spp. (Zhu et al., 2015). As a result, bioaugmentation was found efficient in the removal of quinoline, carbazole, naphthalene, pyridine, and phenol from coking effluent.

3.7 Biostimulation

Biostimulation refers to the enhancement of bioremediation by modifying the edaphic factors, nutrient constitution, oxygen, carbon, nitrogen, phosphorous, and electron acceptors favorable to the microbes. For example, bioremediation of halogenated pollutants involves the supplementation of electron donors to the anaerobes to consume such halogenated pollutants as electron acceptors. Similarly, bioremediation of hydrocarbon-polluted sites, supplemented with inorganic nutrients such as nitrogen (N) and phosphorous (P), enhanced the microbial growth and bioremediation efficiency (Stroud et al., 2007; Zhang & Lo, 2015; Smith et al., 2015). Whereas, nitrate supplementation was found to be efficient for biostimulation to bioremediate hydrocarbon-rich pollutants (Dashti et al., 2015; Bell et al., 2016). Therefore, particular microbes and its favorable nutrient conditions are recommended for the successful degradation of hydrocarbon (Röling et al., 2002; Wang et al., 2012; Zhang & Lo, 2015; Dashti et al., 2015).

3.8 Rhizofiltration

The plant root system has the ability to sequester and precipitate heavy metals from industrial effluent is termed as rhizofiltration and stored it in its biomass. Hence rhizofiltration is a type of phycoremediation (Abubakar et al., 2014). Live and dead biomass of a plant named *Datura innoxia* has been reported to scavenge Ba2+ ions from effluents. Similarly, the roots of a plant, Indian mustard (*Brassica juncea*) was found effective in removing heavy metals, including lead (Pb) from the effluent when grown hydroponically. However, aquatic plants are feasible and much favorable for the recycling of industrial effluents with high heavy metal concentrations in the developing countries for cost-effective bioremediation technology (Fawzy et al., 2012; Galal & Shehata, 2014; Dürešová et al., 2014; Krishna et al., 2012). Heavy metal tolerance or resistance by aquatic plants is a defense mechanism established by plants by metal sequestration, storing it in some cell organelles, and inactivated by some organic compounds (Sarwar et al., 2017). *Pistia stratiotes* is an aquatic plant, resistant to heavy metal concentration, and has been reported to sequester and accumulate higher concentrations of heavy metals such as nickel (Ni), chromium (Cr), lead (Pb), and cobalt (Co) through its root system and stored it in its shoot.

3.9 Bioventing

Bioventing is similar to biostimulation, where both aim to enhance bioremediation. However, oxygen is supplied additional to nutrients in bioventing, for enhanced growth of aerobic microbes to improve the bioremediation process further. This technology is applied to a particular zone which is devoid of sufficient air supply or oxygen, where indigenous aerobic microbes strive to grow. The addition of sufficient moisture and nutrients along with the optimal flow rate of air enhanced microbial conversion of harmful pollutants into the harmless state (Philp & Atlas, 2005), especially spilled petroleum products (Höhener & Ponsin, 2014). This technology is applied only for aerobic microbes to effectively remediate petroleum products such as kerosene, diesel, jet fuel, and gasoline.

3.10 Bioengineering

The base of bioengineering is the evolution and advancement of molecular biology, where a desired genetic material is transferred between two different populations to attain a specific goal. This technology is applied in bioremediation strategy also, where novel and potential microbial strains are produced with selectively desired traits for enhanced bioremediation processes. These include transfer of desired catabolic pathways, modification of enzyme stability, specificity, and affinity to increase the bioavailability of contaminants, and resistance to harmful intermediates during bioremediation. Higher hierarchy organisms prone to heavy metals have their own defense or resistance mechanism like the synthesis of phytochelatins, metallothioneins (Mehra & Mulchandani, 1995), and cysteine-rich peptides such as glutathione (Singhal et al., 1997) to chelate or scavenge toxic heavy metals into non-toxic forms (Hamer, 1986; Bae et al., 2000). Therefore, the transformation of such traits into bacteria was successfully carried out by Pazirandeh et al. (1995), in which, they transferred metallothionein gene from a fungus *Neurospora crassa* into a recombinant *E. coli* and has proved cadmium sequestration up to 75% higher within 20 minutes and attained maximum accumulation in 1 hour. Similarly, expressing polyhistidyl peptides on the surface of recombinant bacteria *Staphylococcus carnosus* and *S. xylosus* have gained efficiency in sequestering higher concentrations of nickel (Samuelson et al., 2000). In spite of searching particular microbes for particular pollutants, bioengineering provides a modern way to produce novel microbial strains for the effective removal of toxic pollutants from industrial effluents. Therefore, bioengineering is a powerful and modern technology to improve and develop microbial strains with desired qualities for feasible and quicker bioremediation and support industrial development in the future.

4 Future Perspective and Conclusion

In the modern era, industrial development will be a backbone for every developing and developed country. Consequently, population explosion is a crucial factor that influences industrial production at a high rate. Therefore, we should be prepared to face such a negative consequence, which is a greater generation of industrial effluents from the food industry, pharmaceutical industry, agrochemical industry, petrochemical industry, tannery industry, heavy metal processing industry, nuclear waste, and sewage. Industrial effluents are the major pollutants of freshwater resources and lead to water scarcity for domestic purposes. However, each industry is equipped with specially designed effluent treatment methods. Henceforth, conventional technologies are costlier and not eco-friendly, as in the case of bioremediation. Therefore, a tremendous paradigm shift has taken place all over the world to evolve bioremediation technologies for the next modern era.

Bioremediation has evolved with many technologies including biosorption, bioreactors, composting, bioleaching, bioventing, rhizofiltration using plants, bioaugmentation, biostimulation, HRAP, and bioengineering. Types of bioremediation had also evolved from microbial bioremediation (bacteria), phycoremediation (plants), mycoremediation (fungi), to phycoremediation (algae). Many indigenous microbes, fungi, and microalgae are being reported with the potential to bioremediate industrial effluents in pilot-scale experiments. Among bioremediation technologies, bioengineering is a powerful technology to produce a viable biocomponent for successful and efficient bioremediation in the near future. Similarly, integrated bioremediation is also a promising methodology to biologically remediate industrial effluents in different stages using different biological organisms like a serial bioremediation strategy from anaerobic microbes, aerobic microbes, photoautotrophs, and terrestrial or aquatic plants for future perspectives.

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A Review on Remedial Techniques for Pharmaceutical Contaminants in Wastewater

R. Seenivasagan and R. Kasimani

Abstract Many pharmaceutical companies utilize confidentiality composition as a means to escape the norms imposed by the pollution regulation control. Derivatives of pharmaceutical compounds (hormones, volatile organic compounds, antibiotics, and surfactants) and their metabolites are toxic (ecosystem of aquatic, terrestrial, and human health), and antibiotic-resistant microbial species are wastewater sources from houses, pharmaceutical industry, and hospitals. The wastewater comprises large quantity of salt, organic matter, microbial toxicity creating COD and BOD, and ever-increasing innovations in the field of medicine also increases the usage of pharmaceutical drugs, thereby increasing the rate of pollution. Pollution begins from the production and processing of pharmaceutical products until the cycle of consumption. This chapter explicates pharmaceutical contamination and pollution created by personal care products and addresses the means of elimination by biological and chemical methods like adsorption / bioadsorption, activated carbon adsorption, sedimentation, coagulation, advanced oxidation processes, photooxidation, ozonation, biological treatment, and electrochemical processes. Eco-friendly approaches are derived from the biological treatment by microbial process (composting, vermicomposting, aerobic and anaerobic techniques), and they do not produce secondary waste and also convert the toxic to non-toxic form. This has also demonstrated the benefits and demerits of the removal measures. This chapter summarizes the important overviews of key publications on pharmaceutical products.

Keywords Pharmaceuticals · Wastewater · Biological methods · Photooxidation

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1 Introduction

Until recently, pharmaceutical manufacturers are generally considered not to contribute considerably to environment pollution, on the other side not posing any threat to the environment (Kummerer, 2001; Babatunde et al., 2014). Drug manufacturing industries are the major cause of pharmaceutical wastewater (Awad et al., 2014; Ng et al., 2014). Nonetheless, new findings, though indicate the conflicting observation: Most processing plants around the globe have been determined to release high levels of APIs, into the environment significantly beyond previously established standards, thereby leading to pollution (Bisarya & Patil, 1993; Kummerer, 2001; Cui et al., 2006; Larsson et al., 2007; Li et al., 2008). Pharmaceutical wastewaters by chemical-based synthesis include a great number of organic and inorganic constituents comprising spent solvents, reactants, additives, catalysts, intermediates in large amounts and products (amoxicillin) with NH_3-N and high COD concentration, reduced biodegradation, recalcitrance, and toxicity from bacteria (Oktem et al., 2008; Chen et al., 2008). Pharmaceutical wastewaters contain tons of inorganic and organic pollutants, for example, antibiotics, released lacking effective treatment; actions like these can lead to large quantity of drugs entering the environment and creating numerous problems in the environment (Lang, 2006; Enick & Moore, 2007; Cunningham & Lin, 2010).

Pharmaceutical products contain compounds of wide range and include antibiotics, cytostatic drugs, anti-inflammatory medicines, β-blockers, hormones, contrast media antiepileptic drugs, and regulators of blood lipids (Mehrabad et al., 2016). Owing to the large range of chemicals produced in drug processing plants, successful elimination of substances in pharmaceutical residual effluents is a difficult task (Zwiener & Frimmel, 2000). Generally, wastewater of pharmaceuticals is characterized by the presence of refractory compounds and increased toxicity, limiting its biodegradability, thereby posing a potential danger to the wastewater treatment plants including natural environment, if handling is not proper (Gros et al., 2010). Volume and variability of created wastes through the pharmaceutical production and processing can considerably be greater than the quantity of the finished genuine product, and approximately 200–30,000 kg of wastes may be produced for each kilogram of dynamic ingredient extracted (NRDC, 2009). Given the immense quantity, scope, and dangerous nature of this waste, successful disposal of waste from pharmaceutical is a significant challenge. The pharmaceutical waste includes residual drugs requiring high need for pharmaceutically active compounds (PhACs), COD, BOD such as surfactants or toxic substances, hormones, volatile organic compounds, and antibiotics that pose possible threat to the environment. Numerous wastes from pharmaceuticals pose a substantial threat to human health and environment due to constant persistence in the ecosystem resulting in uniform progress of antibiotic-resistant microbial strains.

Currently, the involvement of antibiotics, anti-inflammatories, steroids, antiepileptics, estrogens, antihypertensive drugs, blood lipid regulators, antineoplastic agents, antiseptics, painkillers, and additional substances are documented well in lakes, rivers, drinking water, groundwater, urban effluents, treatment plants, and sea coastal water (Reddersen et al., 2002; Steger-Hartmann et al., 1997; Tixier et al., 2003; Sacher et al., 2001; Stumpf et al., 1999; Andreozzi et al., 2003; Atkinsons et al., 2003). This chapter examines the pollution created by personal care products and pharmaceutical contamination and addresses the means of elimination by chemical and biological methods like adsorption / bioadsorption, sedimentation, photooxidation, coagulation, activated carbon adsorption, ozonation, electrochemical processes, advanced oxidation techniques, and biological treatment. The benefits and demerits of the removal method were also demonstrated. This chapter summarizes the overviews of key publications on pharmaceutical products.

2 Sources of Pharmaceuticals in Water

A significant amount of industrial chemicals can be traced from the manufacturing and food product industries. Surface liquid is the principal source of disposed waste in industries. Illegal or untreated processing of effluents has increased the effect of surface water contamination up to 20 times the harmless level of protection and 22 heavily contaminated areas of the world. It should be noticed that most rivers are contaminated by industrial activity or the other in most stretches (Modak et al., 1990; Lokhande et al., 2011). Pharmaceutical manufacturers and hospitals are the major sources of polluted wastewater from pharmaceuticals. The pharmaceutical mixtures are typically produced by pharmaceutical industry in different operations, where abundant volume of water is required to extract and wash the equipment used (Gadipelly et al., 2014). The utmost distinguishing character of pharmaceutical industry effluent is that it comprises not only APIs but includes other intermediates, solvents, catalysts, other raw materials used in synthesizing and developing appropriate dosage form desired. And those things are pretty disruptive to the water from catchment areas where it is eventually disposed (Oktem et al., 2008; Zaman et al., 2014; Fent et al., 2006).

Active pharmaceutical substances are emerging pollutants whose existence in bodies of water has become an increasing environmental issue. Biota, sediments, drinking water, wastewater, and surface water have been identified to differing amounts of pharmaceuticals around the world (aus der Beek et al., 2016). The pharmaceuticals make their way through the ecosystem mainly by the disposal of treated and untreated wastewater from medical facilities or domestic users. Extensively metabolized drugs are excreted via urine and feces to the ecosystem. Nevertheless, the topically added pharmaceuticals (once eroded away) with the discarded and expired ones (while directly disposed into waste or sewage) present a significant danger to the ecosystem as the pollution join sewage by its strong and unmetabolized form. Despite stringent rules and regulations in the manufacture of drugs, pharmaceutically dynamic substances are often released by drug manufacturing plants with the waste.

Pharmaceutical wastewater comprises huge quantities of antiviral, antibiotics, and anti-serum drugs in addition to toxic, highly concentrated, and intermediates of non-biodegradable organic compounds (i.e., nitroimidazoles, ketones, sulfonamides, and phenol) that are over than those found in wastewater treatment plants (WWTPs) and drinking water plants posing potential threat toward human health and ecosystem (Aguilar et al., 2014; Joss et al., 2006). Among the Semi-synthetic β-lactam antibiotic amoxicillin is utmost popular contained pollutant in chemical synthesis and fermentation founded pharmaceutical effluents (Trovo et al., 2008; Wen et al., 2008).

3 Water and Soil Pollution of Pharmaceutical Waste

Scientists note large concentrations of pharmaceutical compounds in wastewater in diverse, that is, ground and surface waters, as well as sources of water used for drinking (Yang et al., 2014). Compounds of pharmaceuticals typically reach the natural water supplies by runoff of numerous sources of non-point water such as agronomic activity or sources of static water such as hospital and municipal treatment plants (Yang et al., 2016). The quantity and diverse generated wastes during pharmaceutical production is substantially greater than the quantity of the finished genuine product and is been estimated that 200–30,000 kg of waste has been created for each kilogram of the active ingredient usually formed (NRDC, 2009). Carbamazepine was the most common noticed drug in surface water bearing in mind the examined research. This drug is the antiepileptic, frequently detected in surface water (Rivera-Utrilla et al., 2013).

Biological materials such as processing waste, residual surplus solvents extraction lasting until the purification and separation of ingredients which are active from the natural sources, pharmacologically dynamic agents such as chemotherapeutic agents and anti-coagulants, along with washing agents and antiseptics are used in equipment sterilization. The emission capacity of the wastewater system too relies on the output of production line in pharmaceuticals (Balcioglu & Otker, 2003). Pharmaceutical wastewater has diverse structure and it contains several types of high concentration organic pollutants, NH_3-N COD, BOD_5, and high amounts of dissolved solids, depth of color, toxicity, and other characteristics (Chen et al., 2013). Around 500,000 cubic meters of wastewater is discharged per day, and waste discharges of about 100,000 tonnes per annum from pharmacy's most toxic chemical synthesis (Xiao et al., 2011). These pharmaceutical by-products from the pharmaceutical processing facilities separate assembly lines and ultimately become a portion of the total pharmaceutical runoff that has chemical oxygen demand (COD) upto 80,000 mg/L (Nandy & Kaul, 2001). Maximum pharmaceutical wastewaters recognize excess concentration of COD and can differ to variation of manufacturing industry which the COD value range starting at 4410 to 40,000 mg/L (Cetecioglu et al., 2015).

In aquatic ecosystems, colloids, soil, suspended solids, and sediments play an important role as basins that decide the conveyance of pharmaceutical mixtures through sorption. Several experiments have demonstrated the potential of pharmaceutical mixtures to adsorb on biosolids (Walters et al., 2010), soils, and sediments (Biel-Maeso et al., 2018). Propranolol, atenolol, and metoprolol have commonly been recognized in wastewaters, in which atenolol was acknowledged in the maximum concentration in few cases reaching up to 1 mg/L (Navarro et al., 2002; Guasch et al., 2004; Serra et al., 2009). Such compounds are also detected in surface waters in a range of low mg/L to ng/L, as a result of insufficient drainage through conventional effluent management (Guasch et al., 2004; Ternes 1998; Ricart et al., 2009, 2010). Few clofibrate analogs like bezafibrate, fenofibrate, and gemfibrozil were identified in the sewage plant trials in concentration to low of mg/L in the influent (Dorigo & Leboulanger, 2001; Guasch et al., 2004; Bonnineau et al., 2010). Drugs like pravastatin, atorvastatin, and mevastatine were identified in different ecological matrices which include treated and raw wastewater including surface water discharge points nearby (Dorigo et al., 2004; Bonnineau et al., 2010; Ricart et al., 2010; Pesce et al., 2010a, 2010b). Antagonists of H2-receptor, carbamazepine, cimetidine, and ranitidine, were commonly found in sludge wastewater. Carbamazepine conjugates of glucuronide can potentially be broken down during the treatment of wastewater, thereby raising its concentrations in the environment (Guasch et al., 2004). Carbamazepine stays heavy, not degraded in treatment of wastewater, and several experiments have identified it as pervasive in diverse environmental matrices (river, soil, groundwater) (Popper, 1972; Hurlbert, 1984; Munoz et al., 2001; Dorigo et al., 2004; Tlili et al., 2008; Laviale et al., 2010). As of most added pharmaceuticals, the recorded concentration ranges from few mg/L to very less ng/L (Hill, 1965; Clements & Newman, 2002; Franz et al., 2008; Bonnineau et al., 2010).

The most prevalent antibiotic ciprofloxacin is prescribed in Indian hospitals. It has been found in India at the highest concentration in wastewater (2830.658 μg/L) and surface water (356.052 μg/L) (Larsson et al., 2007). Yan et al. (2013) detected five classes of antibiotics (tetracycline, chloramphenicol, sulfonamides, macrolide, and fluoroquinolones) in water surface on a concentration range of 0.05–23.5 ng/L. The classes of tetracycline, commonly used as wide band antibiotic (4-epitertracyline), were detected both in treated and untreated wastewater in a concentration from 80 and 110 ng/L (Kim et al., 2014). Ferrando-Climent et al. (2014) verified the incidence of anticancer drugs ciprofloxacin and tamoxifen in the stream at concentrations ranging between 25–38 and 7–103 ng/L, respectively.

4 Health Hazard of Discharged Pharmaceutical Wastes

In the past 15 years, pharmaceuticals are inducing fear as possible bioactive compounds in the ecosystem. Pharmaceuticals are evolving pollutants in most urban wastewater, owing to their imperfect management systems, which extremely disturb the water quality. Additionally, pharmaceutical compounds of water pose serious dangers to ecosystems and health of humans in the extended run (Sires & Brillas, 2012). Pharmaceuticals are contaminants of growing importance because of their possible hazard to the marine biota and human well-being (Schwarzenbach et al., 2006; Boxall et al., 2012; Ebele et al., 2017).

Most pharmaceutical products remain at low concentration for longer periods in marine ecosystem including their lipophilicity, and lethal effects are more possible to be permanent quite more than acute. Such pollutants are similarly exposed to the pollutants during the lifespan which make their prenatal phase more vulnerable to effects of toxicity (Wilkinson et al., 2016). Several pharmaceutical groups pose specific questions, and among them, antibiotics have major environmental effects where they can interrupt wastewater treatment methods and badly influence the environment (Schroder, 1999; Sim et al., 2010). The dumping of treated and raw effluent serves as the principal cause of these pollutants in aquatic ecosystems (Daughton, 2003). Terrestrial drainage is also the secondary source from livestock farms, aquaculture facilities, and agricultural fields (Hong et al., 2018). Bioaccumulation experiments have documented the possible adverse consequences for marine organisms. These contaminants have been found in different tissues of fish, namely, gills (Tanoue et al., 2015), brain (Arnnok et al., 2017), muscles (Zhao et al., 2015), liver (Ojemaye & Petrik, 2019), and blood plasma (Muir et al., 2017). There has also been several studies evaluating bivalves (Burket et al., 2019), antibiotics in algae (Ali et al., 2017), and marine invertebrates (Meredith-Williams et al., 2012).

Pharmaceutical compound, Transformation products (TPs) formed through degradation with their separate toxicity. The essence of TPs is unspecified; certain TPs can be more harmful or permanent than their parental combinations, for example, antiviral drug acyclovir transformation which produces two lethal by-products through treatment of wastewater that showed a 40% decrease in reproduction of *Daphnia magna* and repressed green algae development (Schluter-Vorberg et al., 2015). Carbamazepine, an anticonvulsant drug, remains in marine ecosystem and causes toxic effects to marine species like fish, algae, and bacteria. Numerous human metabolites and processing yields may stance a danger for amplified genotoxicity (Brezina et al., 2017).

5 Physiochemical Treatments of Pharmaceutical Wastes

Physicochemical approaches like adsorption, ion exchange, electrochemical processes, frothing, coagulation-flocculation, chemical reduction, precipitation (Cheng et al., 2007), including the mixtures of these procedures (Torres et al., 1997), are used to handle wastewater at various phases right from primary processing to eventually treating their growing toxic concentrations in varied sewage treatment. Pharmaceutical-generated wastewater has extreme color, harsh odor, low BOD, and high COD (Farhadi et al., 2012). Anaerobic treatments are suitable choice for COD content of pharmaceutical wastewater; nevertheless, it is not mostly possible in precise due to excess total dissolved solids (TDS) content of this wastewater which obstructs methanogenic bacterial action (Lefebvre & Moletta, 2006).

The EC method was successfully suitable for pharmaceutical, restaurant, industrial, and household wastewater treatments. The impurities elimination of wastewater in pharmaceuticals are 72% for reduction in COD and development of COD; BOD ratio by 0.3: 0.18 with electrode of cast iron shows the biodegradability enrichment (Abhijit et al., 2005). Pharmaceutical wastewater (penicillin) treated by anaerobic, sulphate containing (3200 mg/L) was done by Rodriguez-Martinez et al. (2005). UASB showing 85–90% chemical oxygen demand and removal of sulphate above 90% was attained at an HRT of 8.3 d and OLR of 1.5 kg COD.m-3/d. Nevertheless, the reactor's ability was exaggerated (COD elimination fell to 70%) and was impaired when the filling rates amplified to 2.09 kg COD.m-3/d by decreasing the HRT to 7 days. The researchers recommended the sulphides gathering may be a reason for performance reduction. Chelliapan et al. (2011) recorded 45% efficient removal of COD when confirmed using an UASB to handle wastewater of pharmaceuticals with OLR of 3.73 kg, HRT of 2–4 d, and COD·m/3/d. Shi et al. (2014) found that COD elimination performance was 41.3 ± 2.2% for UASB with an OLR of 8.11 ± 0.31 kg HRT of 48 h and COD·m/3/d.

5.1 Coagulation

The process of coagulation and precipitation acts as an important step of pretreatment in the increase of the wastewater biodegradability by elimination of suspended particulate matter, grease, and oil including precise compounds. The unit operation coagulation happens in which colloids are separated as water and wastewater. The key method of operation is colloidal particle destabilization promoting collisions and charge neutralization among neutralized elements causing cohesion. Coagulant use reduces COD stacking at a moderately lesser price, stabilizing some of the components that are prone to leaching. A relative study of widely accessible coagulants like alum, lime, ferric chloride, and ferrous sulfate shows that ferric chloride eliminates COD and BOD to the maximum extent (Cheng et al., 2007). Cheng et al. (2007) achieved a low COD elimination level of 17.2% with polyaluminum chloride on a dose of 0.5 g/L on wastewater concentration after triazine processing capability. The procedure for treating wastewater, coagulating agents, that is, addition of Al_3^+ or Fe_3^+ salts to the chemical aggregates and coagulates the contaminants. Therefore, diverse coagulation systems allow their wastewater removal (Balla et al., 2010). The methods of electrocoagulation were more efficient in removing resistant and pharmaceutically active pollutants (Ensano et al., 2017).

5.2 Chlorination

Regardless of its reduced cost, chlorine (Cl_2), as hypochlorite or gaseous chlorine, has often been widely used in treatment of water (Deborde & von Gunten, 2008; Sharma, 2008) at one or two stages of processing: for preoxidation (to trigger a principal disinfection at the commencement of the treatment) and also for post-treatment (to retain a residual disinfection throughout the delivery method). Acero et al. (2010) worked on chlorination efficiency process in regard to the removal of pharmaceuticals, and their formulation of THMs was also proven. Finally, oxidant exposures (CT) and half-life periods are needed for the elimination of 99% of the four pharmaceuticals that are also measured. Such thresholds are helpful in determining the health doses of chlorine in disinfection or oxidation phases in plants treating pharmaceuticals. 17 β-estradiol and 17α-ethinylestradiol are effectively removed from pharmaceuticals by chlorination (Alum et al., 2004).

6 Adsorption/Bioadsorption

A well-researched procedure adsorption has been used for the extraction of pharmaceuticals from waters (Mestre et al., 2007; Cabrita et al., 2010; Akhtar et al., 2016), considered being an effective and flexible approach because of the low initial cost, non-selective nature, operational simplicity, and also because it does not result in the formation of hazardous products (Rafatullah et al., 2013; Akhtar et al., 2016). Adsorbents may be used in extracting selected oxidizing chemicals as of pharmaceutical treated effluent. Subsequently, wastewater is appropriate for disposal into rivers. It has been shown in the ease of environment friendless and fabrication of adsorbents obtained from plant-focused materials which has been confirmed (Ternes et al., 2003).

Adsorption processes are investigated in WWTPs capable of extracting pharmaceuticals from wastewaters. In addition, sorption may help in establishing resistance to antibiotics through microbes and domesticating genes with antibiotic resistance, pharmaceuticals adsorbed to residues and marine colloids might be tender to microbes, thus preventing degradation and fostering acclimation by microbes (Azuma et al., 2019). The adsorption ability of five pharmaceutical mixtures (diclofenac, propranolol, carbamazepine, sulfamethoxazole, and indomethacin) to marine colloids sediments and suspended particulate matter (SPM) has reported a strong sorption attraction of pharmaceuticals with marine colloids than SPM and sediments indicating that colloids serve as effective pharmaceutical compound sorbents (Maskaoui & Zhou, 2010).

Ravi et al. (2020) considered the adsorption of three new pollutants (carbamazepine, diclofenac, caffeine) developed with porous organic polymers based on synthesizing novel phosphate. The findings exhibited that both treated constituents have extraordinary selectivity for the wastewater mixtures. Zhou et al. (2016) tested the capacity of consumed mushroom substratum, deprived of any chemical or thermal action in removing sulfa-antibiotics (sulfamethoxazole, sulfathiazole, sulfamethazine, sulfamethyldiazine) from the aqueous solution. The result showed the adsorption ability that spent mushroom substratum declined in the following order: sulfamethoxazole > sulfathiazole > sulfamethazine > sulfamethyldiazine that consisted with the variations in structures of chemicals and functional antibiotic classes. Nanotubes of carbon are considered to be superior as mutual adsorbents to extract pharmaceutical compounds like microcystines, trihalomethanes, and 1,2-dichlorobenzene (Peng et al., 2003). Tzeng et al. (2016) experimented carbonization of cow dung for using as the adsorbent for elimination of sulfamethazine from water. A great efficacy in elimination, of equal to 88% (for an adsorbent dosage of 1 g/L), was confirmed at the adsorbents formed. Yi et al. (2016) analyzed the ability adsorption of levofloxacin from aqueous solution by means of wood chip and rice husk as adsorbents, finding which wood chips offered a greater capacity for the antibiotic adsorption. The method of adsorption has been deemed complex and includes both pore diffusion and surface adsorption.

7 Activated Carbon Adsorption

Activated carbon (AC), a generally used adsorbent in the elimination of both inorganic and organic pollutants, has proved capable of removing chosen pharmaceuticals (e.g., clofibric acid, carbamazepine, diclofenac, bezafibrate, caffeine) (Ternes et al., 2002; Sotelo et al., 2012, 2014; Coimbra et al., 2015). Application of GAC or PAC to MBR processes in the literature are: addition of PAC at 50–200 mg/L increased elimination of flufenamic acid, fluoroquinoloic (FQ) acid, moxifloxacin, enrofloxacin and ciprofloxacin (>94%), lower concentrations achieved lower removals (Baumgarten et al., 2007).

8 Advanced Oxidation Processes

AOPs comprise a range of treatment methods like homogenous and heterogeneous photocatalysis built nearby solar visible irradiation or ultraviolet (UV), ultrasonication (US), electrolysis, Fenton's treatment, ozonation, and wet air oxidation (WAO). The new technologies include pulsed plasma, ionizing radiation, and subjecting to microwave treatment (Gupta et al., 2009; Tong et al., 2011; Sharma et al., 2013). AOPs are effective in the elimination of a wide variety of pharmaceutical compounds. Such systems differ in efficiency of treatment. In fact, they are considered to be non-cost-efficient because of the high energy demand of AOPs. Furthermore, the added transformed products produced by these systems result in increased toxicity, for instance, certain oxidative TPs have greater polarity which increases the mobility to the environment, thus the hazard of groundwater contamination (Brezina et al., 2017). This process is considering to be cost-effective, energy-intensive, and helpful in determining the ideally suitable treatment process. A mix of recovery mechanisms seems more favorable. For example, a mixture of UV/H_2O_2 and O_3/H_2O_2 demonstrated superior degradation of pharmaceutical compounds with lower energy consumption and reduction of by-products formation (Lee et al., 2016).

Such methods include modern oxidative treatment in conjunction with titanium dioxide (TiO_2) or UV in grouping with ozone. These technologies need comparatively particle-free water and distinct quantities of reactors. Pharmaceutical compounds can be mineralized using AOP completely, although some are considerably much harder to extract and more resistant (Baresel et al., 2017). Kanakaraju et al. (2018) have widely studied the variety of innovative oxidation methods engaged in variety of studies, namely, pharmaceutical ozonation for NSAIDs (non-steroidal anti-inflammatory drugs) including precursors of NSAIDs like salicylic acid. Solar-photo-Fenton, Fenton, and photo-Fenton approaches are primarily used for the antibiotic treatment like nalidixic acid, ofloxacin, and ciprofloxacin.

8.1 Ozonation

Ozonation (O_3) is an antioxidant therapy in which ozone oxidizes the different compounds. The most commonly used method for the deterioration of organic micropollutants matches the major treatment process or is incorporated into the key treatment procedure as final polishing stage. The rate of degradation of permanent organic compounds relies on factors like contact time and ozone dosage, but it is also determined by the added organic compounds in the effluent treated as well. Ozone has been used in the water treatment mostly due to its sterilization and strong properties of disinfection (Arana et al., 2002).

Gome and Upadhyay (2013) measured ozonation cycle for the wastewater treatment trials starting pharmaceutical industries around Dewas, MP, India, with respect to their biodegradability, that is, percentage of COD / BOD. Unprocessed samples were separately treated both in alkaline or acidic conditions. This needed a dosage of 32.73 mg/L for acidic conditions and 30 mg/L ozone for alkaline situations. Though it was proposed that their findings do not indicate significant biodegradability improvement. Nevertheless, it was proposed that increase in the treatment time would accentuate the biodegradability enhancement. Alharbi et al. (2016) considered the degradation by ozonation of four pharmaceutical substances: trimethoprim, sulfamethoxazole, carbamazepine, and diclofenac and the development of by-products during oxidation. This study showed the full deprivation of trimethoprim, diclofenac, and carbamazepine, when a lesser ozone dosage was applied at 2.3, 2.8, and 1.6 mg/L, respectively.

8.2 Photooxidation

Photooxidation is a chain process of photochemical transition by the act of a substance like as Fenton's reagent or TiO_2 (Dalrymple et al., 2007; Chatterjee & Dasgupta, 2005; Herrmann, 2005). CeO_2, ZnO, TiO_2, CdS, Fe_2O_3, WO_3, and many other nanomaterials for semiconductors are used as photocatalyst for various applications like chemical synthesis environment and energy (Dhananjay et al., 2001; Carp et al., 2004; Shah & Chang, 2018; Rajaraman et al., 2019).

8.3 Electrochemical Processes

In the EC phase, dissolute metal hydroxide ions stay sufficiently capability of removing solvent inorganic pollutants (Solak et al., 2009). The key responses in EC process are aluminum / iron suspension from the processing of hydroxyl and anode ion at the cathode (Liu et al., 2015). In the EC processes, electrodes usually are made of iron (Fe), stainless steel (SS), and aluminum (Al), and the key function is a vigorous precursor of coagulant by anode dissolution and incremental output of hydrogen gas on cathode through gas bubble (Bhatnagar et al., 2013). Typically, three consecutive stages of the EC cycle include the production of coagulant material by oxidized breakdown of sacrificial anode metal, contaminant inconstancy, and particulate deferral, fracturing of emulsions, finally destabilizing phase aggregation to the shape flocks (Kamaraj & Vasudevan, 2016).

Probably, the application of EC pretreatment using anaerobic fixed film bed reactor (AFFBR), known for the efficient contaminant elimination from pharmaceutical wastewater. The final reduction of BOD value is 35–37% and COD value is 23–24%, applies 4, 8, and 12 mA/cm^2 using Al/Al cell (Deshpande et al., 2010). Nariyan et al. (2017) initiated in EC process that electrode of aluminum metal was found to be efficient in eliminating oxytetracycline hydrochloride from the iron electrode. Ahmadzadeh and Dolatabadi (2018) showed that the best elimination effectiveness of metronidazole (MNZ) was initiated to be 100% under ideally different operational parameters of existing density of 6.0 mA/cm^2, early metronidazole concentration of 21.6 mg/L, pH of 8.2, taking 14.60 min of response time, and 3.0 cm of interelectrode distance.

Conventional methods for treating wastewater appear to be inefficient in eliminating several pharmaceutical compounds. Owing to the several advantages compared to progressive oxidation methods by conductive diamond anodes, many chemical and photochemical processes have been extensively studied for the degradation of pharmaceutical compounds (Gherardini et al., 2001; Michaud et al., 2003; Panizza & Cerisola, 2005; Verlicchi et al., 2010). Other studies demonstrate drug-contaminated wastewaters can be efficiently treated using anodic oxidation procedure using a BDD anode. During the process of degradation, the water pollutants were oxidized by huge quantities of hydroxyl radicals, formed from the water electrolysis on exterior of the diamond. Yang et al. (2017) observed that electrochemical aptasensors were developed for the identification of sulfadimethoxine and ampicillin based on displacement of aptamer motioning probe. Low limit of detection (LOD) was achieved by the sensor in square wave voltammetry (SWV) measurement for both antibiotics of 0.28 and 7 nM in spiked lake water. Diclofenac (2-[2-(2,6-dichloroanilino)phenyl]acetic acid), a typical drug used for observing kidney and an essential ingredient of numerous pharmaceutical formulations (Buser et al., 1998) and its toxic material for the identification of surface water in many countries (Yu et al., 2013). Zhao et al. (2009) observed that approximately 72% of the mineralization was obtained for 30 mg/L diclofenac confined in a combined solution of NaCl (0.1 M) and Na_2SO_4 (0.1 M) through an anodic oxidative degradation method with BDD. Merola et al. (2014) established an electrochemical immunosensor for active identification on penicillin G and additional beta-lactam antibiotics by means of two reasonable tests. A H_2O_2 electrode was engaged as transducer.

9 Biological Treatment

Biological approaches are commonly used in the treatment of effluent owing to their effectiveness, low cost (Sirtori et al., 2009), and elimination of refractory pollutants from pharmaceutical wastewaters completely (Inyang et al., 2016). Biological degradation or bioremediation has a benefit over other unsuccessful chemical approaches and has made the water poisonous because of the yield in by-products during the treatment methods. Bioremediation methods are based on the activity of any bacterial, plant, fungal type, or the usage of membrane bioreactors, anaerobic or aerobic to manage and sustain a stable state of chemicals in aquatic environment. The technique of bioremediation seeks to treat plastics and xenobiotics resulting in microbial transformation making toxic less, water less, and added stability compared to its original state of pollution (De Luca et al., 2018; Misal et al., 2011).

Biological treatment system, relay on waste water's chemical composition, preliminary concentration and its physicochemical features. Nevertheless, the recovery efficiency of the biological approaches depends on the suspended/attached growth, hydraulic retention time, sludge retention time (Zupanc et al., 2013; Falas et al., 2013), redox state (Xue et al., 2010; Suarez et al., 2010), and pH (Gulde et al., 2014). Because of their role of nutrient (carbon, P, and N) and elimination of organic pollutant, microbial population is the critical constituent of WWTP.

The connection of non-floc and filamentous making microbes in WWTP influences the management and quality settling by inducing foaming and sludge bulking. WWTP removal of nitrate and phosphate are the main possessions of the microbial populations that defend natural aquatic system from consequent toxicity and eutrophication. Microbial group of beta proteobacteria and few groups of *Gamma proteobacteria* (*Nitrosomonas, Nitrosospira,* and *Nitrosococcus*) contribute to the nitrogen removal responsibility (Wells et al., 2009). Degradation of 25 pharmaceutical compounds includes, hormones, antipyretic, paracetamol, antibiotic, analgesic, ibuprofen only (hydrophobic compounds), 17 beta-estradiol, and achievement of 90% reduction in aerobic process (Joss et al., 2004). *Enterobacter, Pseudomonas,* and *Arthrobacter* use varied and diverse group of organic compounds, for example, pharmaceuticals as source of carbon and energy. *Enterobacter coloacea* with *Enterobacter hormaechei* prove a stimulating degrading ability of the pharmaceutical waste (Nilambari & Dhanashree, 2014). *Phanerochaete sordida* converts diclofenac into 4′, 5-dihydroxydiclofenac, 4′-hydroxydiclofenac, and 5-hydroxydiclofenac by oxidation reactions of cytochrome P450, laccase, and manganese peroxidase, which are sources of diclofenac elimination upto 90% after incubation of 6 days (Hata et al., 2010).

Gonzalez-Gil et al. (2015) testified that for maximum PCPs and some pharmaceuticals, aerobic treatment has quicker degradation kinetics related to anaerobic ones. Sorption (adsorption and absorption) and biodegradation are the principal removal tools involved in aerobic treatment like activated sludge process conventionally used. Prasertkulsak et al. (2019) observed the exclusion of five pharmaceuticals (ibuprofen, diclofenac, naproxen, trimethoprim, triclosan, trimethoprim) in the effluent using microbial sludge of the membrane bioreactors was more than 80%. Chen et al. (2018) established the concentrations of m-Cresol, N,N-Dimethylformamide, and isopropanol decrease as the compounds moved using the pilot-scale anaerobic membrane bioreactor by elimination efficiency fluctuating between 98% (N,N Dimethylformamide) and 96% (m-Cresol) at 15 ± 3 °C. Naghdi et al. (2018) assessed the efficacy of crude laccase, made by growth of *Trametes versicolor*, for carbamazepine breakdown in the presence and absence of the enzyme mediators, ABTS. This finding shows that laccase-ABTS organization can achieve additionally 95% carbamazepine breakdown efficacy in liquid media. Murshid and Dhakshinamoorthy (2019) illustrated the bacterial consortium capability in degrading dual non-steroidal anti-inflammatory drugs (mefenamic acid and sodium diclofenac). The findings indicate the degradation efficiencies for sodium diclofenac and mefenamic acid were 89% and 92%, respectively, within 120 h. These methods of treatment include membrane bioreactors (MBRs) technique. Biological breakdown method is combined via activated sludge with direct solid–liquid partition using membrane for filtration.

A large portion of scientific research has engrossed on using microorganisms to degrade pharmaceutical waste and transform them to either useful or harmless materials. The proposed approaches include anaerobic and aerobic methods, composting and vermicomposting (Amin et al., 2006; Lillenberg et al., 2010) and their mixture, few of which yielded useful by-products (Zhou et al., 2006; Majumdar et al., 2006). Influence of wild strain, purple non-sulphur photosynthetic bacteria was observed by Madukasi et al. (2010). This strain was called Z08, and 16SrDNA was used in identification and was confirmed as *Rhodobacter sphaeroides*. The wastewater from pharmaceuticals was supplemented with 0.1% of yeast extract and 0.5% of ammonium sulphate for a retention time of 5d under micro aerobic optimal light (6000 lx). A COD removal rate of 80% was observed at the end of the test, which clearly indicates the possible usefulness of phototrophic bacteria in the wastewater treatment for the elimination of organic wastes. The method has obtained safe removals of diclofenac (~55%) and bisphenol-A (80–90%). The white-rot fungus-improved MBR augmented by using redox mediator (1-hydroxy benzotriazole, HBT) was explored for elimination of 30 traces organic compounds, including 5 steroid hormones and 11 pharmaceuticals. The synergic effects of combined fungal culture and bacteria resulted in improved outcomes related to fungi without mediator MBR comparison (Nguyen et al., 2013).

9.1 Aerobic and Anaerobic Treatment

An efficient processing strategy is aerobic, anaerobic digestion and anaerobic co-digestion of pharmaceuticals distillates. Using AcoD effects in greater degradation grade of organics with anaerobic digestion on different substrates (Fountoulakis et al., 2008). The activated sludge system is often used as a phase of aerobic suspended growth. While the activated sludge process is operational in treating certain forms of pharmaceutical wastewater with low intensity, it has the downside with sluggish sludge settling (Eckenfelder Jr, 2000). Buitron et al. (2003) analyzed the efficiency of sequencing batch biofilter that combines aerobic-anaerobic environments into single tank to handle pharmaceutical wastewater (O-Nitroaniline and Phenols). The results revealed that a COD reduction of 95–97% was accomplished in the combined method at HRT 8–24 h, COD.m-3/d, and OLR of 4.6–5.7 kg.

Suresh and Abraham (2018) define the activated sludge process as the adding of flocculent suspensions to microbes like ammonia and nitrite-oxidizing bacteria like *Nitrospira* sp. and *Nitrosococcus mobilis* and eventual suspension airing. The activated sludge method can be additionally split into conventional and phased processes of aeration. Also immersed diffuser is used for agitation within the tank. With various types of treatment, model parameters like oxidation ditches, pH, and extended aeration may be modified. Ileri et al. (2003) have used sequence batch reactors (SBRs), an alternate to the active sludge, as this process needs floor of land space and does not yield any return sludge. Additionally, benefits the SBRs provide is that it does not need different units for sedimentation and aeration methods. They analyzed both domestic wastewater and raw mixed pharmaceutical wastewater. Their results were as follows: The COD removal rates were 88% and rate of BOD removal was set up to be 82%, removal rate of 98% for suspended solids (SS), and 96% was observed for NH_3 from the collected pharmaceutical wastewater and domestic wastewater, which was achieved by using a 4-h aerated SBR and 60 min for the sedimentation process.

Fox and Venkatasubbiah (1996) showed the usage of anaerobic baffled reactor in pharmaceutical wastewater treatment containing high sulphate (isopropyl acetate fermentation). Venkata Mohan et al. (2001) established the efficiency of COD eliminating HRT at 1d could be improved upto 50% by adding a sulphide oxidation unit.

The use of anaerobic suspended film contact reactor has been shown in the pharmaceutical wastewater management from bulk drug processing unit (aliphatic and aromatic organic compounds). Organics loading concentrations ranged from 0.25 to 2.5 kg.m-3/day and COD decline ranged from 60% to 80% with methane content ranging from 60% to 70%.

10 Vermicomposting

One of today's promising methods for the management of solid waste is vermicomposting that provides a variety of advantages such as chemical compound degradation, incorporation of the agricultural components of the waste as bio-fertilizer, or improved soil aeration. Worms are used in vermicomposting and produce heterogeneous blend of processed waste. Singh and Suthar (2012) opine that the scientists used the technique of vermicomposting in treating herbal pharmaceuticals residues. Using earthworm for composting *E. foetida*, they treat herbal pharmaceutical industrial wastes mixed using cow dung in various quantities setting under simulated environment in a laboratory condition. During vermicomposting the results revealed major improvements in chemical properties of waste blends, with decrease in the pH content of entire final residues. Upon vermicomposting the finished result became more stable, odor-free with a wide variety of plant available soil nutrient sources, and decreased pH content in all waste mixtures.

11 Conclusion

One of the new micropollutants that endanger the water quality and the environment is pharmaceutical wastewater. Choosing of the treatment methods primarily depends on pollutants' solubility and chemical structure. The literature discloses the quality of the surface water bodies has yet to be successfully secured from the threat of toxic pharmaceutical waste discharge. Pharmaceutically vigorous compounds pose danger to environment through their persistent aggregation, toxicity, persistent nature, and the ability in developing microbial strains that are drug resistant. However, it is crucial that they are handled properly to shield the ecosystem. The discharge of pharmaceutical compounds to ecosystem can cause disruption of marine flora and fauna, hazard to human health, and develop microbial strains of multi-drug resistance. In this review, various approches of removing pharmaceutical pollutant based on biological, chemical, and physical properties were discussed.

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Potential Eco-friendly Techniques for the Management of Organic Pollutants from Industry Effluents

V. Uma Maheshwari Nallal, R. Sitrarasi, C. Thamaraiselvi, and M. Razia

Abstract Bioremediation techniques have become noticeable and valuable tools to reduce, reuse, and recycle different industrial effluents through eco-friendly practices. Industries are well known to release anthropogenic-related chemicals into the environment over the century and consequences are witnessed as contamination of soil, water, and air, respectively. The untreated or impertinently treated wastewater effluents are known to be toxic to plants and animals, including humans that lead to negative impacts on the earth. Remediation has emerged for degrading contaminants using physical, chemical, and biological methods. Bioremediation techniques are used nowadays around the world meticulously. It is technology based along with the combined action of plants and associated microbial communities to degrade, remove, transform, or immobilize toxic compounds in effluents. This chapter discusses the classes of organic effluents, toxicological mechanism, and its environmental impact and also emphasizes the current and advanced eco-friendly techniques in the remediation of organic effluents through microbial, algal bioremediation and phytoremediation. Bioremediation techniques are potential, cost-effective, and in addition to that remains as a solution to the challenge of treating many classes of contaminants, compared to the conventional chemical and physical methods, which are often very expensive and ineffective compared to biological methods.

Keywords Bioremediation · Effluent · Microbes · Nanomaterials · Phytocompounds

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1 Introduction

Environmental pollution has been well defined in various ways and implies to the release of unwanted substance by man into the environment that alters the surrounding and damages either their own health or the resource in turn (Moschella et al., 2005; Wasi et al., 2012). It is regarded that pollutants directly or indirectly have a detrimental effect on the human health when they occur in higher concentrations than the natural levels (Richards & Shieh, 1986). The two major classifications of pollutants are biodegradable and non-biodegradable pollutants: sewage effluents and organic matters constitute the biodegradable pollutants and they are decomposed quickly, whereas plastics, detergents, and heavy metals are considered non-biodegradable and cannot be easily decomposed in natural ways. The major source of anthropogenic wastes that enter water bodies are through industries. Release of xenobiotic compounds has been tremendously influenced by the fast-growing wave of urbanization and simultaneous industrialization that occurs to meet the demands of the population (Tabrez & Ahmad, 2010). Industries cannot be solely blamed for the environmental degradation; utilization of fertilizers, gasoline, aerosol sprays, and pesticides remain a major reason for the direct addition of organic pollutants into the surroundings (Richards & Shieh, 1986).

Among the various types of pollutions, organic pollutants are undeniable contributors of water pollution. Effluents from different industries such as textiles, oil mills, paper and pulp industry, and metal industry are the significant contributors of water pollution (Tripathi et al., 2007; Anjaneyulu et al., 2005). Direct water pollution occurs through point sources, and indirect water pollution is through non-point sources. Pollutants affect the developmental characteristics, reproduction, and behavior of biotic communities. Water is a prerequisite for various activities and purposes such as drinking, irrigation, agricultural use, industrial use, and sanitation entirely depends on these water bodies in developing countries such as India. As the global demand for water increases, improper disposal of residues into water bodies has become a major health concern that has inculcated the need for waste water treatment; reuse of water and improvement in water quality have become overwhelming concerns in the present scenario (Gadipelly et al., 2014; Ahmad et al., 2008).

Expansion of modern society has paved ways for the amplified disposal of organic pollutants that results in increased toxicity of wastes (Gavrilescu et al., 2015). Illegal dumping, inadequate disposal techniques, accidental spillage, careless dumping of hazardous waste, and poor choice of landfall are the main causes of xenobiotic contamination and can result in emergence of fatal disease spreading microorganisms (Aboulhassan et al., 2006). This downfall augments the need of potential and effective methods to protect human life and the ecosystem. The conventional physical and chemical methods that are already in existence and practice demand high cost, are less effective, and can serve as a source of additional residue producers that contaminate the surroundings. Physicochemical methods have a narrow range of selection among pollutants to be removed from industrial effluents and are rarely environmental friendly (Banat et al., 1996; Chen et al., 2015). As the concern toward pollution control increases, the need for environmental friendly, inexpensive, and efficient techniques to remove pollutants has become a notion of many researchers (Petala et al., 2009).

Biological remediation methods have gained attention for their eco-friendly behavior and good performance at affordable costs (Giovanella et al., 2020). Bioremediation involves the absorption, adsorption, degradation, or transformation of pollutants through the use of prokaryotic (microorganisms) or eukaryotes (plants) in a simple, inexpensive, and effective way (Alegbeleye et al., 2017; Ayangbenro & Babalola, 2017). For the past two decades, scientists have developed various bioremediation techniques that operate on both narrow and wide range of pollutants with the ultimate goal to restore the polluted ecosystems in a rather simple and eco-friendly way. It has served as the key in solving various environmental issues that remained a challenge to conventional methods (Verma & Jaiswal, 2016). Degradation, detoxification, mineralization, or transformation of pollutants to an innocuous state has never been too easy through bio-remediation, but requires careful planning and execution of the techniques. The major concerns while planning the techniques are nature of the pollutant (dyes, chemicals, nuclear waste, sewage, and hydrocarbons), degree of pollution, location and type of the environment, and cost and site of application (ex situ or in situ) (Azubuike et al., 2016) The purpose of this chapter is to give a comprehensive idea on the organic pollutants eliminated from various industries, their toxicological mechanisms and their environmental impact, and potential eco-friendly management techniques that are widely being applied along with advantages, limitations, and future prospects.

2 Organic Pollutants in Industry Effluents

Organic pollutants from industry effluents play a major role in water contamination when compared to other surfaces. Polycyclic aromatic hydrocarbons (PAHs), phenols, aliphatic and heterocyclic compounds, pesticides, herbicides, PCB, and PBDEs are the various organic pollutants that are toxic and deleterious to the environment (Fig. 1). Industries that eliminate a major amount of organic pollutants through effluents that contaminate water bodies are sugarcane industries (Razia et al., 2020; Thamaraiselvi et al., 2019; Parvathi et al., 2015), textiles (Parvathi et al., 2018), tanneries (Vaishnavi et al., 2019), and related industries. The probability of treated waste water from industries containing organic pollutants is also high. Their elimination into the nearby water bodies are a major concern for public health. Treatment of the industrial effluents cannot be entitled to specific organic compounds since they can be a heterogeneous mixture of complex organic pollutant with various concentrations. Other than the effluents from the industries, pesticides and herbicides from the farmlands, municipal sewage that contains food, dissolved organic compounds, oils, detergents, and surfactants also alter the environment.

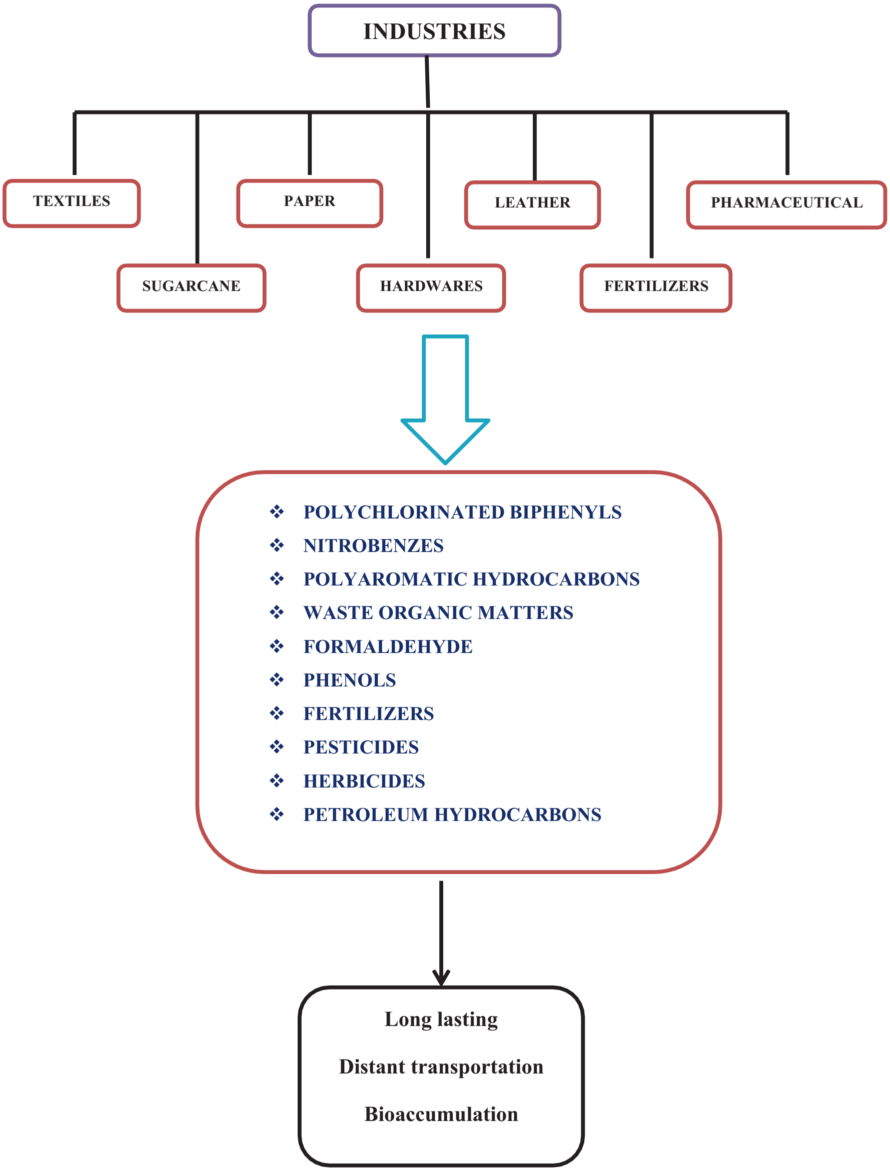

Fig. 1 Organic pollutants from industry effluents and their characteristic features

These organic pollutants not only damage the environment but they also pose a serious threat to the health of humans (Zheng et al., 2013).

The ability to degrade differs from one organic pollutant to another, which is influenced by their structures. Compounds that have simple structures and hydrophobic nature can be degraded readily. Microorganisms such as bacteria, fungi, and algae can easily degrade organic pollutants such as methanol, sugars, and ketones that can only cause acute toxicity when prevalent in water at higher concentrations. Similarly compounds that have complex structures and hydrophobic nature are degraded in a slow phase; they can exist in nature for longer periods that are toxic. For example, compounds such as PAHs, DDT, and PCB degrade very slowly (Clara et al., 2005). Such organic pollutants that can thrive for years are persistent and can enter and get transported in the food chain. Some of the persistent organic molecules are neurotoxic and carcinogenic. Propensity for long-distance travel and higher retention time in the surface without degradation is the major reason that draws attention toward the persistent organic pollutants (POPs). A number of these compounds are major health risk factors as they can cause serious damage to the endocrine system (Hossain et al., 2012). Bioaccumulation and biomagnification with the advantage of circumvention to degradation techniques display POPs as a major threat to human survival (Chiron & Minero, 2007).

The archetypal toxic organic pollutants in industry effluents are as follows.

2.1 Waste Organic Matter (WOM)

WOM consists of sediments and waste water present in the industry effluents. Organic compounds such as protein, carbohydrate, and organic acids are the main components of WOM. Waste organic matter in water bodies can affect their physicochemical properties and the quality of the water that are required for domestic purposes. They are major hindrances in water purification, degradation, and transformation processes (Dignac et al., 2005).

2.2 Formaldehyde

Formaldehyde is made up of organic molecules such as carbon, hydrogen, and oxygen. This organic compound is identified in the effluents of chemical industries, textile industries, paper and pulp manufacturing industries, and paint and fiber industries. Formaldehyde is capable of combining with a multitude of other compounds, which makes the degradation process of formaldehyde tiresome. Moreover, they can affect the skin and the mucous membrane through which they gain entry into the central nervous system of the human body and cause neurodegenerative disorders. The chances of retinal damage are also high when exposed to high amounts of formaldehyde (Panchanathan et al., 2016).

2.3 Nitrobenzene

Nitrobenzene is a similar organic compound such as formaldehyde that consists of carbon, hydrogen, oxygen, and nitrogen. It is one of the important organic compounds used in the chemical industry. Large-scale manufacturing of aniline is possible with the presence of nitrobenzene. Nitrobenzene is the precursor of aniline, and in turn it is indirectly involved in the manufacturing process of phenols. Aniline is also eliminated from chemical industries in their effluents as they are the precursors to phenol manufacture. These organic compounds smell like rotten fish thereby rendering an unpleasant smell to the water bodies and are a major hindrance in the use of water for drinking purpose. Chemical industries are largely involved in the manufacture of such organic compounds due to their use in laboratories as solvents for the preparation of electrophilic reagents. Continuous and long-term exposure of nitrobenzene can cause fatal damage to the human body (damage of central nervous system, vision impairment, lung irritation, and blood-related issues) and is identified as carcinogenic substance (Guo et al., 2014).

2.4 Phenols

Phenolic compounds mainly exist in water surfaces due to the elimination of effluents from the industries. They are highly toxic and can remain on the surface for a long period of time. Phenols are organic compounds with OH as their main functional group that is directly bonded aromatic hydrocarbons. The major sources of phenols are coke plants, oil refineries, industries that manufacture insulation materials, paper and pulp industries, and chemical industries. Many phenolic compounds that enter the water bodies and other environmental surface are carcinogenic in nature. The reason that they have become major health concern is due to the fact that they are toxic even in low concentrations. Phenols can cause serious health issues and can impair the reproductive capacity of aquatic organisms as well as human beings (Villegas et al., 2016).

2.5 PCBs

Polychlorinated biphenyls (PCBs) are biphenyl groups attached to at least two or more than two to ten chlorine atoms. PCBs are commonly employed in industries that manufacture machinery since they are used as coolant fluid and dielectrics in the machines. For example, PCBs are commonly used in transformers, electric motors, and capacitors. Industries that make use of such machineries also tend to discharge PCBs into the environment in their effluents. As far as persistent organic pollutants are considered, PCBs are a major concern to human health. They can cause serious damage to the immune system. Over exposure to these compounds can lead to the accumulation of these compounds in the adipose tissues of the skin. Spread of these compounds from the skin can damage other internal organs such as the brain, kidney, and liver and result in their impairment. They have been reported to cause nervous disorders and affect the immune system. Reproductive issues are of great concern when it comes to these organic pollutants, they act as mutagens that can interfere with the hormones, and studies showed that they can inhibit as well as imitate estradiol. Moreover, they are stable, long persistent, and can withstand extreme temperature and pressure. It is the chemical makeup of the PCBs that determine their degradation process. This manmade chemical has now become a major threat to mankind itself (Yao et al., 2014).

2.6 PAHs

Polycyclic aromatic hydrocarbons (PAHs) occur in clusters, angular or linear arrangements. They are made up of two or more benzene rings and are recalcitrant organic pollutants. PAHs are released during burning of coal, trash, solid wastes, tobacco, wood, and gasoline. High-temperature cooking can release PAH into the environment. They consist only of carbon and hydrogen moles, they are manufactured in several chemical industries, and they are the most common carcinogenic compounds that are used in laboratories for cancer experiments. Coke industries, aluminum manufacturing industries, and motor manufacturing industries are the common sources that eliminate PAH in their effluents. Accidental leaks and tar deposits must also be considered for the deposition of PAH into the environment. PAHs that have high molecular weight are a major threat to the environment and human health as they can accumulate in the environment. They can threaten the life of organisms by causing acute toxicity, mutagenicity, and carcinogenicity (Euvrard et al., 2017).

2.7 Fertilizers, Pesticides, and Herbicides

Pesticides and herbicides are a major threat to water bodies as they are washed away from the farmland and reach the water source thereby contaminating them. Since this chapter is dedicated to the organic pollutants present in the effluents from industries, pesticides and herbicides can be given less importance. The industries that manufacture fertilizers, pesticide, and herbicides are the source of such organic pollutants as the wash off water from such industries can contain them. Organophosphorus pesticides can exist in the water for a long period of time and cause serious environmental pollution. They can be easily degraded in the environment by simple techniques, and they possess acute toxicity on people and livestock (Younas et al., 2017).

2.8 Petroleum Hydrocarbons

The major source of petroleum hydrocarbons is industrial waste water and municipal sewage. Oil manufacturing industries, their refinement, and transportation entertain their presence in the waste water that is eliminated from such industries. They are highly toxic to aquatic organisms as they could deteriorate the water quality and decrease the oxygen exchange between the water surface and the environment (Kuyukina et al., 2020).

3 Toxicological Mechanism of Organic Effluents

Industries are legally bonded to install effluent treatment facilities, yet a significant amount of organic pollutants enter the water bodies and soil surfaces. The major industries that eliminate POPs into the surroundings are petroleum industries, chemical industries, steel manufacturing industries, pulp and paper manufacturing industries, and fertilizer industries (Richards & Shieh, 1986). Fatima and Ahmad (2006), and Tabrez and Ahmad (2010) have reported from India the presence of organic pollutants such as phenols, pesticide, heavy metals, PCBs, and PAHs. Roane et al. (1996) report the presence of pesticides at 37% of sites in the USA. It is not only the large-scale industries that significantly contribute the waste accumulation in the environment; small scale industries also play a major role. Tabrez et al. (2011) have reported large amount of heavy metals into the sewage from industrial effluents from small- and large-scale industries. Heavy metals can amalgamate with the ground water and cause fatal adversities in human bodies. These metals can also disturb the metabolic functions, hormones, and enzymatic reactions.

Organic compounds are the major constituents in pesticides that have become a part of modern agricultural practices. Widespread population has highly increased the need to adopt modern agriculture and alternatively increase the use of synthetic pesticides in the environment. Thus, pesticides have become ubiquitous compounds in the surface and ground waters. Increase in the demand of fertilizers, pesticides, and herbicides among farmers have encouraged such industries to produce large amount of likely products. The effluents from these industries contain the organic pollutants that persist in the environment for a longer period of time. Fatima and Ahmad (2006) report the presence of toxicant organochlorine and organophosphorus in India. Pesticides are highly harmful to aquatic microorganisms as they can enter their body. They can cause neurotoxicity, cardiotoxicity, and ocular toxicity even if exposed to a short period of time. Chronic exposure to pesticides such as endosulfan, DDT, and HCH can attribute to the development of various cancers (Muniz et al., 2008). Herbicide manufacturing industries dispel organic compounds such as 2,4-dichlorophenoxyacetic acid (2, 4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 4-chloro-2-methylphenoxycetic acid in their effluents. Since the ban of chlorinated hydrocarbons to control weed growth, carbamates have gained importance. The mechanism by which the carbamates control the overgrowth of weeds is by inhibiting the cholinesterase enzyme. When these mixtures enter the human body, they can work through the same mechanism and are therefore considered highly toxic to humans (Chaudhaery et al., 2010).

Phenols from chemical industries, petrochemical industries, and pulp and paper industries are commonly found in the effluents that are discharged (Gupta & Ahmad, 2012). The toxic mechanism of phenol involves the disruption of the cytoplasmic membrane in cells. The integrity of the cell wall is lost which leads to the disruption of related functions and cell death (Yap et al., 1999). Phenols can increase the stress levels in microbes that alter their cell membrane fluidity leading to cell death. This has been reported in various microbes such as *Escherichia coli* (Mrozik et al., 2004), *Pseudomonas putida* (Yap et al., 1999; Heipieper et al., 2003), and *Vibrio* species (Heipieper et al., 2003; Mrozik et al., 2004). When stress increases, the degree of saturation of fatty acids increases leading to the conversion of cis-unsaturated fatty acids to trans-isomer and also triggers the alteration of polar groups in phospholipids therefore transforming the stability of the cell membrane.

4 Environmental Impact of Industrial Effluents

Industrial effluents are considered as the manmade curse to the environment. Organic pollutants present in the industrial effluents are the silent killers as they persist in the environment for a long period of time and accumulate on the surface causing permanent impairment to the ecosystem (Alharbi et al., 2018). They are omnipresent in the environment, in water, air, land, animals, plant as well as human beings. Human survival has been possible on earth due to their interaction with the abiotic and biotic components of the environment; any effect on these components can directly or indirectly question the ultimate survival of humans. It is not only the environment that is being affected, but also, we are forced to face interferences in social, cultural, and technological perspectives (Pariatamby & Kee, 2016). Organic pollutants that are eliminated in the industrial effluents deteriorate the ecological balance; thereby, threatening the life of plants, animals, humans, and other organisms leading to mortality. As organic pollutants can persist in the environment for a longer period of time, their resistance toward photolytic, chemical, and biological degradation makes them a great menace to the environment. Organic pollutants have turned out to be a major global concern due to their long-range transport, bioaccumulation in adipose tissues of mammals, and persistency and toxicity at meagre concentration (Tang, 2013). Organic pollutants are not restricted to certain geographical area of earth; they are even identified in the Arctic region as they can travel to longer distances due to their small size, low molecular weight, and stability (Brown & Wania, 2008).

Due to our smart and insane expeditions, humans have tried to conquer and pacify nature, seize infectious agents, and caused extinctions with the discovery of organic chemical compounds. Only in the later years, man has started to realize the harmful effects of these organic compounds that are dispersed into the environment as they begun to cause serious health issues. Myers (2002) suggests that we lag behind in knowledge of the boons and banes of these toxic chemical, and it is highly necessary to adhere to traditional risk assessment. Nevertheless, traditional risk assessment is always subdued since it prevents commercialization of the product in the global market. Sarkar et al. (2003) reported that in India high levels off persistent organic pollutants were detected in fish samples collected from the rivers of Kumaon, Himalayas, Uttarakhand. Some studies were performed in the late 1990s in India that demonstrated the presence of elevated levels of PCBs, DDTs, and HCHs in *Plantanista gangetica* (Ganges river dolphin). Karuppiah et al. (2005) reported that Irrawaddy dolphins contained low concentrations of PCBs when compared to the Bay of Bengal dolphins. High levels of organic pollutants are reported in the Himalayan glaciers (Kang et al., 2009); Kumaon Himalayan region (Sarkar et al., 2003); Kolkata, West Bengal (Purkait et al., 2009); Assam (Bishnu et al., 2009); Karnataka and Andhra Pradesh (Begum et al., 2009); and the Tamiraparani river, Tamilnadu (Kumarasamy et al., 2012). Organic pollutants have unarguably exceeded the limits as contaminants globally, and improper disposal or lethargic remediation strategies can lead to higher level damages in the environment and human health.

5 Eco-Friendly Techniques in the Remediation of Organic Pollutants

The progress in the remediation of organic pollutants from industrial effluents is slower than the progress in the invention of organic pollutants. Organic compounds were discovered for the betterment of human survival, which has now become a major hindrance to the ecosystem and the existence of plants, animals, and humans. Few developed as well as developing countries have new technologies that can effectively degrade the organic contaminant from polluted sites. On the other hand, the cost incurred in developing such physicochemical methods account for rates higher than that which was required to develop the same (Azubuike et al., 2016). These magnified problems in the management of organic pollutants from industrial effluents create the need for eco-friendly and cost-effective methods that can target multiple contaminants at a particular contaminated site. Bioremediation has become the apple of our eye when it comes to successful biological and safe method for degradation of pollutants (Fig. 2).

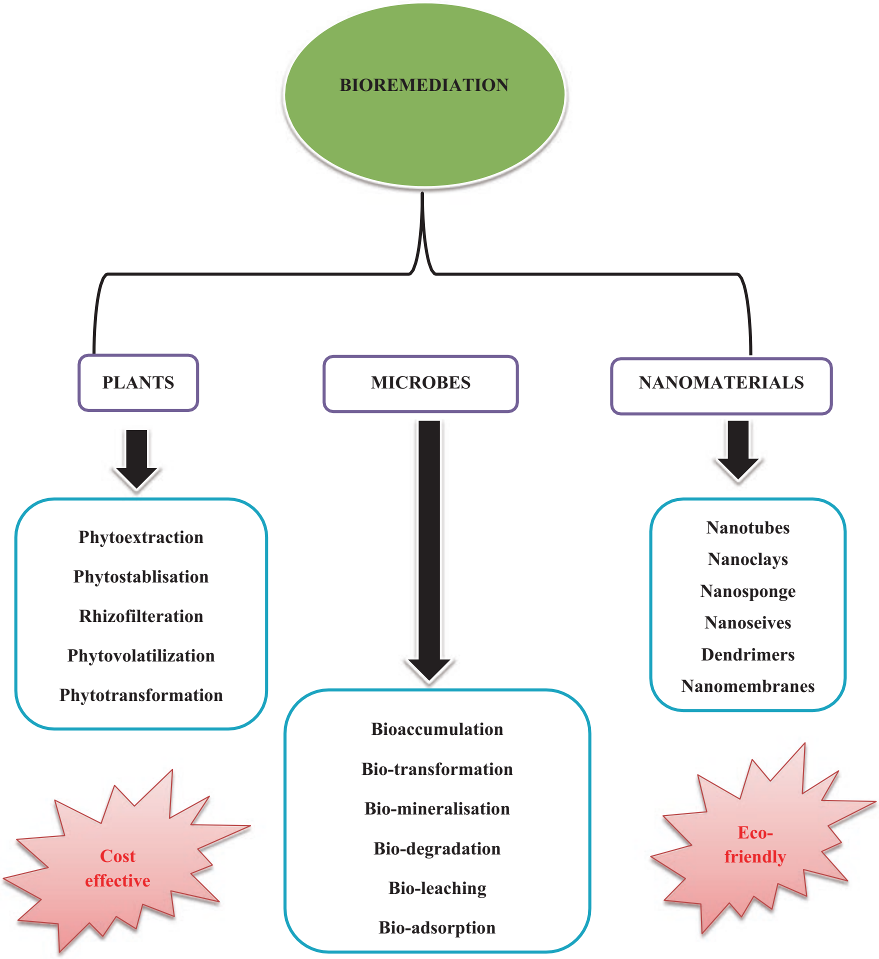

Fig. 2 Potential eco-friendly techniques for the management of organic pollutants and their types

5.1 Phytoremediation

Phytoremediation is a technique to eradicate pollutants and that came into existence approximately three decades ago. Plants have been identified as a unique agent to accumulate and immobilize persistent organic contaminants. The success of phytoremediation in degrading petroleum-based contaminants has been appreciable when compared to other physical and chemical methods that are being employed at contamination sites. Very little success has been achieved in breaking down metal and persistent organic compounds or contaminants, but phytoremediation has been a promising candidate in degrading heavy metal and organic contaminants. It is a common phenomenon for plants to metabolize the substances that are available to them in the surroundings; plants accumulate and degrade complex substance into simpler ones by nature to obtain their requirements from the abiotic environment (Vidali, 2001). Phytoremediation has gained the attention and trust of many researchers to effectively clear the contaminants from the site in a safe and cost-effective manner. Phytoremediation is not limited to the removal of impurities and contaminants from soil alone, but the field has also extended its service in removing the contaminants from water and effluents eliminated from the industries into the surroundings (Raskin & Ensley, 2000).

In the past years, phytoremediation has taken roots in different ways based on the fate of the contaminant. Several classifications of phytoremediation have been evolved and are unique in treating various types of organic contaminants. Either one of these techniques is used at the site of the contaminant, or combinations of the techniques are used to achieve better results. The most commonly employed technique of phytoremediation is phytoextraction or simply known as phytoaccumulation. In this method, the plants take up the contaminant from the site where they are planted through their root system up to their shoots. Heavy metals are accumulated within the plants through this method, and precious metals such as silver, gold, and platinum can also be accumulated within the plant and extracted through laboratory procedures. One of the best ways to remove poisonous heavy metals such as mercury, arsenic, etc. is through phytoaccumulation technique. The next method is phytodegradation or phytotransformation where organic contaminants are ingested from the soil or the site of contamination and transformed or broken down into a less poisonous or less transportable form. Through this method, it is easier to convert hexavalent chromium to trivalent chromium which is less carcinogenic and immobile.

Reducing the mobility and transportability of the contaminants in the location can be achieved by phytostabilization. Leaching of the contaminants from one surrounding into another is a major hindrance in maintaining the quality of the ecosystem. Here leachable particles bind to the plant root or shoot and form a stable mass through absorption. This makes sure that the particles will not re-enter the environment. Rhizospheres found in the roots of the plants help in degrading the particles in the soil to a simpler form which can be easily degraded. The ability to breakdown contaminants in the surrounding through the rhizosperes of the plant roots is known as rhizodegradation. Here a special relationship between microorganism and plants is observed. The mechanism of degradation is facilitated by proteins and enzymes that are associatively produced by soil organisms and plants.

Agricultural lands containing herbicides, pesticides, metals and selenium, industrial sites containing organics, metals and arsenic, mine tailings with metals, and wood treatment sites containing PAHs can also be successfully remediated with plants (Banuelos, 2000; Ferro et al., 1999; Olson et al., 2003; Rock, 2003; Winter & Redente, 2002). Contaminated waters that can be phytoremediated include sewage and municipal wastewater comprising nutrients and metals, agricultural drainage water with fertilizer residues, metals, arsenic, selenium, boron, organic pesticides, and herbicides, industrial wastewater containing metals and selenium, coal pile runoff containing metals, landfill leachate, mine drainage, and groundwater plumes with organics and metals (EPA pub., 1999; Ferro et al., 2001; Hansen et al., 1998; Horne, 2000; Lin et al., 2000; Rock, 2003). Plants can also be used to filter air containing NO, SO_2, ozone, CO_2, dust or soot particles, nerve gases, and/or halogenated volatile hydrocarbons in both outdoor and indoor conditions (Jeffers & Liddy, 2003; Morikawa et al., 2003).

Phytoremediation is solely photo-driven as plants are autotrophs and photosynthesis is a natural process that aids phytoremediation. Phytoremediation is tenfold cheaper when compared to physical and chemical methods. In situ phytoremediation is cost effective and is safe as it reduced the exposure of the workers to the pollutants as well as reduces the exposure of wildlife to deadly contaminants (Glass, 1999). It is a green and clean initiative as bulldozers or harmful chemicals are not employed in this technique. Advantages are greater than the disadvantages in this technique and is popular among the public as mere ethical issues arise in this case (Flechas & Latady, 2003; Negri et al., 2003).

5.2 Microbial Bioremediation

Microbial remediation is an eco-friendly technique to remove the organic contaminants from the industry effluents that are eliminated into the surroundings (Singh & Nagaraj, 2006). Special concern is growing toward the microbial enzyme-based bioremediation techniques that involve oxidoreductase, hydrolases, and other such enzymes (Karigar & Rao, 2011).

Bacterial Remediation

Oil-degrading microorganisms produce biosurfactants that have low molecular weight. This property helps in degrading oils at contamination site and ocean oil spills. The water-oil interfacial tension is reduced through the biosurfactants produced by the microbes. Even high molecular weight biosurfactants can work as biodispersants by preventing amalgamation of oil in water. Lipids and proteins are the active components of the biosurfactants with high molecular weight. The surface area of the hydrophobic water-insoluble contaminants is increased by these surfactants that help in the remediation process. Overproducing bacteria with biosurfactant property is preferred for cleaning the water-insoluble lipid and oil contaminants at the site. Certain bacteria can indirectly help by stimulating the growth of the oil-degrading bacteria as well as improve their ability to degrade the hydrocarbons (Ron & Rosenberg, 2002). Degradation of PAH has been possible in the past years only through the use of bacteria, fungi, and algae that have the ability to degrade such complex molecules and immobilize them. Bacteria are less efficient in degrading PAH when compare to other microorganisms (Albert & Ravendra, 2000).

Poisonous substances can be easily degraded by microorganisms and have a high potential for bioremediation. The effect of bioremediation depends on the modifications that are included to suit the site of contamination. Chemical attraction plays a major role in effective degradation of pollutants (Sudip et al., 2002). Heavy metal contamination is considered as a crucial environmental problem due to the threats that it possesses. They can amplify through the food chain and lead to severe ecological and health-related issues in terrestrial and aquatic organisms. Employing physical and chemical techniques would be expensive and unsafe for the elimination of heavy metals and organic pollutants. Bioremediation using microbes is a safe and cost-effective method (Anushree, 2004).

Mycoremediation

Fungi including mushrooms have many enzymes that are effective in degradation of organic contaminants from industrial effluents. Numerous pollutants of various sizes can be effectively degraded using fungi, and this effective remediation method is known as mycoremediation (Purnomo et al., 2013; Kulshreshtha et al., 2013). Degradation of the impurities by mushrooms improves their biomass and the ability to secrete oxidizing and hydrolyzing enzymes (Kuforiji & Fasidi, 2008; Zhu et al., 2013). Ligninolytic enzymes that are produced by white rot fungi can degrade substrates specifically and have the capability of mineralization and transformation of POP that have analogous structure as lignin. Fungi are effective in degrading effluents from industries such as textiles, paper and pulp industry, chemical industry, etc. (Pointing, 2001).

Phycoremediation

The elimination or deduction of persistent organic pollutants from the surroundings by algae is recognized as phycoremediation and is an encouraging eco-friendly practice for the management of contaminants. More than being eco-friendly, it is a sustainable technique and a natural way to clean the decontaminated sites (Baghour, 2019). Phycoremediation is an effective method to remove heavy metals from the surroundings, and this can be achieved in two processes: biosorption and bioaccumulation. In biosorption technique, the heavy metals are passively bound to the nonliving biomass in an aqueous solution, such as the effluents from the industries, whereas in bioaccumulation technique, the metals are removed or accumulated by the algae through its metabolic activity. Green algae have gained immense interest due to its ability to bioaccumulate or biodegrade organic pollutants at major contaminated sites such as aquatic ecosystems (Iriti et al., 2009). Singh and Olsen (2011) reported that photoautotrophic organisms such as algae are important bioresources that have the ability to grow faster, have easy cultivation methods, and require less water and land resources.

Scenedesmus, *Chlamydomonas*, *Nodularia*, *Arthrospira*, *Oscillatoria*, *Spirulina*, *Botryococcus*, *Cyanothece*, *Chlorella*, *Phormidium*, *Ulva lactuca*, *Kappaphycus alvarezii*, *Desmodesmus* are the few microalgal and macroalgal species used for bioremediation purpose. Macroalgae are utmost beneficial when compared to microalgae as they can assimilate enormous amounts of macro- and micronutrients during their developmental stages. This has an advantage of minimizing the ill effects of anthropogenic activities in regard with eutrophication and algal blooms (Dubey et al. 2013; Rawat et al. 2011). The report of Madadi et al. (2016) shows that *Chlorella vulgaris* is highly potential in treating effluents from industries as they can effectively remove nutrients from petrochemical wastes. The enzymes present in the algae are perceived to play a vital role in the biodegradation of persistent organic pollutants and also the microalgae that are capable of acting as biosurfactants maximize the bioremediation at PAH-containing sites (Baghour 2019). The use of algae as a potential technique in the management of organic pollutants from industrial effluents as an alternative eco-friendly approach will reduce the environmental impact of chemical and physical methods. More than being environmental friendly, they are cost-effective that makes them good candidate in the bioremediation process from an economic perspective.

5.3 Remediation Using Nanomaterials

Nanoremediation methods necessitate the use of reactive nanomaterials of 1–100 nm in size for alteration and decontamination of pollutants. These nanomaterials must retain properties that enable both chemical reduction and catalysis to diminish the impurities of concern. The advantage of this method is the on-site bioremediation of the contaminants; transport of the contaminated soil or water is not required for treating the impurities (Otto et al. 2008). The unique properties of the nanomaterials make them the desired candidate for bioremediation process. Nanomaterials are characterized by small size, large surface area, ability to penetrate through narrow spaces, ability to withstand in ground water, wider distributions, and options of various coating for specific targeting of the pollutants. Their smaller size encourages them to penetrate deep into the ground when compared to large particles of macro size. However, transportation is not possible though penetration can be achieved. Long distance transport of the nanoparticles through the ground cannot be achieved (Tratnyek and Johnson 2006). Zeolites have attracted the researches due to their stubborn character in eliminating the contaminants. Carbon nanotubes and fibers are widely used in removing pollutants at various contamination sites. Enzymes that are biocatalysts and proteins by nature are also used to synthesize nanoparticles that can be effectively used in nanoremediation. Metallic nanoparticles, nanoparticles produced by the amalgamation of two or more metals, by coating polymers unto their surface, titanium dioxide nanoparticle, and nanoparticles synthesized from noble metals are the present stand of researchers worldwide to solve the ever-growing problem of environmental pollution (Theron et al. 2008; Zhang 2003).

Mechanisms through which nanoremediation works is mostly through the Brownian movement or random motion that helps them to move or transport in effluents rather than wall effects. Gravity plays a chief role in controlling the movement of the nanoparticles as they tend to sediment and their movement is further restricted. Density of the nanoparticles is a driving characteristic in nanoremediation as it can force the particle to settle down limiting its ability to degrade the contaminants. Surface electrostatic force does not interfere in manufacturing process since nanosize particles can easily suspend themselves in water which makes these nanoparticles as a versatile remediation tool and provides an option to inject liquid into the surface where the impurities are present. Iron nanoparticles are usually coated with polymers or other substances to improvise their reacting ability and the rate of transport. The small size results in the entrapment of the nanoparticles within the soil, which subsequently restricts their flow along with the groundwater. This has been found as a major setback in in situ bioremediation using nanoparticles (Henn & Waddill 2006).

Aggregation of the synthesized nanomaterials when they are released into the surrounding makes the nanoparticles behave like natural materials. As stated earlier, transport to further areas is a limitation with nanoparticles, but researchers have synthesized nanoparticles taking into consideration the hydrological properties of the water at the site of contamination in order to provide the opportunity of long distance travel to the particles that are used for remediation (Kersting et al. 1999; Novikov et al. 2006; Vilks et al., 1997). Colloids are highly capable of forming nanoclusters that are stable and portable; they can carry the contaminants by absorbing them from the surface. Since they can absorb particles in between the redox zones, they can facilitate the inhibition of pollutant transport. Aggregation, sedimentation, and dispersion are the major factors that determine the effective activity of the nanoparticles without forming clusters to degrade the contaminants in the environment (Waite et al. 1999). Gilbert et al. (2007) reported that inorganic nanoparticles may exhibit the same property of cluster formation as found in natural nanomaterials; hence, it is necessary to study the fundamental properties of the synthesized nanoparticles for better performance. Self-aggregation is regarded as the major problem that hinders the use of the particles in remediation as the fear of particles entering the food chain prevails. They can remain as suspended solids in drinking water through bioaccumulation (Boxall et al. 2007).

Diffusion of nanoparticles to other location generally occurs when the nanoparticles are released into the environment. When nanoparticles such as iron oxide bound to copper are used, they are found to travel for longer distances in mining sites to degrade heavy metals, hydrocarbons, and other organic materials. This shows that these particles can move along and degrade the required particles at the required site (Hochella et al. 2005). Size-dependent reactivity and binding ability is observed in these particles based on their kinetic and thermochemical relationships in regard to the size (Madden et al. 2006). It is studied that nanoparticles are harmless in nature but can possess toxic properties by absorbing the pollutants that they are adhered too and can potentially be toxic to humans, animals, aquatic being, and the environment. Copper which is bound to the iron oxide nanoparticles can be potentially harmful to fungi, algae, and other aquatic plants as they are toxic in general. The only way to surpass copper toxicity is by using mercury or copper which can be harmful in other ways (Sposito 1989). Public believe that nanoparticles that are used for in situ remediation possess risks that are unknown. Nongovernmental and nonprofit groups are against the use of nanoparticles stating that precautions must be taken before the use of these particles for remediation, and until their safety is proved to the public, use of such particles must be restricted. In early 2003, the ETC Group called for the counteractive principle to be functional to the practice of nanotechnology (ETC Group 2003). Their apprehensions were about manifold nanoscale machines that can influence self-replication and change matter into "gray goo" (Drexler 1986).

6 Advantages and Limitations of Bioremediation

Bioremediation techniques are considered as effective and eco-friendly technique to manage organic pollutants from industry effluents, yet they have their own advantages and limitations. This section discusses the various advantages and disadvantages that are experienced in bioremediation techniques.

In ex situ techniques, biopile technique has constructive feature, effective biodegradation strategy, the ability to control and maintain temperature, and aeration is available. But this technique requires space, and the cost of maintenance is also high. Power supply is a prerequisite; hence, loss of power supply in remote areas can be a hindrance and lead to contamination without uniform distribution of air on the effluents (Sanscartier et al., 2009). Windrow treatment methods show higher rate of hydrocarbon removal than biophile method. They can be the best options to remediate the toxic volatiles, yet they are assumed to release methane into the atmosphere due the reduction reaction that occurs which is a harmful greenhouse gas (Coulon et al., 2010). Phytoremediation is so far considered as a best method to treat organic pollutants. Accumulation, extraction, filtration, stabilization, and degradation are the several mechanisms involved depending on the type of the pollutant. Plants provide an easy platform to remove elemental pollutants such as heavy metals and radionuclides that are toxic in nature. Hydrocarbons and chlorinated compounds are removed by mechanisms such as stabilization, rhizoremediation, and degradation. Meagher (2000) and Kuiper et al. (2004) have reported the removal of hydrocarbons and chlorinated compounds by using willow and alfalfa plants for bioremediation.

The major factors that influence the effect of phytoremediation are root system, above-ground biomass, concentration of the pollutant, toxicity of the pollutant, climatic conditions, and location of the site. The important advantage of using plant as remediation agents is the opportunity of bioaccumulating precious metals that can be recovered by phytotoming. Moreover, they are environmental friendly, require low cost of operation and maintenance, and they can also improve soil fertility (Mench et al., 2009). The few limitations that researchers have overcome while using phytoremediation are longer remediation time, toxicity, and slow growth of the plant and depth of the roots.

7 Current Status and Future Prospects of Bioremediation

Bioremediation techniques have proven to be potential sources for the management of organic pollutants from industry effluents without any doubt. Different types of wastes are being treated with different techniques to manage the pollutants in an effective way. Microbes have gained immense attention due to the crucial role they play in restoring the contaminated sites. There is an increased knowledge in identification of microbes and its metabolic pathways involved in degrading the pollutants through bimolecular techniques such as genomics, proteomics, transcriptomics, and metabolomics (Wang et al., 2012). This helps in overcoming the limitation that is observed in bioremediation sites. Nutrient requirements, compatibility among different microorganisms at the study site, and bioavailability of nutrients are being continuously studied by the researchers. Microbes are cost-effective when compared to other physicochemical methods. The major preference for microorganisms when compared to phytoremediation is the fast multiplication rate. Slow growth observed in plants is often a limitation when it comes to degrading the organic pollutants. Biostimulation and bioagumentation are the recent techniques practiced using microbes to degrade pollutants. In biostimulation, nutrients are added to the polluted sit to stimulate the activity of the autochthonous microbes. This method will reduce the limitation of nutrition availability in polluted sites. On the other hand, the method of bioagumentation aims at increasing the number of microbes with degrading capacity at the site of pollutants. Moreover, it was observed that microbial consortium is capable than pure isolates in degrading the organic pollutants efficiently (Silva-castro et al., 2012; Bhattacharya et al., 2015).

Prospects in bioremediation techniques are increasing in the current scenario, which tends to make bioremediation as the most potential techniques to manage organic pollutants from industry effluents. It is regarded that application of more than a single remediation technique at site can help increase the efficacy and decrease the time required for the bioremediation process. By this way, the limitation of one method can be overcome by the advantage of another. Simultaneous application of eco-friendly multiple remediations can reduce the cost and make it feasible (Cassidy et al., 2015). Banitz et al. (2016) suggest that information regarding the spatial configuration of bacterial dispersal through the application of combined metrics can act as an indicator of biodegradation performance.

Genetically engineered microorganisms (GEMs) have earned the attention of researchers in different fields and applications. Bioremediation efficacy can be enhanced by planning the effective and controlled use of genetically engineered microorganisms. GEMs can act as a biocatalyst and effectively target pollutants as well as recalcitrant compounds and degrade then. They can incorporate novel metabolic pathways or use existing pathways for the purpose of degradation. Use of horizontal gene transfer is also a promising approach; use of suicide systems in GEM can kill the microorganisms that try to escape the contaminated sites, and this will help in gaining public acceptance. GEMs can be engineered with special degrading pathways to target a particular compound in a short span of time (Paul et al., 2005). The future of nanomaterials in remediation techniques can reach great heights if the methods are executed precisely. Nanomaterials have increased surface area and require low activation energy, which can help in increasing the potential of nanoparticles at degradation sites. The overall time and cost of remediation can be reduced with the strategic use of nanoparticles (Rizwan et al., 2014; Azubuike et al., 2016).

8 Conclusion

Organic pollutants from industry effluents have become a major stress to the environment. Though industries are installed with treatment plants in recent days, a large amount of the organic pollutants reach the surroundings through the effluents that are eliminated from the industries. Physicochemical methods that have been conventionally used for the management of organic pollutants are costly and require superior maintenance. Eco-friendly techniques such as bioremediation require low cost of installation and maintenance. Microorganisms and plants have been employed as potential bioremediation technique for the management of organic pollutants. The type of the organic pollutants present in the effluent and location of the polluted site are the major factors that determine the efficacy of the bioremediation site. The bioremediation technique that has to be applied must be carefully determined by taking into consideration the nature of the pollutant, feasibility of the procedure, cost of installation, and performance of the particular technique. The effectiveness of the method entirely depends on proper planning and execution of the suitable method.

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An Overview on Eco-friendly Remediation of Toxic Organic Contaminants from Textile Dyeing Industry Wastewater

K. G. Ahila, S. K. Vinodini, A. Ancy Jenifer, and C. Thamaraiselvi

Abstract Textile industries play a crucial role in Indian economy and also cause serious issues on environmental pollution. The demand of colors, fade-resistant garments, and other hue products are increasing in day-to-day lifestyle, triggering the blooming of dyeing industries. These factories utilize colossal volume of water and various chemical substances for dyeing process and release toxic organic pollutants such as organic azo-dyes, surfactants, and phenolic compounds with effluent to the environment which severely disturb the natural balance and affect all forms of living beings. Higher concentration of colored compounds in the effluent mixed with surface water reduces the flow of sunlight and prevents the photosynthetic process of aquatic vegetation. Also, it affects the fertility of agricultural land and health impacts in human and animals. The changes in physicochemical nature of surface and underground water quality due to textile effluent lead to water crisis. Conventional treatment methods are expensive and not sufficient in efficient removal of organic pollutants from the wastewater. Thus, economically and ecologically safe approaches are needed for the treatment of textile industry effluent to prevent and conserve natural resources without affecting the growth of this sector. In this chapter, eco-friendly techniques such as bioremediation, phytoremediation, coagulation process by natural coagulants, and biogenic nanomaterials applied for the removal of organic pollutants from the textile effluent are elaborately discussed.

Keywords Textile effluent · Organic wastes · Toxicity · Biological techniques

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1 Introduction

Globally, environmental pollution is considered as a serious issue due to the rapid escalation of diverse industries as well as human population explosion (Ali et al., 2020). Textile dyeing industries are economically important, and it holds the second place after agriculture sector in India. Among all the type of industries, textile industries are contributing 14% overall production in India (Raichurkar & Ramachandran, 2015). These industries consume huge quantity of water for dyeing and finishing process; generate wastewater with toxic organic contaminants such as unfixed dye stuffs (e.g., xanthenes, Congo red, anthraquinones, phthalocyanines), phenolic compounds, and surfactants (Chanwala et al., 2019; Yang et al., 2019; Fernandez et al., 2010; Mahajan et al., 2019).

Annually, 2,80,000 tons of unfixed dyestuffs waste water from textile dyeing industry is released into the environment with or without partial treatment (Gita et al., 2019). In India, around 10,000 textile factories, 2100 bleaching as well as finishing units are running to produce textile products such as readymade cloth, handlooms, silk, wool, jute, nylon, and polyester and these factories are exporting their produce to various countries (Sachin et al., 2010).

2 Textile Dyeing Process

Textile dyeing industries widely implement a conventional approach known as "wet processing" method for dyeing the cotton yarn and fabric materials. In this process, various complex sequential steps such as sizing, desizing, scouring, bleaching, dyeing, and finishing processes are being employed to manufacture a complete furnished colorful garment (Punzi, 2015; Bisschops & Spanjers, 2003; Mattioli et al., 2002; Verma et al., 2012). Wet dyeing process of cotton fabric materials is summarized in Fig. 1. Before weaving and spinning steps, the yarn or cotton fabrics are subjected to sizing process with diverse kinds of sizing materials (starch, carboxymethylcellulose, polyvinyl alcohol, polyacrylase). The desizing process removes impurities and chemical substances attached to the sized fabrics. Diluted H_2SO_4 (0.5%) is generally used as a desizing agent along with alkali, surfactants, and enzymes.

In the scouring process, the organic impurities such as oil, grease, fats, wax, and other dirt present in the fabric material are removed before dyeing process. This process is carried out by boiling the raw materials with alkaline solution and scouring agents (soaps, detergents, wetting agents, alkalis, lubricants, defoaming agents) to improve the dye fixation ability. After this treatment, the materials are washed thoroughly with caustic soda, sodium silicate, detergents, and water. The bleaching step is a major step which eradicates any natural tint found in the fabric and bleaches it into white by bleaching substances such as hydrogen peroxide, sodium hypochlorite, and optical brightness for efficient dyeing attachment. Subsequently, the

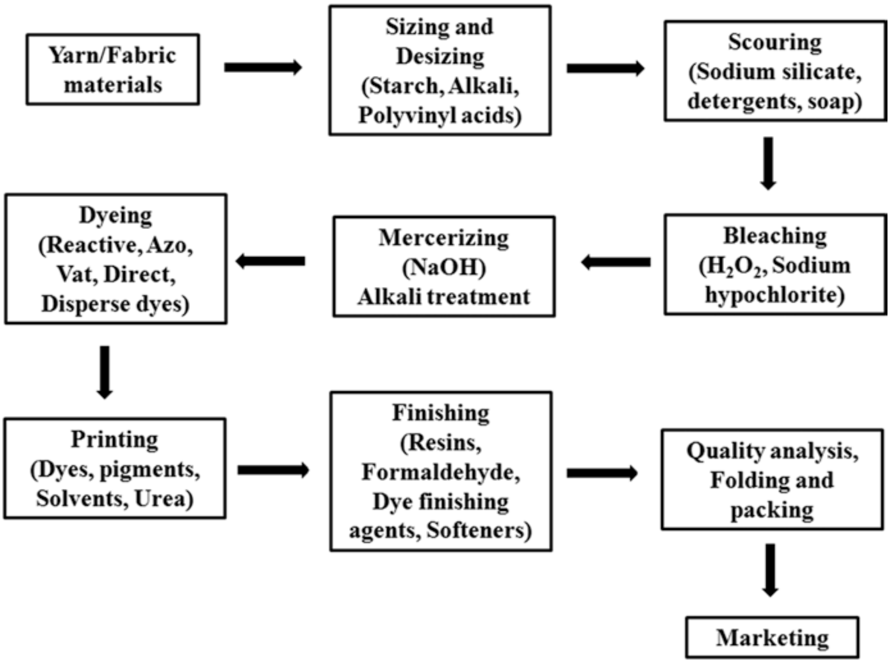


Fig. 1 Steps in the wet dyeing process

Fig. 2 Cotton fabric dyeing by wet processing method

mercerizing process, which is a continuous chemical process, enhances the strength, appearance, luster, and dye binding ability of fabrics toward the dye substances. Sodium hydroxide is commonly used as a mercerizing agent. After this process, alkaline pH of the processed material has to be neutralized by sequential washing with water. Figure 2 shows the wet dyeing process of cotton fabric material.

Dyeing process is an essential step of wet processing, which makes use of various kinds of organic and inorganic dye stuffs (Imtiazuddin et al., 2012) that belong to azo, reactive, disperse, direct, and vat dye classes. The dye fixation with the fabrics takes place under alkaline condition with higher temperature. This method utilizes various organic, inorganic, and polymeric compounds for processing (Robinson et al., 2001). In the printing process, processed materials are headed to print required designs with multi-colored dyes and pigments. The printing paste comprises water, dyes, thickening agents, solvents, surfactants, and urea. Various methods such as flatbed screen, heat transfer, resist style, direct style, and rotary screen are widely employed for printing process (Bisschops & Spanjers, 2003; Wadje, 2009). The finishing process improves and enhances the quality, appearance, durability, and acceptability of the printed fabrics for commercialization. Generally, formaldehyde mixed with dye fixing agents, resins, softeners are used to increase water and flame resistant, antimicrobial, antistatic, antiwrinkling and insect repellent properties of the printed fibers. The finished garments are subjected to quality analysis, folding, packing, and exporting to national as well as international level.

3 Water Consumption for Wet Processing

Wet processing requires large quantity of water for dyeing, washing, chemical processing, bleaching, and finishing process. USEPA reported that a typical dyeing factory utilizes approximately 36,000 L of water for producing 20,000 Ib/day for a fully furnished fabric garment. Nigam et al. (2000) have reported that the textile dyeing units use 200–500 L of water to manufacture 1 kg of processed products. Also, 1 kg of cotton materials dyeing with reactive dyes requires 70–150 L of water, 30–60 g of dye substances, and 0.6–0.8 kg of sodium chloride for dye fixation process.

Marcucci et al. (2002) stated that a classic dyeing industry needs 200–500 L of water to produce 1 kg of processed garments. Mainly, the water consumption level depends on the employing process, raw materials, dye types, and machines used in

Table 1 Overall water requirement for wet processing

Water required for wet processing (cotton)	
Process	Requirements in L/1000 kg of fabrics
Sizing	500–8200
Desizing	2500–21000
Scouring	20000–45000
Bleaching	2500–25000
Mercerizing	17000–32000
Dyeing	10000–300000
Printing	8000–16000

Source: http://www.fibre2fashion.com

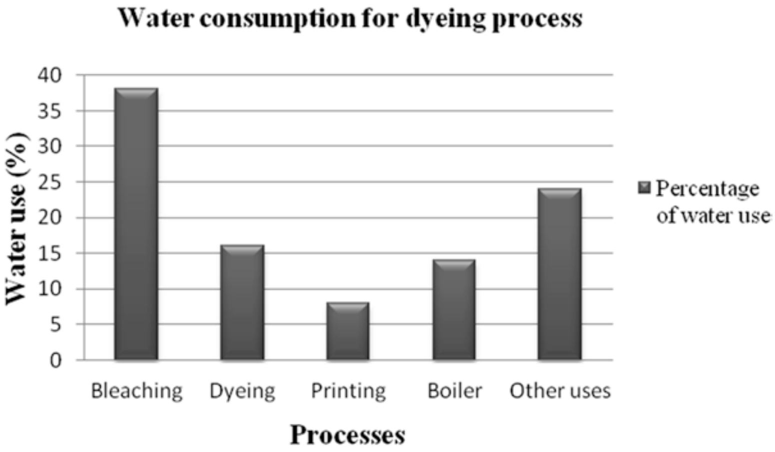


Fig. 3 Overall water usage in a classic textile dyeing industry

the industries. Table 1 illustrates the liters of water required for wet process (http://www.fibre2fashion.com). Figure 3 shows the percentage of water consumption in overall process.

4 Organic Dyes in Textile Dyeing Processes

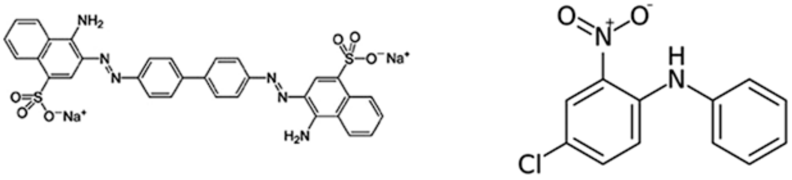
Mankind has used dyes for thousands of years and the earliest known use of a colorant is believed to be with a Neanderthal man about 1,80,000 years ago. Though, the first known use of an organic colorant was much later, being nearly 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs (Gupta & Suhas, 2009). Dye molecules generally comprise chromophore groups, which are responsible for color formation and auxochrome and act as electron acceptor and assist in water solubility nature. In addition to this, it enhances the binding affinity of dye toward the fibers, and it increases the color intensity. Thus, the auxochromes are also represented as “color enhancer.” Chromophore groups are usually found in the organic dyes as carbonyl group (=C=O), =C=C=, C=NH, or C=S sulphur bonding (Hunger, 2003; Pereira & Alves, 2012). Most of the dyes are of synthetic origin with complex aromatic structural property. The dye structures are based on the presence of hydrocarbons such as naphthalene, benzene, toluene, xylene, and anthracene (Rivera et al., 2011). Dye classes and few examples of organic dyes used in dyeing industries are given in Table 2. The structure of some widely used organic textile dyes is shown in Fig. 4.

Table 2 Dye classes and examples of organic dyes used for dyeing purposes

Dye class	Example	Molecular formula	Applications
Acid dye	Congo red	C32H22N6Na2O6S2	Silk Nylon Wool fibers Paper Leather
	Methyl orange	C14H14N3NaO3S	
	Methyl red	C15H15N3O2	
	Acid orange (II) 7	C16H11N2NaO4S	
	Naphthol blue black	C22H14N6Na2O9S2	
	Acid blue	C20H13N2NaO5S	
	Acid yellow	C12H9N3Na2O6S2	
	Acid violet 7	C20H16N4Na2O9S2	
Basic dyes	Basic blue 41	C20H26N4O6S2	Silk Nylon Wool Polyester
	Rhodamine B	C28H31ClN2O3	
	Methylene blue	C16H18ClN3S	
	Aniline yellow	$C_{12}H_{22}N_3$	
	Crystal violet	C25H30ClN3	
Disperse dyes	Disperse blue 1	C14H12N4O2	Polyamide Fibers Polyesters Nylon Poly-acrylonitriles
	Disperse red 1	C16H18N4O3	
	Disperse orange 1	C18H14N4O2	
	Disperse yellow 26	C12H9ClN2O2	
	Disperse brown 1	C16H15Cl3N4O4	
Direct dyes	Direct black 38	C34H25N9Na2O7S2	Silk, cotton Wool Flax, rayon Paper Leather
	Direct orange 34	C33H24N6NaO9S2	
	Direct blue 71	C40H23N7Na4O13S4	
	Direct violet 35	C34H24N5Na3O11S3	
	Direct red 80	C45H26N10Na6O21S6	
Reactive dyes	Procion brilliant blue	C23H14Cl2N6O8S2	Wool Cellulosic fibers Polyamide Nylon Silk
	Reactive black 5	C26H21N5Na4O19S6	
	Reactive red 120	C44H30Cl2N14O20S6	
	Remazol red B	C18H14N2Na2O10S3	
	Reactive yellow 14	C20H19ClN4Na2O11S3	
	Reactive blue 19	C22H16N2Na2O11S3	
Vat dyes	Indigo	C16H10N2O2	Wool Flax Wool Rayon
	Benzanthrone	C17H10O	
	Vat blue 6	C28H12Cl2N2O4	
	Vat green 1	C36H20O4	
	Vat violet 18	$C17H7Cl_4NO2S$	
	Vat black 25	$C_{45}H_{22}N_2O_6$	

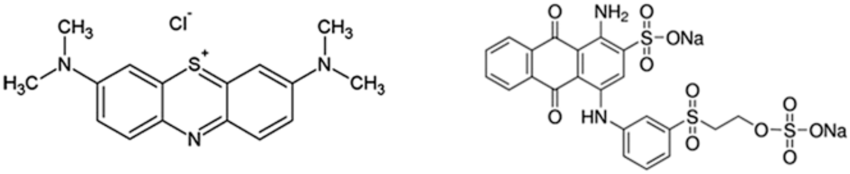
5 Characteristics and Effects of Textile Industry Effluent

The characteristics and composition of waste water generated from dyeing industries depend on the utilization of organic, inorganic chemicals and dye substances as well as processing methods. The physicochemical parameters, such as color, pH, temperature, total solids, total dissolved solids, chemical oxygen demand,



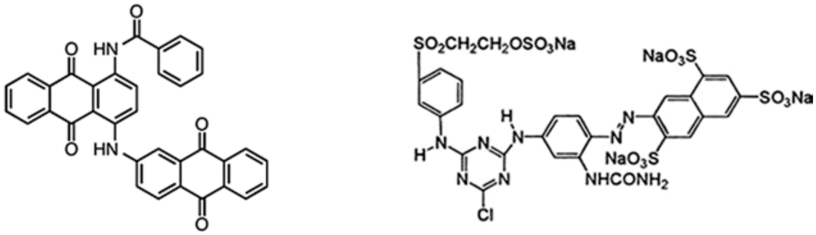
Congo red dye

Disperse yellow 26



Methylene Blue

Remazol Brilliant Blue



Vat Violet 18

Yellow F3R dye

Fig. 4 Structure of some organic dyes used for dyeing applications

biological oxygen demand, chloride, carbonate's heavy metal content in the effluent, show extreme fluctuation in the concentration, which indicates the quality of dyeing wastewater (Phalakornkule et al., 2010; Carmen & Daniela, 2012). The persistent organic dyes are difficult to degrade due to its complex structural feature and higher molecular mass (Verma et al., 2011). The toxic dyeing effluent chiefly contributes to the deterioration of terrestrial as well as aquatic environment (Tehrani-Bagha & Mahmoodi, 2010).

In Tamilnadu, the quality of Noyyal (Erode), Amaravathy (Karur), Cauvery (Trichy), and Bhavani (Coimbatore) river water is drastically polluted by the direct release of treated or untreated dyeing effluent (Sathiyaraj et al., 2017). The wastewater with higher concentration of color and TDS impedes the re-oxygenation potential, prevents sunlight penetration, affects the biological activities as well as photosynthetic process, and leads to destroy aquatic flora and fauna (Zaharia et al., 2009). In addition to this, phosphorous and nitrogen from the industrial effluent mixed into the river cause eutrophication (Qasim & Mane, 2013), reduction in yielding crop in agriculture land, pollution due to the organic contaminants like carboxylate, azo compounds, naphthalene (Annamalai et al., 2014), and cause human health issues like infertility, cancer, skin allergy, and respiratory problems. Fernandes et al. (2018) and Bonet et al. (2018) reported liver damage, inflammatory diseases, and bladder cancer because of the toxic effects of organic dye substances.

The reservoir bed of Orathapalayam dam increased several meters with settling of toxic sludge from textile dyeing industries released with higher TDS content. Due to this harmful effect, about 400 tons of fishes died. In Coimbatore, the Bhavani River has been polluted with dyeing effluent, and the farmers utilize polluted water for the irrigation to cultivate vegetables, paddy, banana, and turmeric. The toxic compounds which enter into the food chain may cause severe health impacts in all trophic levels.

6 Organic Pollutants in Dyeing Wastewater

The processed wastewater discharge during the dyeing as well as finishing process is characterized with higher concentration of organic contaminants, unfixed toxic organic dye stuffs, heavy metals, and various kinds of chemical impurities (Wu et al., 2016; Arslan-Alaton & Alaton, 2007). The recalcitrant organic dyes, surfactants, salts, and chlorinated chemicals used for dyeing purpose are considered as the most important organic pollutants in dyeing effluent (Ben Mansour et al., 2012). Most of the organic toxicants contain different characteristics and include aliphatic or aromatic cyclic rings or halogenated substitution compounds especially chlorine that enhances their persistent nature, which are difficult to remove from the environment; also its carcinogenic properties cause severe health impacts in humans and other animals (Huang et al., 2017). The foremost ingress of organic pollutants to the textile effluent is from the raw materials used for garments production. Natural (cotton, wool) and chemical-based fibers (nylon, polyester) are widely used as a raw material for the production textile products. Natural fibers usually contain organic pollutants like oil, grease, fats, wax which also contributes in the increase of COD and BOD of textile industry wastewater (Le Marechal et al., 2012). In addition to this, the organic chemical compounds of pesticides and herbicides such as pentachlorophenol, diazinon, fenvalerate, cypermethrin, and cyromazine used during the cultivation period remain attached with the natural fibers thereby increasing the organic pollutant load in the effluent. The lipophilic properties of certain pesticides also aided to strong affinity with cotton fibers. Various kinds of pollutants are released from each step of wet processing due to the usage of different organic chemical substances.

In sizing and desizing process, the discharge of organic pollutants depends on the raw materials (cotton, linen, synthetic fibers) as well as chemical substances. Typical organic contaminants produced during these processes are enzymes, hemicelluloses, carboxymethyl cellulose, starch, fats, etc. During the scouring process, anionic, ionic, non-ionic surfactants, formate, wool waxes, and anionic detergents are liberated into the effluent. After the bleaching process, the organic pollutant load increased with the presence of bleaching agents and other chemical matter, including EDTA, polyacrylates, and gluconates. Higher organic contaminants are formed after the dyeing, finishing, and printing processes. Volatile organic compounds like benzene, xylene, and methane used in printing process are also released into the atmosphere. Major pollutants are unfixed lethal organic dyes (contribute to rise of color intensity in wastewater) along with auxiliary chemical components such as alkylphenol, EDTA, methylenephosphonic acid, fatty amine ethoxylates, ammonia, glycerin, polyvinyl alcohol, mineral oil, and halogenated compounds, which dynamically lift the concentration of organic pollutants, TDS, COD, and salts in the textile industry wastewater. Generally, these noxious contaminants present in the contaminated environment are detected qualitatively and quantitatively by spectroscopic (UV-visible spectroscopy and surface-enhanced Raman scattering) as well as chromatographic (LC-MS and GC) instrumental analytical methods (Borah et al., 2020). Dan et al. (2018) detected organic pollutants using UV spectrophotometer in the wavelength ranges from 250 to 300 nm. The persistent, recalcitrant dye components and other organic contaminants entirely alter the nature of dyeing effluent and lead to difficulty in the reduction of pollutants and also cause inefficiency in treatment process. A few examples of organic pollutants released during the wet processing method are presented in Table 3.

7 Eco-friendly Techniques for the Removal of Organic Pollutants

Traditionally, the organic contaminants present in the polluted environment are eliminated by physical (adsorption, reverse osmosis, membrane filtration, photolysis, sonication), chemical (coagulation, flocculation, precipitation, chemical

Table 3 Several organic pollutants present in wet processing wastewater

Process	Organic pollutants
Sizing and desizing	Cellulose, enzymes, starch, fats, oil, polyvinyl alcohol, gelatin, etc.
Scouring	Surfactants, detergents, soaps, petroleum spirit, nitrogenous matter, glycerol, grease, waxes, fats
Bleaching	Gluconates, polyacrylates, cellulose, surfactants
Mercerizing	Alcohol sulphates, cyclohexanol, surfactants
Dyeing	Organic dye substances, amine ethoxylates, ammonium compounds, polymeric substances, ethylenediaminetetra (methylenephosphonic acid), EDTA
Printing and finishing	Aliphatic hydrocarbons, organic dyes, polysaccharides, polyvinyl alcohol, tin organic compounds, methylpyrrolidone, glycols, acrylamide, polyacrylates, etc.

oxidation and reduction), physicochemical (electrocoagulation, ion-pair extraction, electrochemical treatment), biological (aerobic and anaerobic digestion, oxidation ponds, microbial degradation, enzymatic and plant-based treatment), and combination of all these approaches (Robinson et al., 2001; Kabra et al., 2013; Jain et al., 2020; Zhou et al., 2019; Senthilkumar et al., 2018; Santhanama et al., 2019).

Schematic treatment process typically carried out in effluent treatment plant (ETP) is given in Fig. 5. Most of the abovementioned techniques involve high cost; tedious, ineffective, and difficult to degrade certain kinds of toxic dyes; and produce secondary pollutants like intermediate compounds, huge amount of sludge, and alteration in pH of the treated water. Moreover, many of these methods are harmful to the environment. To overcome these disadvantages, various researchers reported biological methods for industrial effluent treatment. In this chapter, eco-friendly treatment techniques such as adsorption, coagulation (plant and animal-based adsorbents and bio-coagulants), microbial biodegradation (bacteria and fungi), phytoremediation (terrestrial and aquatic plants), and green-synthesized nanomaterials (silver, iron, copper, zinc oxide, graphene oxide nanoparticles) adapted to remove organic contaminants from the textile dyeing industry wastewater are provided.

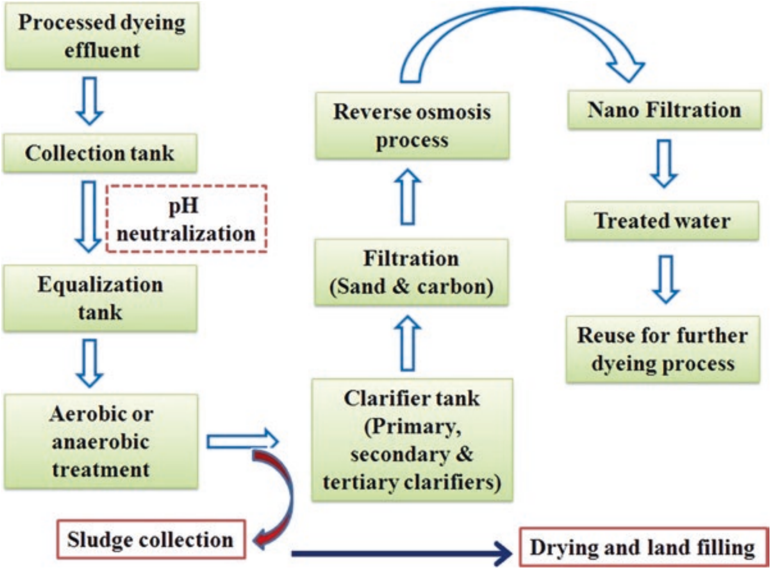


Fig. 5 Typical dyeing effluent treatment process

7.1 Adsorption

Adsorption is referred as the binding substances on the surface of adsorbent through chemical bonding. This treatment is considered as an efficient and non-toxic technique to eliminate soluble and insoluble organic pollutants from the wastewater. Granular or powdered activated carbon is a broadly used commercial adsorbent, but it is expensive. Recently, researchers focus on preparing bio-based adsorbents from various sources like plant wastes (leaf, wood, flower), algae, rice husk, seaweed, hair, mud, zeolite, clay, hydroxides, and metal oxides, as an alternative to activated carbon (Ali et al., 2012; Velmurugan et al., 2011).Importantly, an excellent adsorbent should possess various properties such as porosity, polarity, solubility, surface area, and solution of the pH to enhance the adsorption capacity (Kyzas et al., 2013). Activated carbon from biological-based raw materials is prepared through carbonization and physical as well as chemical activation method. Usually, higher temperature is applied for carbonization process, which eliminates non-carbon compounds like hydrogen, oxygen, and nitrogen (Ali et al., 2012).

Miyah et al. (2018) proved the decolorizing efficiency of walnut powder as a natural low-cost adsorbent and exhibited higher adsorption capability of methylene blue dye from aqueous solution than commercially available expensive adsorbents.

Yang and Hong (2018) reported the adsorption potential of *Glyssogyne tenuifolia* leaves treated with lauric acid toward organic toxic dyes. In another investigation, shells of almond, apricot, and walnut treated with levulinic acid efficiently adsorbed methylene blue dye from aqueous solution (Kocaman, 2020). Likewise, Saeed et al. (2010) reduced the concentration of crystal violet dye concentration in aqueous solution by grape fruit peel powder as an effectual adsorbent through adsorption mechanism. Various researchers prepared bio-based adsorbents for the removal of textile organic dye decolorization (Table 4).

Table 4 Various bio-based adsorbents used for textile dye decolorization

Bio-based adsorbents	Organic pollutants	References
Potato peel	Methylene blue	Taher et al. (2010)
Orange peel	Methylene blue	Velmurugan et al. (2011)
Coconut shell	Reactive dyes	Vieira et al. (2011)
Potato husk	Acid red (AR37)	Hilal et al. (2012)
Garlic peel	Direct red (DR12B)	
Cashew nut shell	Methylene blue	Ponnusamy (2014)
Egg shell waste	Methylene blue	Abdel-Khalek et al. (2017)
Walnut shell	Methylene blue	Miyah et al. (2018)
Cranberry leaves	Lissamine green	Al-Kadhi (2019)
Lignocellulosic waste	Reactive blue 19	Degermenci et al. (2019)
Banana peel	Reactive black 5	Munagapati et al. (2019)

7.2 Coagulation

Coagulation is a widely used conventional treatment technique employed in various industries to reduce organic pollutants and suspended solids and achieve complete decolorization of toxic organic dyes from the dyeing wastewater with the aid of chemical and biological coagulating agents. In addition to this, it evades the formation of toxic intermediate compounds and secondary pollutants during the degradation process (Golob et al., 2005; Verma et al., 2012). Aluminum hydroxide (alum), iron-based salts (ferric chloride, ferrous sulphate), calcium hydroxide, and polyaluminum chloride are broadly used for the pre-treatment of dyeing effluent (Kang et al., 2003; Huang et al., 2009; Patel & Vashi, 2010). The basic mechanism of coagulation is charge neutralization, inter-particle bridging, and destabilization of colloidal particles like soluble dye molecules as well as suspended solids leads to the formation of microflakes or agglomerates. The aggregation of microflocs forms large-sized aggregates and settle down. The separation of settled sludge can be carried out by sedimentation as well as filtration process (Verma et al., 2012; Wang et al., 2018; Manholer et al., 2019). The performance of coagulants crucially depends on the optimum dosage of coagulant, pH of the solution, and characteristics of the effluents or pollutants (Patel & Vashi, 2010).

The application of synthetic polymeric and metal-based coagulants in effluent treatment has some limitations including the production of settled solid sludge after coagulation process, alteration in pH and nature of treated water, inefficient in the decolorization of insoluble dye stuffs, and complications in the disposal as well as limited to recycling of synthetic coagulants (Anjaneyulu et al., 2005; Ramavandi, 2014; Anastasakis et al., 2009). Additionally, researchers reported harmful effect of chemical coagulants such as alum, which leads to Alzheimer's disease in humans (Vijayaraghavan et al., 2011; Flaten, 2001). Natural polymers and coagulants are an alternative source for toxic chemical coagulants because of low cost, eco-friendly nature, biodegradability, easily available, and not causing any detrimental effects on humans or other animals. Furthermore, solid sludge obtained after treatment of effluent using natural coagulants can be used as a soil conditioning agent and manure (Zahrim et al., 2011). In general, polysaccharides, proteins, tannin, and mucilage are extensively used plant-based coagulants (Yin, 2010).

The phytocompounds, namely, polysaccharides such as galactomannan, galactan, galacturonic acid, and mucilage are capable coagulants aided for the removal of suspended solids, color, COD, turbidity, and toxic organic pollutants from the textile industry wastewater. Many researchers validated the coagulation property of mucilage extracted from *Abelmoschus esculentus*, fenugreek, dragon fruit peel, cactus, etc. (Freitas et al., 2015; Anastasakis et al., 2009; de Souza et al., 2014; Le et al., 2020).

Moringa oleifera Lam seed powder is a well-known natural coagulant efficiently used for the treatment of dye related wastewater (Fig. 6). It eliminated 95% of azo dyes from the aqueous solution and shown better performance in the removal of textile dyes such as Blue 71, Acid Yellow 23, and Reactive Red from the effluent

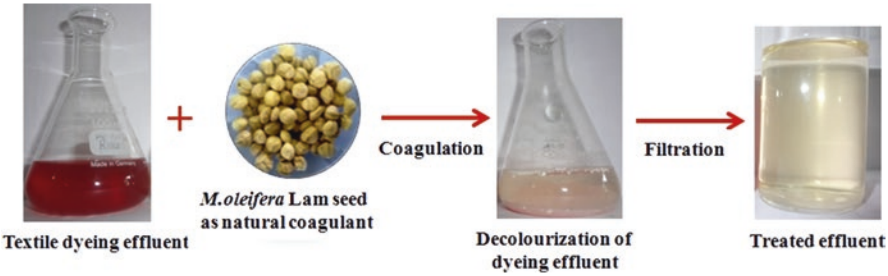


Fig. 6 Treatment of textile effluent using *M. oleifera* Lam seed as a natural coagulant

(Altamirano-Corona et al., 2015). Cationic protein molecules found in the seed extract possess positive charge and are actively participating in the diminution of anionic dye contaminants by means of charge neutralization as well as adsorption mechanism (Sapna et al., 2012).

In another investigation, *M. oleifera* Lam seed powder effectively decreased 74% of color, 84% of TDS, 39% of COD, and 65% of turbidity from the dyeing-related wastewater (Kalaicelvi et al., 2016). Sanghi et al. (2006) achieved 87% decolorization of acid dye form the aqueous solution using coagulant prepared using seed gum of *Ipomeoa dasysperma*. Similarly, Mahmoudabadi et al. (2019a) confirmed the coagulant property of *Plantago major* extract and successfully decolorized Reactive Blue 19 dye.

In contrast to plant coagulants, animal-based materials also encompass effective coagulation property. Chitosan is a major coagulant derived from deacetylated chitin, which is composed of D-glucosamine and N-acetyl D-glucosamine (Yin, 2010; Kurita, 2006; Verma et al., 2012). These natural polymers are capable in the reduction of suspended solids, color causing organic dye substances, COD, and turbidity from the dyeing wastewater (Guibal & Roussy, 2007). Mahmoodi et al. (2011) successfully removed 75% of Acid green 25 dye and 95% of Direct red 23 dye from textile wastewater using chitosan. Likewise, Abdullah and Jaeel (2019) studied the coagulation potential of chitosan and reduced acid dye concentration from textile dyeing wastewater. Some natural coagulants used for the remediation of textile dyeing effluent and organic dye decolorization are given in Table 5.

7.3 *Phytoremediation of Organic Dye Pollutants*

Phytoremediation or green remediation is an ecologically benign, aesthetically pleasant approach, which uses live plants (aquatic and terrestrial) for the treatment of industrial effluent, polluted soil, and restoration of contaminated sites (Sinha et al., 2007; Ekambaram et al., 2018). Naturally, plants contain defense mechanism against toxic compounds or environmental stresses. Through the enzymatic pathways, plants convert toxic compounds to non-toxic compounds, and this property

Table 5 Bio-based coagulants used to remove organic pollutant

Bio-based coagulants	Organic pollutants	References
Chitosan	Acid green 25 and Direct red 23	Mahmoodi et al. (2011)
Moringa oleifera Lam seed, Maize seed, chitosan	Congo red	Patel and Vashi (2010)
Plantago major L.	Neutral red	Chaibakhsh et al. (2014)
Acanthocereus tetragonus	Congo red	Chethana et al. (2016)
Ocimum basilicum seed mucilage	Textile effluent treatment	Shamsnejati et al. (2015)
Dillenia indica	COD, color, and turbidity from textile effluent	Manholer et al. (2019)
Moringa strenopetala	Reactive blue 19, Reactive red 195, Direct red 81, Direct blue 86	Gelebo and Ahmed (2019)
Alcea rosea root mucilage	Disperse red 60 and Reactive blue 19	Mahmoudabadi et al. (2019b)
Hylocereus undatus fruit peel mucilage	TSS, COD, and color from textile effluent	Le et al. (2020)

assists in the degradation of organic contaminants (Govindwar & Kagalkar, 2010). Classically, plants remediate contaminants through various modes including phytoextraction, phytotransformation, phytostabilization, rhizofilteration, phytoaccumulation, rhizodegradation, and phytovolatilization (Ali et al., 2013; Muthusamy et al., 2018; Ali et al., 2020). The remediation capability of the plants mainly depends on the plant species, interaction with root region, bioavailability, nature of the growth medium, characteristics of the pollutants or effluent, selection of chelating agents, and environmental conditions such as pH, temperature, and salt concentration (Tangahu et al., 2011). *Chara vulgaris*, *Eichhornia crassipes, Lemna minor, Pistia stratiotes, Hydrocotyle vulgaris* roots, *Nasturtium officinale, Typha angustifolia, Hydrilla verticillata*, *Azolla pinnata*, *Azolla filiculoides, Medicago sativa* L., *Bacopa monnieri* L, and *Sesbania cannabina* Pers are some plants having remediation potential and used for wastewater and polluted soil treatment.

Kabra et al. (2013) examined the effluent treatment as well as dye decolorization potential of *Glandularia pulchella* (Sweet) Tronc. The toxic dye stuffs in the effluent stimulate the production of several enzymes such as tyrosinase, lignin peroxidase, alcohol oxidase, and dichlorophenolindophenol reductase which enhances the degradation of contaminants from the dyeing wastewater. Vafaei et al. (2012) obtained 99% removal of Basic Red 46 dye from the aqueous solution using *Azolla filiculoides* under optimized pH and temperature. The results concluded that the synthesis of antioxidant enzymes induced due to the chemical stress involved in the decolourization process. Vasanthy et al. (2011) successfully reduced 95% of Red RB and 99.5% of Black B from aqueous solution using the whole plant of *E. crassipes.* The chromatographic (GCMS) analysis of plant extract obtained after treatment confirmed the increased level of hexadecanoic acid and decreased level of chlorophyll and phytol content. In another analysis, *E. crassipes* effectively eliminated 50.64% of total solids, 55.71% of BOD, 40–70% of COD, 94.78% of chromium, 94.44% of copper, and 96.88% of zinc from the dyeing wastewater. The alkaline pH of the effluent was also neutralized by water hyacinth (Mahmood et al., 2005).

The combination of algae (Nostoc) with aquatic plants (*Eichornia crassipes* and *P. stratiotes* L) is used for the elimination of pollutants from the mixture of textile industry effluent, and it removed 65% of COD from the effluent through synergistic mechanism (Roy et al., 2010). *Salvinia molesta* is a submerged aquatic flora which has the dye degradation potential. Chandanshive et al. (2016) effectively removed 97% of Rubine GFL azo dye from the aqueous solution using *Salvinia molesta* by triggering the production of plant enzymes such as laccase, lignin peroxidase, tyrosinase, alcohol oxidase, DCIPR reductase, catalase, and supermutase. The degradation and intermediate compounds were identified using GC-MS, FTIR, and HPLC analysis. The microscopic analysis confirmed the accumulation of dye substances in the stem region after 48 hours. In addition to this, *S. molesta* plant reduced 82% of BOD and 76% of COD after 192 hours from real dyeing effluent.

Mahajan and Kaushal (2016) removed pH, EC, total dissolved solids, COD, and BOD from the different dilution (100%, 75%, 50%, 25%, and 10%) of textile dyeing industry effluent within 7 days through phytoextraction mechanism of *H. verticillata* (L.f) Royle. In the same way, Patel and Adhvaryu (2016) studied the dyeing effluent treatment potential of *E. crassipes* and *P. stratiotes* L. The treatment process was performed for 7 days, and the parameters such as pH, total solids, COD, and dissolved oxygen of the treated effluent was checked. After treatment, the COD level got decreased and the dissolved oxygen got increased. *E. crassipes* showed maximum removal of color than *P. stratiotes* L. The aquatic floating plant *Azolla pinnata* potentially eliminated 90% of methylene blue dye from the aqueous solution which confirmed its phytoremediation potential (Al-Baldawi et al., 2018). As well, Khataee et al. (2012) achieved 80% reduction of Acid Blue dye using *Lemna minor* after 6 days of treatment period. The decolorization process can be assisted by various antioxidant enzymes including ascorbate, peroxidases, and superoxide dismutase produced by *Lemna minor* due the stress caused by toxic effect of dye molecules (Paczkowska et al., 2007). Similarly, Imron et al. (2019) removed 80.56% of methylene dye using *Lemna minor* within 24 hours of duration. *Bacopa monnieri* (L.) Pennell plant potentially degraded 90–100% several reactive and azo dyes after 2 weeks of treatment duration under hydroponic culture (Shanmugam et al., 2019).

Most of the aquatic plants uptake the contaminants through the root region and degrade the pollutants via rhizodegradation mechanism. Moreover, the microorganisms present in the rhizosphere region get stimulated by the production exudates by plants and the degradation of pollutants occurs by synergistic effect. The absorbed toxic contaminants are easily converted into non-toxic compounds. And also, the carbonic compounds present in the organic pollutants are utilized by the plants for growth and metabolic activities (Tangahu et al., 2011; Al-Baldawi et al., 2015; Geoffroy et al., 2004). *Typhonium flagelliforme* significantly removed dye from the solution prepared by distilled water within 4 days duration (Kagalkar et al., 2010).

In another investigation, Rai et al. (2014) analyzed the dye decolorization capability of *Aloe barbadensis* plant extracts and decolorized 27.33% of Congo red dye. Kamat (2014) reported the dye decolorizing potential of two terrestrial plants such as *Arabidopsis thaliana* and *Helianthus annuus*.

Sureshvarr et al. (2010) reported the azo dye degradation potential of *Eucalyptus* plant using GCMS analysis carried out for treated and untreated azo dye–contaminated soil samples. Tetradecanoic acid is a type of carboxylic acid, which has antioxidant property effectively involved in the degradation of organic pollutants from the dyeing effluent (Bodoprost & Rosemeyer, 2007). Chandanshive et al. (2018) treated the dye containing textile wastewater using various plants like *Gaillardia grandiflora*, *Tagetes patula*, *Portulaca grandiflora*, and *Aster amellus* through constructed wetland system. The outcome revealed the dye accumulation capability of the ornamental plants and improved the effluent contaminated soil quality. Microscopic analysis showed the accumulation of dye molecules on the plant cells. And also, the enzymatic characterization of plant tissues revealed the contribution of laccases, peroxidases, and thyrosinases enzyme in the dye decolorization as well as degradation of organic contaminants from the contaminated soil.

Phytoremediation approach is gaining several advantages over conventional treatment techniques such as eco-friendly, less expensive, require solar energy, no need for the requirement of high cost machines as well as technical experts, and efficient to degrade both organic and inorganic pollutants. Alternatively, this method has some limitations including its time-consuming nature, rooted to harmful effects in plants due to the formation of noxious intermediate by-products during the degradation, and lack of proper understanding on the phytoremediation mechanism occur in the plants (Muthusamy et al., 2018). This method can be used with the combination of other physical methods for efficient removal of organic contaminants from the textile industry wastewater. Few plants used for the degradation of organic pollutants and treatment of textile effluent are given in Table 6.

7.4 *Bioremediation of Organic Pollutants*

Bioremediation is a biological technique widely adapted for the treatment of various industrial effluents. It refers to the remediation of wastewater or contaminated soil using microorganisms such as bacteria, yeasts, fungi, microalgae, and biocatalysts. This method is an ecologically benign, low cost, and easier approach for the decolorization and degradation of toxic organic dyes as well as contaminants from dye-related wastewater. Common effluent treatment plants of textile industries typically carried out aerobic and anaerobic treatment using microbial inoculants (Saratale et al., 2011; Vikranta et al., 2018; Patil et al., 2020). Diverse types of microbial strains are capable to absorbing, degrading, or neutralizing organic contaminants by the activation of various enzymes like phenoloxidases, reductases, peroxidases, and monooxygenases are synthesized due to the stress caused by the toxic compounds (Vikranta et al., 2018; Kalme et al., 2007). The dye decolorization

Table 6 Examples of plants used in textile dye and effluent remediation

Plants	Organic pollutants	References
B. malcolmii	Malachite green, red HE4B, methyl orange, and reactive red 5B	Kagalkar et al. (2009)
Eichhornia crassipes	Reactive and acid dyes	Vasanthy et al. (2011)
Ipomoea hederifolia	Textile wastewater	Rane et al. (2014)
Lemna minor	Triphenylmethane dyes	Torok et al. (2015)
Alternanthera philoxeroides	Remazol red dye	Rane et al. (2015)
Azolla pinnata	TDS, COD, nitrate, sulphide from textile wastewater	Ugya et al. (2017)
Lemna minor L	Basic red 46	Yaseen and Scholz (2018)
Azolla pinnata	Methylene blue	Al-Baldawi et al. (2018)
Asparagus densiflorus	Textile wastewater	Watharkar et al. (2018)
Leman minor	Methylene blue	Imron et al. (2019)
Hydrilla verticillata	Phenol	Chang et al. (2019)

mechanism mainly occurs through breaking the bonds such as hydroxyl group, carboxylic acid, amino group found in the chromophore region of dye molecules (Ghosh et al., 2017). Many researchers reported the bioremediation potential of various bacterial strains such as *Bacillus* sp., *Pseudomonas* sp., *Micrococcus*, *Acinetobacter*, *Aeromonas*, *Neisseria* sp., and *Rhodococcus* (Pandey et al., 2019). Buthelezi et al. (2012) demonstrated the treatment efficiency of indigenous bacterial strains isolated from activated sludge have been effectively decolorized whale blue, mediblue, and mixed dyes. The decolorization highly influenced by the characteristics of dye, temperature, pH, and concentration of bio-flocculants.

Sethi et al. (2012) isolated indigenous bacterial strains such as *Klebsiella* sp., *Pseudomonas* sp., and *Proteus* sp. from textile dyeing wastewater and *Klebsiella* sp., *Shiegella* sp., and *Marganella* sp. from textile industry sludge waste and utilized the same for decolorization process under optimized pH, temperature, carbon, and nitrogen sources to enhance the dye decolorization. The effluent isolates reduced 80% of color, and sludge isolates reduced 40% of color. Bafana et al. (2008) separated azoreductase enzyme with 60 kDa of molecular weight through electrophoretic method, which responsible for the decolorization of azo Direct red 2 and converted into benzidine and 4-aminobiphenyl. In another evaluation, *Pseudomonas putida*, *Lysinibacillus fusiformis*, *Comamonas testosteroni*, *Aeromonas hydrophila, P. plecoglossicida,* and *P. monteilii* were isolated from the soil sample collected near dyeing industrial area and used for the decolorization of acid orange, methyl orange, methylene blue, malachite green, and rhodamine B dyes. *P. putida* removed 91% of malachite green after 5 days and decolorized 85% of acid orange and 69% of methylene blue after 7 days of incubation. *Comamonas testosteroni* removed 85% of methyl orange, and *P. monteilii* removed 56% of Rhodamine B dye after 3 days of incubation period (Fulekar et al., 2013). Similarly, Telke et al. (2009) potentially decolorized 100 mg/L of Congo red from aqueous solution and removed 50% of COD from dyeing wastewater within 12 hours optimum pH (8) and temperature (40 °C) using *Pseudomonas* sp. isolated from textile effluent.

Likewise, Kalyani et al. (2008) also isolated *Pseudomonas* sp. SUK1 from effluent and successfully degraded 99.28% of Red BLI under aerobic condition with controlled pH (6.5–7.0) and temperature (30 °C). The significant role of aminopyrine N-demethylase and NADH-DCIP reductase enzyme contributed in the degradation process was determined by UV, FTIR, and TLC techniques. Mahmood et al. (2012) screened green and red dye decolorization efficiency of six indigenous bacterial cultures such as *Bacillus cereus*, *Bacillus mycoides*, *Bacillus subtilus*, *Micrococcus* sp., *Bacillus* sp., and *Pseudomonas* sp. The bacterial consortium BMP1/SDSC-01 removed 84% of green as well as red dye and 85% reduction observed in yellow and black dye solution. In the same way, Desai (2017) studied the decolorizing capacity of native bacterial isolates such as *Klebsiella* sp. and *Staphylococcus* strains by culturing in the media enriched with Direct Red 2B dye and the strains reduced 98.83% and 98.83% of dye, respectively, under specific concentration of carbon and nitrogen sources with optimized pH and temperature. Some of the microbial strains used for the degradation of organic dyes from textile dyeing effluent are summarized in Table 7.

7.5 *Nanoremediation of Organic Pollutants*

Nanotechnology is one of the most fascinating fields of science which deals with the synthesis of nanoscale material size ranging from 1 to 100 nm. These nanomaterials are having vast applications in medicine (drug delivery), environmental cleanup,

Table 7 Microorganisms used for the remediation of organic pollutants

Microorganisms	Organic pollutants	References
Providencia sp. *Pseudomonas aeruginosa*	Red HE3B dye	Phugare et al. (2011)
Candida krusei	Basic Violet 3 dye	Deivasigamani and Das (2011)
Aspergillus niger	Remazol Brilliant Blue R and Acid Red 299	Benghazi et al. (2014)
Bacillus cereus	Acid Red (AR) 151, Orange (Or) II, Sulfur Black (Sb) andDrimarene Blue (Db) K2RL	Bayoumi et al. (2014)
White-rot fungus *Coriolopsis* sp.	Triphenylmethane dyes: Crystal Violet, Methyl Violet, Cotton Blue, and Malachite Green	Chen and Ting (2015)
Bacillus circulans	Methyl orange	
Bacillus pseudomycoides	Acid Black 24	Kumara et al. (2019)

textile, electronics, biosensors, optics pace industries, etc. (Christian et al., 2008; Saif et al., 2016). Moreover, the application of metal and metal oxide nanoparticles in the degradation of organic/inorganic contaminants are gaining crucial part because of their unique properties in terms of larger volume of surface area, reusability, stability, recyclability, and less/non-toxic and facile synthesizing approach (Gautam et al., 2019; Beshkar et al., 2017).

Generally, nanoparticles are synthesized by two strategies such as such as "top-down" and "bottom-up" approaches. The nanoparticles produced from the larger materials by reducing its size is referred as top-down, while in bottom-up, assembling of smaller molecules to hefty structure takes place (Rotello, 2004) (Fig. 7). Synthesis of nanoparticles is carried out by various physical and chemical methods such as co-precipitation, micro emulsion, flame synthesis, laser ablation, and chemical vapor condensation. Most of these methods are having demerits such as higher cost, noxious and are corrosive in nature, explosive properties of precursors, require high temperature, and need of surfactants (Hamed, 2005; Ghaedi et al., 2006; Huang et al., 2008; Mamania et al., 2013; Ghorbani et al., 2017). Due to these limitations, the environmentally benign, facile, and reliable biological materials such as plant, bacteria, fungi, algae, and yeast are applied as precursors and reducing agents to synthesis of nanoparticles (Mandal et al., 2006; Jebali et al., 2011).

The green or biogenic route of nanoparticle fabrication can be aided by various bioactive compounds present in plant and microbial extracts in terms of enzymes, polyphenol, amino acids, vitamins, polysaccharide, and terphenoids which act as stabilizing as well as capping agents through bioreduction or bio-precipitation mechanism (Park et al., 2011). Green nanomaterials facilitate solutions to

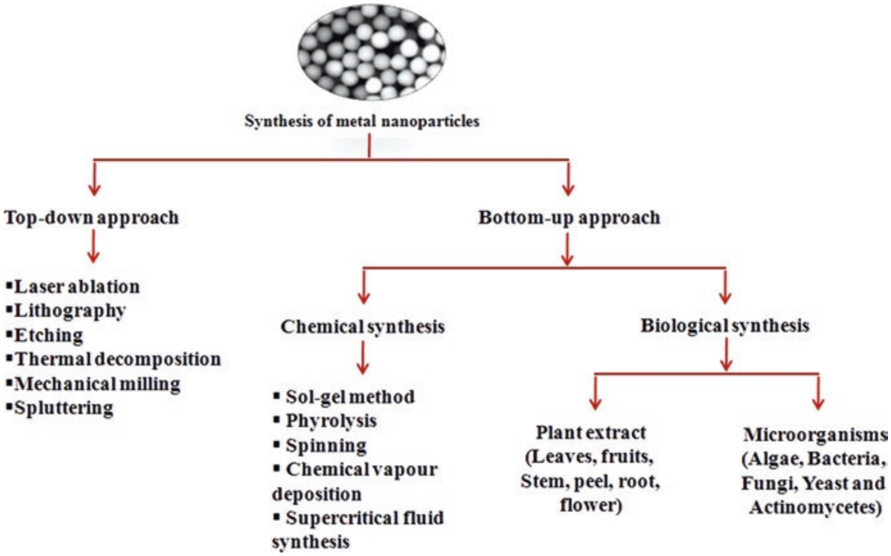


Fig. 7 Methods of metal and metal oxide nanoparticle synthesis

technological and environmental challenges in the field of solar energy conversion, catalysis, medicine, and drinking water and wastewater treatment. Various types of metal nanoparticles like silver, gold, iron, zinc oxide, copper, selenium, tin oxide, and titanium oxide are widely synthesized using plant and microbial biocomponents as reducing agent which are having the potential to degrade organic pollutants from the contaminated site and convert into non-toxic compounds through oxidation or reduction mechanism. Furthermore, biogenic nanoparticles are effective in varied temperature as well as pH and recyclable without the loss of notable reduction on catalytic property. These nanomaterials are used as an efficient nano-adsorbents or nanocatalyst for clean-up purposes (Gautam et al., 2019).

Among metallic nanomaterials, silver nanoparticle is an important one that has been extensively studied by many researchers because of its unique potential as antibacterial activity. Diverse types of plant and microbial extract-based reducing agents are used for the synthesis of biogenic silver nanoparticles and are actively participating in the degradation of toxic organic contaminants. AgNP synthesized using *C. pyrenoidosa* extract acts as a nanocatalyst and efficiently degraded methylene blue dye from aqueous solution (Aziz et al., 2015). Khan et al. (2016) produced *C. japonicum* plant extract–mediated AgNP and applied for the removal of organic dye bromophenyl blue. Similarly, Duran et al. (2007) revealed the textile treatment capability of silver nanoparticles synthesized using extract obtained from the fungi *F. oxysporum*. Bhakya et al. (2015) exposed organic dye degradation potential of silver nanoparticles synthesized with the extract obtained from leaf, bark, and root extracts of *Helicteres isora* plant by means of catalytic activity. Interestingly, the dye degradation process by silver nanoparticles occurred through the adsorption toward the surface of contaminants due to the higher surface volume ratio of nanoparticles and enhancement of catalytic property by the exposure of UV/visible light or sunlight (Ansari et al., 2013).

Gold is a well-known precious metal chiefly used for ornamental purposes. Unlike bulk gold material, gold nanoparticle is tremendously recognized as a competent nanocatalyst because of its unique optical absorption property in the presence of UV as well as visible light. The photocatalytic property of gold nanoparticles can be proficiently utilized for the elimination of noxious organic compounds (Laoufi et al., 2011). As a green route, the leaf extract of *Lagersteroemia speciosa* rapidly reduced precursor gold ions to 41-91 nm nanosized gold nanoparticles, and it hastily decolorized several organic dyes namely Bromophenol blue, bromocresol, methylene blue, and methyl orange via photocatalytic reaction (Choudhary et al., 2016). In another analysis, fungal (*C. oxysporum* extract) mediated gold nanoparticle easily decolorized the toxic dye Rhodamine B within 7 minutes of reaction time (Bhargava et al., 2016). Basically, biogenic gold nanoparticles detoxify or degrade the azo dyes by cleaving the azo bond present in the dye molecules and convert lethal nitroaromatic compounds to non-toxic carboxylic acid by oxidation process (Sharma & Deswal, 2018).

Zinc oxide is an effective superconducting metal, and it is broadly noted for optical, electrical, and photocatalytic properties. Golmohammadi et al. (2019) proved the photocatalytic activity of zinc oxide nanoparticles fabricated using the extract of jujube fruit by degrading organic dyes including methylene blue and Eriochrome black-T from model wastewater. Lemon juice promptly reduced the precursor chemical zinc acetate to zinc oxide nanoparticles through reduction process, and it successfully decolorized certain organic dyes like reactive blue 21, methylene blue, methyl red, and orange via photocatalytic activity (Davar et al., 2015).

Iron is considered as a versatile metal widely used for various applications. Iron nanoparticles are gaining more attention from researchers than bulk iron material because of its distinctive features specifically magnetic property, higher surface volume, less toxicity, low cost, and facile preparation methods (McHenry & Laughlin, 2000; Chin et al., 2011). Iron oxide magnetic nanoparticles include zero-valent iron, magnetite, and maghemite nanoparticles which are extensively used for water and wastewater treatment. The unique properties such as their small particle size, large surface area to volume ratio, magnetism, rapid kinetics, and high reactivity with the pollutants aid efficient purging of contaminants from the water and wastewater. The magnetic property of the iron nanoparticles easily removes the minute contaminants than the well-defined membrane filtration system. The recovery of magnetic iron nanoparticles can be carried out by low-gradient magnetic field or hand-held magnet (Hu et al., 2007; Yantasee et al., 2007; Shen et al., 2009).

Huang et al. (2014) developed 40–50 nm nanosized iron nanoparticles assisted with oolong tea extract as an eco-friendly reducing agent and revealed its decolorizing efficiency by removing 75.5% of malachite green dye from aqueous solution through adsorption mechanism. Bishnoi et al. (2018) degraded methylene blue dye through photocatalytic activity of magnetic iron nanoparticles prepared using fruit extract of *Cynometra ramiflora* plant. In another analysis, iron oxide nanoparticles removed 99.09% of dye from the effluent through adsorption mechanism (Arifin et al., 2017). Cheera et al. (2018) effectively decolorized Congo red dye with the aid of green-synthesized iron nanoparticles using *Acacia nelotica* plant extract. The utilization of biological-based reducing agents facilitates to evade the usage of toxic chemicals and paved toward the preparation of eco-friendly nanoparticles and assist in multipurpose applications including effective removal of organic pollutants from the textile dyeing effluent. Green-synthesized metal nanoparticles used for the removal of organic pollutants are given in Table 8.

8 Conclusion

Textile industries are vitally significant areas which produce more beautiful colored products as well as most dangerous creator of environmental pollution that lead to the deterioration of natural resources. In the current scenario, dyeing industries need to conserve huge volume of water by recycling and reusing remediated water. These dyeing effluents are characterized with higher concentration of harmful organic pollutants that cause lethal effect in flora and fauna of the ecosystem. To eradicate these organic contaminants, industries need less-expensive and eco-friendly treatment approaches. In this overview, promising biological techniques in terms of

Table 8 Application of biogenic metal oxide nanoparticles in organic pollutant removal

Nanomaterials	Organic pollutants	References
Silver nanocomposites	Textile dyes (Reactive red and reactive blue)	Khatoon and Sardar (2017)
Iron nanoparticles	Color and organic matter from textile wastewater	Ozkan et al. (2017)
Nickel nanoparticles	Reactive Yellow 160	Kiran et al. (2020)
Silver nanoparticles	Safranine O, methyl red	Jyoti and Singh (2016)
Magnetic iron nanoparticles	Color, TDS, COD from dyeing effluent	Ahila et al. (2018a, 2018b)
Iron oxide nanoparticles	Color from dyeing effluent	Ahila et al. (2018a, 2018b)
Copper oxide	Rhodamin B from textile wastewater	Rafique et al. (2019)
Silver nanoparticles	Brilliant Blue FCF dye	David and Moldovan (2020)

adsorption, coagulation using natural coagulants, microbial remediation, plant-based remediation, and green-synthesized nanomaterials employed for the treatment of textile effluent were elaborately discussed. However, these biological approaches are having certain limitations that need to be conquered for the proficient reduction of organic pollutants from the contaminated environment.

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Application of Phycoremediation Techniques Toward Nutrients Removal from Wastewaters: Evaluation of Adsorption and Absorption Methods

P. Santhanam, S. Dinesh Kumar, M. Divya, N. Krishnaveni, and P. Perumal

Abstract The industrial effluents are being discharged into the adjacent water bodies without proper treatment. Such effluents contain excessive nutrients, heavy metals, toxic compounds, and non-biodegradable materials which could harm the aquatic environments and their associated flora and fauna. In this chapter, the recent technologies that have been applied to eliminate and/or used to remove excessive nutrients in water ecosystems are discussed with special reference to microalgae. The survey of literature indicates that the microalgae have been used via a wide range of absorption and adsorption methods toward removing the excessive nutrients from the effluents. The use of living cells or dry biomass of microalgae as compared to other currently employed ones toward nutrient removal has been an advantageous one. This chapter discusses the process and enforcement necessities to bring the excess nutrients elimination more possible at a commercial level.

Keywords Nutrients · Microalgae · Mobilization · Immobilization · Absorption · Adsorption

1 Introduction

Our globe would encounter 40% shortfall in water by 2030 (Sun et al., 2016). During the past few eras, the anthropogenic pressure and unsustainable development coupled with urbanization have caused degradation of our environments. The discharge of raw effluents and sewage sludge in to the aquatic ecosystem has been a common practice (Chan et al., 2009). Moreover, fin and shellfish culture practices have been intensively employed to supply the protein to the populations. Such rapid

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growth of waterfront activities led to severe environmental threat to the nearby ecosystems (Chen et al., 2015). The toxic content of the wastewater could enter in to the humans through food chain that could cause serious health problems (Barakat, 2011). Unfortunately, the runoff of high nutrient loaded effluents and abnormally less oxygen level besides harmful algal blooms in the water bodies could potentially harm the aquatic organisms including their mortality (Lau et al., 1997; Chernicharo, 2005; Cai et al., 2013). The commonly employed remediation techniques, namely, physical and chemical methods have their own demerits such as energy consumption, prolonged incubation, and leftover sludge after remediation process are the real barriers during the possible achievement of eco-friendly remediation (Sun et al., 2016). Alternatively, bioremediation of wastewater through microalgae is considered to be an economically viable and environment friendly one. Microalgae-based bioremediation was tried during the 1950s to tap its hidden potential value in industries for its marketable applications including wastewater treatment. In recent times, the phytoremediation process has become an effective technique toward innovative wastewater-remediation and producing valuable biomass for co-product development.

1.1 Wastewater Source and Characterization

Environmental degradation takes place due to the liquid and waste disposal by municipalities as well as corporations (of towns and cities). Discharge from factories, aqua-agri lands, and dumping sites generating large quantity of wastes, and these wastes cause pollution that need solution (Horan, 1990). Aquaculture wastewater was found to contain unusually high amount of nutrients (Yang et al., 2019). Domestic wastewater has been normally found to possess phosphate (0.55 μmol), nitrate (0.81 μmol), nitrite (19 μmol), ammonia (108.63 μmol), and heavy metals such as zinc (2.746 ppm), chromium (0.008 ppm), copper (4.625 ppm), lead (0.198 ppm), and cadmium (0.092 ppm). Also, the industrial wastewaters have been found to possess phosphate, nitrate, nitrite, ammonia, zinc, chromium, copper, lead, and cadmium at the rate of 0.0.0017 μmol, 1.74 μmol, 2.39 μmol, 8.07 μmol, 0.45 ppm, 0.007 ppm, 3.897 ppm, 0.268 ppm, and 0.023 ppm, respectively (Dinesh Kumar et al., 2015a, 2015b, 2020). Metals are being directly discharged into the aquatic environments largely due to petrochemical and other modern industrial activities (Schaller et al., 2011).

1.2 Microalgae Metabolism

The microscopic algae are largely single-cell forms 0.2–2 μm wide and that included even filamentous forms (Barsanti & Gualtieri, 2016). They are important autotropic microscopic organisms that are found in various water ecosystems, namely, fresh, brackish, and marine environments. Microalgae exhibit various shapes and sizes and are the fast-growing aquatic plants (phytoplankton). But they do not have any specialized body parts but with primitive cell wall structure made up of cellulose and silica. They represent cyanophyceae, green algae, dinoflagellates (*Dinophycea*), coccolithophores (*Prymnesiophyceae*) besides the diatoms (Sharma et al., 2011). The type of food synthesis process of algae depends on the availability of intensively of light, concentration of CO_2, etc. (Liang et al., 2009). Their growth depends on their culture condition, and sometimes they undergo many strategies at times (Perez-Garcia et al., 2011). The high rate of CO_2 accumulation could lead to the high rate of photosynthesis, and at the same time organic carbon substrate might retard the respiration. The organic carbon consumption rate might be increased during the dark cycles due to low illumination (Sforza et al., 2012).

1.3 Removal Process

Bio-absorption

Bio-absorption of nutrients by algae is considered a normal biological mechanism (Dinesh Kumar et al., 2013, 2016a, 2016b). The binding of pollutants (adsorption) is mediated by cell wall materials like polysaccharides, mucilage, and other functional groups: carboxy and hydroxyl groups (Mishra et al., 2011; Dinesh Kumar et al., 2019a, 2019b). Biosorption is being considered a non-metabolic and is a rapid process, it may work with living and nonliving microalgal cells and such process may depend on numerous factors such as pH (Naja & Volesky, 2011; Dinesh Kumar et al., 2018), species (Gadd, 2009; Dinesh Kumar et al., 2013; Revathi et al., 2017; Leena Grace Nancy et al., 2019), varieties (De Philippis et al., 2007; Dinesh Kumar et al., 2016a, 2016b), and cell concentration (Naja & Volesky, 2011; Adam et al., 2015; Dinesh Kumar et al., 2018). The biosorption technique involves the accumulation of nutrients by the inner part of the cell. This process may work in a slow manner due to the transporting of the nutrients into the interior part through the cell membrane via binding with proteins and other components (Kaplan, 2013). This method is possible only in living cells and which might be triggered by temperature, nutrient starvations, metabolic inhibitors, and substrates (Wilde & Benemann, 1993). Understanding these mechanisms to remove the excessive nutrients by using various prokaryotic and eukaryotic microalgae could provide eco-friendly strategy to clean the aquatic ecosystems.

Bio-adsorption

During the past four decades, the biotechnological technique like immobilization of microorganisms has been tried for enhanced wastewater remediation. Nowadays, algal immobilization has caught much interest for bioremediation process (Cohen, 2001; Ahmad et al., 2012). Some of the researchers obtained high quantity of biomass with strong metabolic activity and toxic metal resistance which was quite higher than the mobilized microalgal wastewater treatment system (Wang et al., 2006; Zhou et al., 2008; Cai et al., 2011; Liu et al., 2012; Dinesh Kumar et al., 2019a, 2019b). An immobilized microalgal bioremediation technique provides more advantages, namely, low operating cost and reusability without losing their activity (Devi & Sridhar, 2000). Moreover, the harvest of algal biomass after wastewater treatment is easy as they are entrapped in matrix. Therefore, algal immobilization technology has been practiced worldwide for treating the wastewater during the last few years.

The Immobilized Cell Cultivation System

Massive biomass yield of microalgae is mostly obtained through suspension methods of culture with proficient light conversion, and secondary metabolite production has been generated during remedial processes (Lebeau & Robert, 2006; Moreno-Garrido, 2008). However, unfortunately harvesting of microalgal biomass in wastewater treatment plant is a major hurdle during this algal technique. To overcome the harvest-related problem, the immobilization of microalgae in the matrix systems is recommended toward proficient bioremediation. Immobilization has been classified into two types, namely, active and passive immobilization. While adsorption, confinement in liquid-liquid emulsions, capturing with semi-permeable membranes, covalent coupling, and entrapment within the polymer are considered to be active immobilization type, the passive immobilization can work via individual capacity of organisms based on the nature of their surface through biofilm formation. Although the microalgal immobilization technique that is generally employed in was familiar in secondary metabolite industry, its application in effluent treatment is not practiced commercially so far.

1.4 Active Immobilization Methods

Flocculant Agent

The flocculant forms are playing a significant role to avoid centrifugation complication during immobilization of microalgae. The most commonly used flocculant agent is chitosan of lineal polysaccharide possessing randomly distributed standards. It is a crustacean exoskeleton structural component, which possess the flocculation capacity (Chen et al., 2011). This substance has been found to flocculate microalgae under various environments like saline, fresh, and brackish water (Morales et al., 1985). Considering its biodegradable nature, it is mostly the preferable one. Its low chitosan strength is considered as weakness and still it is not yet rectified (Gualtieri et al., 1988). About 76-fold improvement was found when

Phaeodactylum tricornutum cells were treated with $CaCl_2$, but only 30-fold improvement was observed in the same algal cells when they were treated with chitosan (Moreira et al., 2006). The chitosan-based *Scenedesmus* sp. immobilization resulted in 70% NO_3 and 94% PO_4 adsorption during 12 h treatment (Fierro et al., 2008). The usage of Al and $FeCl_2$ for flocculation was rarely used, despite their requirement ten times higher than other flocculent in respect of freshwater microalgae.

Chemical Attachment

The surface of the algal cells was damaged when the chemicals adhered to the cell wall. In this case, immobilization of algal cells via chemical treatment is not advisable and not productive (Codd, 1987). Seki and Suzuki (2002) have stated that the immobilizing algal cells through chemical interference can kill the surface of the cells and could damage their binding efficiency as well as their life.

Gel Entrapment

During algal cell immobilization, the gel entrapment principle is commonly used. The components like acrylamide, gelatin, collagen or egg white, resins, polyurethanes, agars, carrageenan, or alginates are mostly employed for algal entrapment (Codd, 1987).

Synthetic Polymers for Gel Entrapment

Different kinds of biopolymers have been used for morphological study characterization, industrial manufacturing, and effluent remediation (Lebeau & Robert, 2006; Ignacio, 2008). In case of polymeric immobilization, the technique is mainly used for the physical separation between treated effluents and microorganism like biofiltration systems. The polymers are used to immobilize the live microalgae with the help of small apertures in relation to the algal cells. Such pores help the algal cells in fluid transport to sustain their cell metabolism as well as growth rate maintenance (Cohen, 2001). The intrinsic issue of obtaining biomass produced by suspended microalgae during wastewater treatment is resolved through immobilization in polymers (Travieso et al., 1996; Valderrama et al., 2002). Agar, alginate, agarose, carrageenan, and chitosan have been considered as natural polymers and by-products from algae. At the same time, the manmade polymers such as polyvinyl, acrylamide, resins, and polyurethane could also be considered for treatment. Among the natural polymers, carrageenan and alginate were most popular for wastewater treatment (Bashan, 1998; Ignacio, 2008). The natural polymers can have ability to impact the effluents, and they are also susceptible to environmental degradation by microbes, while artificial polymers do not. Their diffusivity rate was higher than the synthetic polymer, and toxic compounds are also low (Leenen et al., 1996).

During immobilization, the polymers are mixed with the algal suspension and then the mixture solidifies into a polymeric gel, and the gel's monomers are linked together to form polymer with the support of algae. Such processes can be achieved by multiple techniques such as physical and chemical treatments. The strength of polymer is directly proportionate to the monomer's concentration. By dropping the alginate mixture via small syringe specific instrument in to the $CaCl_2$ solution, spherical-shaped beads are formed. Finally, the dried beads can act as agricultural inoculants (Bashan et al., 2002). Massive functional changes have been reported inside their immobilized forms. The hydrocarbon-rich immobilized microalgal beads, namely, *Botryococcus braunii* and *Botryococcus protuberans* have revealed the increased chlorophyll pigment and fat content during the pre-immobilization stage (Singh, 2003). Immobilization of *Synechococcus* sp. with chitosan matrix protects the algal cell walls against the NaOH toxicity and which recorded higher growth as compared to mobilized cell cultivation methods (Aguilar-May et al., 2007). Jeon et al. (2002) opined that the polyvinyl alcohols and glutaraldehyde are the superior water-soluble synthetic polymers for microalgal cell immobilization.

Natural Polysaccharides for Gel Entrapment

Natural polysaccharides are the commonly employed ones in the algal immobilization. Among these, carrageenan, agar, and alginate are frequently used. The carrageenan is extracted from the seaweeds of the Rhodophyceae family and used as natural polysaccharides with the help of water alkaline extraction method. It contains cationic compounds, namely, metal ions, amines, amino acid derivates, and water-miscible organic solvent, which could precipitate as a gel (Tosa et al., 1979). From *Aghardhiella subulata* and *Chondrus crispus*, the carrageenan could be obtained as distinctive isomeric forms (Burdin & Bird, 1994). Hardening of cell can enhance strength of the obtained products (Chamy et al., 1990). Travieso et al. (1996) have studied the nutrient removal property of three microalgae, namely, *C. vulgaris, C. kessleri,* and *Scenedesmus quadricauda* that have immobilized in optimized conditions. The red algae like *Gelidium, Pterocladia,* and *Gracilaria* were extracted for sulfated galactan. Agar is known to be a thermo-reversible gel which is a polymer and is found to be a suitable candidate for algal immobilization (Codd, 1987; Papageorgiou, 1987). According to Aksu et al. (1998), the metal adsorption strength of agarose matrix microalgae system was lesser than the Ca-alginate matrix system under optimized conditions. The production of glycerol was found to be high in immobilized *Dunaliella salina* (Thakur & Kumar, 1999). Alginate is a popular polysaccharide (gel to trap the algal cells) and which also formed a group of family with a-L-guluronic acid and 1-4-linked-b-D-mannuronic acid (Smidsrod & Skjak-Braek, 1990). The brown algae are the main candidates for producing alginates, especially the algae genus of the Sargassum. The alginate concentration has been varied from species to species and reaches up to 40% of DW (Ertesvag & Valla, 1998). Araujo and Andrade (1996) stated that the advantage of algal immobilization is that extremes of physical-chemical factors cannot cause any changes in the cells while entrapping algal cells in to the matrix. Hertzberg and Jensen (1989) have defined a standard procedure for algal immobilization especially for marine microalgae by using alginate beads. Pane et al. (1998) reported that the calcium alginate immobilized *Tetraselmis suecica* beads showed higher chlorophyll production. The cellular growth of microalgae immobilized in calcium alginate beads and mobilized microalgal cells were compared and found that the concentration of chlorophyll was higher in immobilized algal cells. Maximum amount of glycerol is being produced from *Dunaliella tertiolecta* by alginate immobilization methods (Grizeau & Navarro, 1986). Jen et al. (1996) have standardized the methodology for microencapsulation (co-encapsulation) with alginate and polylysine.

1.5 Passive Immobilization

Some microalgal cells are having a natural tendency to attach substrates. Polymerized synthetic foams may be tried in passive immobilization techniques for the cell immobilization.

Loofa Sponges

The reticulate type of loofa sponge is obtained via the removal outer tissue of the *Loofa cylindrica* (Cucurbitaceae) (Akhtar et al., 2004). This substance contains a high degree of porosity, unchanging physical properties with recyclable, non-toxic, and low-cost values (Liu et al., 1998). While using loofa sponges for the fine experimentation, it exhibits variety of structures naturally. For example, some of the sponges consist numerous pore proportions during plant growth (Akhtar et al., 2004; Iqbal & Edyvean, 2004; Ahmadi et al., 2006). This could help in easy handling and is statistically more demonstrative, or even possess fragment in fibers (Ogbonna et al., 1996). Microalgae immobilization through loofa sponges is not considered to be cost-effective solution in biotechnological applications. Even though, we use loofa sponge after proper washing and cleaning with dried matter, it will not work well. The length of incubation period depends on the nature of the organisms (that is to be used). The forms like *Chlorella sorokiniana* and *Synechococcus* sp. can be passively immobilized through loofa sponges under the incubation periods of 2 weeks as reported by Nasreen et al. (2008) and Saeed et al. (2009).

Adherence to Wood Plastic and Glass

Some algal forms have the habit to naturally attach with the bottom substrata, and they are called as periphyton or epiphytes forms. Hence, Gosh and Gaur (1998) prepared specific glass slides to study the ecological and ecotoxicological characteristics with the help of glass rods. They have placed the slides into the devices for 4 or 5 weeks for achieving high biomass in the glass slides during low-current locations. Likewise, Admiraal et al. (1999) have prepared 1.5 cm and 2 length glass disks and kept in small low land river at northern Belgium for 10–20 days. The glass tubes are the better substrates than the wood substrates (Danilov & Ekelund, 2001). Plastics are being covered only by bacteria, and not by algae. For increasing the attachment concentration, the etching agents are being used. The glass beads (3 mm dia) for microalgae attachment, etched with hydrofluoric acid, showed better attachment. The persistent chemical such as TIO_2 is used to assess the light-inducing nature of attachment concentration of algae (Franke & Franke, 1999). This method is not being extensively practiced for lower algae. Silane coupling reagent was used for the better adhesion of *Chlamydomonas* sp. immobilized in glass fiber (Laurinavichene et al., 2006)

Twin Layer Recirculation System

It is one of the passive immobilization bioreactors for the microalgae cultivation and treatment of effluent. Twin layers are harmless and constant in effluents. It is economically viable and easy to operate. This novel laboratory-scale TLRS comprised of very thin micro- and macro-porous layers and they are water attaching ones. They act as light reactor by utilizing artificial light. Non-oven polyester filter, PTFE filter, printing paper, nylon mesh, and nitrocellulose membrane are being used as a substrate layer for immobilization of microalgae (Shi, 2009). The microalgae are provided with wastewater as a culture medium through source layer, being made up of a stainless metal wire water flow via mesh. The topmost part of the twin layer has the mechanism to receive the six evenly viable flow supplier. The immobilized algae receive the culture medium (effluent is received via peristaltic pump). The changed organisms get the O_2 and CO_2 from immediate environment. The treated liquid is being collected below the system. The culture is being maintained under the temperature of 26 ± 1 °C up to 15 days under illumination with an irradiance of 300 $\mu mol\ m^{-2}\ s^{-1}$ and a light/dark period of 12L:12D. This study in line with the established mechanisms of nutrient uptake by the algae.

Agar Alginate Algal Block System (AAABS)

Dinesh Kumar et al. (2016a, 2016b) have developed agar-alginate algal block (AAAB) system to eliminate excessive nutrients from shrimp farm wastewater as a semi pilot-scale treatment system. This treatment has dealt *L. vannamei*-cultured wastewater (3 months old) with an agar alginate algal block biofilter system consisting marine microalga *Picochlorum maculatum* in immobilized form. Finally, AAABS removed 89.6% of nitrite, 98.5% of ammonia, 46.4% of nitrate, and 57% of phosphate from the effluent by ten cycles of treatment, and this system revealed the promising outcome in terms of nutrient removal as well as operating system while facing the cost of agar, alginate, and tube as a challenges.

2 Bio-absorption

The microalgal production through carbon synthesis requires many sources (Costa & de Morais, 2013). The microalgae growth can be accomplished through three different pathways, namely, heterotrophic, autotrophic, and mixotrophic.

2.1 Heterotrophic Growth

Heterotrophic growth is a non-light method that requires organic substrates. Such heterotrophic mechanisms are involved in assimilation, activation, and storage/consumption of metabolites (Morales-Sánchez et al., 2013). Glucose undergoes glycolysis, tricarboxylic acid cycle, and glyoxylate cycle pathways. During heterotrophic growth process, the microalgae consume nitrogen for synthesis of amino acids. Nitrogen sources for algae culture are ammonium, nitrate, nitrite, urea and amino acids, peptone, purines, and yeast extract (Morales-Sánchez et al., 2013; Chen & Chen, 2006). Urea and other biological nitrogen compounds are also good extracts for heterotrophic growth regime (Leena Grace Nancy et al., 2020).

2.2 Autotrophic Growth

The algal pigments, chlorophylls, phycobilins, and carotenoids accumulate lights and generates electrons that could be moved to PSI, II, and cytochrome b6f complexes, ADP+ and NADP+ that could be modified as ATP and NADPH. The ATP and NADPH are used during dark cycle to assimilate the CO_2 via Calvin Benson cycle in the chloroplast. The high amount of CO_2 delivers satisfactory quantities of CO_2 to stroma in chloroplast and which could decrease the O_2 interference on ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO). Microalgae are involving in CO_2 consumption carbonic anhydrase, inorganic carbon transporters, sequestered RuBisCOs in elevated CO_2 micro-compartment and in carboxylation mechanism (CAM and C4-photosynthesis) (Giordano et al., 2005; Wang et al., 2011, 2014; Baba & Shiraiwa, 2012; Nelson et al., 2008; Dinesh Kumar et al., 2015a, 2015b, 2017; Leena Grace Nancy et al., 2019, 2020). Therefore, the microalgae can be gainfully employed in remediating the effluents.

2.3 Mixotrophic

During mixotrophic production, the algae use both the abiotic and biotic carbons (Cerón-García et al., 2013). A mixture of autotrophic and heterotrophic growth is known as mixotrophy that can result in an increased growth rate (Wang et al., 2011). By simultaneous utilization of carbon dioxide and organic carbon, assimilation would offer an opportunity for successful algal culture by proficiently utilizing the available light and organic carbon. This method of microalgae culture have high productivity as compared to the autotrophic methods as agreed by Yang et al. (2000). Rate of light intensity, oxygen, carbon dioxide, least quantity of energy conversion rate, and CO_2 fixation rate are considered as important factors during mixotrophic culture (Perez-Garcia et al., 2011). Zhan et al. (2017) have reported the major merits and demerits of mixotrophic cultivation with reference to the energy efficiency and pigment fixation.

2.4 Mechanisms of Bio-absorption

Ammonium (NH_4^+) is considered a major nitrogen source for algal growth as it is the most dynamically effective source, with only limited energy requirement to accumulation (Kaplan et al., 1986). It could be passing through surface skins for the proteins from ammonium transporter family under autotrophic and heterotrophic conditions. Nitrate is considered as important source and its influence in plant growth is very high. It is being transmitted through plant cell membrane, subsequently reduced the ammonia and the process involves substantial spending of energy (Crawford et al., 2000). In algae, the nitrate is being catalyzed to ammonium via the nitrate and nitrite reductase enzymes (Fernandez & Galvan, 2007). Usually, nutrients and minerals are major components in algae cultivation. Absorption of nutrients especially nitrogen and phosphorus are key components during algal growth (Cai et al., 2013). Axenic culture of algae may efficiently fix the atmospheric CO_2 for their growth and other body mechanisms (Cai et al., 2013). Hadiyanto et al. (2013) stated that the huge quantity of ammonia, nitrite, and nitrate is a part in the many types of effluents. Conversion of inorganic to organic has been performed by eukaryotic microalgae. During the conversion process, inorganic nitrogen has been adsorbed by plasma membrane through algal cells and possible outcome was reduction of NO_3 as NO_2 followed by ammonium as amino acids (Fig. 1).

Martinez et al. (1999) stated that the growth and energy metabolism are fully dependent on the phosphate which was formed as inorganic phosphorus. In phosphorylation process, the inorganic phosphorus, that is, the hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate (H_2PO_4) are then incorporated into organic compounds by involving the production of ADP and ATP. Further, the properties of wastewater or aqueous solution also serve as a major contribution to the elimination of nutrients. The suitable removal methods to be followed depend on the nutrients' type and their concentration.

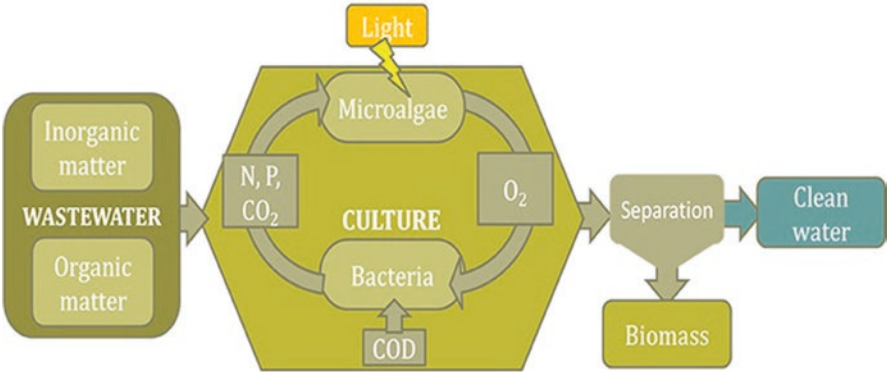

Fig. 1 Nutrient recovery from wastewater using microalgae (Cai et al., 2013)

In conclusion, the variety of prokaryotic and eukaryotic live algal cells and dried biomass could be profitability used to eliminate the nutrients from the different type of effluents. More information is available on the wastewater type and pollutant type that have to be considered to implement the bio-adsorption and bio-absorption methods on a commercial-scale level, because the effluents have been generally found to contain mixture of inorganic and organic compounds. So far, many laboratory-level and mass scale-level demonstrations were made and experiments have been carried out to understand the effluent characteristics in relation to the efficiency of microalgae absorption and adsorption techniques. In view of the above, it is recommended for the adoption of technology involving the algae toward the nutrients' removal from the polluted industrial effluents, in future.

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A Review on Technological Approach for Obtaining Nutrient from Solid Waste

A. Karthika, R. Seenivasagan, and M. Vasanthy

Abstract Globally the huge amount of solid waste creates the ecological and technical problems. As the human population increases, there is simultaneously increase in waste generation. Hence waste management strategies are considered most important in gaining organic nutrients from it. Farmyard manure, biochar, poultry manure, vermicompost, biogas digest, and urban compost are rich sources of vitamins, growth-promoting substances, macro-, and micro-nutrients. Numerous technologies are followed nowadays to recover organic nutrients and utilize them for the agricultural field to retain the soil fertility, improved tillage, reduce irrigation of soil, obtain high porosity, better aeration, water holding capacity, and plant growth-promoting factor, etc. Among them composting, vermicomposting technologies, and aerobic digestion play major roles. These processes are able to collect microbes, macro-nutrients, and all micro nutrients from the waste degradation. At the end of process, compost and digestate obtained are eco-friendly and cost-effective compare to other bio products. This chapter deliberates the methods followed in managing solid waste and their importance in gaining nutrients. This could also substantiate the significance of micro- and macroorganism helpful in increasing the rate of degradation. Other new technologies such as biochar, osmosis, and electro-dialysis are also discussed. This chapter summarizes over all case studies and key publications regarding solid waste management and nutrient recovery from organic waste with no further costs.

Keywords Solid waste · Vermicompost · Compost · Organic nutrients

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1 Introduction

The World Bank Report by the year 2020, about 2 billion tonnes of waste would be generated. This could be expected to increase by 3.4 billion tonnes by the year of 2050 (Luis et al., 2019). According to the Associated Chambers of Commerce and Industry (ASSOCHAM), in India about 5.2. million tonnes of waste is estimated to be generated every year. Generation of waste has been categorized into food and green, glass, metals, plastics, paper and cardboard, rubber, wood, and others. In the developed countries, among 34% of waste generation about 16% went for recycling. But in the developing and underdeveloped countries, about 90% of waste are not disposed properly and hence leads to pollution and disasters.

Recently the disposal of organic solid waste creates more attention by collecting and recycling. With increasing population, there would be increase in the generation of waste annually (Vinay et al., 2018). Therefore, managing the solid waste is one of the major needs to avoid the consequences caused by the waste generation. Solid waste management includes activities such as generation, storage, collection, transfer and transport, treatment, and disposal of solid wastes. Due to unavailability of suitable facilities, there is a lack of collection and transportation. Therefore, there is a deposition of waste accumulated in every nook and corner of the city. All this happened due to the unplanned maintenance and poor financial status of the municipal corporation of the country. The MSW management system should involve planning, engineering, organization, administration, financial and legal aspects of activities related with generation, storage, collection, transport, processing, and disposal in an environmentally compatible manner thereby adopting the economy, energy conservation, aesthetics, and opportunities (Sharholy et al., 2008). It should provide maintenance charge for proper infrastructure facilities and requirement needed for all activities.

1.1 Solid Waste Generation

About 2.0 billion metric tons of municipal solid waste (MSW) are produced annually worldwide. According to the World Bank Report, overall waste generation increases up to 3.40 billion metric tons by 2050 (https://www.wastedive.com/news/world-bank-global-waste-generation-2050/533031/). About 13.5% of waste get recycled; 5.5% went on composted; 40% of waste has not been managed properly, and it went on open dumping and burning which pollute soil, water, and air. Among 217 countries worldwide, India influences maximum waste generation. About 62 million tonnes of waste with growth rate of 4% was generated in India. All types of waste including organic waste, plastic waste, and textile waste come under municipal solid waste (MSW). Organic waste is a major contributor to MSW, as organic waste gets decomposed easily and it may also cause harm to environment due to wild deposition of waste in land without proper treatment. Hence it pollutes soil and ground water and accumulates greenhouse gases (Sisto et al., 2017). Therefore, solid waste management should be necessarily practiced to overcome the problem.

1.2 Amount of Municipal Solid Waste Generation

The quantity of the waste depends up on the influence of food habits, living standards, commercial activities, and seasons of a particular area. An increase in population will increase the waste generation. Currently, it must be higher in comparison to the previous years (Pappu et al., 2007). MSW generation is lower in small towns when compared to metro cities. The solid waste generation in urban area must be 1.15 lakh tonnes; in mega cities, it must be 21,100 tpd; in metro cities, it must be 19,643 tpd; in towns, it must be 42,635.28 tpd, respectively.

1.3 Collection and Generation of MSW in India

According to Planning Commission Report (2014), urban India generates 165 million tons of waste annually and by 2050 it could reach 436 million tons. It requires around 1175 hectare of land per year to dispose waste in a systematic manner (Bhide & Shekdar, 1998; CPCB, 2000; Pappu et al., 2007; Shekdar, 2009). This must be based on 0.45 kg/capita/day waste generation. During the last decade, solid waste generation has increased 2.44 times (CPCB, 2013).

1.4 Types of Waste

Municipal solid waste is generally categorized into residential, industrial, commercial and institution, construction and demolition, municipal services, and agriculture and mining. Physical characteristics of MSW include paper, textile, leather, plastic, metal, glass, ash, and dust. Chemical characteristics of MSW shows carbon (0.64 ± 0.8)%, phosphorus (0.67 ± 0.15)%, potassium (0.68 ± 0.15)%, and C/N ratio (26 ± 5)%. The composition of MSW include compostable waste (fruit and vegetable peels, food waste), recyclable (paper, plastic, glass, metals, etc.), toxic substances (paints, pesticides, used batteries, medicines), inerts, moisture, soiled waste (blood stained cotton, sanitary napkins, disposable syringes) respectively. According to NEERI MSW, India has approximately 40–60% compostable, 30–50% inert waste, and 10% to 30% recyclable.

1.5 Rag Pickers

The role of rag pickers provides an important scenario in MSWM. The rag pickers pick up the recyclable material such as paper, plastic, and tin and sell it to scrap merchants to generate income, so that they can save 14% of the municipal budget annually and reduce up to 20% load on transportation and on landfill (Pappu et al., 2007).

1.6 Solid Waste Management Practices in India

According to CPCB Report 2013, there is an action plan execution and enactment for municipal solid waste management. Due to lack of segregation, only 12.45% waste is scientifically processed and rest is disposed in open dumps. Main features such as land requirement, environment friendliness, cost-effectiveness, and acceptability to the local community block efficient solid waste management system. The following practices are carried out to manage generation of solid waste.

Segregation

Segregation is the process of separating waste into different elements. It can accomplish by sorting manually at household; curbside collection schemes; automatic separation; mechanical biological treatment separating systems, etc. Since segregation of waste is not organized properly, three-fourth of the generated waste does not get disposed suitably (Kaushal et al., 2012).

Collection

Waste collection is a part of the process of waste management. It is the transfer of solid waste from the point of use and disposal to the point of treatment or landfill. The waste produced in household is transferred into communal bin. Waste from other complex sectors, complexes, and industries that come under municipality also transfer their waste to disposal site (Kumar et al., 2009).

Three Rs : Reduce; Recycle; Reuse

It helps to cut down on the amount of throw-away waste. It conserves the natural resources by landfill space and energy. Retrieving useful materials from waste, utilizing them for making new products, sorting out and taking recyclable material such as plastics and glass lead to income generation. In India, in union territories such as Pondicherry, rag pickers collect all the recyclable material and send these materials for recycling process (Pattnaik & Reddy, 2010).

Transportation

Small to heavy vehicles are utilized for transportation. In villages, bullock carts, hand rickshaws, compactors, trucks, tractor, trailers, and dumpers were used. In small towns, trucks, stationary compactors, mobile compactors/closed tempos, and tarpaulin-covered vehicles are used in the transportation of MSW. Without the transport system, disposal of waste decreased drastically (Joseph, 2002).

Disposal

In India, 59 cities followed the disposal techniques for solid waste generation. The following techniques were followed to carry out the disposal waste material.

1.7 Nutrient Recovery from Solid Waste

Stabilizing organic solid waste retrieves nutrient-rich manure. The organic matter degradation is attained by microbes and earthworm thereby maintaining aeration and fertility of the soil (Garg et al., 2012). Enormous amounts of nutrients have been recovered from organic solid waste such as distillery industry sludge (Suthar & Singh, 2008), agricultural wastes (Suthar, 2009), bagasse (Pramanik, 2010), and water hyacinth (Varma et al., 2016). Soobhany et al. (2015a). Degradation of organic solid waste retrieves all beneficial plant macro-nutrients and micro-nutrients. Techniques involved in degradation of organic solid waste help to minimize the pathogenic compounds (Soobhany, 2018) and reduce the heavy metals (Soobhany et al., 2015b) to produce better quality products with enriched nutrient content.

1.8 Techniques in Treating Organic Waste

There are several techniques followed for treating waste materials. The organic waste material can be directly digested anaerobically to produce biogas or it may undergo aerobically followed by reverse osmosis to produce enormous amount of micronutrient. It can be further subjected into composting or vermicomposting to produce organic fertilizer. It may undergo gasification or pyrolysis to produce biochar and syn gas.

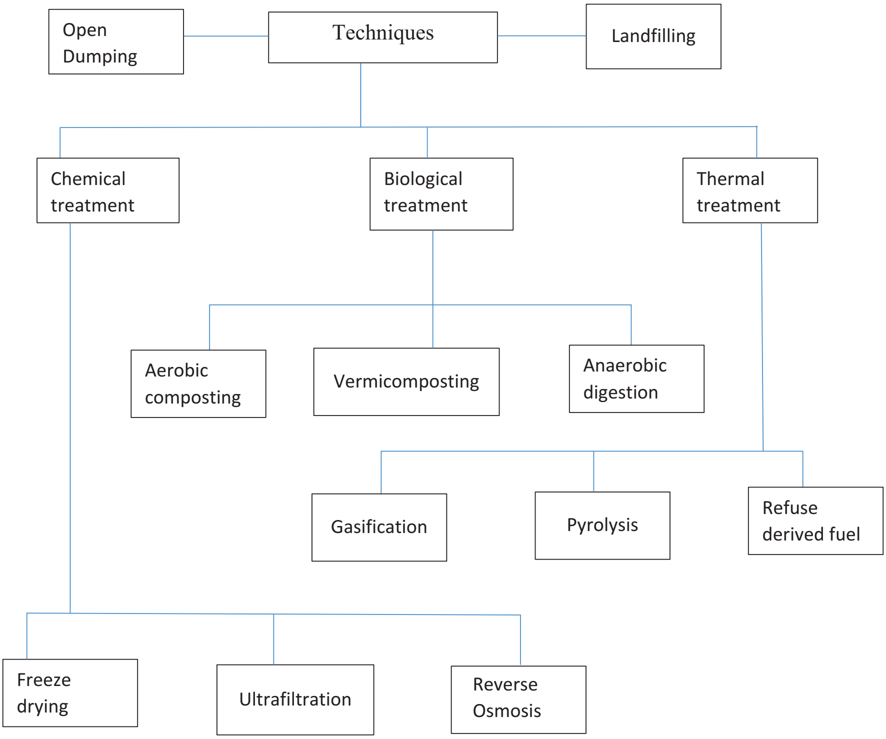
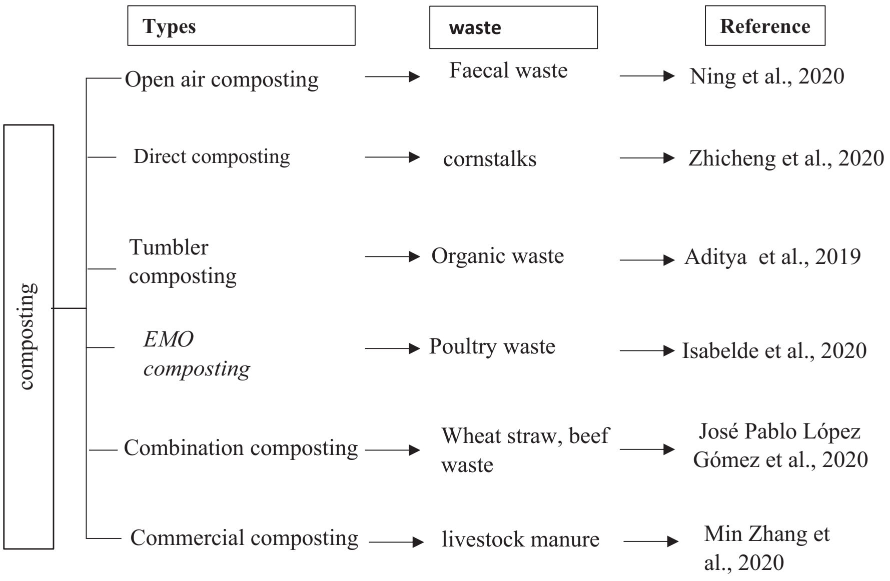


Fig. 1 Methods followed for treating municipal solid waste

1.9 Techniques for Treating Solid Waste

Composting

Organic waste decomposed in aerobic method to produce fertilizer a humus like material. It contains all major and minor nutrients which help in increasing plant growth and soil fertility. This natural fertilizer is dependent upon numerous microorganisms such as bacteria, actinobacteria, protozoa, fungi, and rotifers. All kinds of degradable waste such as municipal solid waste, green waste, human and animal waste, and sewage waste can be degraded by composting. Compost is performed as soil improver and fertilizer. Production of good compost depends on the temperature, humidity, turning, and moisture, so that efficient organic matter with numerous nutrient content could be obtained (Ahmed et al., 2019).

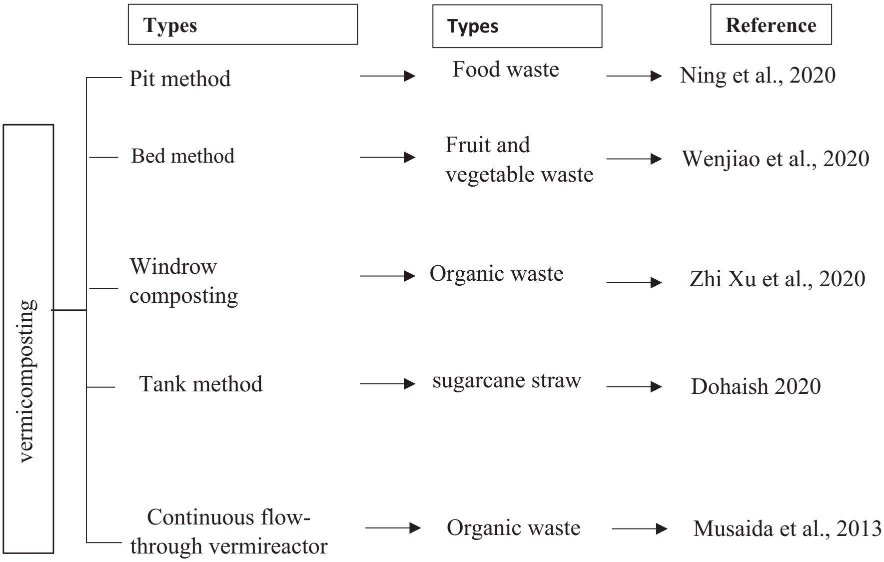


Nutrient Recovery from Composting

According to Paliza et al., compost rich in nutrient content such as phosphorus and nitrogen helps to recycle or maintain the nutrient content where there is loss in leachate and also helps to maximize potential social, economic, and environmental benefits. The compost contains carbon, nitrogen, phosphorus, potassium, magnesium, sodium, and organic matter and thereby improves the soil fertility. The nutrient content can be enhanced by the application of wood ash, lime water, phosphate-solubilizing culture, and broken animal bones. It enhances the physical, chemical, and biological properties of soil. It is an eco-friendly method offering several potential benefits to society. It reduces the utilization of pesticides, fungicides, and herbicides. It develops the entrepreneur in producing new organic products (Joseph et al., 2020) (http://agritech.tnau.ac.in/org_farm/orgfarm_composting.html).

Vermicomposting

Vermicomposting is the process of stabilizing organic waste into value-added product by utilizing microorganism and earthworm under mesophilic condition. It is more effective than composting because of utilization of earthworm. Many earthworm species such as *Eisenia fetida, Eisenia hortensis, Lumbricus rubellus,* and *Eudrillus eugenia* have been used to bring about nutrient-rich manure. It acts as a conditioner in improving the fertility of the soil. The digestive system of the earthworm has numerous of microorganisms which helps to grind and mix the waste material uniformly to produce compost. It consists of water-soluble nutrients which play relatively easy way for the plants in absorption (Syed et al., 2019)

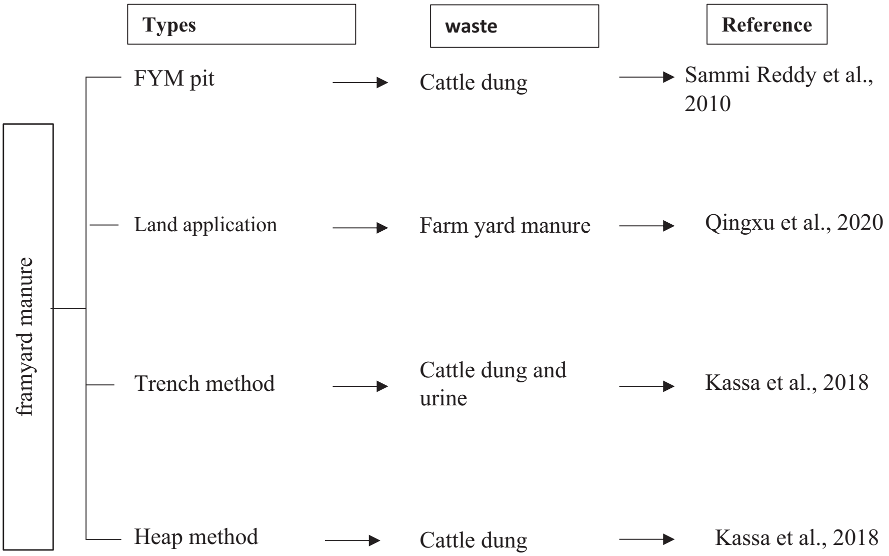


Nutrient Recovery from Vermicomposting

Vermicompost contains numerous nutrients such as pH, organic carbon, organic matter, c/n ratio, TKN, sodium, phosphorus, potassium, calcium obtained from different sources of organic waste such as kitchen waste, green waste, lignocellulosic waste, and municipal solid waste. The nutrient recovery from vermicompost can be enhanced by addition of microorganism along with earthworm, combining different kinds of waste, maintaining pH, and temperature. It acts as a better tool to recover nutrient from organic waste. The nutrient gained through vermicomposting will differ depending on the type of waste that has been degraded. For example, organic waste degradation will be able to gain more nutrient value while comparing the cellulosic waste. Hence by combining the types of waste, there would be better improvement results (Joseph et al., 2020).

Farmyard Manure

Farmyard manure is defined as a decomposed mixture of farm animals such as dung and urine along with leaf litter. It contains complex organic nutrients compared to normal fertilizer. Waste such as cattle waste, human waste, and slaughterhouse waste come under farmyard manure. In addition, the crop wastes, water hyacinth, weeds, and green waste also get mixed. Sheep and goat manure, oilcakes, blood meal, and fish manure contain enormous nutrients which can be directly applied in the field in the form of organic nitrogen. This nitrogen is converted into ammoniacal nitrogen and nitrate by the soil microorganisms before it is consumed by the plants (Walid et al., 2016).

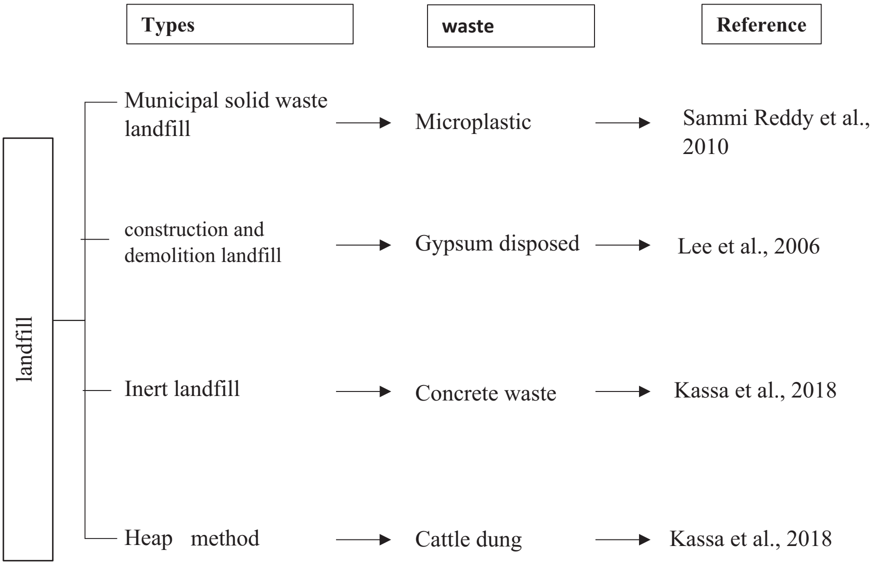


Nutrient Recovery from Farmyard Manure

Enormous nutrients are present in farmyard manure. About 30% nitrogen, 60–70% phosphorus, and 70% potassium were present initially in freshly prepared farmyard manure. Farmyard manure prepared by sheep and goat dung contain 3% nitrogen, 1% phosphorus pentaoxide, and 2% potassium dioxide. Poultry manure contains 3.03% N; 2.63% phosphorus pentaoxide, and 1.4% potassium dioxide. Plant crops such as potato, tomato, sweet-potato, carrot, radish, onion, sugarcane, rice, orange, banana, mango grow well in farmyard manure (Singhal et al., 2017).

Landfill

Landfill is termed as disposal of waste material that is buried in underground. It is one of the oldest methods of disposing the waste material. Landfill should be constructed by not affecting the groundwater. Municipal waste, industrial waste, and hazardous waste can be subjected to landfill. The components of landfill are bottom liner, cells (old and new), leachate collection system, storm water drainage, methane collection system, and ground water monitoring station. Though disposing waste by means of landfill may cause environmental issues, proper protocols should be followed before constructing the landfill (Pinjing et al., 2019).



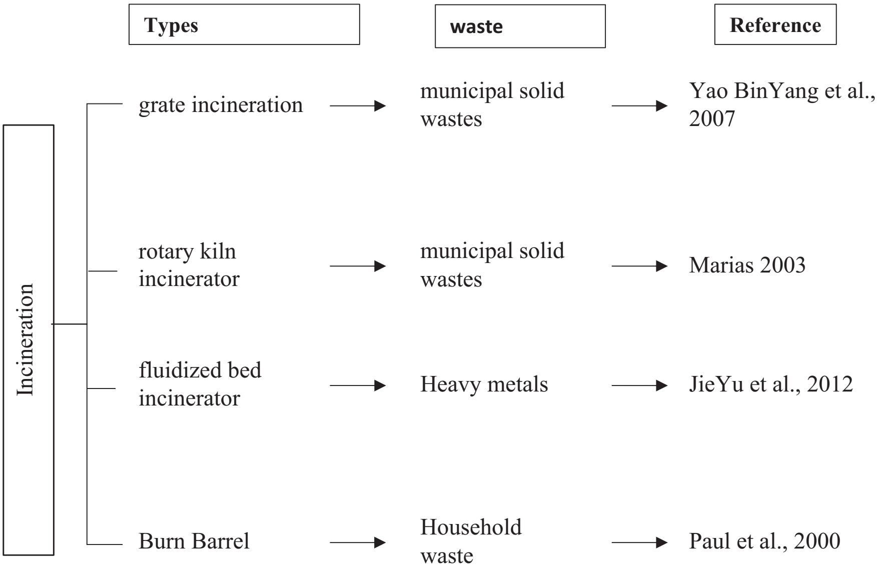
Types	waste	Reference
Municipal solid waste landfill	Microplastic	Sammi Reddy et al., 2010
construction and demolition landfill	Gypsum disposed	Lee et al., 2006
Inert landfill	Concrete waste	Kassa et al., 2018
Heap method	Cattle dung	Kassa et al., 2018

Nutrient Recovered from Landfill

According to the Environmental Protection Agency (EPA), the gas that is generated from landfill should be eco-friendly, which can be utilized as energy resource. Gas to energy facilities by landfill is as follows: (i) to generate electricity for small power plant; (ii) landfill gas in combination with fossil fuel, oil may used for heating purpose; and (iii) natural gas derived from landfill may processed though transmission pipeline for utilization (Naveen et al., 2017).

Incineration

Combustion of organic substance in waste material with the help of thermal treatment is termed as incineration. Through this process, the waste is converted into ash, flue, and gas. The heat generated by this process is used to generate electricity. During incineration, it converts the organic content to potential energy and remaining part is converted into ash. Particular type of waste such as clinical waste, hazardous waste, pathogenic waste, and toxic waste can be destroyed (Luke et al., 2018).

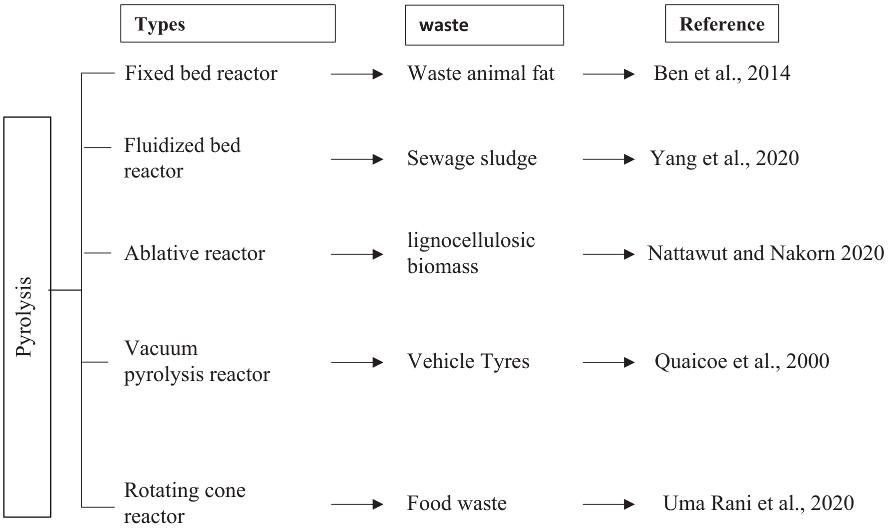


Nutrient Recovery from Incineration

Enormous amount of resources has been recovered from incineration such as silicate, aluminum, and iron oxide. By this process, phosphate recovery from ash is a very useful method. From the incinerated sludge, biofuels are leached from solid waste. After the completion of incineration process, the remaining ash material is either mixed with cement or concrete, and brick can be used as building material. The ash can also be melted and solidified as a ceramic material (Hongwei et al., 2019).

Pyrolysis

Pyrolysis is the process in which waste materials get decomposed at elevated temperature so that the volatile products are produced and leave carbon and char which can be used as soil-enriched material. This process is mainly used in chemical industries to produce ethylene, petroleum, coal, wood, etc. The main advantage of pyrolysis is to help convert the waste plastic to useable oil. Also, syngas and biochar are the by-products produced by the pyrolysis method (Muhammad et al., 2020).



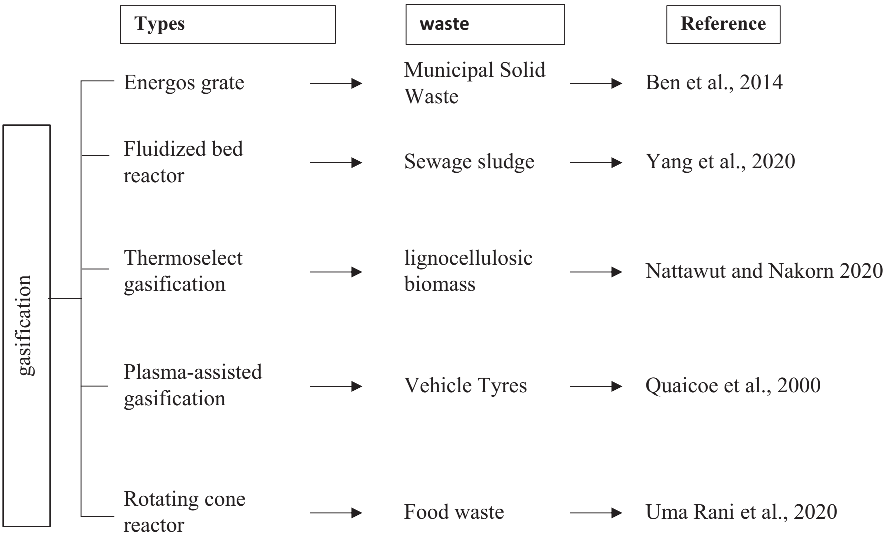
Types	waste	Reference
Fixed bed reactor	Waste animal fat	Ben et al., 2014
Fluidized bed reactor	Sewage sludge	Yang et al., 2020
Ablative reactor	lignocellulosic biomass	Nattawut and Nakorn 2020
Vacuum pyrolysis reactor	Vehicle Tyres	Quaicoe et al., 2000
Rotating cone reactor	Food waste	Uma Rani et al., 2020

Nutrient Recovery from Pyrolysis

Nutrients recovered from pyrolysis are syngas, biochar, bio oil, etc. Other nutrients such as carbon, hydrogen, nitrogen, and sulphur were determined after combustion. Main elements such as Na, Mg, Al, P, K, Ca, ash, and trace elements (V, Cr, Mn, Co, Ni, Cu, As, Cd, Sn, Sb, Tl, P) are recovered from pyrolysis. The biochar obtained from pyrolysis, alkali-pyrophosphates and sylvine, which were soluble to a sufficient proportion in water and/or in neutral ammonium citrate also act as good organic fertilizer. Also, syngas obtained from pyrolysis have enormous applications from households to industries (Tamer et al., 2020)

Gasification

The process of conversation of organic waste into carbon monoxide, hydrogen, and carbon dioxide is termed as gasification. This technique is accomplished by heating the material at high temperature with controlled amount of oxygen or steam. It acts as a feedstock for chemical conversion of valuable commercial products such as transportation fuels, chemicals, fertilizers, and even substitute natural gas. Many materials like metals and glass can be removed from MSW before it is subjected to the gasifier. The plastic that is removed from the solid waste can be utilized as feedstock for gasification (Shahabuddin et al., 2020)

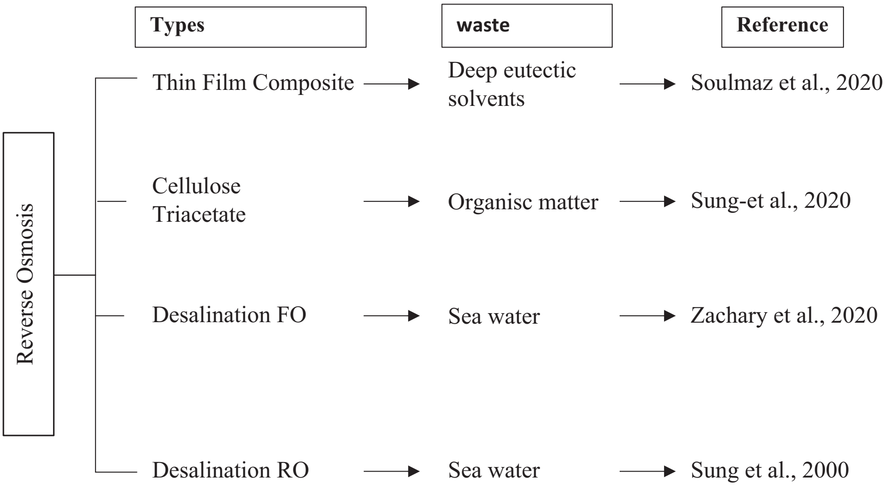


Nutrient Recovery from Gasification

During gasification processing, MSW utilize feedstock to produce syngas and recover energy from a steam circuit, seeking to recover more energy. Other products such as non-combustible material (ash) with carbon fused into glassy or vitreous residue. Volatile gases and steam are largely produced by gasification system. Steam cycle, engine, and gas turbine are generated by this system (Shayan et al., 2018)

Reverse Osmosis

It is the process of purification of drinking water by removing ions, large particles, and unwanted materials using permeable membrane. It works on the principle of thermodynamic parameter. Reverse osmosis is involved in the production of potable water by dissolving chemical and biological substances. The permeable membrane allows pure solvent across the membrane by retaining the ions and larger compounds (Gilles et al., 2018).



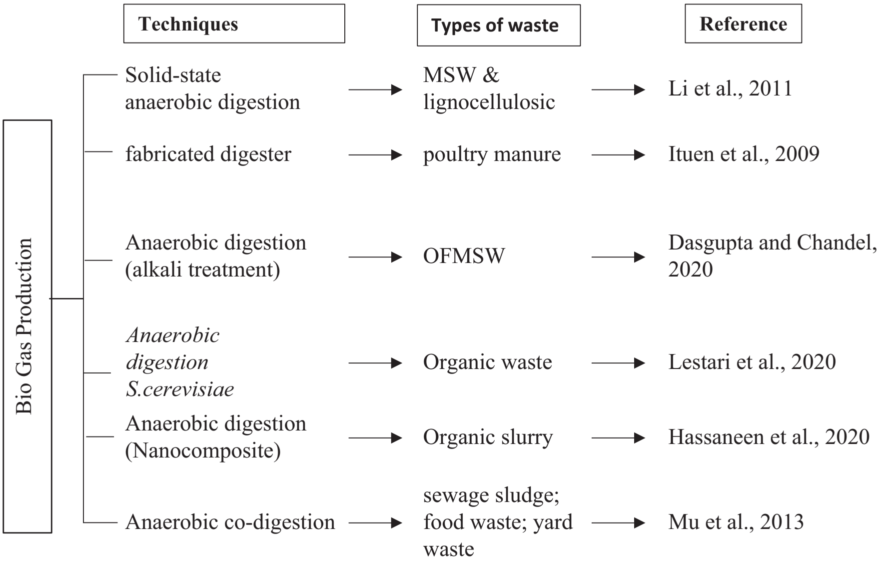
Nutrient Recovery from Reverse Osmosis

During this process, nutrients get recovered from the digested waste water due to the osmotic pressure gradient between the semipermeable membranes. By this way, various nutrients such as ammonium, phosphorus, sodium, magnesium, and sulphate can be obtained from the water digestate. It can be used to remove all the impurities present in wastewater and can be left as a safe disposal. It removes the contaminants present in water. This process used is in industries to clean water, or to convert brackish water, or to recover salts from water needed for industrial applications.

1.10 Nutrients Gain in Treating Solid Waste

Biogas Production

Organic waste such as agricultural waste, manure, municipal waste, plant material, sewage, green waste, or food waste get decomposed in the absence of oxygen and produce mixture of gases consisting of methane and carbon dioxide. Some examples are as follows.



Advantage of Biogas Plant

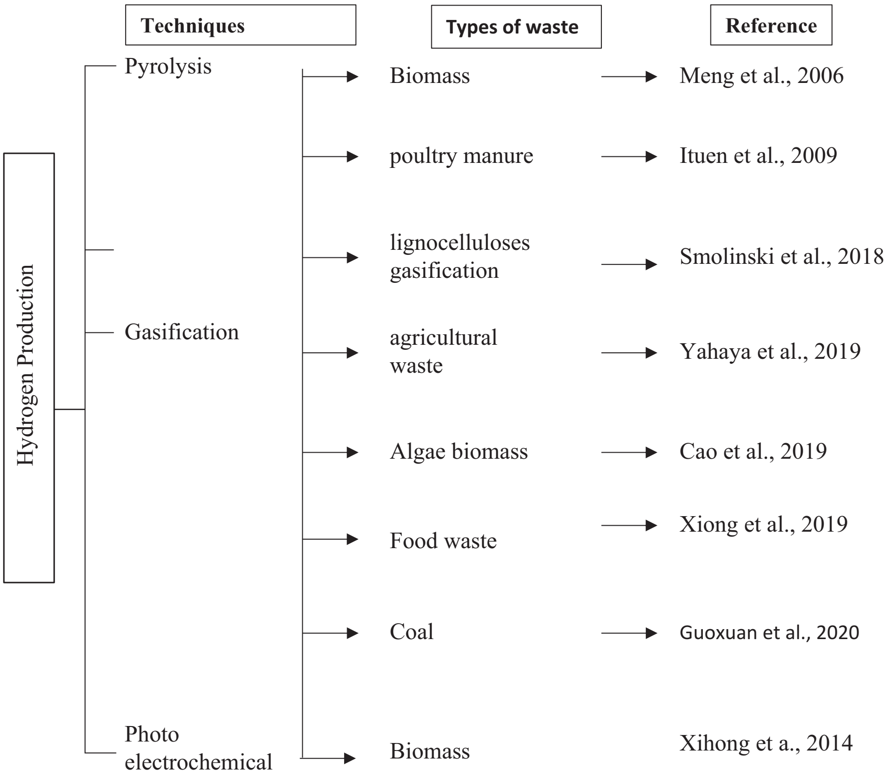
In a biogas plant, nutrient digestate is collected along with biogas. This digestate is rich in organic matter containing macro- and micro-nutrient, which act as a good plant fertilizer. The substrate, pH, and temperature greatly influence the nutrient recovery of digestate. The main substrates utilized in biogas plant are livestock manures and slurries, crop residues, and organic residues from agri-food processing industries (Peter, 2010).

The digestate processing consists of three main steps: (i) Solid phase from the liquid phase, the obtained solid material can be composted, or it straight act as a biofertilizer. (ii) Liquid phase obtained from digestate can follow nanofiltration, ultrafiltration, and reverse osmosis. This membrane technology can be used to produce purified water. (iii) Ammonia stripping, ion exchange, or struvite precipitation techniques can be applied to obtain complete digestate which requires high investment cost due to consumption of chemical reagents. The nutrient-rich digestate can be directly used in the field of biogas processes; hence, the end product is complete biofertilizer and marketable (Pooja et al., 2020).

Hydrogen Production

Overall 95% of hydrogen production is obtained from fossil fuels, stream, natural gas, coal gasification, electrolysis of water, etc. Hydrogen is produced from renewable energy sources by two ways: (i) power to gas; (ii) landfill to gas. Hydrogen gas is utilized in the production of ammonia, hydrodesulphurization, aromatization process, transport fuel, and compressed form is used in pipeline, cylinder, and trucks. The research undergone by the hydrogen production is as follows (Demei et al., 2020).

The first is blue hydrogen, which can be generated from natural gas with a carbon capturing unit; the second is green hydrogen, which can be produced from renewable sources; and the last one is gray hydrogen, which may be obtained from fossil fuels.

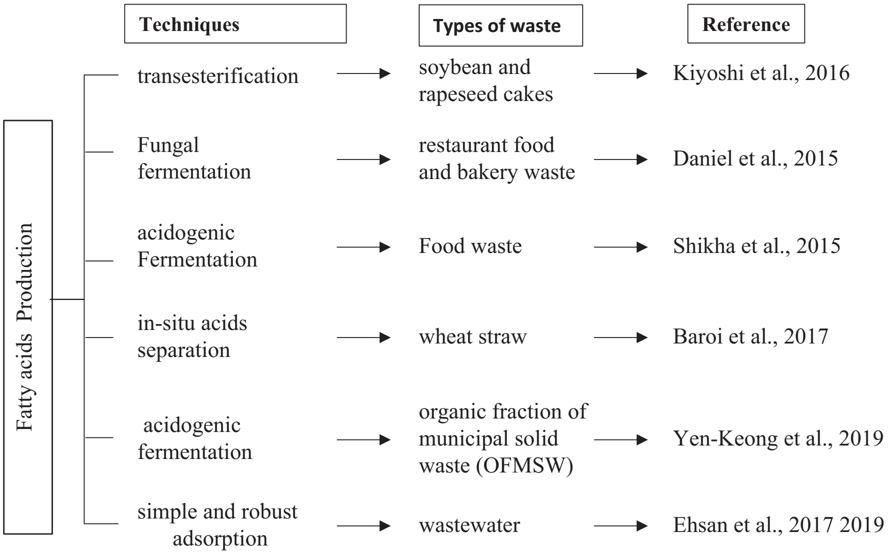


Advantage of Hydrogen Production

Hydrogen production could be obtained from different kinds of wastes such as cellulosic, starch, agriculture, food industry, olive mill, algal, and agricultural. Thus, preparing biohydrogen utilizing varieties of microorganisms helps to gain energy nutrient from the waste. Many kinds of technologies such as photolysis of water; dark fermentation, and photofermentation are involved in production of hydrogen. The nutrients present in all types of waste could be predominantly converted into energy (Yanan & Jianlong, 2016).

Fatty Acid Production

Fatty acids are high-caloric food stuff used for human consumption. It is primarily produced from raw materials such as plant seeds, soybean, rapeseed, and corn. During the manufacture of fatty acids, fats and oil, alkali foots, and spent clay were discharged at the end. It is further processed and utilized as synthetic resin paints, PVC plasticizers, textile oils, oils for rolling of iron and steel, printing inks, and food sugar esters. Fatty acids can also be prepared from baobab seeds, and aquatic algae act as feedstock for biodiesel production (Lijie et al., 2020).



Techniques	Types of waste	Reference
transesterification	soybean and rapeseed cakes	Kiyoshi et al., 2016
Fungal fermentation	restaurant food and bakery waste	Daniel et al., 2015
acidogenic Fermentation	Food waste	Shikha et al., 2015
in-situ acids separation	wheat straw	Baroi et al., 2017
acidogenic fermentation	organic fraction of municipal solid waste (OFMSW)	Yen-Keong et al., 2019
simple and robust adsorption	wastewater	Ehsan et al., 2017 2019

Advantage of Fatty Acid Production

Enormous amounts of nutrients were recovered from fatty acid, used vegetable oil, olive oil, and palm oil promisingly converted into biofuel (Dorado et al., 2002). Various techniques such as adsorption, solvent extraction, electrodialysis, reverse osmosis, nanofiltration, and membrane contractor were used to recover fatty acids. Wen-Yong Lou states that cooking oils containing 27.8 wt% high free fatty acids (FFAs) can be converted into biodiesel. Carbon and nitrogen source can also be generated from volatile fatty acids (Yan et al., 2018). The study by Bengtsson et al. (2017) reveals that a mixture of fermented VFA substrate having acetic, propionic, butyric, valeric, and caproic acids is utilized to produce PHA. Hence, many resourceful nutrient recovery has been gained from waste steam (Merve et al., 2018).

Lactic Acid Production

Lactic acid is produced from lactic acid bacteria by fermenting waste products such as molasses, fruit waste, and agro waste. It play an important role in dairy, baking technology, fish and meat processing industries, energy generation, agriculture, and bioremediation. About 1.3 billion of food get wasted from agriculture to human consumption. The food waste rich in carbohydrate acts as good source for lactic acid bacteria to grow (Sebastian et al., 2019).

Lactic acids production

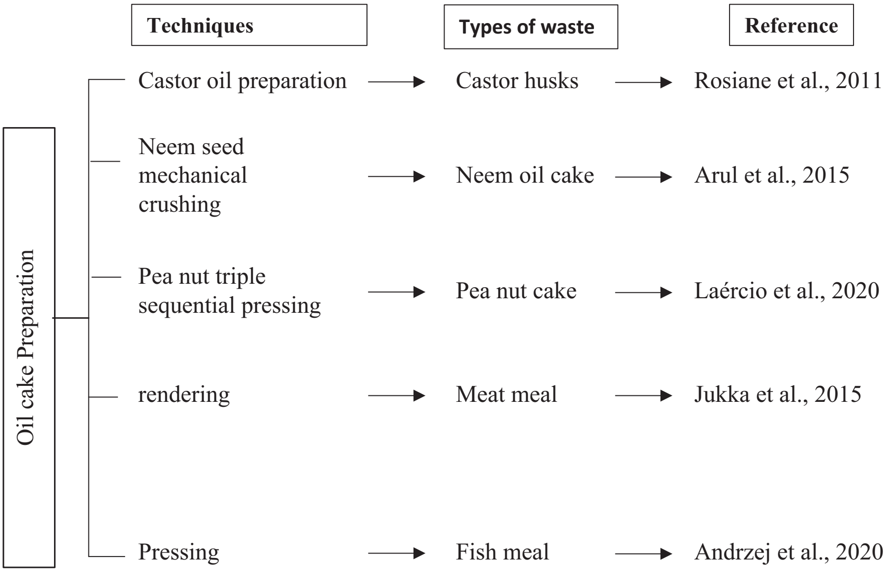
Techniques	**Types of waste**	**Reference**
saccharification and fermentation	sugarcane bagasse	Mukund et al., 2007
fermentation	agro-industrial waste	Parmjit and Shubhneet, 2015
saccharification	cardboard waste	Remedios et al., 2005
fermentation	range Peel Waste	Isabelde et al., 2020
acidogenic fermentation	organic fraction of municipal solid waste (OFMSW)	José Pablo López Gómez et al., 2020
fermentation	gelatinized starchy waste	Kridsada et al., 2020

Advantage of Lactic Acid Production

It acts as a descaling agent and antimicrobial agent. It is used as acidulant for deliming, in tanning industries. It has very useful medical applications as electrolyte and surgical sutures. Lactic acid has a wide variety of applications in food industries such as bakery products, soft drinks, dairy products, jams, jellies, and egg processed foods (Joachim et al., 2018).

Oil Cake

Oil cake is produced by separating the remaining solid portion in extracting oil from oilseeds and used as manure. Oil cakes are of two types: edible oil produced from groundnut cake, coconut cake, cotton seed cake, linseed cake, niger cake, rape seed cake, safflower cake, and sesamum cake; non-edible oil produced from castor cake, neem cake, kanranj cake, and Mahua cake. Oil cake could be used as feed for cattle or fertilizer for crops in horticulture. All the non-edible oil contains about 2–4% of nitrogen, 1% of phosphorus pentaoxide and potassium di oxide; edible oil contains 3–7% of nitrogen, 1–2% phosphorus pentaoxide and potassium di oxide (Rachana & Naik, 2018; Zineb et al., 2019)

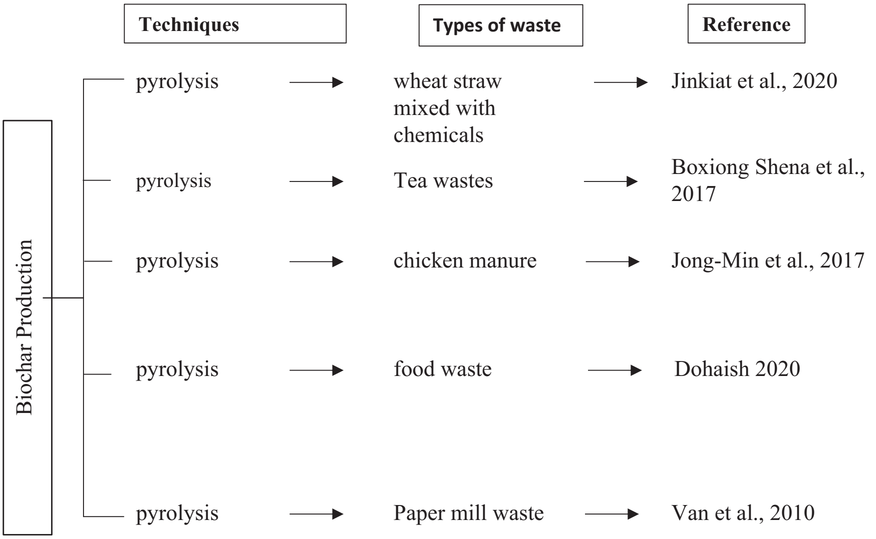


Advantage of Oil Cake

Oil cakes are rich in carbohydrates, fats, proteins, and minerals. It can be a valuable feed for poultry and other animals for proper functioning of metabolic processes. Therefore, the yield of milk, meat, and egg get increased. Feed oil cakes from certain seeds such as castor beans and tung nuts are toxic and are used as fertilizers. The husk that remains after the process of oil cake is enormously rich in fiber content. The fat in oil cakes is also usually a good source of linoleic acid, which is essential for animal metabolic processes (http://collections.infocollections.org/ukedu/en/d/Jnr18se/7.3.html).

Biochar

It is stable solid-rich carbon undergone in soil for more than thousands of years and obtained from thermochemical conversion of biomass with oxygen-limited environment. It is used as best amendments for soil to improve its fertility, agricultural productivity, and restrict the soil-borne diseases. It maintains the pH, nutrient, organic matter, and structure of the soil. It also enhances the growth of microorganism in the soil (Nai-Yun et al., 2020).



Biochar Production

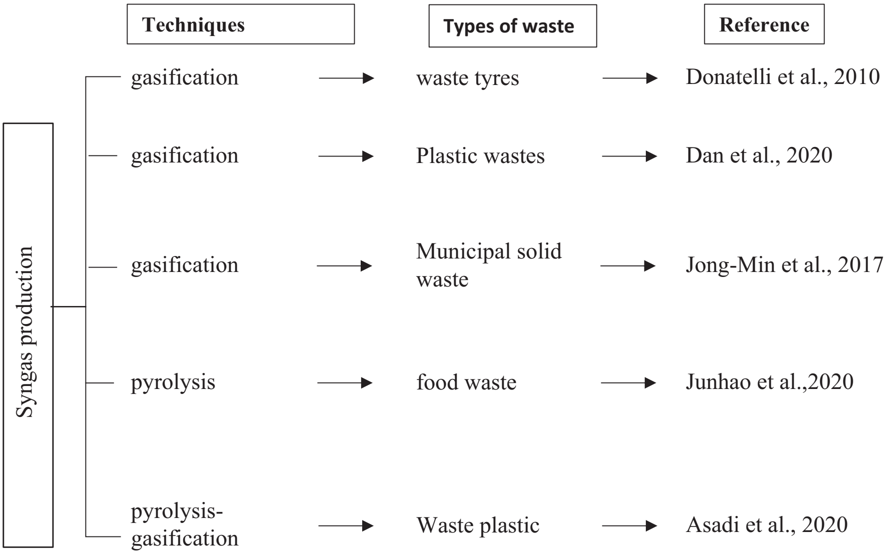
Techniques	Types of waste	Reference
pyrolysis	wheat straw mixed with chemicals	Jinkiat et al., 2020
pyrolysis	Tea wastes	Boxiong Shena et al., 2017
pyrolysis	chicken manure	Jong-Min et al., 2017
pyrolysis	food waste	Dohaish 2020
pyrolysis	Paper mill waste	Van et al., 2010

Advantage of Biochar

During pyrolysis the solid residue get reduced. It results in the production of potential fuel with high energetic value. Biochar produced through pyrolysis acts as good fertilizer. It minimizes the use of chemical fertilizer. It improves the soil fertility by enhancing the nutrient level and also reduces acidity of the soil. Many organic pollutants are being sequestered by using biochar. Soil improved using biochar will able to retain the soil nutrients such as magnesium, calcium, phosphorus, nitrogen, and carbon (Ahmed et al., 2019).

Syngas

Syngas is the mixture of hydrogen and carbon monoxide also with small quantity of hydrocarbon, carbon dioxide, and methane. It is produced by anaerobic digestion or biogasification by degrading organic substrate by bacteria. Among total generation of municipal solid waste, three-fourths of them went for landfill or incinerated. As these methods lead to many environmental problems, gasification process was chosen by many countries. Municipal solid waste can be converted into usable syngas through gasification process. Therefore, many commercial products such as transportation fuels, chemicals, and fertilizers can be produced. The ash generated through gasification process is used for making cement, roofing shingles, and as an asphalt filler. Non-degradable plastic waste can act as excellent feedstock for gasification (Gabriele & Siglinda, 2020).



Advantage of Syngas

Syngas is used for the production of ammonia and fertilizer. During this process, ethanol produced from syngas is a marketable and needed product. The generation of hydrogen during the process may be used as fuel for combustion engines. Potential biofuel produced during syngas production may be used for generating electricity and household usage. It is considered to be independent power supply. It is economically efficient by combining heat and electricity (Steven et al., 2018).

2 Conclusion

Even though various techniques are followed for managing solid waste generation, still we cannot reduce the problem. More attention has to be paid to initiate the nutrient recovery by means of different techniques. Apart from nutrient recovering technique 3Rs should be followed by the people to minimize the generation of waste. Not only single techniques were effectively involved in recovering nutrient numerous techniques such as landfill, pyrolysis, gasification, vermicomposting, and composting. By this nutrient, there is increase in soil amendment, fertility of soil, and plant growth promotion can be achieved. Considering the economic feasibility, the technique should be selected to recover maximum nutrient recovery with minimal input. As we are in a developing country, practicing eco-friendly techniques such as composting, anaerobic decomposition, and the usage of biodegradable materials is advisable for a sustainable future. This chapter presents the methods and technical approach of nutrient recovery form solid waste.

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A Bird's Eye View on Sustainable Management Solutions for Non-degradable Plastic Wastes

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Abstract Plastics are inert materials that are resistant to environmental and mechanical stress. The immense use of plastics has increased over the past decade. In addition, utilization of non-degradable polymers showed the impact on health of the terrestrial and aquatic lives. In general physical or chemical recycling process, which reduces the accumulation of plastic wastes while the decomposition of the plastics was majorly attained by the process of incineration. Pyrolysis, chemical degradation, and biological degradation are widely explored methods to reduce the precipitation of polymer waste. Energy recovery through chemo-pyrolysis of plastics aids by the chemical degradation to produce liquid fuel, wax, and other by-products which might be used in various applications. The depolymerized plastics can be made into a value-added product by combining it with biodegradable substance which changes the physical and chemical characteristics of plastics. The current management of plastic waste might be a tentative relief, but we need a completely sustainable solution. This chapter is intended to combine chemical and biological methods developed for plastic waste management.

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1 Introduction

Plastics are polymers synthesized from the respective monomers and they exhibit two-dimensional linear to three-dimensional branched or cross-linked structure. Plastics are carbon compounds derived from renewable and non-renewable sources including biomass. The characteristics of polymer are low molecular weight, economical production, transparency, hardness, and processability. The unique characteristics of plastics, namely, its resistance to high temperature and its resistance to chemicals and light have revolutionized the world as it is also available at low costs. It has increased the demand for plastics to several million tons. During the course of the development, which was considered as a revolution, it became a threat over a while. Today plastic is extensively utilized for household, textile, packing equipment in electricity and transportation, aerospace, and sheets. In Europe, about 39.9% of plastics are used for packaging and 19.7% for construction of buildings. Plastic waste not only causes serious health problems but also creates social and environmental problems (Banu et al., 2020). Plastics are mostly non-biodegradable polymers along with other components (Santaweesuk & Janyalertadun, 2017). The plastics industry has had steady growth for more than 50 years. The estimation of overall plastic manufacturing and its market is expected to be 311 MT in 2016 and US dollars 654 billion respectively. In particular, half of the US dollars 375 billion tons of the plastics at a projected 2020 market value has seen tremendous growth in packaging. Globally, 8 billion tons of polymers is disposed in the oceans each year. Microplastics, a form of plastics enter the ecosystem, are eventually consumed by humans and aquatic animals (Fox & Stacey, 2019). European Union (EU) promoting plastic recycling of municipal packaging waste must be, improved from 65% to 75% of packing waste, including plastics by 2030 (Fivga & Dimitriou, 2018). PET is a polyfunctional polymer that has numerous applications in both domestic and industries. Large amounts of post-consumer PET generated as a major municipal solid waste cause environmental problems due to overuse. These include soft drink bottles, food containers, and many others (Al-Sabagh et al., 2016a, 2016b).

Apart from the danger caused by plastic, its hydrophobicity attracts pollutants such as pesticides, metals, and PAHs which are mostly categorized under persistent organic pollutants (POPs). Plastic waste hence requires treatment methods instead of management techniques. PET waste can be recycled through alternative use: the ensuing process re-extrusion as a primary, mechanical method as secondary, chemical depolymerization as tertiary, and energy recovery as quaternary for the management of polymer wastes (Drah et al., 2016). Almost 70% of post-consumer PET is utilized by fiber industries and 4% is used to recover terephthalic acid using chemical depolymerization method. These polyethylene terephthalate waste recycling methods are more sustainable compared to usual land filling and combustion (Jeya et al., 2020). Recycling through biological and chemical procedures along with physical methods are necessary to reduce pollution as an economic alternative.

The diversity of microplastics present a challenge to study them as synthetic analogs obtained from petrochemical sources that have globally accepted definition over 5 nm in size. Plastics refer to a broad range of materials, each with their own rare physical properties and chemical composition. About 90% of the plastics produced worldwide are among one of six types namely - polyethylene terephthalate, polypropylene, HDPE, polyvinyl chloride, LDPE, and polystyrene - (Zhou et al., 2019; Kosuth et al., 2018). The physical method is used in both primary and secondary recycling techniques. The products of plastic waste are processed in primary recycling, according to original material. Nevertheless, in secondary recycling, polymer waste is transformed to another product without changing the nature of the polymer. Tertiary recycling is converting polymer waste into new products. Catalyst degradation refers to heat or gas fractions being liquid or gaseous fractions (Nisar et al., 2020). Plastics are primarily made from the petrochemicals, and plastics become a source of energy by using the pyrolysis process that is then reused as an alternative fuel (Wang et al., 2017). Catalytic pyrolysis is an encouraging technology that converts polymer wastes into liquids (plastic fuel) as a value-added product (Fang et al., 2018a). Therefore, it is commonly viewed as eco-friendly technology to dispose plastic waste.

2 Health Impairments of Plastics and Microplastics

Human exposure to plastic waste damages human health by direct ingestion or tapping animals and their various additives and contaminated foods (Cook & Halden, 2020). For instance, land filling and incineration were the conventional methods used to treat the plastic wastes. Incineration of plastic wastes is the commonly used method which produces toxic gases that cause severe illness to living beings (Pramila & Ramesh, 2011; Moharir & Kumar, 2019). Apart from the danger caused by the plastic, the hydrophobicity of the polymer networks attracts pollutants such as pesticides, metals, and PAHs which are mostly classified under POPs (Rochman et al., 2013; Paço et al., 2018). The plastic wastes hence require treatment methods instead of management techniques.

Nowadays, particles of microplastics contains various types of polymers in different sizes, shapes, and concentrations in marine and freshwater environment (Campanale et al., 2020), atmosphere (Prata, 2018), drinking water (Pivokonsky et al., 2018), food, and biota (Rezania et al., 2018). Human exposure to microplastics results in a greater personal vulnerability as they release toxic contaminants and pathogenic organisms to freshwater (Rodrigues et al., 2018), soil (Watteau et al., 2018), and sediment (Abidli et al., 2018; Reed et al., 2018). A study revealed an evidence of microplastics in fish species (Barboza et al., 2020). All the biochemical analysis revealed that microplastics were found in the gastrointestinal tract, spinal muscles, and gills. The microplastics found in adipose tissue of fish (i.e., spinal muscles) also highlight the need for further evaluation of the human diet. The estimated microplastics intake are from 39,000 to 52,000 particles per person per year, based on food consumption (Cox et al., 2019). The human body parts affected by microplastics are digestive and excretory systems (Stock et al., 2019; Liao & Yang, 2020; Inkielewicz-Stepniak et al., 2018; Smith et al., 2018). Exposure to different groups of experimental animal models such as fish, crustaceans, and molluscs have suggested that concentration may be triggered by exposure to 0.001 mg/L- including microplastic physical and chemical toxicity, changes in behavior, genetic toxicity, antioxidant, reproductive disorders, oxidative stress, and decrease in population growth rate- (Zhu et al., 2019; Qiao et al., 2019; Yin et al., 2018; Guilhermino et al., 2018; Barboza et al., 2018; Sá et al., 2018).

The balance of microplastic in the fish species causes danger to consumers' health as small plastic transfer contaminants can enter into fish tissues (Fossi et al., 2018). A total of 90% of the detected microplastics and pigment particles <5 μm and approximately 40% <1.5 μm are considered toxicological features in humans with oral intake of microplastics (Oßmann et al., 2018). Microplastic, pigmented, and additive particles are found in mineral water bottled samples with the least analyzed particle size of 1 μm. Ingestion by one person per one day is estimated to be 26–130 air bone microplastics and therefore affects the human respiratory system (Prata, 2018). Humans encounter health hazards from microplastics through food, drink, and air; hence the human respiratory system is affected (Catarino et al., 2018; Gasperi et al., 2018). Based on the air model using a mannequin, only a male with light activity is expected to inhale 272 small polymers per day (Vianello et al., 2019). Skin permeation by microplastics is speculated that nanoplastics (<100 nm) may cross the skin (Revel et al., 2018).

3 Physical Recycling Methods

3.1 Primary Recycling

This method is reprocessing of post-consumer plastic wastes to provide recycled material for similar application (Rahimi & García, 2017). Manufacturing of plastic bottles in combination with recycled PET (rPET) and maiden polymer is a significant example of primary recycling. Primary recycling takes place due to its low cost, and it is the easiest and the most popular method (Grigore, 2017). The product refers to being reused as its original system.

3.2 Secondary or Mechanical Recycling

Secondary recycling is also called mechanical recycling. Plastic waste can be cut, shredded, or washed into granulated flakes or quality particles for production and then melted to produce new products (Singh et al., 2017). The end products would be re-melted and reprocessed; the alteration of the polymer does not involve the

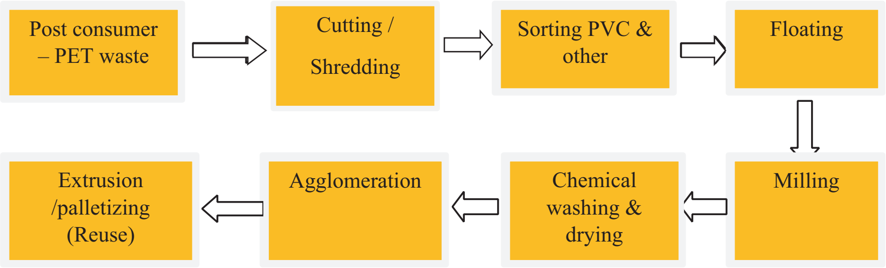


Fig. 1 Mechanical recycling methods

mechanical recycling method (Grigore, 2017). Mechanical recycling steps include the cataloguing and separating wastes, eliminating contaminants, and reducing volume by crushing and grinding, extrusing by heat, and renovating (Chen et al., 2015). Further contaminated and complex the waste is, the tougher it is to recycle mechanically. Secondary (mechanical) recycling provides materials for various applications from the pure plastics that was made from most post-consumer plastic wastes recovered are reused through this process (Rahimi & García, 2017). The recycling plastic waste protects higher energy than the burning process plastic waste can be created. Mechanical recycling of PET waste in melting and extrusion of PET waste into fibers produces the product with limited application (Diaz-Silvarrey et al., 2018).

Mechanical recycling, in particular, can contribute up to 15–20% of all plastic waste categories (Fig. 1). Mechanical recycling mechanism made up of converting plastic waste into a useful product exhibits an identical character in comparison with maiden polyester (Sági et al., 2018; Vanapalli et al., 2019). Mechanical recycling can be used in thermoplastics, and it can be easily reused in manufacturing process. Mechanical recycling involves the following steps (Thomas et al., 2020):

Plastic is extruded into strands and then cut into pellets before it is sold in the market. By doing so, a clear grade PET of high quality is produced which can compete with virgin PET. Upgrade the molecular weight of the recycled PET pellets. Removing impurities from post-consumption PET in an important step in the process of mechanical recycling. Elimination of polyethylene terephthalate contamination involves several processes, and post-consumption PET bottles are sorted, ground, and washed clean (Ragaert et al., 2017).

Disadvantage:

(i) The main problem with melting re-processing of any PET or any other polymer wastes is to reduction of melting viscosity caused by thermal and hydrolytic decomposition of the polymer chain.
(ii) Mechanical recycling produces low quality materials upon continuous recycling (Vollmer et al., 2020).

4 Tertiary or Chemical Recycling of Polymer Wastes

Chemical recycling is also known as, 'tertiary recycling' promoted by chemical degradation to retrieve the raw material or depolymerised products of the polymer component in the plastic or getting oligomers from the polymers, for example pyrolysis, which means converting plastic waste into monomer, another chemical fuel with the help of mostly heterogeneous catalysts such as metal oxides or zeolites containing metal sites, heat and/or pressure (Rahimi & García, 2017). Chemical recycling or depolymerization involves breaking down the chemical binding in the polymer chains using high temperature and pressure with the support of chemical catalysts and/or biological enzymes at ambient conditions (Pohjakallio & Vuorinen, 2020). For example, in terylene and nylon (PA), the common depolymerization is to break down the ester (-COO-) or amide (-CONH-) linkages, respectively, using proper acidic/basic/catalytic/thermal conditions. Whereas polyolefin's (polyethylene and polypropylene) most stable carbon bonds need to be broken down using cracking catalysts. For polyesters or polyamides, commonly the solvolytic chain cleavage could be used in the existence of protic solvents such as water, alcohols, and glycols. By using this procedure either complete depolymerization or degradation into its monomers or a limited depolymerization to its oligomers can be achieved under optimized conditions or by employing suitable cracking catalysts (Fig. 2).

4.1 *Hydrolysis of Post-Consumer PET Waste*

Acid- or base-catalyzed degradation of hydrolysable polymers is one of the chemical recycling methods (Grigore, 2017). This includes the reaction of polyethylene terephthalate waste and water in an acid, alkali, or neutral environment. The monomer leads to total polymerization. The disadvantage of using the hydrolysis method is design cost of the reactor to withstand high pressure, high temperature (200–250 °C) and pressures (1.4–2 MPa), and the longer time to complete depolymerization (Fig. 3).

The hydrolysis under alkaline condition is very suitable for green chemistry, and in this method, the efficiency of the hydrolysis process is required for a mild reaction condition. The main products of the reaction are terephthalic acid (TPA) and ethylene glycol (EG) (Zanela et al., 2018). Acid hydrolysis of the PET waste, with water and acid catalysts, then react to produce TPA and EG. This reaction is performed under strongly acidic conditions (87% of H_2SO_4, H_3PO_4, and 7–13 M HNO_3). The disadvantage of hydrolysis is that the reaction condition is high pressure and temperature (1.4–2 MN/m^2) (Raheem et al., 2019). The neutral hydrolysis method is without using the catalyst in the reaction carried out at sub (300 °C) and supercritical (385 °C). The reaction time is 1–60 min and the yields are obtained TPA 62.9% and 93.5% (Goto et al., 2010).

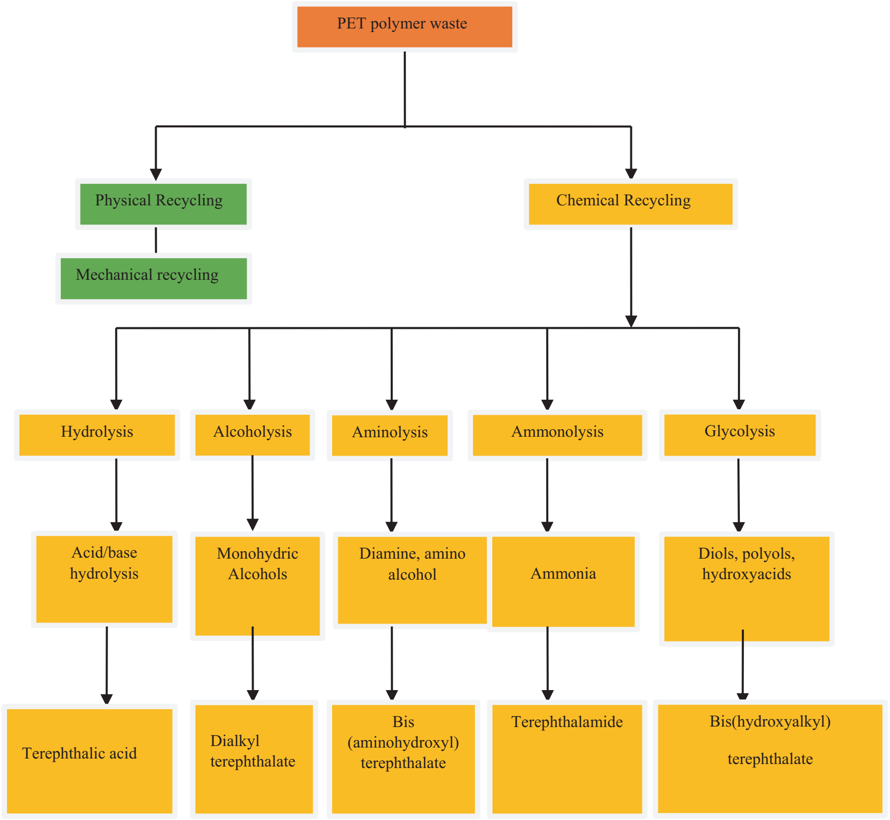
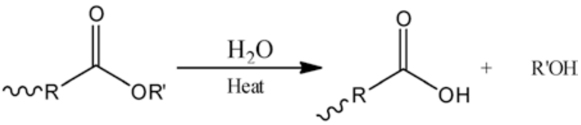


Fig. 2 Recycling methods of PET polymer wastes recycling method

Fig. 3 PET hydrolysis reaction



4.2 Recycling of PET Wastes Through Alcoholysis or Solvolysis

Alcoholysis or solvolysis is involved in the degradation of hydrolysable polymers such as polyester or polyamides using protic organic solvents such as methanol and ethanol; dihydric alcohols such as glycols and polyols such as glycerol. This process is also called transesterification process. Most of these reactions are catalyzed by Lewis acid catalyst like Zn-salts. Three types of dihydric alcohols are used in an investigation for the alcoholysis of PET wastes with different temperatures and degradation catalysts (Zhou et al., 2019). Higher alcoholization activity is found good with lower alcohols, whereas dipropylene glycol (DPG) alcoholization activity is lower. However, dihydric alcohols exhibit good thermal stability and are environment friendly, and hence they are used in the chemical industry for the degradation of PET wastes. Alcoholysis of PET waste using methanol and ethylene glycol dispersion in ultra-small ZnO nanoparticle having diameter of 4 nm in size is used as a pseudo homogeneous catalyst. The methanolysis and glycolysis of PET using ZnO nanoparticles at 170 °C at 15 min yielded 95% dimethyl terephthalate (DMT). The efficiency of PET methanolysis is found to be 553 g of PET h^{-1} (g ZnO)$^{-1}$, and the advantage of using pseudo homogeneous ZnO catalysts is that it can be easily recovered and reusability is highly efficient, economical, and environment friendly (Du et al., 2020). In methanolysis process, the PET degradation at high pressures 20 and 40 atm and degradation of PET at 180 and 280 °C yielded dimethyl terephthalate (DMT) and ethylene glycol. This process requires high cost due to high pressure reactor design (Ragaert et al., 2017).

4.3 Ammonolysis and Aminolysis of PET Waste into Terephthalamides

Chemical recycling is an effective method namely aminolysis of hydrolysable polymer wastes in which aqueous ammonia, aliphatic amino alcohols, and diamines are commonly used as solvents for the aminolysis. However, in most of the cases, different amines have been used to get derivatives of terephthalamides (Fig. 4) (Goje

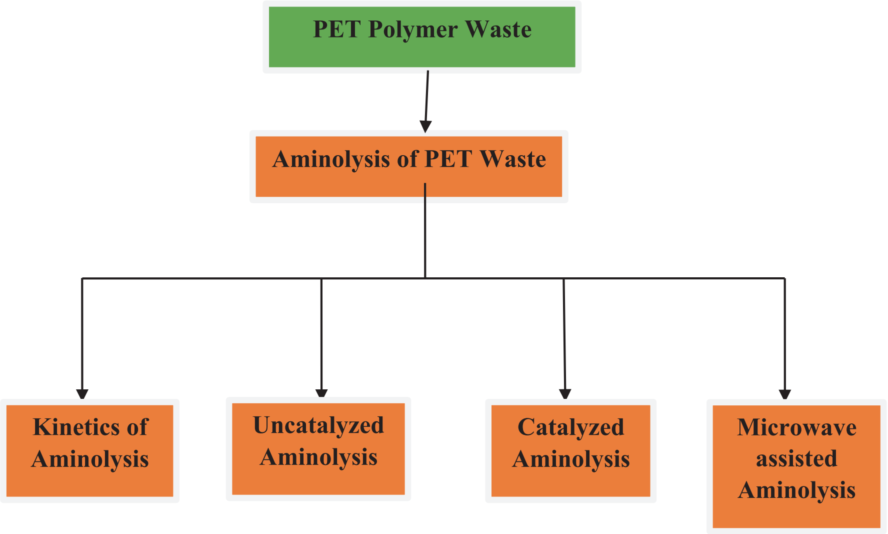


Fig. 4 Scheme of aminolysis of PET waste

et al., 2005). There are many amine derivatives used as the solvents in the aminolysis degradation and amino alcohols of ethyl and propylene, ethylenediamine (Hoang & Dang, 2013) 3-amino-1-propanol, and hydrazine monohydrate (HMH) have been reported (George & Kurian, 2016). Sodium acetate catalyst is used in all cases of the depolymerization method. Diethanolamine and 1-amino-2-propanol yielded pure products of terephthalamide (THETA) derivative and terephthalic acid (TPA) (Shah et al., 2012).

Aminolysis of PET waste effected by ethylene diamine, which produced α, ω-amino-oligo (ethylene terephthalamide) derivative under UV radiation required 24 h for degradation, microwave 6–7 min, and solar power 8 days. Microwave and ultraviolet radiation yielded 100% depolymerized product and 100% conversion, but solar energy is the most eco-friendly as compared to all three techniques (More et al., 2016).

Aminoethylene ethanolamine (AEEA) has served as a good aminolyting agent at temperature of 180 °C using zinc acetate as a catalyst and the same aminolyting agent showed complete degradation within 30 min in 500 watts MW irradiation (Jamdar et al., 2017). The oligomer product is obtained by yield (53%), and then the product is applied to the coating. Some of aminolyting PET degradation have been studied utilizing deep eutectic solvents. For instance, depolymerization of PET waste combined deep eutectic solvent (DES) using diethanolamine, ethanolamine, and the choline chloride-$ZnCl_2$/urea as a catalyst for the high yield of the three monomer diamide products is 82%, 95%, and 83%, respectively, in shorter reaction time. This is a high activity and relatively degraded reaction state (Musale & Shukla, 2016).

Aqueous ammonia reacts with polyethylene terephthalate in an ethylene glycol to produce terephthalamide as a single monomer which can be further transmuted into terephthalic acid or dehydrated to form dinitrile derivative followed by reduction to p-xylylene diamine or 1,4-bis (aminoethyl) cyclohexane (Raheem et al., 2019). The PET: NH_3 ratio at 70 °C is 1:6 and the low pressure and EG yields an 87% yield at 80 °C temperature. Ammonolysis has been used successfully for post-consumer PET waste.

4.4 Depolymerization of PET Wastes Using Glycolysis

Glycolysis is a class of transesterification depolymerization of hydrolysable polymers such as polyesters and polyamides using glycols or diols catalyzed by Lewis acid catalysts (Fig. 5). It is one of the primary chemical recycling methods for PET fiber wastes into the BHET, a monomer used for PET synthesis (Sheel & Pant, 2019; Bary et al., 2019).

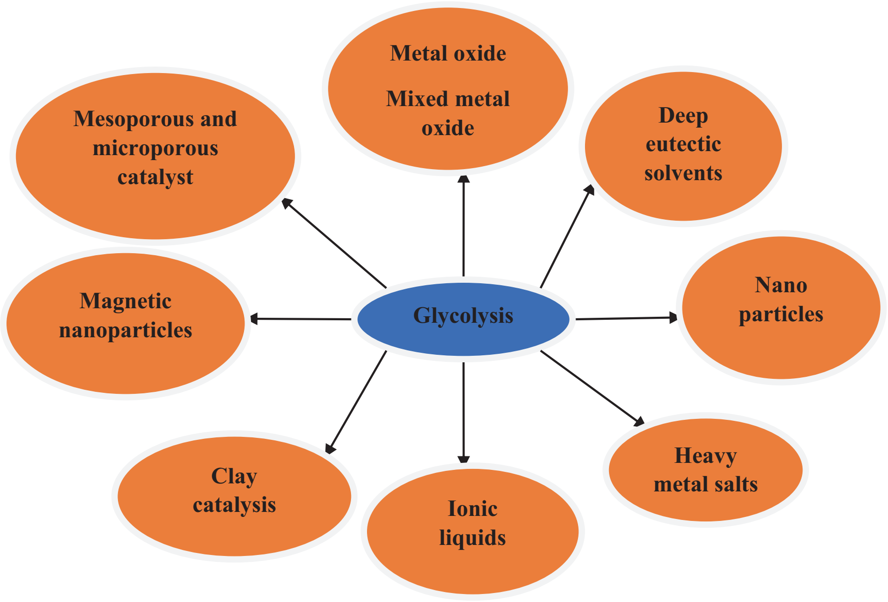


Fig. 5 Scheme of glycolysis

Heavy Metal Salt and Ionic Liquids

Polyoxometalates are used as catalysts. The catalyst is easily separated from the solvent and the atmospheric pressure is 185 °C for 30 min. Zinc and lead are both heavy metal salts with a negative effect on the environment, which can be used as a high-pressure catalyst for PET glycolysis (Al-Sabagh et al., 2016a, 2016b). Zinc acetate catalyst depolymerized PET with thiodiglycol to yield bis [2-(2-hydroxyethylthioethyl terephthalate)], and the depolymerized product has been explored for anti-corrosion activity for steel (Yasir et al., 2017). Mixed metal oxides are an innovative catalyst of spinal yielding a high proportion of BHET (92.2 mol %) under mild reaction conditions (260 °C and 5 atm), and mixed oxide spines have shown excellent catalytic performance toward glycolysis (Imran et al., 2013).

Metal-containing ionic fluids were scrutinized as an effective catalyst for PET glycolysis. For instance, copper and zinc acetate comprising ionic liquids such as 1-butyl-3-methylimidazolium were used for the digestion of 100% PET (Al-Sabagh et al., 2014a, 2014b). In another investigation, Co and Zn containing ionic liquids have exhibited excellent catalytic activity under the milder reaction condition, and yield of BHET was found to be higher and it can be easily separated from the reaction medium. These ionic liquid catalysts have high purity and have good thermal stability under reaction conditions (Wang et al., 2015a).

Deep Eutectic Solvent and Microwave Promoted Depolymerization

The deep eutectic solvents (DESs) comprised of urea and $ZnCl_2$ have been used to depolymerize PET into BHET. The DES of urea-$ZnCl_2$ is a low cost and has the similar properties of the ionic liquids (Wang et al., 2015b). The maximum yield of bis(2-hydroxyethyl) terephthalate was accomplished up to 88% using DES at 180 °C (Sert et al., 2019). The DES containing DBU as an organic base combined with $Zn(OAc)_2$ is used as catalyst for glycolysis. This catalyst showed the acid-base synergistic effect between 1,3-DMU and $Zn(OAc)_2$ in which the acidic site can activate ester carbonyl and the basic site can facilitate ester bond cleavage. The investigation showed DES is an effective catalyst for PET glycolysis. The catalytic system is a shrink-core model, which showed the activation energy upto 148.89 KJ/mol (Liu et al., 2018).

The glycolysis of PET wastes can be promoted in shorter reaction time under microwave irradiation using the 5:1 ratio of EG:PET and $Zn(OAc)_2$ catalyst with microwave power of 500w and induced temperature at 196 °C afforded 78% of BHET (Sangalang et al., 2015; Chen et al., 2015). A novel imidazolium halometallate ionic liquid is found as a very exciting catalyst for the depolymerization of PET (Cot et al., 2019).

Porous and Non-porous Recoverable Nanoparticle Catalysts

The catalytic system based on porous materials always provides effective catalytic support owing to its higher surface area, shape selectivity, and tunable catalytic activity. Non-porous metal oxides including alumina and silica could also be used as support for loading catalytic sites. A recoverable superparamagnetic γ-Fe_2O_3 nanoparticle used for glycolysis, which carried out at 300 °C and 1.1 MPa pressure with 0.05 wt% of catalysts/PET ratio (Bartolome et al., 2014). Ultra-small cobalt nanoparticles have been used for the glycolysis of PET wastes using ethylene glycol (Veregue et al., 2018). Apart from acidic metal oxides, the basic metal oxides could also be used for the glycolysis of PET wastes. For instance, the hydrotalcites containing Mg-Al mixed oxide catalysts have been used as a base catalyst for PET depolymerization (Chen et al., 2012).

Microporous aluminosilicate materials such as zeolites are developed to replace conventional heavy metal catalysts (Shukla et al., 2008). Y-zeolite is more active for PET depolymerization due to the high Si/Al ratio. The common clay material such as bentonite and kaolin impregnated with Al^{3+}, Fe^{3+}, and Zn^{2+} have been used as a catalyst for the depolymerization post-consumer PET waste (Jeya et al., 2017; Jeya et al., 2020). The composite catalysts containing ionic liquid and clay have been used for PET waste depolymerization (Al-Sabagh et al., 2015).

Fe_3O_4 magnetic nanoparticle is deposited on boron nitride nanosheet (h-BNNS) and is used for glycolysis. The graphene-type nanosheets with boron and nitrogen act as Lewis acidic and basic sites for activating the ester linkages in the polyesters (Nabid et al., 2019). Super paramagnetic γ-Fe_2O_3/nitrogen-doped graphene is used as a hybrid material and bifunctional catalyst as the first report appeared for glycolysis of PET wastes (Bartolome et al., 2014). Silica-coated magnetic Fe_3O_4 as a magnetic recoverable nanocatalyst provides nearly 100% of yield in the glycolysis at 180 °C (Cano et al., 2020). The efficient nickel nanocatalysts are synthesized using the Pechini method at 500 °C with 5 h of the reaction (Rezende et al., 2019). Some of the catalytic systems announced for the glycolysis of PET wastes are catalogued in Table 1.

Metal Oxide Catalysts

The basic catalyst derived from 1% of ostrich eggshells used for PET glycolysis at 192 °C for about 2 h with fraction of catalysts-PET at 1:10 and the weight ratio of PET-ethylene glycol 1:15 yielded 76.4% of BHET (Yunita et al., 2019). The presence of Zn/Al mixed oxide as a bimetallic catalyst has been used for evaluation of glycolysis reaction of PET waste fiber (Chen et al., 2012). The metal oxides derived from disposed materials have been employed as the catalyst for depolymerization of PET wastes. The mixed oxide (Co/RZnO) from spent Li-ion batteries was prepared by mechanical milling of 2.5 wt% of RCoO on RZnO the Co/RZnO as catalyst the high yield of the BHET (80%) (Fuentes et al., 2019). Supercritical ethanolysis was catalyzed by simple and cheapest metal oxide, cobalt and nickel oxide catalysts in the conversion of PET to give 93% yield (Fernandes et al., 2020).

Table 1 Comparison of reported nanoparticle catalysts

Catalysts	Temp (°C)	Amount of catalysts/PET	Time (mins)	Amount of EG/PET	BHET yield	References
Fe_3O_4-MWCNT	190	20/2	120	20/2	100	Al-Sabagh et al. (2016a, 2016b)
γ-Fe_2O_3	255	0.01	60	_	>90	Bartolome et al. (2014)
$ZnMn_2O_4$	260	1.0	60	17.2	>90	Imran et al. (2013)
[bimim] MCl_4	178	1/5	240	20/5	100	Wang et al. (2015a, 2015b)
[Mg-Zn]-Al LDH	190	½	180	20/2	100	Eshaq and Elmetwally (2016)
Go-Mn_3O_4	300	0.003/0.3	80	1.1/0.3	>96	Park et al. (2012)
POMS $Na_{12}[WZnM_2(H_2O_2)(ZnW_9O_{34})_2]$	190	0.018	40	¼	>84.5	Fang et al. (2018b)
Fe_3O_4NPs@h-BNNS	200	0.002/0.3	300	10/0.3	100	Nabid et al. (2019)

5 Quaternary Recycling

Quaternary recycling recovers energy content from plastic waste by combustion or thermal catalytic pyrolysis (Langer et al., 2020). This is usually done by the combustion of the pyrolysis process. This method has ecological problems, i.e, plastic burning leads to airborne toxins and poses health hazards. As compared to incineration, thermal or catalytic pyrolysis yields fuels for the application.

5.1 Pyrolysis of Plastic Waste

Pyrolysis is a common procedure and the most promising economical way to dispose polymeric wastes (Fivga & Dimitriou, 2018). Though it is better than land filling, it generates toxic gases during incineration. However, controlled pyrolysis using suitable cracking catalysts could be used as a sustainable solution as the alternative fuels. Catalytic pyrolysis process efficiently converts the polymeric waste into alternative fuels through hydrogenation process. In this section, the use of pyrolysis in managing various polymeric wastes is discussed (Budsaereechai et al., 2019).

Pyrolysis of Poly(Ethylene Terephthalate) (PET) Wastes

The role of metals such as Pd, Pt, Ni, Co, metal oxides, and mixed metal oxides have major roles in the hydrocracking of C-C linkages and hydrodeoxygenation of polymeric wastes into hydrocarbons. For instance, at 700 °C, Pt-catalyzed pyrolysis yielded 17% and 56% polycyclic compounds and biphenyl derivatives. Pt-catalyzed pyrolysis of PET produced supported the formation of more aromatic compounds as compared to non-catalytic PET pyrolysis (Kim et al., 2020). Pyrolysis products of gases are mainly pyrolysis products, and synthesis of benzoic acid by catalytic pyrolysis of PET on sulphated zirconia at 525 °C produced benzoic acid and gaseous products (Dziwiński et al., 2018; Honus et al., 2018a, 2018b; Diaz-Silvarrey et al., 2018). Pyrolysis of PET under ammonia produced terephthalonitrile (TPN) using 50% N_2 and 50% NH_3 as a carrier gas. Alumina catalyst (γ-Al_2O_3) at 500 °C yielded 58.1% of TPN (Xu et al., 2019a).

Pyrolysis of High-Density Polyethylene (HDPE)

High temperature pyrolysis of HDPE at 500–800 °C is proven to be an efficient method in a fixed bed reactor (Al-Salem, 2019). A liquid hydrocarbon yield (70%) at 550 °C and gas product at 36% at 750 °C were obtained. The gas chromatography mass spectrometry (GC/MS) analysis showed C2 to C4 obtained as the major product in 70% and C8-C12 in liquid form. The CCFP of MP and HDPE over both HY-zeolite and HZSM-5 achieved extra aromatics due to the more effective Diels-Alder reaction (Park et al., 2018). Activated carbon support on Ni used for HDPE pyrolysis may be an economical catalyst for producing H_2 from gasification. The pyrolysis of PP, 900 °C has been converted to 66.88 wt% of the gaseous has turned into substance (Honus et al., 2018a).

Pyrolysis of Low-Density Polyethylene (LDPE)

Based on GC-MS analysis, the thermal process of LDPE at 474–520 °C yielded liquid oil hydrocarbon containing C_8-C_{24} and C_7-C_{20} (Abdulkareem et al., 2019). The combination of CaO blended with HZSM-5 has been found useful for increasing monoaromatics during catalyzed pyrolysis of hemicellulose along with LDPE (Ding et al., 2019). It has been reported that MgO is loaded with different acid and basic metal oxides (i.e., ZrO_2, Al_2O_3) for better conversion of lignin with LDPE as compared to cellulose pyrolysis. It is noteworthy that MgO supported in carbon produced large quantities of aromatic hydrocarbons (Ryu et al., 2019a, 2019b). The catalytic activity on pyrolysis of kraft lignin and LDPE using ZSM-5 and Al-SBA-15 (weak and strong acid site) has been investigated by Shafaghat et al. (2019).

Pyrolysis of Polyvinyl Chloride (PVC)

The pyrolysis of PVC using a layered double hydroxide catalyst, CuAl-LDH 4% yielded two different fractions at 50–400 °C and 400–600 °C, respectively. The first stage is the dehydrochlorination and the evaporation of the plasticizer and more degeneration of the molecular chain after the second dichlorination. The catalyst, CuAl-LDH exhibited efficient pyrolysis of PVC flares (Chen et al., 2018; Pang et al., 2020). Zeolite catalysts and mesoporous materials like MCM-41 can be used for catalysed pyrolysis of PVC (Souza et al., 2019).

Pyrolysis of Polypropylene (PP)

Basic oxides of alkaline earth metals such as CaO catalysts have been explored for the pyrolysis of PP to produce the liquid fuel oil. The analysis using GC/MS showed the carbon content in the range C_2 to C_{18} with 60% quality, which is the compound in gasoline and diesel fractions (Alam et al., 2019). Hydrogenation of feedstock containing PPO, waste mixture showed a complete transformation of unsaturated compounds into vegetable oil and straight-acting gasoline saturated compounds. Thermal cracking of waste polypropylene provide diesel fuel bimetallic catalyst made from sulfide catalysts such as $NiMo/Al_2O_3$, the product has high carbon-hydrogen content, low emission, and excellent combustion in their structure

(Sági et al., 2018). Polypropylene is converted by pyrolysis oil using the Ni-impregnated ZSM-5 as a catalyst when hydrogenation of PPO at a temperature 350 °C at 70 bar to produce the diesel (Mangesh et al., 2020).

Pyrolysis of Polystyrene (PS)

CuO is found to be a catalyst for the degradation of polystyrene (PS) into pyrolysis oil. The fractions are C_1 and C_4 as gases and C_3 to C_{24} as the liquid (Nisar et al., 2020). The performed polystyrene pyrolysis is catalyzed by solid acid catalysts, namely, HZSM-5, HY, Hβ, active Al_2O_3, and two mesoporous Al-silica MCM-41. HY and Hβ reduced the liquid yield of the pyrolysis process, whereas HZSM-5 and all silica MCM-41 are well suited for producing treasonable single ring aromatic compounds such as toluene, ethylbenzene, and cumene (Ma et al., 2016, 2017).

5.2 *Other Pyrolytic Process*

Microwave-Assisted Technology (MAP)

Microwave-assisted pyrolysis of LDPE is performed at the same time to enhance the yield and grade of petrol outcome products using MAP then NiO and HY-zeolite. The optimum oil yield at 56.4 wt % and oil quality with higher hydrocarbons at temperature of 450 °C was obtained by using HY-zeolite on LDPE ratio at 1:10 (Ding et al., 2019). Soap stocks have been used for hydrocarbon production promoted by microwave using SiC downdraft furnace. The optimum pyrolysis conditions are the catalyst temperature at 400 °C with soap stock to catalyst ratio of 2:1. It is shown that HZSM-5 performed better after five applications where the rate of hydrocarbon decreased by 7.05% (Wang et al., 2019).

Co-Pyrolysis of Polymers with Other Biomass

The high yield of pyrolysis oil is obtained in a furnace and a catalytic stable bed reactor using high density polyethylene catalysed by ZSM-5, which produced mainly C_{10} to C_{24} hydrocarbon compounds (Ghaffar et al., 2020). WPC wood fibers have a large amount of plastic and are an excellent feedstock for producing aromatic compounds. The in situ and ex situ catalytic pyrolysis of wood-polyethylene composite (WPC) on numerous microporous catalysts is performed as follows: HBeta (25), HY (5.1), and HZSM-5 (23). HBeta (25) revealed the very big performance for the production of aromatic hydrocarbons because it demonstrated a suitable pore size for the diffusion of plastic molecules (Park et al., 2018).

Characteristic of Plastic Pyrolysis Oil

The kinetics of pyrolysis of polystyrene under nitrogen or helium atmosphere using TGA showed activation energy at heating rate of 10, 15, and 20 °C/min is found to be in the range of 82.3–202.8 KJ mol^{-1} and 3.5×10^{6}–7.6×10^{14} min^{-1}as the pre-exponential factor (Nisar et al., 2019). The yield and quality of various plastics waste products, namely, PS, PE, PP, and PET, the liquor oil from the pyrolysis process is prepared by a small pilot-sized pyrolysis furnace for this purpose and handled at an optimum temperature and retention time of 450 °C and 75 min progressively. Polypropylene waste produced a higher amount of oil (80.8%) and gases (13%) than 6.2% formation of charcoal as compared to other plastic wastes. Liquid oil from PP pyrolysis uses styrene (48.3%), ethylbenzene (21.2%), and toluene (25.6%) as zeolite catalyst (Miandad et al., 2017). A study on maximum bio-oil yield can be achieved at 773 K, lignin pyrolysis using FBR and RKR (Park et al., 2019a, 2019b).

6 Biological Treatment of Plastics

The present topic concentrates exclusively on the biological treatment approaches of plastic waste. There are possibilities to degrade the plastics which consist of ester or urethane bonds, and as these bonds are hydrolysable, it can be cleared by using enzymes, namely, lipases, hydrolases, and proteases (Wierckx et al., 2018; Drzyzga & Prieto, 2019). Plastic degradation using abiotic and biotic factors, in which the degradation of the polymers can be achieved through hydrolysis by enzymes or oxidation of the polymer leading to monomers (Shah et al., 2008; Magnin et al., 2020).

The biomagnification of plastic waste is a more remarkable menace to the full ecological organization as is the consumption of plastics by aquatic and terrestrial organisms (Denuncio et al., 2011; Moharir & Kumar, 2019). Further pollution of the environment can be prevented using the biodegradable products, but the resistivity to shear stress by the organic products will not be on a par with the plastics. To make it similar to plastics except for the non-degradable characteristic, the researchers started utilizing the polymers produced by microorganisms and plants, as shown in Fig. 6 (EU Strategy on plastics, 2018).

The other options mentioned above might ensure plastic pollution limits. The regular monitoring of the plastic waste disposed of, accumulated, used, and recycled would decide the better alternative. Figure 7 summarizes methods used in each choice (Paço et al., 2018; Bassi, 2017).

The microorganisms enable plastic degradation from various sources such as mangroves, municipal solid wastes, dumpsites, marine areas, and places contaminated with plastics. These sources contain microbes *Pseudomonas sp., Streptomyces sp., Rhodococcus sp., Clostridium sp.,* and *Comamonas sp*. The fungi *Aspergillus niger, A. flavus, Fusarium lini, Pycnoporus cinnabarinus* and *Mucor rouxii* were

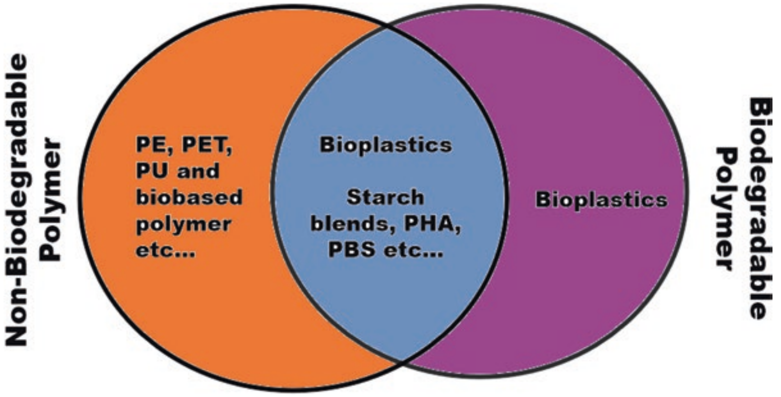


Fig. 6 Biodegradability of polymers. (Credit: European Bioplastics, 2018)

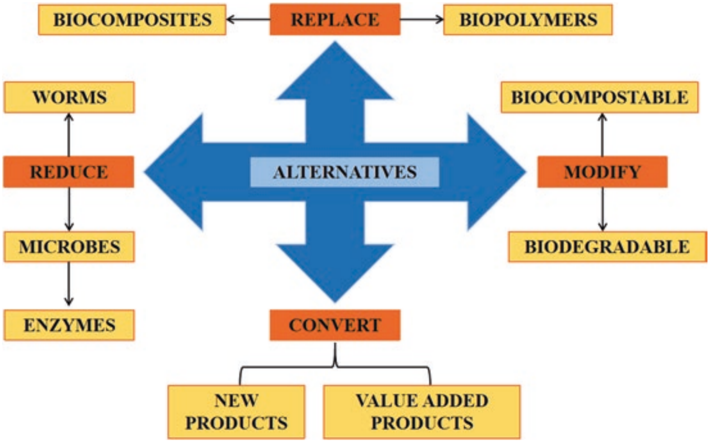


Fig. 7 Alternatives for plastics. (Credit: Bassi, 2017, Permission granted)

reported in the plastic degradation by Pathak (2017). Abiotic factors such as temperature, UV light, and heat seem to ease the biodegradation process by causing chemical and mechanical changes to the plastics (Lucas et al., 2008). Distorted plastics with reduced molecular weight become more accessible to oxygen, and water molecules ultimately make the oligomers readily available for microorganisms (Lambert et al., 2014). Apart from macroplastics, the nanoplastics in the oceans and seas appear to be an attraction of pollutants, mainly the persistent organic pollutants (POPs) according to their higher surface area (Liu et al., 2016; Anjana et al., 2020).

6.1 Biodegradation of Plastic Wastes

The biodegradation of plastics mainly facilitated by biofilm formed on the surface of the plastics involves adsorption, immobilization of microorganisms, followed by micro- and macrofouling. Among the microbes, the primary attachment aided by bacteria further comprise other bacterial species, fungi, or diatoms (Selim et al., 2017). Zettler et al. (2013) stated that the microorganisms found on the plastic surfaces as plastisphere contained lesser microbes than the surroundings. It excites us that the biofouling microbes are abundant on the plastic surface compared to the surroundings. The studies suggest the linear relationship between biofilm and plastic degradation (Carson et al., 2013). The process of biofilm formation and plastic degradation is shown in Fig. 8.

Biofilm formation is known as the survival mechanism of bacteria under changing environmental conditions, especially in the marine environment. The mechanism involves consortium formation, nutrient uptake, horizontal gene transfer, and defense against toxic substances (Junge et al., 2004; Rummel et al., 2017). The production of fibrin, collagen, and laminin by the microorganisms aids in cell signalling and cell-cell adhesion (Bryers et al., 2006; Simoes et al., 2010). Extracellular

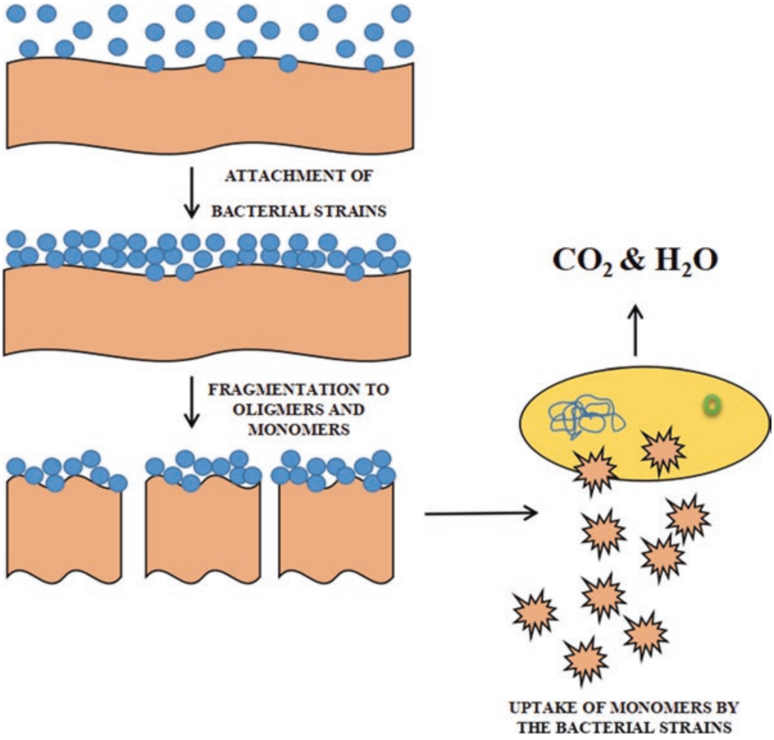


Fig. 8 Biofilm formation and plastic degradation

polymeric substance production by biofilm aids in cell-cell adherence, water retention, and as time progresses the biofilm serves as a matrix for EPS (Simoes et al., 2010; Pathak, 2017). Kokare et al. (2009) reported that the alginate producing gene (*algC*) increases the chances of biofilm formation by fourfold by a sigma factor regulating it positively. The attachment of the Gram-positive bacteria on the hydrophobic surface is achieved by the hydrophobic amino acid and mycolic acid in the fimbriae. It justifies the ability of Gram-positive bacteria to degrade plastics over Gram-negative bacteria, which is mostly aided by EPS production (Prakash et al., 2003).

In the marine environment, the biofouling process attracts invertebrates which adds to the plastic degradation. It increases the weight of plastic waste and sinks to the seafloor (Reisser et al., 2014; Pauli et al., 2017). The early attachment of the bacteria on the plastic surface does not explain its degradative capacity (Lobelle & Cunliffe, 2011). The *Vibrio* colonization on the marine microplastic specifies the involvement of pathogenic microorganisms in plastic degradation (Frère et al., 2018; Oberbeckmann & Labrenz, 2020). The exciting facts, apart from the biofouling in microplastics, are the development of antibiotic-resistant bacteria. The bacteria forming the biofilm transferred plasmid coding to trimethoprim resistance at a higher rate (Arias-Andres et al., 2018). Even though the process of conversion of macro-sized synthetic polymers to micro- or nano-sized polymers does not change the availability of plastic pollution in the environment. Alexander mentioned the biodegradation of xenobiotics (1975) and stated conditions that microorganisms could not degrade the pollutants. The commandments of Alexander specify the requirements based on synthetic polymer, as mentioned below.

- Higher molecular size decreases the rate of penetration to the cell – commandment 5.
- The degradation will not be effective if the aqueous solution concentration is low – commandment 6.
- Relatively less access to the pollutant – commandment 10.

The commandments correlate with the biodegradation of plastics as the bioavailability and surface hydrophobicity increase difficulties. The biodegradation of plastics depends on the bioavailability and surface hydrophobicity increases difficulties. The well-known fact of conversion of microplastics to nanoplastics is scientifically unproven (Klaeger et al., 2019).

6.2 *Enzymatic Degradation Process*

Among plastics, linear low-density polyethylene (LLDPE) is more prone to microbial damage. A class of oxidase enzymes aids the degradation by the microorganisms by cleaving the chains of polyethylene (PE) to low molecular weight compounds that enter the microbial cell following the alkane degradation pathway (Gravouil et al., 2017). Hydrolase enzymes, which includes ureases, proteases, and esterases, are also involved in plastic degradation (Ashter, 2016; Anjana et al., 2020). The enzymes such as PHB depolymerase (Ishii et al., 2007), Lipase B (Shibasaki et al., 2009), MHETase, PETase (Palm et al., 2019), styrene monooxygenases (Pu et al., 2018), dehydrogenase (Kawai & Hu, 2009), polyurethenases (Howard et al., 2007), lipase (Hung et al., 2016), PEG-dehydrogenase (Sugimoto et al., 2001), hydrolase (Müller et al., 2005), and peroxidases (Sudhakar et al., 2008) were reported in the plastic degradation produced by bacteria and fungi. The C-C bond breaking occurred by the transfer of free radicals induced by P40 monooxygenase enzyme was studied using quantum mechanics (Xu et al., 2019b). Ma et al. (2018) reported a mutant PETase enzyme with PET specificity to the wild enzymes. The hydrolases are known to contain α/β-hydrolase fold with serine, histidine, and aspertate residue as a catalytic triad. Cystine residues form disulfide bonds promoting binding and thermal stability, as in *Ideonella sakaiensis* (Yoshida et al., 2016). The structure of PETase and cutinases are similar due to the narrowing down of the active site as a result of double mutation (Austin et al., 2018). PETase binds with the substrate-binding cleft cleaving PET to MHET, and the MHETase further hydrolyzes it to ethylene glycol and terephthalic acid (Palm et al., 2019). MHET and BHET inhibit the activity of the thermally stable Ca^{2+}-dependent actinobacterial enzymes (Barth et al., 2015). PET hydrolases from various sources were developed by motif-based search globally using hidden Markov model (HMM) with genomic and metagenomic databases (Danso et al., 2018). Danso et al. (2019) state that there were no studies involving the mechanisms and enzymes used in PE degradation. The degradation of the high molecular weight polystyrene (PS) by Gloeophyllum strains resulted in weight reduction by 50% in 20 days of incubation. Fungal strains such as *Pleurotus ostreatus, Phanerochaete chrysosporium,* and *Trametes versicolor* depolymerized the PS. But there are no studies on the enzymes involved in PS degradation (Krueger et al., 2015).

6.3 Polymer Degradation Using Algae

The pollution of plastics in the aquatic ecosystem, especially the marine environment, could have made algae resistant. There are reports on the algae in various aquatic sources, but there are hardly any reports of algae growing in plastics and plastic-contaminated environments. Sharma et al. (2014) reported the degradation of polythene by ten species of algae which includes *Bacillariophyceae, Chlorophyceae*, and *Cyanophyceae*. Suseela and Toppo (2007), studied the degradation of polythene using algal biofilms in the region of Rajasthan and Uttar Pradesh. The algal species includes *Monoraphidium* and *Selenestrum*, not previously reported in Rajasthan (Sharma et al., 2014). The degradation occurring in aerobic conditions produces CO_2 and H_2O as final products if its anaerobic condition results in the production of methane. In the case of depolymerization under anaerobic condition such as methanogenic conditions (when methane is produced) or sulfidogenic conditions H_2S is produced (Gu, 2001; Gu & Mitchell, 2006).

6.4 Aids for Enhancing Biodegradation of Plastics

There are conventional methods involved in the degradation of plastics, namely, thermal degradation, photo-oxidation, and biological degradation. The thermal production of peroxide radicals causes a change in the structure of the polymer which in turn changes the malleability, optical property, and other characteristics of plastics (Ghosh et al., 2013; Shah et al., 2008). The nanoparticles identified enhance the biodegradability of the polymer by nourishing the growth of the polymer-degrading microorganisms. The synthesis of oxo-degradative polymer to enhance the photodegradation process was also studied (Krueger et al., 2015). González et al. (2015) have studied the degradation of plastic using TiO_2 particles as nanofillers. The deterioration of polyolefins utilizing the process of oxo-degradation, which oxidizes the C-C backbone changes the hydrophobic plastic surface to hydrophilic surfaces. This aids in the absorption of water by plastic and aids in the degradation of the polymer by microorganisms. The process of initialization of plastic disintegration aided by photo-oxidation led to free radical generation; hence, the bioavailability for the biodegradation was increased (Feldman, 2002; González et al., 2015).

6.5 Biodegradation Process: Key Factors

The biodegradation of pollutants influenced by various biotic and abiotic factors such as pH, temperature, salt concentrations, the bioavailability of the contaminants, concentration of the contaminants, microorganisms involved in the degradation of the pollutants, nature of the pollutants, nutrient availability, and presence or absence of oxygen (Arutchelvi et al., 2008). During the enzymatic degradation process, the enzyme activity is inhibited by direct inhibition as the competition between the microorganisms for the available resources. The rate of degradation is also affected by the adsorption and absorption of the pollutants by the microbes. The transfer of gases such as oxygen, methane, and CO_2 is reduced in the soil mainly when it attains saturation with water in the environment. Thus, the low electron density in the site of degradation determines the oxidation of the aerobic condition, whereas the higher electron density indicates a reduction of the anaerobic condition.

6.6 Methods for Determination of Polymer Degradation

The depolymerization of the polymer (plastic) is analyzed by determining the weight loss, change in mechanical strength, tensile strength, CO_2 production, change in the functional groups (addition/modification), leaching of additives, etc. Thus, the degradation of the polymer by biological agents using various methods or aids for enhancement and determining using different ways throws light on the development of S&T toward a sustainable environment.

7 Conclusion

This chapter addressed the environmental impact arising from plastic waste, showing the current evaluation of recycling methods. The benefit and recycling potential of catalysts in plastic waste chemical recycling, mechanical recycling, and energy recovery are comparatively mildly harmful to the environment and more environmentally benign. PET chemical recycling method requires potential and inexpensive PET decomposition system with shorter reaction period, high yields, and pollution recovery under reusable solvent and catalysts. The environmental impact of microplastics is discussed in this chapter. Microplastics directly affect all kinds of living beings due to ingestion of food, water, and air containing microplastic contaminants found in seawater, fresh water, drinking water, atmosphere, terrain, sediment, and then the soil. Digestive and excretory systems of the human body are mainly affected by microplastics through ingestion that can lead to metabolic disease, bladder cancer, diabetic and liver disease, and also affect the skin and respiratory system. The range of particles detected to affect most humans in the body are particles smaller than 135μm that is found in environment to a large extent. Catalytic pyrolysis is much advantageous in the thermal process because it improves efficiency by reducing the processes. Catalytic cracking using zeolite catalysts resulted in high quality of the depolymerised products in the range of motor engine fuels and with the further optimisation of the pyrolysis process, it recommended be for the thermal pyrolysis for the oil refineries. Nature has its way of dealing with pollutants. Biodegradation is one such process used to eliminate toxic waste from the environment. It takes a better understanding and endless exploration, which undermines the previous one.

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Determination of Partition Coefficient of Pesticides: A Short Review and Application of DFT Method

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Abstract Pesticides are chemicals that are used to kill pests. Partition coefficient in n-octanol and water distribution (log $P_{o/w}$) is one of the useful parameters to understand mobility in biological systems. This chapter consists of a short review of the experimental and computational methods used for the determination of log $P_{o/w}$. It also includes the application of density functional theory (DFT) method to calculate the log $P_{o/w}$ for 23 pesticides. A comparison of the computed and reported log $P_{o/w}$ of these pesticides resulted in $R^2 = 0.88$, and it improved to 0.96 after excluding two outliers. The findings from this work can be useful to compute log $P_{o/w}$ of novel pesticides.

Keywords Pesticides · N-octanol – water distribution · Partition coefficient · DFT

1 Introduction

Pesticides are chemical compounds that are used to kill pests, including insects, rodents, fungi, and undesirable plants (https://www.who.int/topics/pesticides/en/). Pesticides can be classified as organic, inorganic, synthetic, and biological (Lyznicki et al., 1997). Some common families of pesticides are organophosphates, carbamates, and organochlorines (Lyznicki et al., 1997).

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Society has benefited with the enhanced food production and disease prevention in the last decades upon the introduction of various pesticides (Vlahovic et al., 2017). Countries facing scarcity of food have implemented the use of pesticides as an approach to improve their harvest yield and the recurrence so that crops can be planted on the same land (Vlahovic et al., 2017). The implementation of bio farming resulted in the use of biopesticides with less of harmful effects.

Pesticides are toxic, specifically to humans, with both acute and chronic effects (Karami-Mohajeri et al., 2013). Thus, assessing the fate and effects of pesticides on the environment and human health are of major concern (Kookana, 2010). Since pesticides are lipophilic, they interfere with biological processes that involve chemical intake including absorption, distribution, biological membranes, receptor interactions, toxicity, and metabolism (Lushchak et al., 2018). The mobility of pesticides within the biological systems may be investigated by taking into consideration the lipophilicity of these pesticides (Rodrigo et al., 2014). Lipophilicity can be interpreted in terms of the partition coefficient (Cevc, 2015), and the coefficient in n-octanol and water distribution (log $P_{\mathrm{o/w}}$) is commonly used (Kraszni et al., 2003).

This chapter provides a short review of the experimental and computational methods used to determine partition coefficient. It also consists of the applications of density functional theory (DFT) method to calculate log $\mathrm{P}_{\mathrm{o/w}}$ of 23 pesticides. A statistical analysis of the computed and reported log $\mathrm{P}_{\mathrm{o/w}}$ was carried out. The findings from this work can be useful to compute log $\mathrm{P}_{\mathrm{o/w}}$ of novel pesticides, which are emerging in view of pests becoming resistant to existing pesticides (Hawkins et al., 2018).

2 Experimental Methods to Determine Partition Coefficient

There are different experimental methods which are used to calculate partition coefficient. Table 1 summarizes some of the relevant literature, and this is followed by a detailed analysis.

The shake-flask method is the basis of several experimental methods used to determine partition coefficient. This method involves adding the solute to the solvent system and partitioning until equilibrium is reached. The concentration of the solute in each solvent is determined (Berthod & Carda-Broch, 2004; Noble, 1993).

Liu et al. (2005) used reversed-phase high-performance liquid chromatography (RP-HPLC) for the calculation of partition coefficient in 1-octanol/water system with 1-octanol as the stationary phase and water as the mobile phase for 46 drugs and flavonoids. This study generated results that showed that RP-HPLC is a useful method to determine the logarithm of partition coefficient. Another method employed to measure the octanol/water partition coefficient is enzymatic hydrolysis with the solutes being sucrose, glucose, and trehalose. The solute was hydrolyzed using enzymes, and the concentration of the sugar in 1-octanol was measured.

Table 1 Literature relevant to experimental methods for determining partition coefficient

Title of research paper	Reference
Partition coefficients (n-octanol/water) for pesticides	Noble (1993)
Determination of liquid-liquid partition coefficients by separation methods	Berthod and Carda-Broch (2004)
Determination of lipophilicity by reversed-phase high-performance liquid chromatography: Influence of 1-octanol in the mobile phase	Liu et al. (2005)
Octanol-water partition coefficient of glucose, sucrose, and trehalose	Mazzobre et al. (2005)
Salting-out phenomenon and n-octanol/water partition coefficient of metalaxyl pesticide	Saab et al. (2011)
Rapid determination of octanol-water partition coefficient using vortex-assisted liquid-liquid microextraction	Román et al. (2014)
Octanol-water partition coefficient measurement by a simple ^{1}H-NMR method	Cumming and Rücker (2017)
A comparison of log K_{ow} (n-octanol/water partition coefficient) values for non-ionic, anionic, cationic, and amphoteric surfactants determined using predictions and experimental methods	Hodges et al. (2019)

The partitioning of pesticides is an aspect to consider as humans are exposed to them, and this has been elaborated in a study which determined the partition coefficient of the metalaxyl pesticide in 1-octanol/water system. The method used was the static shake-flask method (Saab et al., 2011).

Vortex-assisted liquid-liquid microextraction (VALLME) combined with HPLC was used to measure the octanol/water partition coefficient for six model compounds. This method required vortex mixing until equilibrium was reached, and then microdrop was collected from the organic phase and analyzed using HPLC. The results obtained were consistent with literature with this method being reliable (Román et al., 2014).

Proton nuclear magnetic resonance (^{1}H-NMR) was used to measure the octanol-water partition coefficient with a combination of the shake-flask method. The^{1}H-NMR spectrum was obtained for a known concentration of analyte in water. This was followed by the addition of 1-octanol, and the tube was inverted at least 40 times to allow for equilibrium. After separation of the two phases, the NMR spectrum was recorded for the aqueous phase (Cumming & Rücker, 2017).

Two direct methods to calculate the partition coefficient of surfactants, namely, HPLC and the slow-stirring method were compared in a study. Two Organisation for Economic Co-operation and Development (OECD) test guidelines, 117 and 123, were used for HPLC and slow stirring, respectively. The results showed a higher partition coefficient value with HPLC compared to the slow-stirring method with the latter being the mostly used method for all the four classes of surfactants (Hodges et al., 2019).

3 Computational Methods to Determine Partition Coefficient

Table 2 summarizes the studies carried out to determine partition coefficient using computational methods, and this is followed by a detailed discussion.

Partition coefficients of small molecules were studied in two solvent systems, namely, octanol/water and cyclohexane/water (Bannan et al., 2016). They used the Generalized Assisted Model Building with Energy Refinement Force Field (GAFF) and the Dielectric Corrected GAFF (GAFF-DC) to calculate the partition coefficient. A new solvation toolkit was created to automate the process of creating input files for any combination of solutes and solvents for many software packages in molecular dynamics, and this was used in this analysis combined with other software. The log P was calculated using Eq. 1.

$$\log P = \frac{-\Delta G_{\text{transfer}}}{RT\ln(10)} = \frac{\Delta G_{\text{hydration}} - \Delta G_{\text{solvation}}}{RT\ln(10)} \tag{1}$$

R is the molar Boltzmann constant and T is the temperature in Kelvin.

To simplify the analysis, two assumptions were considered: (i) the solvent system was immiscible and (ii) the solutions were diluted. The root-mean-squared error (RMSE) of about 1.2 log units was obtained for both the GAFF and GAFF-DC methods.

The cyclohexane/water partition coefficient of 53 organic compounds investigated the (SAMPL5) challenge using several DFT functionals with solvation model based on density (SMD) in conjunction with the cc-pVnZ ($n = D, T, Q$) basis sets (Jones et al., 2016). Single point computations on the optimized geometry were performed to determine the hybrid DFT functional that would be most appropriate.

Table 2 Literature relevant to computational methods for determining partition coefficients

Title of article	Reference
Calculating partition coefficients of small molecules in 1-octanol/water and cyclohexane/water	Bannan et al. (2016)
Partition coefficients for the SAMPL5 challenge using transfer free energies	Jones et al. (2016)
Partition coefficients of methylated DNA bases obtained from free energy calculations with molecular electron density derived atomic charges	Lara et al. (2018)
Calculating the partition coefficients of organic solvents in octanol/water and octanol/air	Nedyalkova et al. (2019)
QSPR modelling of octanol/water partition coefficient for vitamins by optimal descriptors calculated with SMILES	Toropov et al. (2008)
log P prediction performance with the SMD solvation model and the M06 density functional family for SAMPL6 blind prediction challenge molecules	Guan et al. (2020)
Predicting octanol-water partition coefficients: Are quantum mechanical implicit solvent models better than empirical fragment-based methods?	Kundi and Ho (2019)
Density functional theory calculation of lipophilicity for organophosphate type pesticides	Vlahovic et al. (2017)

To improve accuracy, the “Ultrafine” integration grid criterion was considered. The B3PW91 functional was selected to predict the transfer free energy due to its consistent behavior across the periodic table. A good estimation of the log P values with a mean absolute deviation of 1.9 log P units was obtained.

Nedyalkova et al. (2019) calculated the partition coefficient of 55 organic solvents in octanol/water and octanol/air systems. This study was based on the fact that the partition coefficient of a solute can be calculated by using the difference in Gibbs free energy of the solute in different solvents. Three DFT functionals, namely, M06-2X, M11, and B3LYP, were used. The structure of each molecule was optimized using each DFT functional with the 6–311+G(d,p) basis set in combination with SMD as solvation model. The results obtained agree with the experimental data with the M11 functional having the most agreeable match for octanol/water with a Pearson correlation coefficient (R) of value 0.99 and the M06-2X functional had the best results for octanol/air system.

A study of the partition coefficient of the methylated DNA bases in chloroform/water was performed using atomic charges with implicit and explicit solvation models. The atomic charges were obtained using two partitioning methods, namely, the Hirshfeld and Minimal Basis Iterative Stockholder. It is analogous to the AMBER force field method except for the fact that this method considers the effect of different environments on the polarization of the molecular electron density. The results were in good agreement with the experimental data upon consideration of polarization factor (Lara et al., 2018).

Quantitative structure-property relationships and quantitative structure-activity relationships (QSPR/QSAR) can be employed to calculate the physicochemical property and biological activity of substances. Optimal descriptors are the basis of these calculations which can be calculated using various ways such as molecular graphs and the simplified molecular-input-line-entry system (SMILES). Toropov et al. (2008) calculated the octanol/water partition coefficient using QSPR models based on optimal descriptors obtained from the SMILES notation. The study was carried out on a set of vitamins and organic compounds. Each group, vitamins and organic compounds considered, was randomly divided into two sets, namely, the training set and the test set. The best results were obtained with the group of vitamins with $R^2 = 0.9872$, and the organic compounds yielded good results with $R^2 = 0.9841$. Upon comparison with the method derived from molecular graphs, relatively similar results were obtained which may indicate the use of SMILES as an alternative.

The M06-2X density functional with def2-SVP as the basis set and SMD as solvation model is one of the methods used to predict the log P of small protein-kinase inhibitor fragments. One of the objectives of this work was to be included in the SAMPL6 blind prediction challenge. With the model named *dqxk4* in the SAMPL6 challenge, it identifies as the third-highest performing. The model was used to calculate the log P of 11 compounds from the set, and an RMSE of 0.49 log units was obtained. They also investigated for the deficiencies in models and used a physical model mixed with an empirical one, which in turn lead to an improved performance with 0.34 log RMSE. The mixed model proves to be a path to efficiently improve chemical simulations difficult for ab initio methods (Guan et al., 2020).

Two methods that can be used to predict the log P are the quantum mechanical implicit solvent models and the empirical fragment-based method. In 2019, the two methods were applied and a comparison of both methods to determine the more reliable method was done on two test sets obtained from literature. The implicit solvent models considered consisted of the SMD, SM8, ADF-COSMO-RS, and SM12 which lead to overall good performance with a mean absolute error (MAE) of 0.6 log unit. Numerous empirical fragment-based methods were used including ALOGPS, miLOGP, and iLOGP. Upon comparison, a lower mean absolute error was obtained for the fragment-based methods with a value of 0.2 to 0.4 log unit which made the fragment-based method the better one. Furthermore, testing of the ALOGP method was done with a set of 11 molecules from the SAMPL6 challenge obtaining a MAE of 0.32 log unit, which is near to the best performing COSMOtherm model with the MAE of 0.31 log unit (Kundi & Ho, 2019).

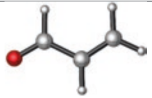
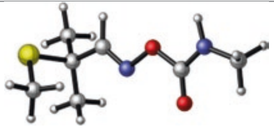
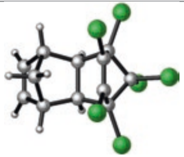
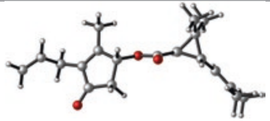
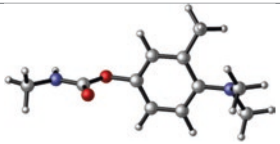
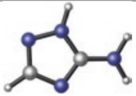
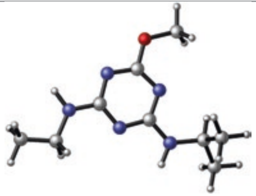
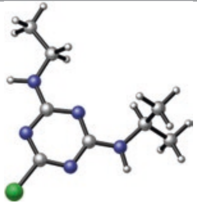
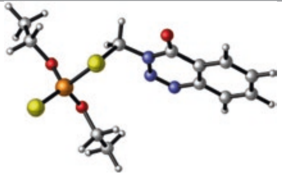
Pesticides can be studied by classifying them as per their chemical aspects. One such study consisted of a group of 22 pesticides classified as organophosphate. Two pure and one hybrid DFT functional, M06L, PBE, and M06-2X, respectively, were used with a combination of the universal solvation model, SMD, and the 6-31+G(d,p) as the basis set. Similar to other research, the molecules were optimized in both solvent and gas phase and the Gibbs free energy of transfer was obtained. For better comparison, various parameters including mean signed error (MSE), MAE, RMSE, mean absolute deviation (MAD), root-mean-square deviation (RMSD), and largest error in absolute value (LE) were calculated. Upon analyzing the results, the M06L functional produced results that match better with experimental values with an MAE of 0.44. However, when comparing the two Minnesota functionals applied, results from M06-2X are closer to the experimental values while results from M06L lead to an overestimation (Vlahovic et al., 2017).

4 Application of DFT to Calculate (log $P_{o/w}$) of Pesticides

We performed DFT computations for 22 pesticides. The functional used was B3LYP in conjunction with the 6–311+G(d,p) basis set. The 3D conformer of each pesticide was generated from PubChem as an SDF file. The file was opened using Mercury 3.9 (Macrae et al., 2020), the structure was saved as .xyz file and opened using notepad to obtain the pesticide's Cartesian coordinates. Each structure was fully optimized in the gas phase and n-octanol as the solvent (Table 3). Solvent computations were based on the continuum solvation model, SMD. Frequency computations were carried out with the optimized structures to ensure ground state conformation. All computations were carried out by using resources from SEAGrid (Pamidighantam et al., 2016; Shen et al., 2014; Dooley et al., 2006; Milfeld et al., 2005).

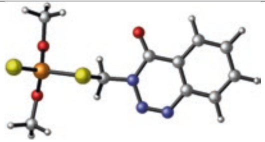
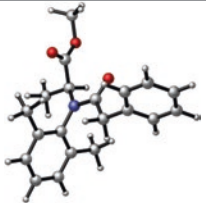
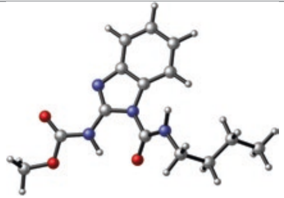
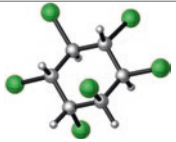
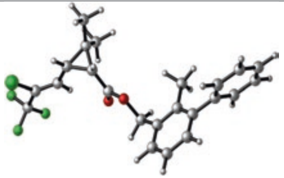
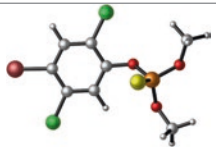
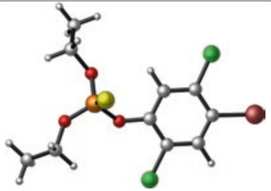
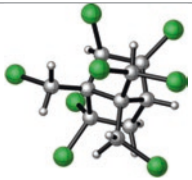
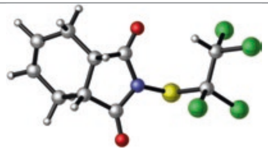
The partition coefficient is related to the difference in Gibbs free energy in the two solvents. The Gibbs free energy obtained in n-octanol, ΔG^{o}_{o} and water, ΔG^{o}_{w} at 298.15 K was retrieved from the output file as "free energy." The two values obtained were used to calculate the standard Gibbs free energy, $\Delta G^{o}_{o/w}$. All the calculations

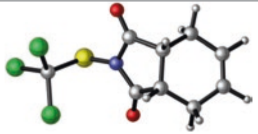
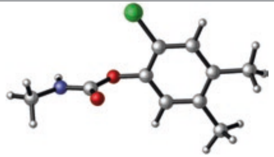
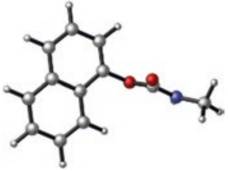
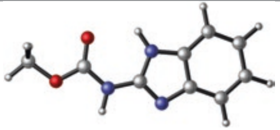
Table 3 Structures of pesticides used for the DFT calculations

Acrolein	Aldicarb	Aldrin
		
Allethrin	Aminocarb	Amitrole
		
Atraton	Atrazine	Azinphos ethyl
		
Azinphos methyl	Benalaxyl	Benomyl

(continued)

Table 3 (continued)

		
BHC	Bifenthrin	Bromophos
		
Bromophos ethyl	Camphechlor	Captafol
		
Captan	Carbanolate	Carbaryl

		
Carbendazim		
		

were performed considering the transfer of the solute from water (w) to octanol (o) as per Eq. 2.

$$\Delta G^{o}_{o/w} = \Delta G^{o}_{o} - \Delta G^{o}_{w} \tag{2}$$

The relation of the Gibbs free energy to the equilibrium constant, Eq. 3, is obtained after merging equations from thermodynamics and the ideal gas equation.

$$\Delta G^{o} = -RT\ln P \tag{3}$$

The log P value for each pesticide was calculated according to Eq. 4.

$$\log P = -\frac{\Delta G^{o}_{o/w}}{2.303RT} \tag{4}$$

Table 4 $\Delta G_{o/w}$, log P (experimental), and log P (DFT) of the pesticides considered in this work

Pesticide	$\Delta G_{o/w}$	log P	log P (DFT)	Modulus of difference in log P
Acrolein	−1.41	0.90[a]	0.25	0.65
Aldicarb	−0.37	1.08[b]	0.07	1.01
Aldrin	−35.03	5.66[c]	6.14	0.48
Allethrin	−29.71	5.00[d]	5.21	0.21
Aminocarb	−19.65	1.73[e]	3.44	1.71
Amitrole	5.80	−0.87[f]	−1.02	0.15
Atraton	−14.29	2.69[g]	2.50	0.19
Atrazine	−16.39	2.40[h]	2.87	0.47
Azinphos ethyl	−12.79	3.40[e]	3.44	0.04
Azinphos methyl	−2.89	2.69[e]	0.51	2.18
Benalaxyl	−20.84	3.40[i]	3.65	0.25
Benomyl	−10.99	2.12[j]	1.93	0.19
BHC	−24.88	4.14[k]	4.36	0.22
Bifenthrin	−40.83	6.00[l]	7.16	1.16
Bromophos	−24.30	4.88[e]	4.26	0.62
Bromophos ethyl	−34.08	5.68[e]	5.97	0.29
Camphechlor	−32.30	5.50[a]	5.66	0.16
Captafol	−19.46	3.83[m]	3.41	0.42
Captan	−18.01	2.54[m]	3.16	0.62
Carbanolate	−10.41	2.30[m]	1.82	0.48
Carbaryl	−8.52	2.34[n]	1.49	0.85
Carbendazim	−4.16	1.40[o]	0.73	0.67

[a]Isnard and Lambert (1989), [b]Briggs et al. (1982), [c]Kenaga (1980), [d]Briggs et al. (1974), [e]Bowman and Sans (1983), [f]Bromilow et al. (1987), [g]Finizio et al. (1991), [h]McDuffie (1981), [i]Abbott et al. (1986), [j]Austin and Briggs (1976), [k]Kurihara et al. (1973), [l]Worthing (1987), [m]Briggs (1981), [n]Bracha and Oƅrien (1966), [o]Lord et al. (1980)

The calculated log P values are summarized in Table 4. The results are also illustrated in the form of a graph (Fig. 1) of the calculated log P values against the log P values from the literature.

The slope of the line of Fig. 1, y-intercept, and linear regression parameters were calculated and collected in Table 5.

An attempt to detect the outliers using the 4-sigma rule was carried out using the limits as given in Table 6. However, no outliers were detected using the 4-sigma rule possibly due to a high standard deviation.

An alternative, visible detection was used for the anomalies which resulted in Fig. 2. The outliers were the pesticides aminocarb and azinphos methyl.

Table 7 summarizes the effect of removing the outliers on the R^2 value and other parameters calculated related to errors analysis. Thus, the R^2 was improved and the MSE value decreases.

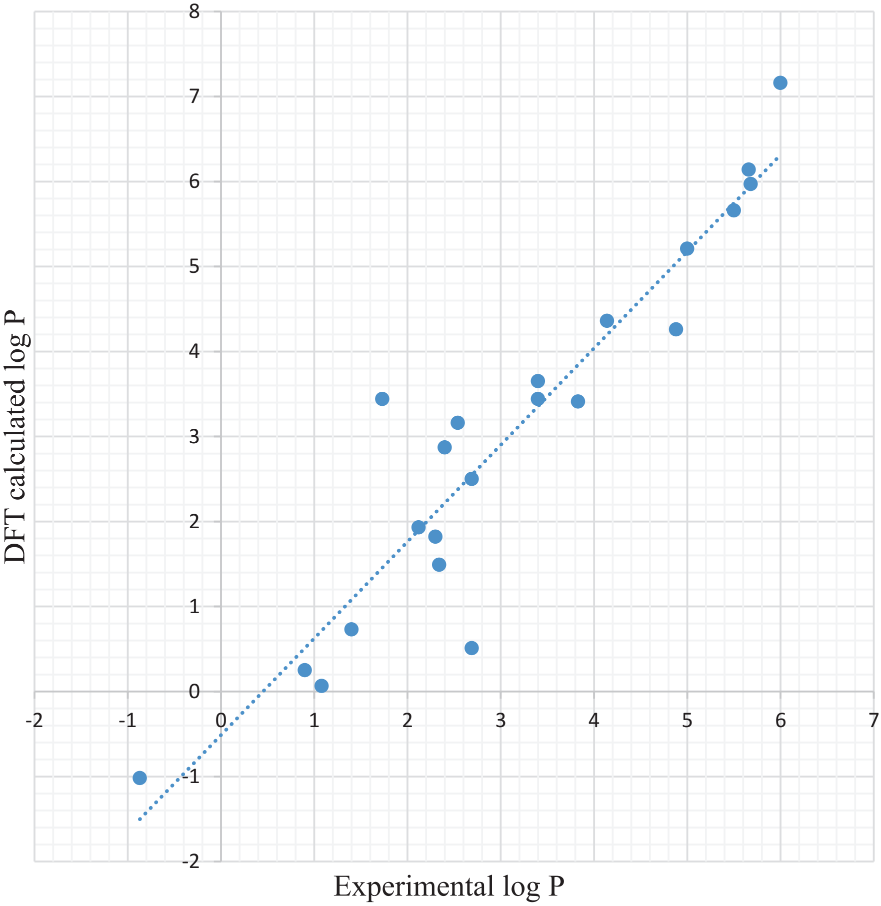


Fig. 1 Plot of log P values calculated using DFT against experimental literature values

Table 5 Linear regression parameters and statistical metrics

Parameter	Value
Gradient	1.138
Intercept	−0.552
R^2	0.88
MSE	0.593
RMSE	0.770
MAD	1.681

Table 6 Mean, standard deviation, and limits for the 4-sigma rule

Mean (μ)	3.044
Standard deviation (σ)	2.144
Upper limit (μ + 4σ)	11.620
Lower limit (μ − 4σ)	−5.532

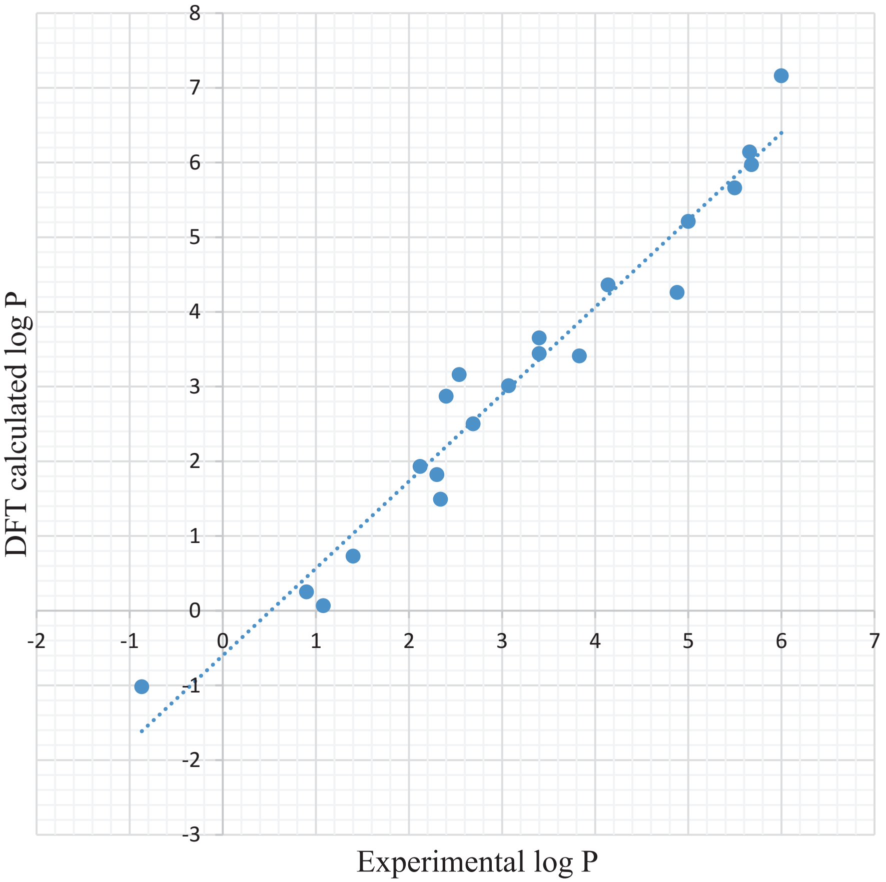


Fig. 2 Plot of DFT calculated log P values against literature experimental values after removal of two outliers

Table 7 Linear regression parameters and statistically calculated errors upon removal of two outliers

Parameter	Value
Gradient	1.166
Intercept	−0.600
R^2	0.957
MSE	0.284
RMSE	0.533
MAD	1.697

5 Conclusion

In this chapter, we presented a short review of the experimental and computational methods used to determine partition coefficient. We also report the of n-octanol-water partition coefficients of 23 pesticides using DFT method. The calculated partition coefficients were compared with experimental values available in the literature. A satisfactory comparison was obtained, and this work can be useful for the application of DFT method to calculate partition coefficient of novel pesticides. The latter are important as pests may become resistant to existing pesticides.

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Microplastics – Pollutants' Interactions, Mechanisms, and Potential Toxicity

T. G. Sunitha, V. Sivasankar, M. Prabhakaran, and K. Omine

Abstract Microplastics are small plastic fragments, flakes, or beads of size less than 5 mm diameter. Due to the anthropogenic activities, these persist ubiquitously in the environment. The high surface area and functionalized surface due to aging and weathering persuade the sorption of toxic contaminants to the microplastics. The microplastics with the adsorbed chemicals are ingested and accumulated by the terrestrial and aquatic organisms. The ingested microplastics and the adsorbed chemicals cause endocrine disruption, reproductive failure, and other developmental disorders. When humans are exposed to these microplastics through food chain, inhalation, and dermal contact, this exposure can lead to an array of health impacts, including inflammation, genotoxicity, oxidative stress, apoptosis, and necrosis. This chapter highlights the interaction mechanisms of the sorption process between the microplastics and the toxic chemicals, factors influencing the sorption process, and the combined toxic effects of microplastics and their adsorbed chemicals on ecosystem.

Keywords Microplastics · Sorption · Interaction mechanisms · Toxic pollutants

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1 Introduction

The global production of plastics is about 381million tons every year, and it will get doubled by 2034 (Plastic in the Ocean Statistics, 2020). Over 10 million tons of plastic wastes is dumped into our oceans every year and 150 million tons into the soil and in internal waters (Axel Barrett, 2020). Low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC), nylon, acrylic, polyurethanes, polylactic acid, polycarbonate, and other biodegradable plastics are the generally used polymers across the world (Ajith et al., 2020). These plastic wastes persist in the environment for decades because of its durability and become the ubiquitous pollutant even in the most isolated areas of the world causing a global threat. The fragmentation of larger plastic particles due to physical, chemical, and biological weathering process when discharged into the environment leads to the formation of microparticles (Andrady, 2011).

Microplastics (MPs) are fine plastic particles of size lesser than 5 mm in diameter (GESAMP, 2015, 2016). Depending on their source, they are classified as primary and secondary microplastics. Primary microparticles are designed intently in microscale for commercial use. The microbeads, microfibers, capsules, and nurdles used in the personal care products, textiles, pharmaceuticals, and plastic manufacturing industries became the main source of primary microplastic. The secondary microplastics enter the environment through the breakdown of larger plastic materials such as water bottles, fishing nets, and household items. Due to the anthropogenic activities, these microparticles are flushed into the terrestrial, aquatic, and atmospheric environment.

When microplastics are discarded into the environment, it detrimentally affects the humans and animals through the consumption of seafood and drinking water, contact with food packaging, or inhalation of particles (Hwang et al., 2019). The living organisms that ingest microplastics are at a high health risk such as reduced growth rates, cytotoxicity, hypersensitivity, increased mortality, decreased reproductive ability, unwanted immune response, ulcers, abrasions, and oxidative stress and acute response like hemolysis (Ajith et al., 2020).

Microplastics absorb and accumulate toxic chemicals and carry harmful bacteria due to their strong sorption capability. Microplastics can store more pollutants than macroplastics because of their larger specific surface area (Lee et al., 2014). These plastics when ingested by the living organisms exert ecological effects, either from the plastic particle, the pollutants trapped to them, or both, and many studies have confirmed this (Wang et al., 2018). The high surface area of microplastics not only sorbs organic and inorganic contaminants but also supports chemical transport of plasticizers, other plastic additives, and constitutional monomers to the ecosystem through leaching (Teuten et al., 2009).

Studies have reported the sorption of various contaminants to microplastics, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxin-like chemicals, polybrominated diphenyl ethers (PBDEs), toxic metals, hydrophilic organic compounds (ciprofloxacin), and pharmaceuticals (antibiotics and anti-depressants) (Fred-Ahmadu et al., 2020). The most common plastic additives include phthalates, bisphenol A (BPA), polybrominated diphenyl ethers (PBDE), nonylphenols (NP), and antioxidants (Hermabessiere et al., 2017). Table 1 stretches some common toxic pollutants sorbed to microplastics and their toxic effects. Several studies imply the interaction between toxic pollutants and microplastics and their potential toxicological impact on the ecosystem.

2 Interaction Mechanisms

Microplastics act as a vector for the hazardous pollutants; therefore, the interaction mechanisms are necessary for the toxicity perspective of these pollutants in living organisms.

2.1 Adsorption of Hydrophobic Organic Pollutants onto Microplastics

Hydrophobic Attraction

Microplastics have low polarity on their surface due to electrostatic interactions, and this enables higher sorption capacity for the hydrophobic pollutant's adsorption of chemicals onto their surfaces (Liu et al., 2018). Hydrophobic chemicals such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and other benzene-ring derivatives adsorb and concentrate on the surface of the microplastics and form a micelle shape-like structure (Verla et al., 2019). The octanol-water partition coefficient (K_{ow} or log K_{ow}) is commonly used as a hydrophobicity parameter. Substances with high log K_{ow} values tend to absorb more readily to organic matter due to their low affinity for water (Mei et al., 2020).

Hydrogen Bonding

Hydrogen bonds are relatively weak electrostatic interactions, involving hydrogen ion H^+, and can affect the sorption of polymers when proton donor and proton acceptor groups are involved (Tourinho et al., 2019). PA and PU have a highest sorption capacity for BPA. It is attributed by the formation of hydrogen bonding between hydrogen donating BPA and hydrogen accepting groups in PA and PU (Liu et al., 2019).

Table 1 Common toxic pollutants sorbed to microplastics and their toxic effects

Toxic pollutants	Sources/uses	Toxic effects	References
Organic pollutants			
Pyrene	Dye and dye precursor, combustion of fuels	Toxic to kidneys and liver, carcinogenic	Shukla et al. (2014)
Naphthalene	Industrial application	Carcinogenic, hemolytic anemia	Shukla et al. (2014)
Phenanthrene	Coal tar, pesticides	Carcinogenic	Shukla et al. (2014)
Benzo(a)pyrene	Industries, coal tar, automobile exhaust fumes	Mutagenic, carcinogen	Shukla et al. (2014)
Polychlorinated biphenyls, PCBs	Electrical insulators, lubricants, paints	Disruption of Ah receptor; endocrine disruptor	Sánchez-Bayo (2011)
Organochlorine pesticides (OCPs)	Insecticide and pesticide	Xenoestrogenic, endocrine disruptor, potential carcinogen	Sánchez-Bayo (2011)
Polybrominated diphenyl ethers (PBDE)	Fire retardants	Thyroid hormone disruptors	Wang et al. (2018)
Nonylphenols	Detergents and pharmaceutical industries	Endocrine disrupters	Sánchez-Bayo (2011)
Octylphenols	Used to in rubber, in pesticides and paints	Endocrine disruptor with estrogenic	Miyagawa et al. (2016)
Bisphenol A (BPA)	In the production of synthetic polymers and thermal paper	BPA exhibits toxic, endocrine, mutagenic, and carcinogenic effect in living organisms	Michałowicz (2014)
Perfluoroalkyl substances (PFASs)	Semiconductors, waterproof materials	Reproductive and developmental, liver and kidney, and immunological effects in laboratory animals	Sánchez-Bayo (2011)
Toxic metals			
Copper	Electrical motors, metal alloy, architecture, and industries	Wilson's disease, liver cirrhosis, DNA damage	Shukla et al. (2014)
Zinc	Phosphate fertilizers, distillery, pharmaceuticals	Fever	Sarma and Joshi (2015)
Cadmium	Batteries and electroplating	Carcinogenic, poisonous, pneumonitis, pulmonary edema, DNA damage, oxidative stress	Shukla et al. (2014)
Chromium	Leather/tanner, thermal power plant, mining fertilizers, textile photography	Allergies, bronchial asthma	Sarma and Joshi (2015)
Lead	Battery, architectural metal, oil paints, gasoline	Neurotoxic. Produces ROS, DNA damage	Shukla et al. (2014)

(continued)

Table 1 (continued)

Toxic pollutants	Sources/uses	Toxic effects	References
Titanium oxide	Additive in plastic product	Cytotoxicity on human epithelial lung and colon cells	Campanale et al. (2020)
Arsenic	Mining, ore smelting	Cancer to the urinary bladder, lungs, liver, and kidneys	Campanale et al. (2020)
Mercury	Thermometers, switches, and some light bulbs	Mutagen or carcinogen, disruption of DNA molecular structure and brain damage	Campanale et al. (2020)

π–π Interaction

π–π interactions are attraction forces also called non-covalent interaction between conjugated structure. Aromatic polymers, such as PS, can undergo **π–π** interactions. Rochman et al. (2013a) showed polystyrene plastics sorbed higher concentration of PAHs than PET, HDPE, PVC, LDPE, and PP because of the contribution of $\pi - \pi$ and strong hydrophobic interactions.

Electrostatic Interactions

Electrostatic interaction occurs when microplastics and the pollutants are oppositely charged and repulsion occurs when they are of same charge. The charge of the microparticles is affected by pH and point of zero charge (pH_{pzc}). When the pH of point of zero charge being lower than most environmental pHs, MP becomes negatively charged otherwise it is positively charged. The negatively charged MP attracts the positively charged pollutants. Wu et al. (2019) showed that bisphenols undergo partial ionization. Bisphenol F shows higher ionization due to low pK_a value. The low pH_{pzc} of PVC indicates the surface is negatively charged; therefore, the adsorption is electrostatic repulsion between PVC MPs and anionic fraction ionized from bisphenols.

Van der Waals Force

Van der Waals forces are weak interactions occurring between molecules not involving covalent or ionic bonding. Hüffer and Hofmann (2016) observed that the aliphatic PE microplastics without any specific functional group can only undergo non-specific van der Waals interaction.

Pore Filling

The microparticles consist of a number of pores of different sizes, and the hydrophobic organic pollutant enters the polymer matrix and is trapped inside. It depends on the pore diameter of a polymer structure and the molecular size of the pollutant. Pollutants with lower molecular weights will easily travel into a polymer matrix with larger pores (Lambert & Wagner, 2017).

Halogen Bonding

Wu et al. (2019) studied the sorption of bisphenols on PVC microplastics. The halogen bond promotes adsorption of bisphenol to PVC. The –Cl on the branch of PVC which act as an electron acceptor and the benzene rings with hydroxyl group act as electron donor generate the halogen bond.

2.2 Adsorption of Hydrophilic Organic Pollutants onto Microplastics

Hydrophilic organic pollutants are polar, ionizable compounds used as pesticides, plasticizers, flame retardants, etc. Due to anthropogenic activities, these pollutants are washed off and enter water streams. Hydrophilic organic pollutants act as endocrine disruption at trace concentrations, which poses immense threat to the ecosystem and human health.

When microplastics enter the environment, their properties get changed, and photo-induced surface oxidation takes place and oxygen-containing functional groups are formed. Liu et al. (2019) investigated the adsorption of hydrophilic organic pollutant ciprofloxacin on pristine and aged PS and PVC microplastics. The adsorption in the aged microplastics was mainly through hydrogen bonding because of the presence of oxygen-containing functional groups. The pristine microplastics were negatively charged and CIP was cationic in lower pH and the adsorption was due to the electrostatic attractions. The pristine PS sorbed through π–π bonds, because the π–π bond strengthened the interactions between microplastics and CIP.

Xu et al. (2018b) observed Van der Waals interaction between sulfamethoxazole and PE microplastics. Sulfamethoxazole is a hydrophilic compound and exists as anion under pH 6.8. PE microplastics carry a negative charge; hence, there exist electrostatic repulsion than attraction. So, the sorption process would have more interactions such as electrostatic interaction and chemical bonds interaction. Guo et al. (2019) also reported the electrostatic interaction of sulfamethoxazole onto microplastics. In acidic environment, sorption of sulfamethoxazole to microplastic increases because microplastics tend to protonate with decreasing pH. Similar trends were observed in the sorption of perfluorooctanesulfonate (PFOS) on PE, PS, and PVC (Wang et al., 2015) and tylosin on PS and PVC (Guo et al., 2018).

Xu et al. (2018a) studied the interaction of tetracycline with three types of microplastics (polyethylene (PE), polypropylene (PP), and polystyrene (PS)) in batch sorption experiments. The interaction depends on the pH, at neutral medium hydrophobic, and at lower or higher pH, electrostatic interactions takes place. The sorption of tetracycline on PS microplastics was due to the presence of polar interactions and π–π interactions.

2.3 Adsorption of Metals onto Microplastics

Microplastics are negatively charged due to low polarity on their surface and metal ions are positively charged. The negatively charged microplastics bind to the positively charged metal by electrostatic attraction and neutralize their charge by forming a micelle shape-like structure (Verla et al., 2019).

Zou et al. (2020) observed electrostatic interaction in the sorption of Pb^{2+} to MPs and electrostatic interaction and complexation in the sorption of Cd^{2+} and Cu^{2+}. When the metal ions enter the solution, they exist in hydrated form. Pb^{2+} has a minimum hydrated ionic radius and therefore has the largest electrostatic interactions with the MPs. While in Cd^{2+} and Cu^{2+}, the electrostatic interaction, together with surface complexation, takes place onto the plastic surface. The sorption of Cd^{2+} and Cu^{2+} could also affected by the pH and ionic strength of the solution.

3 Factors Affecting the Interaction of Microplastics and Toxic Chemicals

3.1 The Materials of Microplastics

The structural properties of the polymer influence the process of sorption between the microplastics and contaminants. Polymers consist of crystalline and amorphous regions. The molecular segments of crystalline region are regularly packed, whereas in the amorphous region it is randomly packed. The crystalline region needs a high amount of energy for the chemical absorption. The amorphous region has a larger degree of free volume because of the distance among polymeric chains which allows the contaminants to diffuse readily through the polymer. The glass transition temperature (T_g) is related with amorphous domain of the polymer. Below the T_g, polymers are in glassy state so the molecules can only vibrate, and above T_g, polymers are in rubbery state so they have higher freedom of movement and hence absorption of pollutants is enhanced. The properties of polymers such as surface charge, surface area, molecular chain arrangement, functional group, and acid-base character also affect the sorption of chemicals (Fred-Ahmadu et al., 2020).

In the sorption studies of microplastics, PE has the highest affinity for sorption of pyrene followed by PS and PVC. The nonpolar nature and rubber-like character could be reason for maximum adsorption (Wang & Wang, 2018). When compared to PS and PVC, PE has greater segmental mobility and free volume in its molecular structure which enhances its sorption efficiency, whereas in PVC the chlorine atoms in the polymeric structure cause a reduction in free volume and make difficult for the migration of adsorbate diffuse into the polymer. The presence of benzene backbone in PS restricts the segmental mobility thus lower the transport of chemicals into the matrix (Wang et al., 2018).

Planar molecules can be easily sorbed to the polymer surface than the non-polar molecules because planar molecules can easily travel to the plastic surface than bulkier non-planar molecules (Velzeboer et al., 2014). The pore size affects the sorption process and small pores leads to the formation of monolayer while large pore size forms mono and multilayer adsorption (Tourinho et al., 2019).

3.2 The Size of the Microplastics

The sorption capacity depends on the MP's particle size, and a decreased particle size increases the surface area to volume ratio. Wang et al. (2019b) studied the size effect of polystyrene microplastics in the sorption of phenanthrene and nitrobenzene. The log K_d values increase with decreasing particle size of MPs and hence adsorption increases. The log K_d value of 50 nm polystyrene was significantly lower because its aggregation greatly reduced the effective surface area available for sorption. Teuten et al. (2007) showed PE, PP, and PVC of same size (200–250 μm) have different sorption capacities due to varying BET surface area. Since PE possess larger log K_d value and surface area than those of PP and PVC, it has higher sorption capacity.

3.3 The Aging and Weathering of Microplastics

The environmental conditions enhanced fragments and cracking of aged or weathered plastic particles into smaller particles due to the degradation process, namely, thermal, mechanical, biological, radiative, oxidative breakdown, or hydrolysis. The change in the property of the plastic surface enhanced the sorption of contaminants. The weathering increases polymer crystallinity and decreases hydrophobicity due to surface oxidation which affects the sorption of contaminants. Aging of polymer decreases its molecular weight which affects the sorption properties (Pèrez et al., 2010). The formation of biofilm on aged MPs due to biological effects also affects the sorption of contaminants.

The concentration of pollutants was higher on yellow plastic than the white. The yellowing of plastic is due to photooxidative weathering, the phenolic antioxidant added as additive results in the formation of quinonoidal structures. Black pellets have polyurethane as a constituent which increase the sorption of chemicals (Veerasingam et al., 2016).

3.4 The Chemical Properties of Contaminants

The organic pollutants present in the environment are mostly hydrophobic in nature. The sorption of organic pollutants mainly depends on hydrophobicity, molecular weight, and molar volume. The sorption of different organic pollutants onto polymers is related to their octanol-water coefficient (K_{ow}) values. The sorption of different contaminants has different octanol-water coefficient (K_{ow}) values for the same type of polymer. The molecular weight of the contaminant is more significant than K_{ow} if diffusion is the rate-limiting process (Tourinho et al., 2019).

3.5 The Environmental Factors

The environmental factors such as temperature, pH, salinity, and ionic strength affect the sorption of pollutants on microplastics. The sorption increases with increase in temperature. Xu et al. (2019) showed the K_d value increases with increasing the temperature from 5 °C to 15 °C indicating that the sorption of PBDEs on MPs was affected by temperature. Above 20 °C, Qiu et al. (2019) showed a decrease in sorption which could be due to an increase in ionic activity, which may compete with polyhalogenated carbazoles for sorption on MPs' surface in the simulated seawater.

When the pH of aqueous system increases, electrostatic repulsion between the contaminant and the microplastic decreases. A high pH can also increase the π–π interaction between the sorbate and the sorbent. Wang et al. (2019a) showed that increase in the pH of Cd solution led to an increase in the adsorption of Cd to PE microplastics. At PH >8, $Cd(OH)_2$ precipitates out which attributes to the adsorption of Cd.

Salinity also plays an important role in sorption of pollutant in aqueous system. Salinity is based on the degree of electrostatic interaction or ion-exchange mechanism. Zhang et al. (2020) in their study showed high salinity decreased the surface zeta-potential of the MPs and enhanced PHE sorption to MPs due to the salting-out effect. Ionic strength is the total ion concentration which is due to the dissolved salts in the water bodies. Zhang et al. (2018) showed a decreased sorption of oxytetracycline to PS MPs with increase in ionic strength. This is because of the competition for sorption between the ions in solution and toxic chemicals. The presence of DOM could also affect the sorption processes of chemicals by plastics as DOM competes with other chemicals for adsorption sites on the surface of the plastics by entering the pores or cover the surface of the polymer matrix (Mei et al., 2020).

4 Toxic Effects of Chemicals Adsorbed on Microplastics

4.1 Toxicity of Organic Pollutants

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are chlorinated organic compounds that vary in the number of attached chlorine atoms, with the general formula $C_{12}H_{10\text{-}x}Cl_x$. There are about 209 congeners of PCBs with different physical and chemical properties (Pascal et al., 2005). The international treaty on persistent organic pollutants, in the Stockholm Convention of 2001, listed PCBs in one of the "dirty dozen" chemicals. Environmental Protection Agency classifies PCBs as a "probable carcinogen." It also affects immune system, reproductive system, nervous system, and endocrine system in humans and animals (EPA, 2000). Although PCBs were banned in the 1970s, their residues are still present in the environment through biomagnifications due to their stability, lipophilicity, and high toxicity. Microplastics have greater affinity for PCBs due to their relatively high surface area to volume ratio (Velzeboer et al., 2014).

The concentrations of PCBs have been reported in many field studies. Frias et al. (2010) collected samples from two Portuguese beaches and found PCB concentration in the range from 0.02 to 15.56 ng g^{-1} on microplastics. Mendoza and Jones (2015) collected microscale plastic particles in September 2007 in the North Pacific Central Gyre and identified PCBs in the range of 1–223 ng g^{-1}. The main fragments of plastics collected in North Pacific Central Gyre were polypropylene (PP), polyethylene (PE), nylon, and polyurethane.

Gassel and Rochman (2019) investigated the chemical contaminants and microplastics in lanternfish (Myctophidae) in the North Pacific Gyre. Fish samples were collected from the North Pacific Subtropical Gyre and the California Current and the tissue concentrations of various chemicals sorbed from microplastics were examined. Lower chlorinated PCB congener's concentrations were higher in lanternfish, and it was about 11 ng g^{-1}lw compared to the other fish whose concentration is 0.87–4.04 ng g^{-1}lw.

In the beaches around San Diego, California, plastic debris were analyzed, and PCBs range was from 3.8–42 ng g^{-1} (Van et al., 2012). Total PCB concentrations were in the range 0.04–124 ng g^{-1} in the Tokyo bay, and it was higher in the urban areas (Yeo et al., 2019). Lo et al. (2019) examined PCB samples in Hong Kong and the total PCB concentration was in the range 13.0 and 1083 ng g^{-1}. Bouhroum et al. (2019) investigated the PCB concentrations in the open ocean and coastal debris and weres found to be 12.2 ng g^{-1} and 1.4×10^4 ng g^{-1}, respectively. Fraser et al. (2020) studied the distribution of PCBs and microplastics in sediments from the

Qiantang River and Hangzhou Bay, China. The sediment in the microplastics mainly contains PET, PS, and PET. These sediments contain PCB concentrations in the range from 1.13 to 1.65 ng g^{-1}.

Besseling et al. (2013) studied the exposure effect of *Arenicola marina* for 28 days to natively PCB contaminated sediment pre-equilibrated with PS. The effects of polystyrene (PS) microplastic on survival activity, and bodyweight, as well as the transfer of 19 polychlorinated biphenyls (PCBs), were assessed in bioassays with *A. marina* (L.). The uptake of plastic particles showed the weight loss of *A. marina* and also reduces the feeding activity. A low PS dose of 0.074% increased bioaccumulation of PCBs in tissues by a factor of 1.1–3.6. Norway lobster (*Nephrops norvegicus*) when ingested with PCB-spiked polyethylene shows limited bioaccumulation of PCB in *Nephrops* tail tissue, whereas PCB-spiked polystyrene shows no bioaccumulation (Devriese et al., 2017).

Grigorakis and Drouillard (2018) evaluated the diet assimilation efficiencies of goldfish (*Carassius auratus*) when exposed to microplastics spiked with PCBs and fish pellets spiked with PCBs. When these were fed to the fish, the microplastic-associated PCBs showed lower diet assimilation efficiencies compared to food matrix-associated PCBs. Jiang et al. (2018) examined the bioaccumulation of PCBs on *Daphnia magna* when incorporated in polystyrene nanoparticle. The PCBs accumulated 1.4–2.6 times more in *D. magna* than PCBs in the absence of polystyrene particles during the 24-h exposure. Asian clams (*Corbicula fluminea*) were exposed to PE, PET, PVC, and PS microplastics with and without PCBs and their predator's white sturgeon (*Acipenser transmontanus*) exposed to the calms. Tubular dilation occurs to the clam by the microplastic, and it has been enhanced by the presence of PCBs. The predators when fed with clams exposed to PCB spiked MP shows less vitellogenin proteins and glycogen depletion (Rochman et al., 2017).

Van der Hal et al. (2019) studied the viability for the transfer of PCBs when incorporated with polypropylene microplastic to herbivorous rabbitfish (*Siganus rivulatus*). The incorporated microplastics were mixed with dough and fed to the fish in two concentrations 500 ng g^{-1} and 5000 ng g^{-1}. PCB congener 194 was found in muscle tissue in the concentration of 200 ng g^{-1} after 2 weeks of exposure to 5000 ng g^{-1} PCB concentration. Lin et al. (2019) studied the toxicity of PCB-18 and 100 nm PS on *Daphnia magna* in water. The combined toxicity to *D. magna* depended on the relative concentration of nano-sized PS and PCB. At high PS concentration, lethality increased due to PS instead of PCB. The ingestion of PCB-spiked microplastics by the marine organism even in small amount led to bioaccumulation harm in them in long run.

Polyaromatic Hydrocarbon (PAHs)

Polyaromatic hydrocarbons (PAHs) are a group of toxic organic pollutants composed of two or more benzene rings bonded in linear, cluster, or angular arrangements (Abdel-Shafy & Mansour, 2016). About 16 PAHs have been listed as priority pollutants in the environment, due to their high toxicity for living organisms

(USEPA, 1980). The main source of PAHs is from petroleum industry. PAHs are well-known carcinogens and their toxicity includes genotoxicity, immunotoxicity, oxidative stress, and endocrine disruption (Honda & Suzuki, 2020). Its hydrophobic nature allows it to sorb easily to the hydrophobic surfaces of most MPs.

Lo et al. (2019) identified 19 PAH species in microplastics collected from the sandy beaches in Hong Kong. Total PAH concentration ranged from 70.8 ng g^{-1} to 1509 ng g^{-1}. Among the 16 PAHs in microplastics, phenanthrene has the highest average concentration of 121 ng g^{-1}. In Bandar Abbas, Iran, three urban intertidal regions, Khor-e-Yekshabeh, Gorsozan, and Suru were selected to study the relationship between microplastic and toxic chemicals accumulated in the sediment. The MPs ranged from 3542 to 33,561 items per m^2 in different regions with variety of shapes and colors. Among the different PAHs found, naphthalene was the predominant component. The total PAH concentration was in the range from 75.80 to 116.10 ppb (Yazdani Foshtomi et al., 2019).

Chen et al. (2020) collected the MPs from the surface waters of estuary in the southwestern coast of Taiwan and analyzed the PAHs accumulated with the MPs. The average PAH concentration was 818 ± 874 ng g^{-1}. Tan et al. (2019) analyzed the spatial distribution of microplastics, as well as microplastics and their adsorbed PAHs in the surface water of the Feilaixia Reservoir. Among the 16 identified PAHs, chrysene, benzo [ghi] perylene, and phenanthrene were the predominant. The total concentration of the 16 PAHs was ranged from 282.4 to 427.3 ng g^{-1}.

Sharma et al. (2020) reported the existence of carcinogens in microplastics which act as vector of PAHs originated from e-waste. The cancer risk in terms of lifetime of microplastic ingestion was 10^{-5} which is higher than the recommended value of 10^{-6}. The smaller microplastics of size smaller than 5 mm show a higher adsorption capacity of about 110 mg g^{-1} which is 40% higher than big size particle.

Phenanthrene

Phenanthrene is a polycyclic aromatic hydrocarbon that occurs in fossil fuels, and due to incomplete combustion, it is present ubiquitous in the environment. Phenanthrene is one of the PAHs in EPA's priority pollutant list. Karami et al. (2016) analyzed the biomarker responses of African catfish (*Clarias gariepinus*) when exposed to LDPE microplastics loaded with phenanthrene for 96 h. The degree of tissue change, the plasmaglobulin, total protein levels, and the content of glycogen-positive material in the liver were increased, while the transcription levels of forkheadboxL2 (foxl2) and tryptophanhydroxylase2 (tph2) in the brain were decreased when exposed to Phe-loaded MPs.

Ma et al. (2016) studied combined toxicity of phenanthrene with five different sizes (from 50 nm to 10 mm), of polystyrene microparticles. The combined toxicity shows an additive effect on the *D. magna* species. The presence of NPs significantly enhanced bioaccumulation of phenanthrene-derived residues in daphnid body and inhibited the dissipation and transformation of phenanthrene in the medium, while 10-mm MPs did not show significant effects on the bioaccumulation, dissipation, and transformation of phenanthrene. The differences may be attributed to higher adsorption of phenanthrene on 50-nm NPs than 10-mm MPs. The MPs aggravate the toxicity of organic pollutants, whereas in some cases it contradicts. Li et al. (2019) studied the toxicity of phenanthrene-induced polystyrene microplastics to fertilized eggs of marine medaka (*Oryzias melastigma*). The combined exposure increased the hatchability, decreased malformation and mortality rates, and restored Phe-induced abnormal expressions of cardiac development-related genes.

Pyrene

Pyrene is a polyaromatic hydrocarbon that consists of four fused benzene rings. It is ubiquitously present in the environment due to the incomplete combustion of fossil fuels. It is also used in the manufacturing of dyes, plastics, and pesticides. Animal studies in mice shown that it is toxic to kidneys and liver. Oliveira et al. (2013) studied the combined toxicity effects of pyrene – microplastics on juveniles (0+ age group) of the common goby (*Pomatoschistus microps*). The exposure resulted in lethargic swimming behavior which is due to the decrease in AChE activity. The reduced isocitrate dehydrogenase (IDH) activity decreases the antioxidant defense and reduces the organism fitness in the environment.

The study of Avio et al. (2015) reveals that PS and PE adsorb pyrene, and when it is exposed to mussels (*Mytilus galloprovincialis*), accumulation of pyrene was observed in hemolymph, gills, and digestive tissues. The adsorption of chemical to the PS and PE does not differ much. The cellular response hazard is severe for those exposed to pyrene-contaminated PE or PS, respectively. Guven et al. (2018) revealed that tropical fish juveniles (*Lates calcarifer*) when exposed to PS-divinylbenzene MP spiked with pyrene for 24 h showed no effect of feeding, but the swimming speed decreased.

Benzopyrene Toxicity

Benzopyrene comes under PAHs. International Agency for Research in Cancer (IARC, 2011) classified benzo [a] pyrene in group 1 human carcinogen. The benzopyrene metabolite produced by cytochrome P450 enzymes (CYP) covalently binds to DNA and causes mutation. The lipophilic nature of benzopyrene makes it adsorbs onto sediments and particulate matter which then undergoes slow degradation.

Batel et al. (2016) developed an artificial food chain with *Artemia* sp. nauplii and zebrafish (*Danio rerio*) to study the transport of microplastic particles and associated persistent organic pollutants (POPs). The transfer and retention time of microplastic-associated benzopyrene via nauplii to zebrafish was analyzed by fluorescence tracking technique. The fluorescence tracking of benzo[a]pyrene indicates that the POP is transferred to the intestinal epithelium and liver from the intestine of fish. O'Donovan et al. (2018) found out after 14 days exposure of LDPE+BaP to calms, a considerable increase in BaP concentration was observed in the whole tissues, reaching a concentration of about 7.3 ± 2.0 ng g^{-1} dw. An increase in superoxide dismutase (SOD) activity was noticed after exposing the calms to spiked microplastics for 7 days which results in increased oxidative stress and deficiency of antioxidant.

Dietary exposure of different sized polystyrene microplastics sorbed with benzo[a]pyrene to mussels *Mytilus galloprovincialis* (González-Soto et al., 2019) shows smaller sized MPs (SMPB) with higher toxicity than the larger MPs. After 7 days exposure to SMPB, the transfer of BP to *M. galloprovincialis* shows 66-fold increase and after 26 days there was a 150-fold increase in mussel's tissues when compared to the control. The smaller size microplastics caused higher toxicity to DNA damage and cell type composition of digestive tubules than larger size microplastics.

Cousin et al. (2020) studied the transfer of MPs and associated contaminants to the larvae of zebrafish and the marine medaka via *Paramecium* and *Artemia* plankton. The larvae incubated with waterborne MPs did not feed directly on MPs. Ingestion of *Paramecium* and Artemia nauplii containing MPs was recorded inside the gastrointestinal tract of both the fishes using Cyp1a induction and fluorescent analysis. Pittura et al. (2018) in their study on combined chemical and physical hazards to mussels *M. galloprovincialis* found a potential transfer of BaP from MPs to hemolymph, gills, and especially digestive tissues which resulted in alterations on the immune system, on the oxidative status, neurotoxicity, and genotoxicity.

Fluoranthene (FLU)

Fluoranthene is one of the US Environmental Protection Agency's 16 priority polycyclic aromatic hydrocarbons. Fluoranthene is released into the environment by burning of fossil fuels and wood. It is used as an ingredient in dyes, pharmaceuticals, and insulating oils. Long-term exposure to fluoranthene causes nephropathy (kidney disease), increased liver weight, and increases in liver enzymes. Paul-pont et al. (2016) evidenced that micro-PS exhibited higher sorption capacity for fluoranthene than marine algae *Chaetoceros muelleri* as indicated by the partition coefficient log K_d values, and this confirmed a strong affinity of fluoranthene for polystyrene. After 14 days exposure of combined exposure to marine mussels *Mytilus* spp. shows highest histopathological damages and levels of antioxidant markers.

Magara et al. (2018) examined the effect of polyethylene MP on the accumulation and related oxidative stress response to fluoranthene in blue mussel, *Mytilus edulis*. Individual exposure of fluoranthene or MP shows antioxidant response more in gills than in digestive gland but co-exposure did not yield additive or synergistic effects. Magara et al. (2019) investigated the possible effects of PHB microplastics as a single contaminant and in combination with fluoranthene on the oxidative stress system of blue mussel *M. edulis*. The study revealed the inhibition of CAT, SeGPx, and GST activity and also modified the antioxidant responses in both gills and digestive glands. The combined effects of microplastics with fluoranthene were not significant compared with those exerted by MPs alone.

Nonylphenol (NP)

Nonylphenol is used in the manufacturing of antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers, and solubilizers. It persists in the environment, and it is extremely toxic to aquatic organisms. NP has been detected in human breast milk, blood, and urine due to its ability to mimic estrogen and in turn disrupt the natural balance of hormones in affected organisms. Beiras et al. (2019) exposed polyethylene MP to 4-n-Nonylphenol and the 4-Methylbenzylidene-camphor to marine zooplankton organisms, meroplanktonic larvae, and holoplanktonic larvae of the copepod *Acartia clausi*. Microplastics did not increase the bioaccumulation and toxicity of 4-n-NP or 4-MBC to zooplankton and sea-urchin larvae compared to the water-borne exposure.

Beiras and Tato (2019) studied the vector effect of PE MP in transferring NP to marine planktonic organism sea-urchin larvae and their toxicity. The ingestion of MPs by larvae does not increase the toxicity of NP, but in the absence of MPs NP was toxic. The effective concentration of NP reduces the larvae growth. The combined toxicity of PE, PS, PA, PE1000, and PA1000 microplastics and nonylphenol on microalgae *Chlorella pyrenoidosa* was investigated. The microplastics alleviate the nonylphenol toxicity to microalgae. The smaller size MPs has higher adsorption and led to oxidative damage. Antagonistic effect on *C. pyrenoidosa* growth was influenced by microplastics and NP (Yang et al., 2020).

Polybrominated Diphenyl Ethers (PBDEs)

PBDEs are organobromine compounds used as a flame retardant which is added as an additive during the manufacturing of plastics. On aging, PBDEs tend to leach out of the plastics. PBDEs are endocrine-disrupting chemicals, since they interfere with the endocrine system function of animals. Tanaka et al. (2013) examined oceanic seabirds (short-tailed shearwaters, *Puffinus tenuirostris*) collected in northern North Pacific Ocean. All the examined sea birds contain plastic in their stomach. PBDEs were measured in the abdominal adipose of the 12 birds and in the ingested plastics, and in the whole tissues of 6 lanternfishes and one squid. The lower-brominated congeners such as BDE47, BDE99, and BDE154 were dominant. These lower-brominated congeners were accumulated in the body of the seabird through the food web.

Granby et al. (2018) investigated PCB- and PBDE-associated microplastic contaminants can alter toxicokinetics in European seabass (*Dicentrarchus labrax*). The microplastics increased the accumulation of the sorbed contaminants in the seabass. The contaminants altered the gene expression and increased the toxic effects.

Pthalates

Li et al. (2020a) studied the combined toxicity of polystyrene microplastics and dibutyl phthalate (DBT) on the microalgae *Chlorella pyrenoidosa*. The mixtures of MPs and DBP intensify the morphological damage of the cell. The distorted and deformed thylakoids show that photosynthesis was inhibited and the Antagonistic effect is caused by the combination of hetero- and homo-aggregation of microalgal cells.

Deng et al. (2020) examined that MPs adsorb phthalate esters and desorb into mouse gut and cause intestinal accumulation. The Di(2-ethylhexyl) phthlate (DEHP)-contaminated MPs cause intestinal inflammation and metabolic disorders due to accumulation of DEHP in the intestine. Schrank et al. (2019) examined morphology, reproductivity, and mortality of *Daphnia magna* when exposed to rigid PVC and PVC with Diisononyl phthalate. The leached DiNP from flexible PVC significantly affects the number of offspring as well as the growth of *D. magna*. The marine copepod *Tigriopus japonicus* exhibits antagonistic effect for acute and chronic reproduction tests when exposed to DBP and polystyrene microplastics (Li et al., 2020b).

Bisphenol (BPA)

Chen et al. (2017) studied the uptake and distribution of BPA in the tissues of zebra fish and neurotoxicity in the presence of PE nanoplastic. The neurotoxic effect in CNS and dopaminergic systems increased in the co-exposure of NPs and BPA. The co-exposure shows no significant reduction of AChE activity because the associated BPA molecules on NPPs cannot interact with AChE directly.

Daphnia magna a fresh water zooplankton was exposed to polyacrylamide and BPA. The daphinds ingested PA MPs loaded with BPA and cause lower BPA body burden (Rehse et al., 2018). Yu et al. (2020) studied the sorption behavior of tetrabromobisphenol a (TBBPA) and PE microbeads and their effect on zebrafish. The co-exposure induced alteration in antioxidant level indicating higher antioxidative stress in liver when compared to either PE or TBBPA alone. The methane production from the anaerobic digestion of waste-activated sludge (WAS) was influenced by the presence of PVC microplastics. The BPA leached from the microplastics ruptured microbial cell walls and extracellular polymeric substances and decreased the methane production by inhibiting the hydrolysis–acidification process (Wei et al., 2019).

Chlorpyrifos (CPF)

Chlorpyrifos is an organophosphate pesticide, and its toxicity leads to neurological dysfunctions, endocrine disruption, and cardiovascular diseases. Bellas and Gil (2020) investigated the toxicity of polyethylene MP and CPF to *Acartia tonsa*, a calanoid copepod. The survival rates, fecundity, feeding, and egg viability were studied. The combination of CPF and MP caused a 70% decrease in egg production than alone. CPF-loaded MP shows decrease in survival and feeding rate.

Garrido et al. (2019) assessed the toxicity of MPs and the pesticide chlorpyrifos (CPF) to the microalgae, *Isochrysis galbana*, clone t-ISO. The microalgae growth rate was monitored. The exposure to MPs alone does not affect the microalgae growth. However, CPF affects the microalgae growth. When microalgae exposed to CPF sorbed to MPs, lower percent on inhibition of growth rate was observed. MPs reduced the toxicity of CPF because MPs were too big to penetrate into the microalgal cell wall. Bour et al. (2020) exposed *Gasterosteus aculeatus* to polyethylene MPs spiked with CPF via prey ingestion. The fish exposed to MP-CPF shows AChE inhibition and hyperactivity.

Triphenyltin Chloride

Triphenyltin chloride is an organotin compound used as a fungicide and antifoulant. Yi et al. (2019a) studied the combined toxicity of polystyrene MPs and triphenyltin chloride to the green algae *Chlorella pyrenoidosa*. The exposure to 0.55 μm PS led to the structural damage of algal cell which facilitates the uptake of TPTCl and increased its toxicity.

Yi et al. (2019b) investigated the effect of polystyrene (PS) particles on the toxicity of triphenyltin (TPT) to the marine diatom *Skeletonema costatum*. MPs with smaller size of 0.1 μm have larger surface area for adsorption of TPT than with larger size PS particles. The PS microplastics decreased the toxicity of TPT to the diatom as the IC_{50} value increased in the presence of PS.

Rainieri et al. (2018) studied the organ toxicity of zebrafish (*Danio rerio*) when exposed to the mixture of PCBs, BFRs, PFCs, and methylmercury combined with LD-PE 125–250 μm of diameter for a period of 3 weeks. The differential gene expression of selected biomarker genes and quantification of perfluorinated compounds in liver, brain, muscular tissue, and intestine of some selected samples were analyzed. The combined toxicity affects their organ's homeostasis to higher extent than the contaminants alone. The liver is the most affected organ, and it also has highest concentration of perfluorinated compounds followed by brain and then muscles.

Rochman et al. (2014) showed early-warning signs of endocrine disruption in Japanese medaka (*Oryzias latipes*) fish exposed to a mixture of contaminants such as PAHs, PCBs, and PBDEs sorbed on polyethylene deployed in San Diego Bay. In a similar study (Rochman et al., 2013b), PBT exposure inhibits AhR activity and decreases expression of CYP1A. Since the fish exposed to the sorbed chemicals in the PE causes bioaccumulation of chemicals leading to liver toxicity.

4.2 Pharmaceutical Toxicity

The European Environmental Agency identified pharmaceutical toxicity as emerging environmental problem. The widespread use of pharmaceutical products increased their discharge into the waterbodies and its toxicity begins to increase. The discharged waste into the environment interacts with the MPs, and when these mixtures are ingested by the organisms, their toxicity increases.

Cefalexin

P. microps juveniles at 25 °C when exposed to cefalexin and microplastics mixtures induced mortality rate (Fonte et al., 2016). The mortality rate of the mixture manifests when the temperature increases. The MPs containing higher concentration of cefalexin indued the predatory performance up to 66%. The presence of microplastics in the water influences the toxicity of cefalexin to *P. microps* juveniles, decreasing it to a relatively small extent. The temperature rise increased the toxicity of microplastics and of cefalexin, alone and in mixture with microplastics, to *P. microps* juveniles.

Roxithromycin (ROX)

Interactive effects of microplastics and roxithromycin on red tilapia (*Oreochromis niloticus*) fish were studied by Zhang et al. (2019a). Compared to roxithromycin exposure, the co-exposure shows bioaccumulation of roxithromycin in gut, liver, brain, and gills. The co-exposure induced the oxidative damage and AChE activity.

Zhang et al. (2019b) studied the toxicity impacts of ROX combined PS microplastics on *Daphnia magna*. The mortality rate and oxidative stress using SOD, CAT, GST, and GPx were assessed. The smaller size (1-μm) PS might immobilize to daphnids and cause physical damage than 10-μm PS. Hence the co-exposure to 1-μm PS and ROX was more toxic and led to the strongest biological responses in *D. magna*. Further it induces oxidative damage to cells in combination or microplastics and ROX alone.

Florfenicol (FLO)

Guilhermino et al. (2018) exposed fresh water *Corbicula fluminea* to the individual and mixtures of the antimicrobial florfenicol and MPs. The toxicology studies show that the mixture of MPs and florfenicol were more toxic than their components separately. MPs-florfenicol mixture caused significant feeding inhibition, neurotoxicity through cholinesterase enzyme (ChE) inhibition, isocitrate dehydrogenase IDH inhibition, and increased oxidative stress and lipid peroxidation levels.

Zhou et al. (2020) investigated the toxicity of oxytetracycline (OTC) and florfenicol with or without the presence of MPs in the blood clam. MPs are easily ingested by blood clam so they easily carry antibiotics into the body and increase the concentration of OTC and FLO. The MPs suppress the GST activity and gene expression by detoxification. The consumption of antibiotic accumulated clams by humans develops antibiotic resistance in the human gut microbiota.

Sertraline

The immune response of bivalve mollusk *Tegillarca granosa* was studied when exposed to polystyrene MPs (diameters 500 nm and 30 μm) and sertraline antidepressants alone and in combination (Shi et al., 2020). A synergistic immune-toxic effect was observed for Ser and nanoscale MPs, which may be due to the size-dependent interactions.

Sulfamethoxazole (SMX)

Huang et al. (2021) studied the interactive effect of aged and virgin microplastics (MPs) with the antibiotic sulfamethoxazole on red tilapia (*Oreochromis niloticus*). The co-exposure causes changes in enzyme activities and gene expressions. The red tilapia exposed to aged MPs and SMX causes severe stress lower neurotoxicity, reduced lipid peroxidation damages, and higher inhibitions of cytochrome P450 enzyme activities.

Triclosan (TCS)

Zhu et al. (2018) studied the toxicity of triclosan with four kinds of microplastics, namely, polyethylene, polystyrene, polyvinyl chloride, and PVC on microalgae *Skeletonema costatum*. The growth inhibition and oxidative stress including superoxide dismutase (SOD) and malondialdehyde (MDA) were determined. The TCS had obvious inhibition effect on microalgae growth within the test concentrations, and single microplastics also had significant inhibition effect which followed the order of PVC800 > PVC > PS > PE. However, the joint toxicity of PVC and PVC800 in combination with TCS decreased more than that of PE and PS. Browne et al. (2013) showed when lugworms are exposed to contaminated chemicals with PVC, they transfer chemicals from microplastics to gut. The results showed that survivorship and feeding were diminished by triclosan associated with PVC.

Syberg et al. (2017) showed that the mixture of PE microbeads and TCS has more toxic effect than TCS alone in marine copepod *Acartia tonsa*. The presence of MP in the mixture potentiates the toxicity of TCS. Nobre et al. (2020) studied the combined effect of TCS-spiked PE microbeads on oyster *Crassostrea brasiliana*.

The gills, digestive glands, and adductor muscles were dissected and biomarkers responses were studied. Glutathione S-transferases were inhibited in the gills when exposed to PE and TCS-spiked PE. The increase in dibenzylfluorescein dealkylase (DBF) activity was observed in the tissues of oyster.

Venlafaxine

Venlafaxine is a chiral antidepressant. Qu et al. (2019) examined the interactions and ecological impact of PVC MP and venlafaxine and its metabolite O-desmethylvenlafaxine on aquatic ecosystem. MPs may help to transport pollutants to liver subcellular structure and decrease the contaminant's metabolism. The MPs combined with chemicals enhance the oxidative stress in loach (*Misgurnus anguillicaudatus*). Enantioselective effects of the co-exposure might cause more adverse effects to organisms.

Procainamide Doxycycline

Microplastics-procainamide and microplastics-doxycycline mixtures were more toxic to marine microalga (*Tetraselmis chuii*). The mixture enhanced the toxicity significantly than each of the substances tested alone. Interaction of MPs with cell wall facilitates the uptake of chemicals in higher amount. The mixtures significantly affect the average growth and chlorophyll concentration (Prata et al., 2018).

4.3 Toxicity of Heavy Metals

Copper

Copper significantly decreased the average specific growth rate of *Tetraselmis chuii*. In the presence of MP, no significant differences among the toxicity curves were found. These results indicate that MP did not influence the copper-induced toxicity on *T. chuii*. The copper interacts with environmental aged microplastics (plastic particles) significantly than virgin ones (Davarpanah & Guilhermino, 2015).

Fu et al. (2019) investigated the interaction of copper with PVC microplastics and cell growth, physiological and biochemical responses of microalga *Chlorella vulgaris*. Mixture exposure enhances the cell growth, whereas single treatments significantly inhibit the growth of *C. vulgaris* and cause oxidative stress.

Chromium

Toxicology interaction between chromium and polyethylene was examined by exposing early juveniles of *Pomatoschistus microps* (Luís et al., 2015). The simultaneous exposure shows decreased predatory performance and inhibition of AChE activity. AChE inhibition was lower in the test with Cr(VI) alone and MP alone. From this study, it is evident that joint exposure increases the AChE inhibition.

Mercury

Mercury is very toxic at even very low concentration. Barboza et al. (2018a) studied the short-term toxic effects of microplastics and mercury exposures, individually and in binary mixtures, on juveniles of the European seabass *Dicentrarchus labrax* (Linnaeus, 1758). Microplastics and mercury when exposed individually caused neurotoxicity through acetylcholinesterase (AChE) inhibition (62–74%), increased lipid oxidation (LPO) in brain and muscle, and changed the activities of the energy-related enzymes, namely, lactate dehydrogenase (LDH) and isocitrate dehydrogenase (IDH). The binary mixtures caused significant inhibition of brain AChE activity (64–76%), and significant increase of LPO levels in brain (2.9–3.4 fold) and muscle (2.2–2.9 fold).

In another study, the swimming velocity and resistance time of juveniles of the European seabass *Dicentrarchus labrax* and *Dicentrarchus labrax* were studied. A significant reduction in swimming velocity was observed in fish exposed to the highest concentration of microplastics (64%), and mercury (53–76%) individually, and in the mixtures (80–87%). A considerable decrease in resistance time was observed in animals exposed to microplastics alone (5–28%), mercury alone (45–53%), and in the mixtures (52–64%). These results may be due to negative effects induced on metabolic, endocrine, and nervous systems that are known to be targets of microplastics and mercury. Since these substances are ubiquitous pollutants, their combined effects may adversely affect wild populations, ecosystem functions, and human health (Barboza et al., 2018b).

Silver

Khan et al. (2015) reported an increased proportion of intestinal silver and significantly lower silver in the body tissue when exposed to Ag-incubated PE microbeads in zebrafish (Danio rerio). Further, Khan et al. (2017) reported that the co-exposure of particulate plastics and Ag, and Ag-incubated particulate plastics, had no effect on the uptake of Ag in the intestine of rainbow trout fish.

Biofouling affects the properties and toxicity of microplastics. The changes in properties and the microplastic toxicity to daphnids *Daphnia magn*a and duckweed *Lemna minor* were evaluated by Kalčíková et al. (2020). Higher concentration of silver was adsorbed on MPBIO than MP and more silver was leached from MPBIO which was probably due to the weak adsorption of Ag on the algal and bacterial biomass. A decrease in root length and root cell viability of duckweed was observed with MPAg and MPBIOAg at higher concentration when compared to MP and MPBIO.

Zinc

The microplastics generated from the HDPE bags act as a vector for heavy metal adsorption. Hodson et al. (2017) established that microplastics generated from HDPE plastic carrier bags can accumulate Zn and act as a source of exposure to soil fauna. *Lumbricus terrestris* earthworms when exposed to Zn adsorbed microplastics, but there was no evidence of Zn accumulation, mortality, or weight change. This study signifies that the microplastics act as a vector and increase the metal exposure of the earthworm.

Cadmium

Wen et al. (2018) studied the exposure of MPs and Cd to juvenile *S. aequifasciatus*. This study shows the reduced bioaccumulation of Cd in the body of the fish which might be due to size, nature, and concentrations of MPs and metal. However, the mixture of MPs and Cd induced severe oxidative damage and stimulate the innate immune responses.

Gold Nanoparticle

The microplastics increase the toxicity of gold nanoparticles to the marine microalgae *Tetraselmis chuii* (Davarpanah & Guilhermino, 2019). The cultures were exposed to the mixture of microplastic gold nanoparticle for 96 h. AuNP alone and MP alone did not cause significant decrease of average specific growth rate of *T. chuii*. The mixture significantly reduced the average specific growth rate of the microalgae. The increased toxicity of the mixture relative to the effects caused by the substances alone may have been due to some damage in the cell wall induced by microplastics that facilitated the entrance of AuNP into the cells, resulting in increased toxicity.

A decreased predatory performance which results in delayed growth and reproduction was reported in fish *Pomatoschistus microps* when exposed to Au-NP and MP (Ferreira et al., 2016). Pacheco et al. (2018) studied the chronic effects of mixtures of citrate-stabilized gold nanoparticles (AuNP) and microplastics on *Daphnia magna*. The mortality caused by the mixture was higher than the AuNP and MP alone. The higher mortality rate indicates toxicological interactions between AuNP and MP in *D. magna*.

Lead Chromate

Lead chromate is added as an additive in the plastic manufacturing. Lead chromate toxicity arises due to the leaching of Pb and Cr from the aged microplastics because of surface cracks and fragmentation. Higher concentration of leachate inhibited the cell growth and photosynthesis in *Microcystis aeruginosa* (Luo et al., 2019).

Arsenic

The US Environmental Protection Agency recognized arsenic as one of the five most harmful soil pollutants. Dong et al. (2020) conducted a study to investigate the effects of microplastic particles of polystyrene and polytetrafluoroethylene and arsenic on leaves and roots of rice seedlings. Microplastic particles and As(III) inhibited the biomass accumulation, photosynthetic rate, chlorophyll fluorescence, and the chlorophyll-a content of rice. Further it induced an oxidative burst in rice tissues through mechanical damage and destruction of the tertiary structure of antioxidant enzymes.

4.4 Health Effects on Humans

Humans are exposed to microplastics and the adsorbed chemicals through ingestion, inhalation, and dermal contact in products, foodstuff, and air. The major source of MP ingestion is through the sea food. Humans could also ingest microplastics by consuming contaminated fruits and vegetable through the uptake from polluted soil (Galloway, 2015). During inhalation, airborne microplastics enter the lungs causing localized biological response, and the main source of airborne microplastics is textile fibers. The dermal exposure occurs through skin pores by the interaction of MPs with contaminated water or soil contaminated or from contact with particulate MPs (Enyoh et al., 2020).

Currently, there are no literatures related to the health effect on the direct or indirect consumption of MPs contaminated with endocrine disruptors. The toxicokinetics of absorption and distribution are only available, and no information is available on metabolism. The MPs and their contaminant chemicals are primarily ingested by lower trophic levels and bioaccumulate. The monomers and additives that leach from the surface of microplastics even in lower concentration act as endocrine disruptors (Cole et al., 2011). The transfer of these chemicals to higher trophic levels including humans raises the possibility of biomagnification. Bakir et al. (2014) showed that desorption of POPs under gut condition could be 30 times greater than in sea water. The gut microbiome is linked with the immune health function and lead to adverse effects such as the proliferation of harmful species, increase in intestinal permeability, and endotoxemia. However, contribution of microplastics to the exposure to POPs seems negligible when compared to the intake from food and water (Bakir et al., 2016). The release of chemicals or microorganisms adsorbed to microplastics will be highly dependent on the types associated with ingested particles, the clearance time and translocation of vector microplastics, the release rate and extent of the contaminant, and its translocation and noxious effects in human tissues. Greim et al. (2001) showed that stable and unstable lesions may arise after metabolism of microplastics associated with PAHs.

The exposure to PS and polyethylene in cerebral and epithelial human cells was not able to induce cytolysis, but increased reactive oxygen species (ROS) to high concentrations, contributing to cytotoxicity (Schirinzi et al., 2017). Furthermore, exposure of macrophage and lung epithelial cell cultures to PS (60 μm) caused ROS and endoplasmic reticulum stress leading to autophagic cell death (Chiu et al., 2015). The medical literature on impact of micro- and nanoplastics originating from inhalation or released from wear debris from plastic prosthetic implants shows diverse effects varying from DNA damage, changes in gene and protein expression, cell clotting, necrosis, apoptosis, and proliferation. However, human health impacts on monomers, additives, and degradation products migrating from plastics and microplastics should be further explored.

5 Conclusion

Microplastics are considered as a harmful potential threat to the aquatic and terrestrial environment as well as to the human health. The sorption of organic chemicals, trace elements on microplastics, and its exposure to the ecosystem led to the accumulation in food chains through agricultural soils, terrestrial, aquatic food chains, and water supply and augment its toxic effects. Several researchers assessed the synergistic effects and the potential transfer of microplastics and associated toxic chemicals to the living organisms. However, the harmful human health effects when exposed to the microplastics and the adsorbed toxic chemicals were mostly unknown which should be further examined.

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Correction to: A Bird's Eye View on Sustainable Management Solutions for Non-degradable Plastic Wastes

Gopal Jeya, Sridharan Rajalakshmi, Krishnaswamy Veena Gayathri, Ponmudi Priya, Pachagounder Sakthivel, and Vajiravelu Sivamurugan

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The original version of this chapter was inadvertently published without updating the Figs. 1 (Pg-507) and 2 (Pg-509) as per the author's request. Although they are correctly present on the online version.

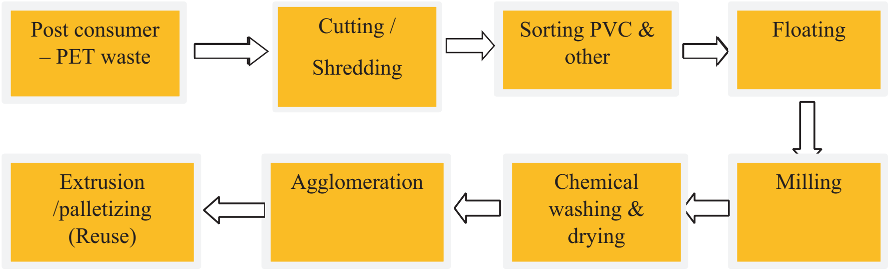

Fig. 1 Mechanical recycling methods

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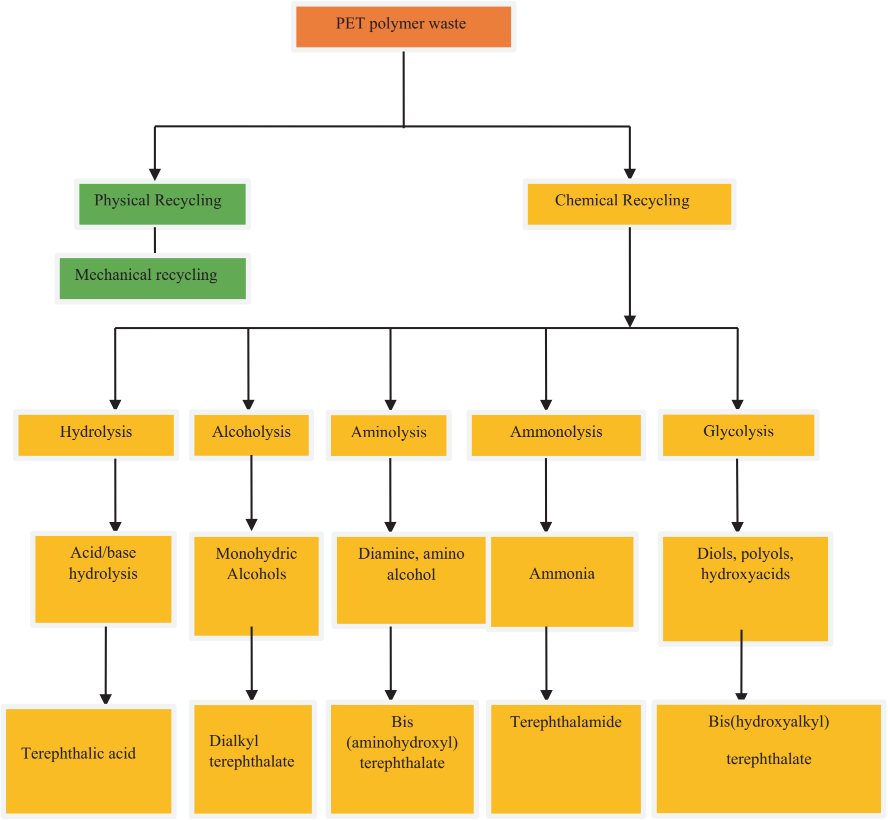

Fig. 2 Recycling methods of PET polymer wastes recycling method

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