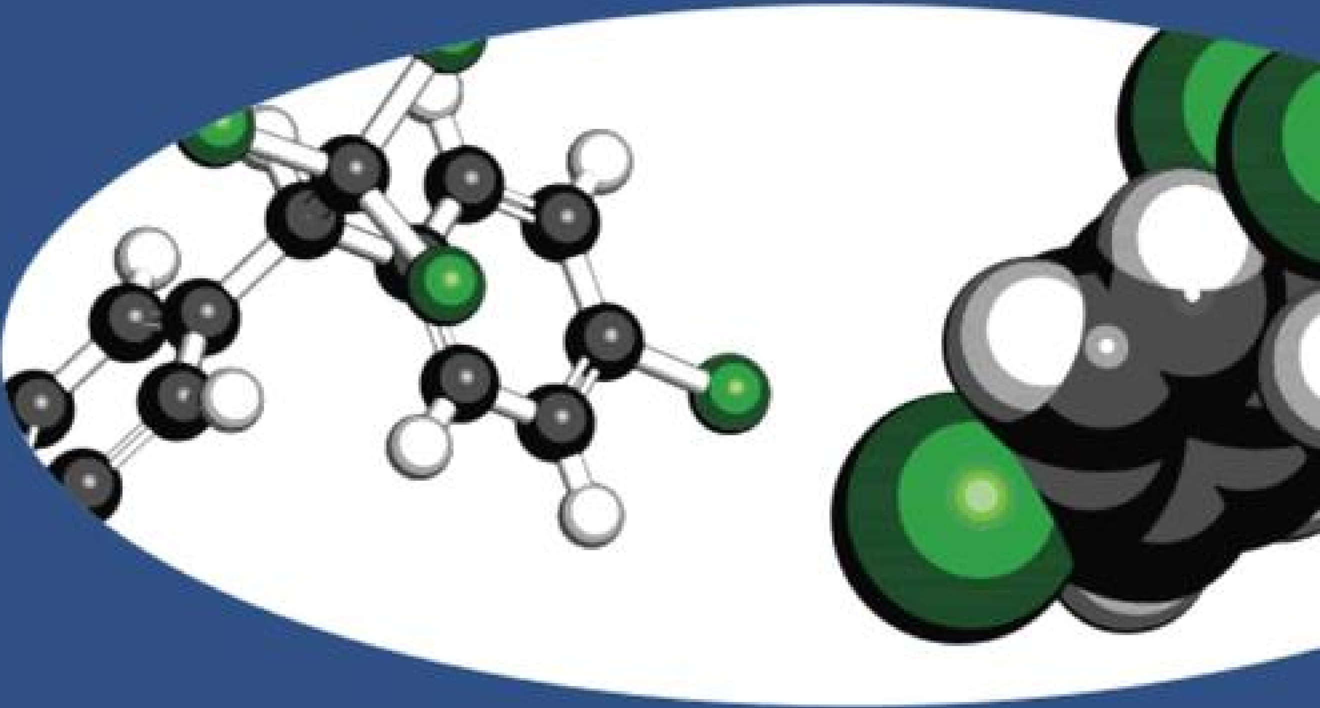
Current Developments in Biotechnology and Bioengineering



Bioremediation of Endocrine Disrupting Pollutants in Industrial Wastewater

Editors

Izharul Haq • Ajay S. Kalamdhad • Ashok Pandey

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Contents

Preface

The book titled *Bioremediation of Endocrine Disrupting Pollutants in Industrial Wastewater* is a part of the Elsevier book series on *Current Developments in Biotechnology and Bioengineering* (Editor-in-Chief: Ashok Pandey). This book intends to cover various aspects of endocrine-disrupting pollutants while discussing their toxic effects on human and animal health and state-of-the-art treatment technologies.

The endocrine-disrupting pollutants are widely distributed in respective environments such as water, wastewater, sediments, soils, and atmosphere. These are highly diverse that include synthetic chemicals used as industrial solvents/lubricants and their by-products (polychlorinated biphenyls, polybrominated biphenyls, dioxins), plastics, plasticizers, pesticides, fungicides, phytoestrogens, pharmaceutical agents, and certain industrial or commercial products. These pollutants are emerging from various industries such as pulp and paper, tannery, distillery, textile, pharma, etc. and have been considered as major sources of contamination. The endocrine-disrupting activity of these compounds is well-documented to have an adverse effect on the environment and human–animal health. Thus, there is an urgent need to cope with this challenge and develop sustainable methods for the treatment of endocrine-disrupting pollutants in industrial wastewater before its release into the environment.

The aim of this book is to comprehensively explore the current status of industrial pollution, its source, characteristics, and management through various advanced treatment technologies. The individual chapters will provide detailed updated information about endocrine-disrupting pollutants including occurrence, source, characteristics, distribution, health risk, and their remedial strategies through the conventional and advanced treatment process for environmental safety.

Covering multiple facets of pollutants and their management through the sustainable, advanced, and eco-friendly treatment process, this book is meant to serve as a single terminus for students, researchers, scientists, professors, engineers, and professionals who aspire to work in the field of environmental science, environmental biotechnology, environmental microbiology, civil/environmental engineering, eco-toxicology and other relevant areas of industrial waste management for the safety of the environment.

All chapters in this book have been contributed by global experts in the field of hazardous pollutants toxicity, its characteristics, effects, and emerging detection and treatment methods. There are 12 chapters in this book. Chapter 1 deals with the detailed study of pharmaceutical pollutants removal and its characteristics in industrial wastewater. Chapter 2 covers the harmful implications of the endocrine disruptive pollutants found in wastewater generated from bio-refineries and discusses the current status of their treatment processes. Chapter 3 includes fate, effects, source of bisphenol A from industrial wastewater and the removal through biodegradation using bacterial community. Chapter 4 focusses on the phytoremediation of endocrine disruptive pollutants from industrial wastewater and different actors of phytoremediation have been highlighted. Chapter 5 provides a discussion on the sources, application, toxicity of alkylphenol, and its removal through various conventional and advanced or combination of methods at the urban and industrial scale. Chapter 6 discusses updated information on phthalate esters occurrence and their toxicity on human, animal, and environmental health as well as their aerobic and anaerobic biodegradation in various wastewaters. Chapter 7 details provide a current description of the generation, characteristics, and toxicity of androgenic and mutagenic compounds and removal or degradation techniques, including biological methods. Chapter 8 elucidates the potential toxicological impacts (e.g., phytotoxicity, genotoxicity, and metabolic fate) of endocrine-disrupting pollutants upon plant life and its remedies that should take to solve these problems. Chapter 9 provides an insight into the occurrence, classification, characteristics, health, and societal impacts of endocrine-disrupting pollutants along with emerging bioremediation techniques, challenges, and future research prospects. Chapter 10 illustrates bacterial and microalgal degradation of endocrine-disrupting estrogens with focusing on removal efficiencies and metabolic mechanisms. Enhanced removal of estrogens by different strategies has been summarised. Chapter 11 covers the nature and type of endocrine disrupters in paper industry wastewater and their possible adverse effect, and various treatment approaches. Chapter 12 discusses an overview on endocrine-disrupting pollutants generation, their characteristics, impact on ecology and health, and their sequestration via bioadsorption techniques. The chapter also reviews the recent development of potential adsorbents and the different remedies applied to remove endocrine-disrupting pollutants.

We are grateful to the authors for compiling the pertinent information required for chapter writing, which we believe will be a valuable source for both the scientific community and the audience in general. We are thankful to the expert reviewers for providing their useful comments and scientific insights, which helped shape the chapter organization and improved the scientific discussions, and overall quality of the chapters We sincerely thank the Elsevier team comprising Dr. Kostas Marinakis, Former Senior Book Acquisition Editor, Bernadine A. Miralles, Editorial Project Manager, and the entire Elsevier production team for their support in publishing this book.

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Treatment of pharmaceutical pollutants from industrial wastewater

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1.1 Introduction

Environmental pollution through pharmaceutical industries is a matter of concern today as some of these industries still do not follow proper guidelines for waste disposal. Variety of toxic effluents produced as by-products during synthesis by fermentation and nonfermentation techniques, formulation operations, and packaging are released in the environment (Annesini et al., 1987; Alum et al., 2004). India pharmaceutical industries also keep discharging this effluent which leads to pollution and develops potential risk to the ecosystem (Arana et al., 2002; Balcioglu and Otker, 2003; Bellona and Drewes, 2007; Bokare and Choi, 2014).

The components present in effluents can be heavy metals, organic and inorganic substances, creating toxicity in the environment (Annesini et al., 1987; Chelliapan, 2006; Chang et al., 2008; Chelliapan, 2011). Population living near these pharmaceutical industries and those working in such industries are at direct risk due to these toxic chemicals which have accidentally intruded into the food web causing the imbalance of the ecosystem (Chen, 2004).

Global industrialization and its consequences also have led to the recognition and understanding of the side effects of pollution concerning public health and the environment. Millions of people die every year due to waterborne diseases which also include toxicity due to industrial effluents besides microbial diseases (Cokgor et al., 2004; Deegan et al., 2011; Damodhar and Reddy, 2013). Groundwater and surface water pollution have risen 20 times above the threshold level in those cities where there are many pharmaceutical companies. The water coming out as effluent from these industries is either untreated or undertreated which leads to the

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accumulation of wastes in surface water as well as groundwater (Deegan et al., 2011; Deepali and Joshi, 2012).

India also has registered an exponential rise in pharmaceutical industries since last 25 years and the use of raw materials for production has too increased causing more discharge of toxic by-products which sometimes have a very intensive color and bad odor (Enright et al., 2005; Dixit and Parmar, 2013). Pollution is mainly caused by some recalcitrant compounds which escape the treatment process and the nature of these compounds is different depending on the variety of medicine produced during any given manufacturing process (Garcia et al., 1995; Choudhary and Parmar, 2013; Gome and Upadhyay, 2013; Guo et al., 2017). Despite having very low levels of these recalcitrant compounds the pollution increases due to the presence of several nonbiodegradable organic matters such as hormones, antidepressants, antibiotics, and plenty other compounds which also contain some heavy metals like mercury, cadmium, nickel, chromium (Hrubec et al., 1983; Helmig et al., 2007; Idris et al., 2013). Central Pollution Control Board (CPCB), Government of India is authorized body for proper assessment and characterization of wastewater providing the standard limits of these effluents to be discharged into the environment (Tables 1.1 and 1.2).

Table 1.1 Summary of typical material inputs and pollution outputs in the pharmaceutical industry.

Process	Inputs	Wastewater	Residual wastes
Chemical synthesis			
Reaction	Solvents, catalysts, reactants, e.g., benzene, chloroform, methylene chloride, toluene, methanol, ethylene glycol, xylenes and hydrochloric acid	Process wastewaters with spent solvents, catalyst, reactants. High in BOD, COD, TSS with pH of 1–11	Reaction residues and reactor bottom wastes
Separation	Separation and extraction solvents, e.g., methanol, toluene, acetone, and hexanes	Spills, leaks, spent separation solvents	Separation residues
Purification	Purification of solvents, e.g., methanol, toluene, acetone, and hexanes	Spills, leaks, spent separation solvents	Purification residues
Drying	Drying Finished active drug and intermediates	Spills, leaks, spent separation solvents	-
Natural product extraction	Plant roots, animal tissues, extraction solvents, e.g., ammonia, chloroform, and phenol	Equipment cleaning, spills, leaks, spent solvents. Low BOD, COD, TSS, and pH of 6–8	Spent raw materials (plants, roots, etc.)
Fermentation	Inoculum, sugar, starches, nutrient, phosphates, fermentation solvents, e.g., ethanol, amyl alcohol, methanol, acetone, and MiBK, etc.	Spent fermentation broth, wastewater containing sugar, nutrients, etc. High BOD, COD, and pH 4–8	Waste filter cake, fermentation residues
Formulations	Active drug, binders, sugar syrups, etc.	Equipment cleaning, Spills, leaks, spent solvents. Low BOD, COD, TSS, and pH of 6–8	Particulates, waste packaging, rejected tablets, capsules, etc.

Effluent limitations guidelines and standards for the pharmaceutical manufacturing point source category, US EPA, Washington DC, Feb 1995.

Table 1.2 Pharmaceutical (manufacturing and formulation) industry.

Parameter (effluent standards)	Standards limiting concentration in mg/L, except for pH
Compulsory parameters	
pH	6.0–8.5
Oil and grease	10
BOD (3 days at 27°C)	100a
COD	250a
Total suspended solids (TSS)	100
Total dissolved solids (TDS)**	-
Bioassay testb	0% survival after 96 h in 100% effluent
Additional parameter*	
Mercury	0.01
Arsenic	0.2
Chromium (hexavalent) Lead	0.1
Cyanide	0.1
Phenolics	1.0
Sulfides	2.0
Phosphate	5.0

[*] Parameters listed as "Additional parameters" shall be prescribed depending upon the process and product
[**] Limits for total dissolved solids in effluent shall be prescribed by the concerned pollution control board/pollution control committee depending upon the recipient water body. [a] The BOD and COD limits shall be 30 mg/L and 250 mg/L, respectively, if treated effluent is discharged directly into a freshwater body, i.e., stream, canal, river, or lake. [b] The bioassay test shall be conducted as per IS: 6582-1971.

1.2 Characteristics of pharmaceutical industries' wastewater

A suitable treatment method for the pharmaceutical industry wastewater can be designed once we know the characteristics of the effluent (Ikehata et al., 2006). As discussed initially in this chapter manufacturing drugs depends upon raw materials used and later on the compounding and formulation processes employed (Imran, 2005). Manufacturing processes being the most important need to be stringent enough in the selection and availability of the raw materials keeping in mind their toxicity and their by-products and emissions generated.

According to Kansal (2011), there is a negative effect of the pharmaceutical industries treated effluents on the water quality. They studied the effect in samples of River Uppanar situated southeast coast of India. Their findings were as follows: pH range (7–8), temperature (26.25–28.87°C), electrical conductivity 694.08–1733.13), TDS (354.38–873.81 mg/L), TSS (50–348.75 mg/L), BOD (3.69–5.78 mg/L), COD (131.31–218.42 mg/L), Ca (36.75–55.86 mg/L), Mg (16.43–23.52 mg/L), hardness (162.97–236.1 mg/L), Na (70.69–100.12 mg/L), and chloride (131.20–176.97 mg/L). Tables 1.3 and 1.4 list down the studies done by various researchers on the characterization of pharmaceutical effluents.

Another important study was done by Kaushik et al. (2012) on assessing the physicochemical parameters and heavy metal concentration in the effluents of pharmaceutical industries from city Selaqui, Dehradun, Uttarakhand, India. Sampling was done from the selected five sites monthly and the study was carried out for 12 months. The compounds which were found

Table 1.3 Characterization of pharmaceutical industry wastewater (PIWW).

				References			
Parameters	**Gome and Upadhyay (2013)**	**(Choudhary and Parmar 2013)**	**Wei et al. (2012)**	**Lokhande et al. (2011)**	**Saleem (2007)**	**Idris et al. (2013)**	**Imran (2005)**
pH	6.9	5.8–7.8	7.2–8.5	3.69–6.77	6.2–7.0	5.65 ± 0.65–6.89 ± 0.12	5.8–6.9
TSS (mg/L)	370	230–830	48–145	280–1113	690–930	29.67 ± 4.22–123.03 ± 4.56	761–1202
TDS (mg/L)	1550	650–1250	-	1770–4009	600–1300	136.33 ± 5.83–193.05 ± 5.35	1443–3788
Total solids	1920	880–2040	-	2135–4934	-	-	-
BOD (mg/L)	120	20–620	480–1000	995–1097	1300–1800	-	263–330
COD (mg/L)	490	128–960	2000–350	2268–3185	2500–3200	-	2565–28,640
Biodegradability (BOD/COD)	0.259	-	0.20–0.39	-	-	-	-
Alkalinity (mg/L)	-	130–564	-	-	90–180	-	-
Total nitrogen (mg/L)	-	-	80–164	-	-	-	-
Ammonium nitrogen (mg/L)	-	-	74–116	-	-	-	-
Total phosphate (mg/L)	-	-	18–47	-	-	-	-
Turbidity (NTU)	-	-	76–138	-	2.2–3.0	17.22 ± 0.78–28.78 ± 1.18	-
Chloride (mg/L)	-	-	-	205–261	-	-	-
Oil and grease (mg/L)	-	-	-	0.5–2.9	-	-	1925–3964
Phenol (mg/L)	-	-	-	-	95–125	-	-
Conductivity (lS/cm)	-	-	-	-	-	157 ± 115.84–1673 ± 119.36	-
Temperature (°C)	-	-	-	-	-	32 ± 2.23–46 ± 3.41	31–34

Table 1.4 Characterization of different metal contaminants in pharmaceutical industry wastewater (PIWW).

	References					
Parameters	**Ramola and Singh (2013)**	**Rohit and Ponmurugan (2013)**	**Rao et al. (2004)**	**Mayabhate et al. (1988)**	**Vanerkar et al. (2013)**	**Sirtori et al. (2009)**
Iron (mg/L)	8.5–10.8	–	–	–	–	–
Chromium (mg/L)	0.12–0.31	0.01	-	-	0.057–1.11	-
Lead (mg/L)	0.158–0.262	0.03	-	-	0.559–6.53	-
Cadmium (mg/L)	0.16–0.56	-	-	-	0.036–0.484	-
Nickel (mg/L)	0.05–0.12	0.02	–	–	0.892–2.35	–
Zinc (mg/L)	1–1.3	0.20	—	–	0.583–0.608	-
Dissolved organic carbon (mg/L)	-	-	-	-	-	775
Copper (mg/L)	–	0.02	–	–	0.649–1.67	–
Selenium (mg/L)	-	-	-	-	0.428–0.666	-
Arsenic (mg/L)	-	-	-	-	0.0049–0.0076	-
Manganese (mg/L)	-	-	-	-	6.41–8.47	-
Sodium (mg/L)	-	-	-	-	155–266	2000
Potassium (mg/L)	-	-	-	-	128–140	-
Oil and grease (mg/L)	-	10.27	-	-	140–182	-
Calcium (mg/L)	-	-	-	-	-	20
BOD (mg/L)	-	410	7200	1200–1700	11,200–15,660	-
COD (mg/L)	-	548	25,000	2000–3000	21,960–26,000	3420
Dissolve phosphate (mg/L)	-	-	6.80	-	-	10
Nitrogen (mg/L)	-	185	-	-	389–498	-
TDS (mg/L)	-	622	20,000	-	2564–3660	-
TSS (mg/L)	-	110	7500	300–400	5460–7370	407
Total solids (mg/L)	-	-	-	-	8024–11,030	-
Electrical conductivity (lS/cm)	-	945	-	-	-	-
pH	-	6.01	7.5	6.5–7.0	3.9–4.0	-
Phosphate (mg/L)	-	-	100	–	260–280	10
Sulfide (mg/L)	-	-	100	–	42–54	-
Sulfate (mg/L)	-	-	360	–	82–88	160
Nalidixic acid (mg/L)	-	-	-	-	-	45
Color	-	White	Orange	–	Dark yellow	-
Chloride (mg/L)	-	-	200	-	-	2800
Alkalinity (mg/L)	-	-	2500	50–100	-	-
VFA (mg/L)	-	-	-	6000	-	-
Phenols (mg/L)	-	-	-	65–72	-	-
Volatile acids (mg/L)	-	-	-	50–80	-	-
Total acidity (mg/L)	-	-	-	-	3000	-

to cross the prescribed limits were phenolic compounds, BOD and COD whereas the rest of the compounds were within the prescribed limits. Later an appropriate model treatment plan was designed using the microbial consortia to eliminate the organic pollutants.

1.3 Advanced treatment methods used in pharma industries

In current years, pharmaceutical industries emphasize in particular on an increase remedies strategies for pharmaceutical wastewater (Shaik et al., 2011). Such strategies encompass neutralization/pH adjustment, oxidation, sand filtration (Saleem, 2007), ozone use, Fenton's method, coagulation/flocculation, electrocoagulation (Dixit and Parmar, 2013), photoelectrocoagulation, peroxi-electrocoagulation, peroxi-photoelectrocoagulation, sedimentation, membrane separation, UV irradiation, adsorption, chlorination, distillation, sun photo-Fenton, opposite osmosis, bacterial treatments (Madukasi et al., 2010), fungal treatment (Spina et al., 2012), algal treatment, phytoremediation and strategies the use of membrane bioreactor (MBR) (Chang et al., 2008), anaerobic constant movie reactor (AFFR) (Rao et al., 2005), cardio sequencing batch reactor (ASBR), membrane-aerated biofilm reactor (MABFR) (Li et al., 2012), and activated sludge (Gupta et al., 1988).

1.3.1 Physical treatment methods

1.3.1.1 Coagulation and sedimentation

The coagulation method includes iron or aluminum salts, such as aluminum sulfate, ferric sulfate, ferric chloride, or polymers, to the water. These chemical compounds are known as coagulants, carry a positive charge which neutralizes the dissolved and suspended debris within the water having a negative charge. When this reaction occurs, the debris binds together or coagulates this manner is every so often additionally known as flocculation. The large debris is heavy and speedy settle to the bottom. This settling manner is known as sedimentation. The mechanism of coagulating is complex. For superior treatment of pharmaceutical wastewater, the secret is a way to squeeze and eliminate certain water spherical hydrophilic colloids. So the flocculent is important, which is related to the impact of coagulation. Inorganic metallic salts and polymers are often used as flocculants. This approach can eliminate chromaticity and poisonous natural matter (Qi et al., 2017).

Meanwhile, it's ready to enhance the biodegradability of pharmaceutical wastewater. Sedimentation is the maximum used approach after coagulation. Under gravity, pollution could also be separated, which has more density than wastewater. Coagulation and sedimentation have a couple of advantages, including clean operation and mature technology, however, it's miles tough to eliminate dissolved natural matter.

1.3.1.2 Flotation

Except for sedimentation, flotation also can put off suspended solids of secondary effluent. The characteristic of this technique is generating an enormous range of small bubbles with the help of using injecting air into wastewater, forming floating floc with smaller density than wastewater. And it's going to float to the surface of wastewater to separate.

1.3.1.3 Chlorination

Chlorination has proven to be powerful for the elimination of prescription drugs along with 17α-ethinylestradiol and 17β-estradiol (Alum et al., 2004) and sulfonamides (Qiang et al., 2006). Chlorine dioxide is likewise powerful for the elimination of sulfamethoxazole, roxithromycin, 17α-ethinylestradiol, and diclofenac (Khetan and Collins, 2007). Acetaminophen, diclofenac, sulfamethoxazole, and fluoroquinolone all emerge as oxidized at some point of chlorination. By-merchandise of acetaminophen encompasses the poisonous by-products N-acetyl-p-benzoquinone imine and 1,4-benzoquinone. Both metoprolol and sulfamethoxazole form cancer agents consisting of chloramines as one in all their oxidation process and this will be because ammonia chlorination is approximately a thousand times faster than phenol chlorination (Pinkston and Sedlak, 2004).

1.3.1.4 Activated carbon adsorption

Activated carbon is an acknowledged traditional method for the elimination of each herbal and artificial natural contaminant (Hrubec et al., 1983; Annesini et al., 1987). It has a huge surface area, multilevel pore structure, excessive adsorption capability, and stable chemical property. Therefore, it's far broadly used as an adsorbent or catalyst provider to dispose of pollutants. It is maximum typically carried out as a powdered feed or in granular shape in packed mattress filters. Granular activated carbon (GAC) may be used as a substitute for anthracite media in traditional filters, supplying each adsorption and filtration. However, carbon regeneration and disposal are environmental considerations (Snyder et al., 2007).

In pharma effluents treatment, activated carbon is used for effluent that is poisonous and difficult to obtain discharge standard. It is a crucial approach of superior remedy of pharmaceutical wastewater as well. Activated carbon adsorption may be categorized as physical adsorption and chemical adsorption. Physical adsorption is reversible, and no selectivity to adsorbate. When activated carbon saturated with the aid of using adsorbates, it is easy to desorb. On the contrary, chemical adsorption adsorbs one or numerous particular adsorbates, which is irreversible and difficult to desorption. For cyclic utilization, a saturation of activated carbon restores its adsorption belongings with the aid of using regeneration. This approach is broadly used for advanced treatment, due to the fact it could be recycled, its higher remedy impact, and huge suitability. But there are a few disadvantages, inclusive of excessive prices relatively, the low performance of regeneration, and complicated operation, which restriction application (Fig. 1.1).

1.3.1.5 Advanced oxidation processes

The organic and physiochemical treatment techniques defined formerly have proven confined achievement for the treatment of pharmaceutical wastewater. However, the improvement of oxidation procedures is displaying better elimination rates. Oxidation reactions have primarily supplemented rather than replace conventional systems to enhance the treatment of refractory

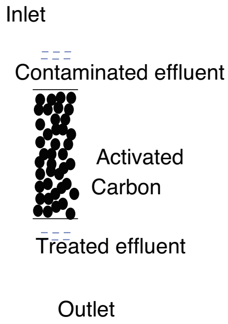

FIG. 1.1 Activated carbon adsorption.

organic pollutants (Balcıoğlu and Ötker, 2003). This technique has been correctly implemented in the treatment of pharmaceuticals (Khetan and Collins, 2007).

Advanced oxidation processes (AOPs), which could oxidize pollution via way of means of forming free radicals. Those forms of pollution can't be degraded via way of means of a common oxidizing agent. A chemical agent like hydrogen peroxide, ozone, transition metals, and steel oxides are required for AOPs. In addition, ultraviolet-seen radiation, electric-powered current, gamma-radiation, and ultrasound are required as an energy source (Ikehata et al., 2006). AOPs are primarily based totally on the manufacturing of free radicals, particularly the hydroxyl radical and facilitate the conversion of pollution to much less dangerous and greater biodegradable compounds (Naghashkar et al., 2006).

Wet air oxidation (WAO)

WAO has been recommending via way of means of F.J. Zimmer Mann in 1958, which became used for papermaking black liquid treatment. By the use of air or oxygen as an oxidant, this system decomposes naturally to rely on inorganic or small molecules at excessive temperature (150–350°C) and excessive pressure (0.5–20 Mpa). WAO is usually utilized in the pretreatment of wastewater advance treatment. This technique has a huge sort of applications, excessive-performance of COD removal, that would even reach greater than 90% slightly below suitable conditions, low strength consumption, much less secondary pollution, and it is straightforward management.

Supercritical water oxidation (SCWO)

SCWO is a chemical response to dissolved oxygen and natural pollution in supercritical water. Organic matter, air, and supercritical water had been whole blended at 24 Mpa strain and 400°C temperature, turning into a homogeneous phase. In those situations, natural compounds spontaneously provoke the oxidation process. With the expansion of the method temperature, 99.9% or greater of the organic matter is unexpectedly oxidized into easy nonpoisonous small molecules in a duration of time, accomplishing the explanation for getting rid of obviating pollution. SCWO has excessive oxidation efficiency, will now no longer cause secondary pollution. However, this technique features a few shortcomings, such because it requires excessive running situations and excessive cost.

Fenton reagent

Fenton chemistry requires the reactions of H_2O_2 in the presence of a catalyst (Fe) that leads to the production of hydroxyl (–OH) radicals. Ultraviolet (UV) light stimulates this process by helping in generating –OH radicals through the photoreduction of Fe (III) to Fe (II). Fenton device changed into first of all utilized in organic synthesis, with the deepening of people's knowhow of it, the device changed into steadily implemented to industrial wastewater treatment. Fenton reaction may be achieved at normal temperature and pressure, and much less harm to the environment (Pignatello et al., 2006). It is a sophisticated oxidation method, that's simple, mild reaction conditions, and excessive oxidation efficiency. However, the shortcomings of the Fenton response cannot be ignored. One is because of free radical scavenging and decomposition of H_2O_2 itself, result in loss of oxidant. Another is the formation of iron mud in natural conditions, making it difficult for subsequent processing (Bokare and Choi, 2014).

Photocatalytic oxidation

Photochemical oxidation, additionally referred to as ultraviolet photocatalytic oxidation, is a combination of UV radiation and oxidant. In the excitation of ultraviolet light, oxidative decomposition of oxidants produces a more potent oxidative potential of free radicals that could oxidize extra tough to the decomposition of refractory natural pollution with oxidants only (Vogna et al., 2002). According to the varieties of oxidants, photochemical oxidation may be divided into UV/O_3, UV/H_2O, UV/H_2O_2/O_3, and so on. At present, the steps of the process can't be described. However, the impact of this approach on the remedy of refractory natural count numbers is undeniable.

Ultrasound oxidation

Ultrasonic degradation of organic compounds in wastewater is a physical and chemical degradation process, in particular primarily based totally on ultrasonic cavitation effect and the ensuing physical and chemical changes, which incorporates the subsequent three ways: loose radical oxidation, pyrolysis, and supercritical water oxidation. Many elements affect the impact of ultrasonic degradation of natural pollution in wastewater. The foremost elements are ultrasound frequency, sound power, ultrasonic time, answer temperature, and pH, and the character of natural be counted.

Electrochemical oxidation

Electrochemical oxidation is a quite new approach for the treatment of wastewater (Chen, 2004). The use of electrochemical response to eliminate poisonous and dangerous pollution in the water is referred to as the electrochemical method. The principle of the approach is as follows: within the electrochemical reaction process, the reactant will release electrons and be oxidized in the anode. Conversely, the reactant in the cathode will lose electrons and be reduced. In general, the elimination of refractory organic matter, especially because of the oxidation of the anode. Conventional electrochemical wastewater treatment strategies include electrolytic recovery, electrochemical oxidation, electrolytic air flotation, electrodialysis, and microelectrolysis. The electrochemical approach is likewise referred to as the "Environmentally Friendly" process, has an extraordinary benefit in comparison with different methods. For example, the electrochemical approach is normally finished below ordinary temperature and stress and has excessive efficiency, may be used alone or in mixture with different strategies, and it covers a small location and no secondary pollution, has quite an excessive diploma of automation. In the future, the main research focus of the electrochemical response is the studies of the anode and electrochemical reactor.

Ozonation

For a long time, ozone is taken into consideration to be a completely powerful oxidant and disinfectant (Arana et al., 2002). The important mode of motion in the ozonation method is the formation of OH– radicals because of ozone decay within the water, however, there are also ozone molecules available for the chemical attack. This will increase the oxidation capability (Ternes et al., 2003). Ozonation has been applied because of the precept treatment approach or to increase the biodegradability and performance of the next treatment (Cokgor et al., 2004). Ozone manufacturing is an energy-intensive method, making it expensive to implement.

In acidic conditions, ozone is the main oxidant. But in neutral and alkaline conditions, it specifically relies on free radical reactions. It may be visible that the oxidation capability of ozone is drastically better than different traditional oxidants. The oxidation ability of numerous oxidants oxidant half-response oxidation ability (V). Ozone can fast oxidize and decompose maximum of the natural count within the water, which may correctly dispose of pollution in water. However, it's miles tough to without directly mineralize. Instead, a biodegradable product may be produced. At the same time, it can additionally correctly dispose of turbidity and pathogens in wastewater. Ozone may be blended with different wastewater treatment technologies, forming ozone superior oxidation technology. This approach has a more potent oxidation capacity and decreases selectivity to reactants.

1.3.2 Membrane separation

Several membrane sorts and packages have been evaluated for the elimination of APIs at pilot and full-scale, consisting of microfiltration, extremely filtration, nanofiltration, opposite osmosis, electrodialysis reversal, membrane bioreactors, and mixtures of membranes in series (Bellona and Drewes, 2007; Snyder et al., 2007). Microfiltration and ultrafiltration are commonly now no longer powerful in removing organic contaminants as pore sizes range from 100-one to a thousand times large than the micro pollution that may slip thru the membranes.

Under positive using pressure throughout the membrane, a component in water selectively permeates it via the use of permselective membrane keeping apart media, that's known as membrane separation. In this way, attain the separation, purification, concentration of the target substance from the mixture. There are numerous membrane separation strategies in wastewater treatment. Such as microfiltration, ultrafiltration, opposite osmosis, and electrodialysis.

1.3.2.1 Microfiltration (MF)

MF is primarily based totally on static pressure because the driving force and the separation procedure is completed via way of means of the movement of the sieve separation of the membrane, which precept is much like conventional filtration. The mild difference is that the pore size of MF is smaller. This technique can successfully remove SS and microorganisms in wastewater.

1.3.2.2 Ultrafiltration (UF)

UF driving force is the pressure difference among the membranes on each side, the medium is the ultrafiltration membrane. Under positive pressure, while water passes through the membrane surface, water, inorganic salts, and small molecules penetrate, different macromolecules are trapped. This technique is specially used for the elimination of macromolecules and colloids in wastewater. The utility of this technique is thought to be ensured that the membrane has good enough membrane flux and is without difficulty disassembled, replaced, cleaned.

1.3.2.3 Reverse osmosis (RO)

There are mainly two classes of RO membrane, cellulose ester, and fragrant polyamide. Its components consist of a tube, plate and frame, roll, and hole fiber type. RO procedure can remove an extensive variety of impurities, dissolved inorganic salts, and lots of organic matter. Meanwhile, it has an excessive performance of salt elimination and water reuse rate. However, this approach calls for an excessive pretreatment of the feed water. With the improvement of RO, nanofiltration (NF) has been proposed as a brand new approach.

1.3.2.4 Electrodialysis (ED)

ED may be a mixture of electrolytic and dialysis diffusion processes. Under the movement of the DC electric powered field, anions and cations of the dissolved salts within the wastewater are moved to the anode and the cathode respectively. During this way, the concentration of anions and cations within the intermediate compartment is steadily reduced, and separation and recovery are achieved. This approach has many advantages, alongside much less electricity and pharmaceutical consumption, much less environmental pollution, ease of work, and automation. But it could handiest remove the salt in water, and desalination performance is decrease than RO.

1.3.3 Biological treatment

Biological treatment strategies have traditionally been used for the control of pharmaceutical wastewater. They can be subdivided into aerobic and anaerobic processes. Aerobic packages encompass activated sludge, membrane batch reactors, and sequence batch reactors (LaPara et al., 2002; Raj and Anjaneyulu, 2005; Noble, 2006; Chang et al., 2008). Anaerobic strategies encompass anaerobic sludge reactors, anaerobic film reactors, and anaerobic filters (Enright et al., 2005; Rao et al., 2005; Chelliapan et al., 2006; Sreekanth et al., 2009). The wastewater traits play a key function within the choice of biological treatments.

Solvents, APIs, intermediates, and raw substances constitute biologically recalcitrant materials that affect the performance of biological treatment systems (Oz et al., 2004; Helmigg et al., 2007). Activated sludge (AS) treatment is fallacious for the treatment of wastewater in which the COD tiers are extra than 4000 mg/L (Raj and Anjaneyulu, 2005). In theory, after secondary treatment, pharmaceutical wastewater must now no longer be treated through biological strategies, due to its negative biodegradability. However, we can't forget about the benefits of biological treatment, consisting of low cost, strong remedy effect. It may be used as a manner of pretreatment in the advance process.

1.4 Conclusions and perspectives

The pharmaceutical industry is essential for modern. Consequently, pollutants are generated during the production of medicines. The tremendous increasing number of pharmaceutical industries lead to hazardous adverse impact on water quality and surrounding environment with human health. Assessment and characterization of pharmaceutical industrial wastewater are to the need time to time with the increased level of water pollution highlights the environment pollution issues. Due to the rapid decrease in the level of water resources and increasing demand for water for consumption in our daily life, it is necessary to reuse the wastewater by developing a sustainable treatment process to clean up contaminated wastewater economically and safely, which could be easily adopted by the common masses.

Various treatment methods for pharmaceuticals in water and wastewater found in the literature have contributed greatly regarding the fate of these recalcitrant organic compounds in different treatment systems. The behavior of these compounds in these systems would allow further characterization of the fate and risk associated with pharmaceuticals in the environment. The pollutants generated during the manufacturing process are easier to handle, as an industry is a point source of pollution and it is possible to install pollutant-specific treatment facilities.

Some auspicious new treatments including advanced oxidation processes such as oxidation, ozonation, per ozonation, direct photolysis, TiO_2 photocatalysis, solar photocatalysis, Fenton reaction, and ultrasonic irradiation. These significantly enhance the removal rate and biodegradability of pharmaceuticals from wastewater. Most of these physicochemical processes removed the majority of the colloidal organic substances and suspended materials; however, refractory compounds remained in the water effluent. The pharmaceutical industry is one of the most important for modern civilization. Apart from this, pollutants are also generated during the manufacturing process of medicines. Thus, the pharmaceutical industry has become one of the major causes of concern. Biological treatments methods have traditionally been used for the management of pharmaceutical wastewaters. They are categorized into aerobic and anaerobic processes which include the use of activated sludge, membrane batch reactor, sequential batch reactor, anaerobic sludge reactors, anaerobic film reactors, and anaerobic filters. The characteristic of wastewater plays a prime role in the selection of biological treatments. However, hydraulic retention time (HRT), temperature, pH, dissolved oxygen (DO), organic load, microbial community, presence of toxic and recalcitrant substances, and the batch operation of the pharmaceutical products are the few variables that require modifications for adaptation to pharmaceutical wastewater to enhance the efficiency of the biodegradability and mineralization capability of biological processes.

The bioremediation processes are technological tools that hold the great prospect for the future. They produce almost no waste residue and have the potential of being economical and in combination with the different physicochemical and advanced oxidation processes, offer better treatment of pharmaceutical industrial wastewater, and thus help in sustainable utilization of available water resources. This could most likely become a potential way to clean up the environment in near future.

Conflict of interest

The author has declared no potential conflict of interest with respect to the research and/or publication of this article.

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2

Elimination of endocrine disrupting pollutants from refinery wastewater

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2.1 Introduction

The ongoing urban development and industrialization in the world from decades have turned the environment into litterbin of synthetic chemicals which are often escorted by the effluents of wastewater treatment plants and refineries. Endocrine disruptive pollutants (EDPs) are one of the prominent categories of compounds existing in these synthetic chemicals. These EDPs are defined as the substances that affect the endocrine system of humans and animals by interfering with the production and release of the hormones. As these hormones are crucial for the physiological processes such as synthesis, metabolism, release, transport, and storage; the abnormalities in these key processes can create serious health concerns for humans and animals. As shown in Fig. 2.1, EDPs can disrupt the functionality of endocrine system through multiple routes. The EDPs can impact the endocrine system through mechanisms such as (1) impersonating or hindering the activity of hormones released from endocrine glands, (2) changing the levels of hormones by altering their production rate, (3) acting as competitive chemicals of hormones for binding proteins, coactivators, and receptors, (4) epigenetic reprogramming (Alofe et al., 2019).

The major sources of EDPs for their accumulation in environment are pharmaceuticals, synthetic and natural hormones, pesticides and herbicides (dichlorodiphenyltrichloroethane, dicofol), personal care products, plastics, and food preservatives. Phenolic compounds, phthalates, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons are some of the examples of EDPs. These EDPs can be introduced in the environment directly through anthropogenic activities. The indirect accumulation of EDPs in environment is occurred via accidental or deliberate discharge from wastewater and industrial effluents. Waste effluent released from petroleum refineries is one such major source for releasing EDPs in environment as polycyclic aromatic hydrocarbons.

Petroleum refineries are essential for sustaining the global prerequisite of fuel pertaining to the necessity of transporting goods, food as well as people. The petroleum products derived from the oil and gas are also crucial for production of electricity and other commercial materials such as plastics, synthetic products, food preservatives, and household objects. Though, the

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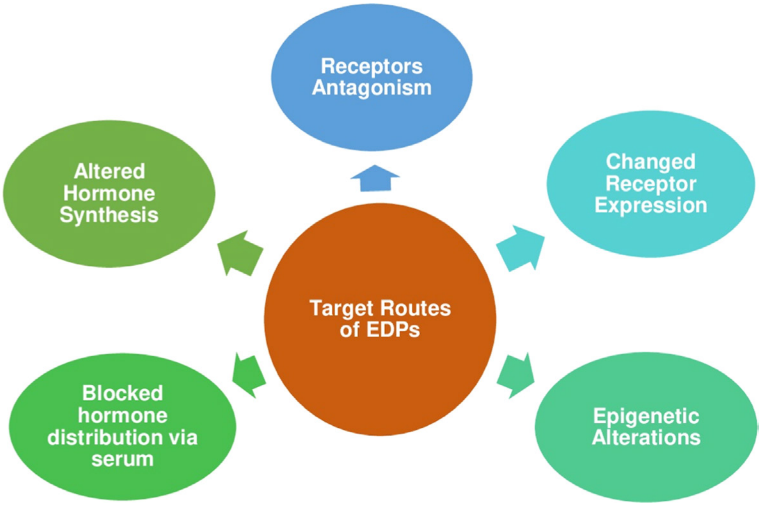

FIG. 2.1 Routes adopted by EDPs to disrupt the endocrine system.

refining process to transform crude oil into commercial products employs as well as generates the chemicals which can be classified as EDPs. As per the International Energy Agency (IEA), the daily amount of crude oil refined worldwide was nearly 13 million m^3 in 2019 (IEA, 2020). Consequently, significant amount of refinery wastewater is continuously generated globally and released in the environment. These oil and petroleum refineries are located all around the world and the refinery wastewater generated on each refining site may have significant harmful effects on the adjacent ecosystems receiving the released wastewater. Therefore, the quality of refinery wastewater needs to be monitored and maintained from the perspective of environment and health.

Biorefineries employing the third-generation technology encompasses the conversion of lignocellulosic biomass to liquid fuels (i.e., biofuel, biodiesel), biodegradable plastic and a wide range of value-added products. However, the bioprocessing of lignocellulosic biomass conversion results in the release of wastewater consisting heavy metals, polycyclic aromatic hydrocarbons, phenols, acrylic polymers, and the other toxic organic compounds. The breakdown of lignin present in the biomass leads to the production of phenolic compounds which may further form polyphenols through polymerization (Kumar et al., 2020). In the wastewater, phenols may also exist in its derivative forms, that is, chlorophenols and bisphenol A, which are known endocrine disruptors (Villegas et al., 2016; Barrios-Estrada et al., 2018). The macro and micro levels presence of these pollutants and the high chemical oxygen demand of lignocellulosic biorefinery wastewater complicates the process of its treatment (Chen et al., 2018). Hence, there is a demand to investigate the various treatment methodologies to pick the suitable route for the treatment of refinery wastewater before it is exposed to the adjacent environment and the living beings.

The present book chapter elaborates the effect of these EDPs originated from refinery wastewater on the various systems and metabolism of human body as well as animals. The chapter further discusses the types of method for their removal.

2.2 Implications of endocrine disruptive pollutants

2.2.1 Vulnerability of endocrine system

Endocrine system comprises of endocrine glands and receptors which regulate key physiological functions such as reproduction, metabolism, homeostasis, emotional behavior, growth rate, and development of body through production and secretion of hormones. Fig. 2.2 depicts the network of body organs and systems susceptible for adverse effects of EDPs. The endocrine system is located throughout the body including the endocrine glands viz. pituitary gland, hypothalamus, pineal gland, thyroid and parathyroid, thymus, adrenal, ovaries, testes, and prostate glands (Kumar et al., 2020). Hence, the proper functioning of endocrine system is associated with the stability of all other systems including nervous system, digestive system, reproductive

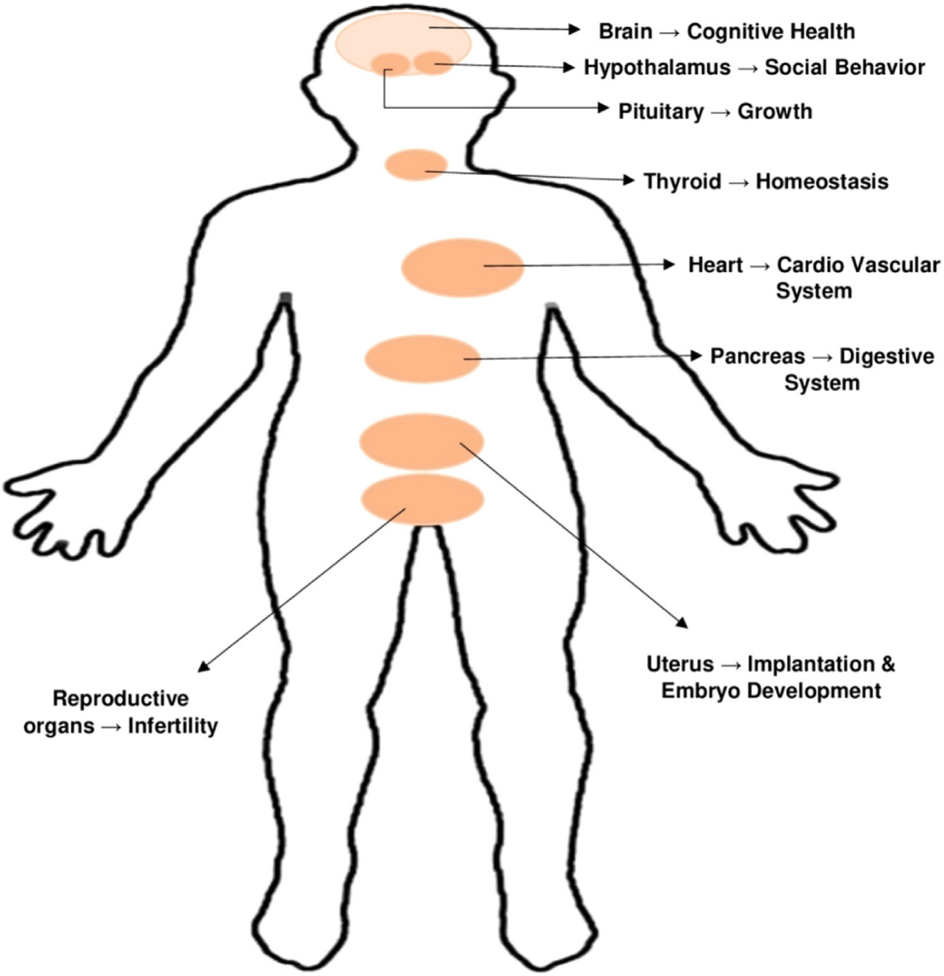

FIG. 2.2 Body organs and systems susceptible for adverse effects of EDPs.

system, etc. Endocrine system influences the overall growth, development, and maintenance of homeostasis in the body either directly or through other systems. Therefore, the adequate operation of endocrine system is crucial for controlling as well as coordinating the various functions and processes of human body. The hormones released from endocrine glands such as estrogen, testosterone, corticosteroid, adrenaline, insulin, thyroxine, and triiodothyronine are not only involved in the day-to-day body function but they also regulate the human life starting from conception to all stages of development and maturation.

EDPs tend to target and imbalance the hormonal homeostasis in the body. Hence, their consequences are expected to be more noticeable in the life stages marking the hormonal changes such as pregnancy, gestation period, child birth, and puberty. These time periods are critical as the process of tissue differentiation as well as maturation leading to organs development occur during these times (Palanza et al., 2016). Exposure of pregnant women to EDPs during pregnancy may influence the growth of fetus growth and its weight during birth (Woods et al., 2017). The children exposed to EDPs such as phthalates during gestation period may also prone to weight gain and obesity during the later stage of their life (Valvi et al., 2015; Buckley et al., 2016). Several studies have associated the neurological disorders and behavioral concerns in children with the EDPs exposure at prenatal stage (Braun et al., 2017; Lim et al., 2017; Kim et al., 2018). Exposure to EDPs during the pre- and perinatal stage may also influence the individuals during the time of puberty (Harley et al., 2017; Watkins et al., 2017). On the basis of these studies, it can be concluded that the interference caused by EDPs in endocrine system may affect the life of humans and animals at all crucial stages of growth and development.

2.2.2 Effect on human and animal health

The negative implications of EDPs on human health are a serious concern which calls for the mitigation of these pollutants from the environment. Presence of EDPs in human system beyond the threshold quantity can trigger multiple disorders through altering the hormones level in the body. Complications in the reproductive system, thyroid disorders, obesity, Alzheimer's disease, and other neurological disorders can be triggered by the presence of these pollutants in human body (Vieira et al., 2020). EDPs may also weaken the immune system and cause tumor. Table 2.1 summarizes the health concerns associated with the prominent EDPs in refinery wastewater.

EDPs can interrupt with the physiology of reproductive system by changing the work flow of the hypothalamic–pituitary–gonadal system. This combined system of glands produces and secretes hormones that control reproductive function. The impact of chemicals and reagents (EDPs) used as well as generated in petroleum refineries have been evaluated in terms of their association with reproductive system malfunctions. The studies revealed that the exposure to these EDPs can exhibit harmful influence on female reproductive functions in humans as well as the animals (Sirotkin and Harrath, 2017; Harville et al., 2018). The high quantity of benzene was detected in the ovarian follicular fluid collected from subjects undergoing in vitro fertilization. This elevated level of benzene was found to be associated with fewer oocytes retrieval and the abnormal levels of follicle stimulating hormone (Alviggi et al., 2014). Similarly, exposure to polycyclic aromatic hydrocarbons present in the effluent of petroleum refinery has been

Table 2.1 Major EDPs in refinery wastewater and the associated health concerns.

S. No.	EDP	Health concerns	Mechanism	References
1.	Bisphenol A	• Polycystic ovarian syndrome • Depression anxiety • Abnormal brain development in fetus	• Decreasing the antral follicle count • Disturbing the thyroid homeostasis • Interfering with steroid hormones and receptors	Zhou et al., 2017; Rashidi et al., 2017
2.	Diethanolamine	• Infertility • Abnormal development of embryo	• Decreased estrogen level • Decreased choline level	Alofe et al., 2019
3.	Phthalates	• Cognitive disorders • Obesity and weight gain • Disturbed thyroid hormone levels	• Decreasing the level of serum thyroxine • Decreasing levels of thyroid stimulating hormone	Buckley et al., 2016; Romano et al., 2018
4.	Benzene	Infertility in women	Reducing levels of follicle stimulating hormones	Alviggi et al., 2014
5.	Polycyclic aromatic hydrocarbons	• Gonadal dysfunction • Infertility	Reducing ovarian germ cells	Vignet et al., 2016

associated with gonadal dysfunction (Vignet et al., 2016). In mouse, the exposure to polycyclic hydrocarbons during early life has been reported to be the cause of lesser ovarian germ cells (Lim et al., 2016).

The study conducted on the samples collected from the women suffering from infertility was investigated for the presence of bisphenol A and its association with reproductive system abnormalities. The studies revealed that the presence of bisphenol A was accompanied with the decreased ovarian reserve, polycystic ovarian syndrome, low antral follicle count as well as with increased incidences of implantation failure (Souter et al., 2013; Zhou et al., 2017; Rashidi et al., 2017). Similarly, diethanolamine have also been allied to the abnormalities concerning the fertility and developmental process. In mice, diethanolamine has been observed to reduce the choline levels which were attributed to the changes in their reproductive functions (Resseguie et al., 2007; Alofe et al., 2019). Since choline biosynthesis is regulated by the estrogen, the reproductive defects were also suggested to be occurred due to repressed estrogen activity by diethanolamine.

Exposure to EDPs during the prenatal stage has been stated to influence the process of brain development which may result in occurrence of neurological abnormalities in the fetus. Prenatal exposure of fetus to bisphenol A has been associated with the incidences of depression and anxiety as well as the unusual social behavior in later stage of life (Braun et al., 2017; Lim et al., 2017). Similarly, other EDPs viz. organophosphates, perfluorinated compounds, and polychlorinated biphenyls have also been attributed to hostile neurological performance, low

IQ, and behavior problems (Kim et al., 2018; Kumar et al., 2020). The process of brain development may be affected by the exposure to EDPs via various mechanisms including interference with receptors and steroid hormones and creating epigenetic changes (Gore et al., 2015). Thyroid hormone homeostasis which is perilous for smooth development of fetal brain has also been stated as a prominent route for EDPs to cause neurodevelopment disorders (Mughal et al., 2018). Thyroid hormones play a vital role in regulation of numerous biological processes. These hormones are regulated by the hypothalamic–pituitary–thyroid system which can be interrupted by the EDPs. EDPs such as phthalates and phenols have been reported as the antagonist compounds for thyroid receptors. Lower thyroxine levels caused by phenols during pregnancy may lead to the adverse effects on the cognitive functions of the newborns (Berbel et al., 2009; Kumar et al., 2020). Similarly, phthalates have also been linked to the decrease in levels of total serum thyroxine as well as the thyroid stimulating hormone in pregnant women (Romano et al., 2018).

Recently, studies associated with EDPs influence on the health of living beings have also suggested the modifications in the gene expression by EDPs without causing mutations in the associated gene. This process of altering the gene expression is termed as epigenetic transformation (Cruz et al., 2014). These epigenetic transformations can be caused by EDPs through various mechanisms such as (1) causing methylation of cytosine residues in the DNA strands (2) altering the micro RNA expression (3) causing post-translational modification in histones. The transfer of epigenetic changes to next generations may depend on the quantity of EDPs present in the system (Rissman et al., 2014). The transfer of epigenetic changes to future generations is termed as epigenetic trans generational inheritance. In this phenomenon, the exposures of a pregnant woman to harmful pollutants result into the mutations in germline which get transmitted to the newborn and thereby the succeeding generations showcasing the altered phenotypic expression (Kumar et al., 2020). Bisphenol A is the EDP which is most commonly associated with epigenetic changes (Santangeli et al., 2017). Apart from bisphenol A, dioxins and phthalates were also observed to cause epigenetic variations (Messerschmidt et al., 2014; Chen et al., 2015; Kumar et al., 2020). In some cases, the epigenetic variations occurred due to exposure to EDPs in early life may remain latent for a long time and become observable in the later stage of life (Kumar et al., 2020).

2.2.3 Effect on ecosystem: the indirect route of bioaccumulation of EDPs

Due to the release of improperly treated refinery wastewater in environment, these EDPs are accumulated in the organisms through exposure and dietary route. This process is called bioaccumulation which has been detected at all levels of food webs in aquatic ecosystem including biofilm to fishes and predatory invertebrates (Ruhi et al., 2016; Yao et al., 2018). These EDPs are first consumed by the lower-level consumers of food webs upon their exposure to aquatic environment. Subsequently, these EDPs travel from one trophic level of food web to the next trophic level. Since Food webs are generally interrelated across different ecosystems and habitat boundaries, these EDPs transfer from aquatic to terrestrial ecosystems through aquatic insects, seafood and other anthropogenic activities. The magnification of EDPs such as polychlorinated biphenyls may cause adversities during the transformation of aquatic insects, which poses elevated risk to higher level biomagnifications through terrestrial predators (Previšić et al., 2021).

The studies regarding EDPs in wastewater are mostly concerned with the impact of these chemicals on human health. Hence, researches are mostly focused on developing methods for removal of these compounds from waste stream. However, attention is required to establish a deeper understanding of the bioaccumulation routes of these chemicals in humans. The knowledge of EDPs transfer via ecosystem will enable to develop research strategies for preventing their bioaccumulation through mass flow between trophic levels.

2.3 Removal of endocrine disrupting pollutants from refinery wastewater

The methods for removing the EDPs from refinery wastewater can be classified broadly in three categories—physical methods (filtration), chemical methods (chemical adsorption and oxidation), and biological methods (microbial degradation). Tables 2.2 summarizes the working principle, advantages, and disadvantages of these removal methods. These methods may also be combined in sequential or simultaneous manner to achieve higher EDPs removal.

2.3.1 Physical methods

The physical methods of removing the EDPs from the refinery wastewater consisted of using a physical separator such as filters or membranes. These filters and membranes separate the pollutants from the wastewater on the basis of particle size (filtration method) or the concentration gradient which controls the flow of particle through the permeable membrane (osmosis method).

2.3.1.1 Filtration

Filtration is the method of separating the chemical compounds on the basis of size exclusion. Depending upon the pore size of filters, the filtration may be classified in three categories—microfiltration, ultrafiltration, and nanofiltration.

The microfiltration process uses the filters of large sized pores and hence it is used to remove the pollutants of high molecular weight. Though microfiltration process has been reported to be ineffective in removing the EDPs alone, it is often used in combination with other removal methods (Bodzek and Konieczny, 2018). Microfiltration is usually used as first step to remove the colloidal contaminants and followed by nanofiltration or osmosis for effective EDPS removal. Here the microfiltration serves as checkpoint to protect as well maintain the quality of membrane used in nanofiltration and osmosis (Vieira et al., 2020).

Ultrafiltration is the more advanced form of filtration as compared to microfiltration as it uses the membranes with comparatively smaller pore size. Though, beside size exclusion, the ultrafiltration method also relies on the mechanism of pollutant removal through adsorption on membrane. Hence the interaction between the pollutants and membrane plays a crucial role in the ultrafiltration process of EDP removal. The previous studies reported ultrafiltration as an effective removal method for water soluble EDPS such as organic acids and estrogen. Further,

Table 2.2 Removal methods for EDPs and their comparison.

S.No.	Type of removal method	Removal techniques	Working mechanism	Advantages	Disadvantages
1.	Physical	Filtration	Size exclusion	Cost effective	Prone to filter fouling, less reusability
2.	Physical	Osmosis	Separation on the basis of concentration gradient	Wider range of removable EDPs as compared to filtration	Prone to membrane fouling, high energy consumption in reverse osmosis method
3.	Chemical	Chemical adsorption	Surface adsorption	Fast process	Costly due to chemical adsorbents
4.	Chemical	Chemical oxidation	Oxidation of EDPs by oxidizing chemical	Fast process, more efficient than adsorption	Costly due to the use of chemical reagents
5.	Chemical	Electrochemical oxidation	Chemical oxidation under influence of electric field	More efficient for separation of charged pollutants	High energy consumption High cost due to chemicals
6.	Chemical	Advanced oxidation	Oxidation of EDPs by using ultraviolet, microwave irradiation, ozone, and photons, etc. for excitation of electrons	Oxidation of wider range of EDPs	High energy consumption High cost due to chemical reagents or catalysts
7.	Biological	Bioadsorption	Surface adsorption of EDPs on naturally occurring biomaterials or their derivatives	Affordable utilization of waste biomaterials	Inherent selectiveness narrows down the range of removable EDPs
8.	Biological	Biodegradation	Degradation of organic EDPs by using bacteria, fungi, or algae	Environment friendly and natural approach	Longer time period Require monitoring of several operating parameters for efficient removal
9.	Biophysical	Membrane bioreactors	Combined biodegradation and filtration through membranes	Cover wider range of EDPs removable by both physical and biological degradation method	Maintenance of membranes and operating parameters

combining the ultrafiltration with other advanced oxidation methods such as ozonation has been stated to enhance the removal efficacy to as high as 99% (Si et al., 2018).

The nanofiltration method uses negatively charged membrane with pore size smaller than ultrafiltration membranes. The process enables the removal of mono and multivalent ionic compound on the basis of size exclusion and electrostatic interaction between the membrane and the pollutants. The selectivity of nanofiltration membranes can be further improved by functionalizing them with other compounds. The nanofiltration membrane functionalized with polydopamine and silver nanoparticles reported to showcase better RDP removal efficiency as compared to unfunctionalized membrane (Guo et al., 2019).

The filtration methods for EDPs removal are cost effective and easy to operate as there is no requirement of maintaining any specific operational parameters or adding chemicals. However, the dependence of separation on size of molecules is the limiting factor which makes filtration unfeasible for a wide range of EDPs. The fouling is another undesirable factor associated with filtration which reduces the reusability of membrane filters. The fouling of membrane can be addressed by either reducing the contamination or by adopting membrane cleaning methods (Gul et al., 2021). Though a better understanding of membrane types as well as fouling mechanism is required to reduce the membrane fouling.

2.3.1.2 Osmosis

Osmosis method employs semipermeable membranes having pore size smaller in comparison to nanofiltration membranes. The driving force in this method that aids in separating the contaminants is osmotic pressure which in turns depends on the concentration flux. The osmosis method can be categorized in two types—forward osmosis and reverse osmosis. Forward osmosis simply encourages the flow of water from low concentration to high concentration flux under the influence of osmotic pressure. Whereas, in reverse osmosis method, the hydraulic pressure is introduced to counteract the osmotic pressure to reverse the flow of water from high concentration to low concentration (Fig. 2.3). Both forward and reverse osmosis methods have

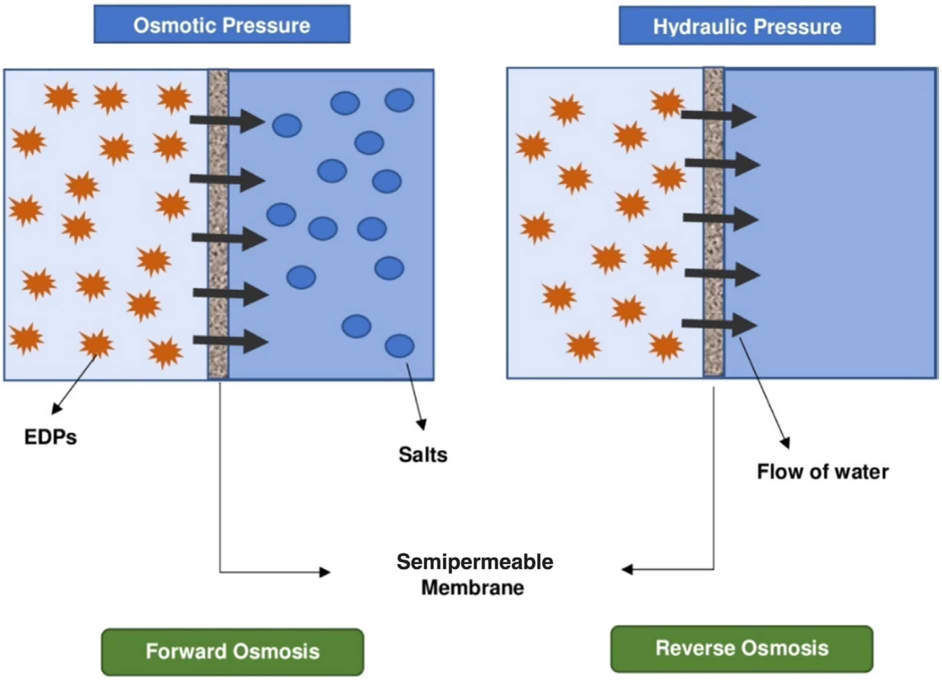

FIG. 2.3 Forward and reverse osmosis.

Table 2.3 Comparison of physical removal methods.

S. No.	Method	Pore size of membrane (μm)	Operational pressure (bar)	Selectivity for EDPs
1.	Microfiltration	0.1	0–2	Low
2.	Ultrafiltration	0.01	1–10	>Microfiltration
3.	Nanofiltration	0.001	5–35	>Ultrafiltration
4.	Forward osmosis	0.0001	1–2	>Filtration, <reverse osmosis
5.	Reverse osmosis	0.0001	15–150	>Forward osmosis

been reported to be highly efficient in removing the EDPs from wastewater (Rodriguez-Narvaez et al., 2017). In both type of osmosis methods, the rejection of EDPs by membrane is achieved through multiple mechanisms including size exclusion, adsorption as well as interactions (electrostatic or hydrophobic) of EDPs with membrane. The underlined mechanism also depends upon the acidic and alkaline nature of the environment in which the osmosis is performed (Vieira et al., 2020).

Though reverse osmosis has associated drawbacks such as high energy consumption owing to the application of hydraulic pressure. Further, in reverse osmosis method, the semipermeable membrane is reported to be more prone for fouling and concentration polarization. However, the application of hydraulic pressure increases the range of removable pollutants as compared to the forward osmosis. Using reverse and forward osmosis in combination has also been suggested to create double barriers for EDPs which may result in higher removal efficiency. Table 2.3 outlines the difference of operating pressure, pore size of membrane and the selectivity of above-mentioned physical removal techniques.

2.3.2 Chemical methods

2.3.2.1 Chemical absorbents

Removal of contaminants through their absorption on the surface of absorbents is an intensively explored method. The choice of absorbents depends upon its absorption capacity as well as the characteristics of the pollutants to be removed. Activated carbon prepared from the raw carbon-based material such as wood is the most commonly used absorbents for removal of pollutants from wastewater (Crini et al., 2019; Ndagijimana et al., 2019). Graphene and their derivative are other carbon-based absorbents used for removal of EDPs. As compared to the activated carbon, the graphene absorbents are reported to showcase better selectivity of EDPs (Khan et al., 2019). Similarly, carbon nanotubes are also appropriate to be used as absorbent for EDPs removal due to their high specific surface area and physiochemical properties.

Beside the carbon-based materials, aluminum- and silicon-based chemical absorbents are also used for the removal of EDPs from wastewater. Zeolite, an alumino-silico-based microporous structure is known to exhibit remarkable selectivity as well as ion exchange ability (Vieira et al., 2020). Hence, zeolite is conventionally used as an absorbent for EDPs removal.

For the refinery wastewater, the polymer absorbents are the most relevant absorbents as they are generally used to remove the aromatic hydrocarbons and polyphenolic compound which are the prominent pollutants in refinery effluents (Vieira et al., 2020). The polymeric adsorbents have the ability to alter and adapt the mechanical and physicochemical properties through polymerization which increase their adsorption selectivity (Lee and Kwak, 2020; Vieira et al., 2020).

Surface adsorption through chemical adsorbents is a fast process for removal of EDPs. However, the use of chemicals as well as the associated cost makes the process less economical and environment friendly. Hence, the researchers are focused on exploring the cost-effective natural adsorbents which are present in the nature in abundant amount such as agri-waste and algae.

2.3.2.2 Chemical oxidation

The chemical method to remove the EDPs from wastewater consists of employing a chemical oxidizing agent such as chlorine, chloramines, ferrate and permanganate to oxidize these EDPs (Villegas et al., 2016). Ferrate is considered to be highly efficient for EDP removal due to its ability to exhibit oxidizing properties over a wide range of pH. For EDPs such as bisphenol A, permanganate compounds, that is, potassium permanganate have been reported to be highly efficient by showcasing approximately 99% bisphenol A degradation (Zhang et al., 2013).

Electrochemical oxidation is also another method to remove EDPs in which pollutants are adsorbed on anode (Pt, SnO_2, PbO_2, etc.) in effect of electrostatic force. This method saves the cost of reagent requires for oxidation. However, it also has the drawback of high energy consumption (Tasic et al., 2014; Villegas et al., 2016).

The advanced chemical oxidation methods employ ultraviolet/H_2O_2 and microwave irradiation, wet oxidation, Fenton oxidation and ozonation (Gao et al., 2020). All these techniques involve the formation of hydroxy free radical in the reaction which mineralizes the phenolic and other organic contaminants present in the wastewater. The combined or solo irradiation treatment with microwaves and ultraviolet may be employed to reduce the treatment time as well as the activation energy of oxidation process. In Fenton treatment, the Fenton reagent, ferrous ions and H_2O_2 are used for oxidation of aromatic EDPs (Villegas et al., 2016). The ferrous ions react with hydrogen peroxide to oxidize in ferric ions with simultaneous formation of hydroxyl radicals which in turn oxidize the aromatic pollutants. The Fenton method can be combined with the exposure of ultraviolet treatment to increase the efficiency of oxidation process and decrease the pH dependence as the ultraviolet photon are consumed to ensure the continuous regeneration of ferrous ions from ferric ions (Villegas et al., 2016).

In the wet oxidation method, the wastewater comprising organic pollutants are mixed with gaseous oxygen under high temperature (150–400°C) and pressure (2–40 MPa) (Weber et al., 2015). The reaction process results in the oxidation of organic EDPs into carboxylic acids and other compounds of low molecular weight. Transitional metal oxides are generally used as catalysts in wet oxidation method of EDP removal (Gao et al., 2020).

As compared to chemical adsorbents, the oxidation method is much more efficient as it covers a wider range of EDPs to be removed from wastewater. Though the chemical oxidation method requires costly reagents which reduce the economic feasibility of the process. Further the electrochemical and advanced oxidation methods increase the demand of energy consumption. Hence, the chemical oxidation methods need to be optimized to balance the process in terms of high removal efficiency through minimum energy consumption. Researches need to focus on exploring more efficient chemical oxidants which are able to oxidize the EDPs at milder operational conditions with less by-product generation.

2.3.2.3 Photocatalytic degradation

Photocatalytic degradation is one of the most promising techniques in the category of advanced oxidation methods. Photocatalytic degradation method employs sunlight to decompose the hydrocarbon pollutant present in the refinery wastewater and turn these pollutants into carbon dioxide and water (Fig. 2.4). During the reaction, semiconducting materials such as metal oxides (titanium oxide, zinc oxide, etc.) are used as photocatalysts. The most commonly used

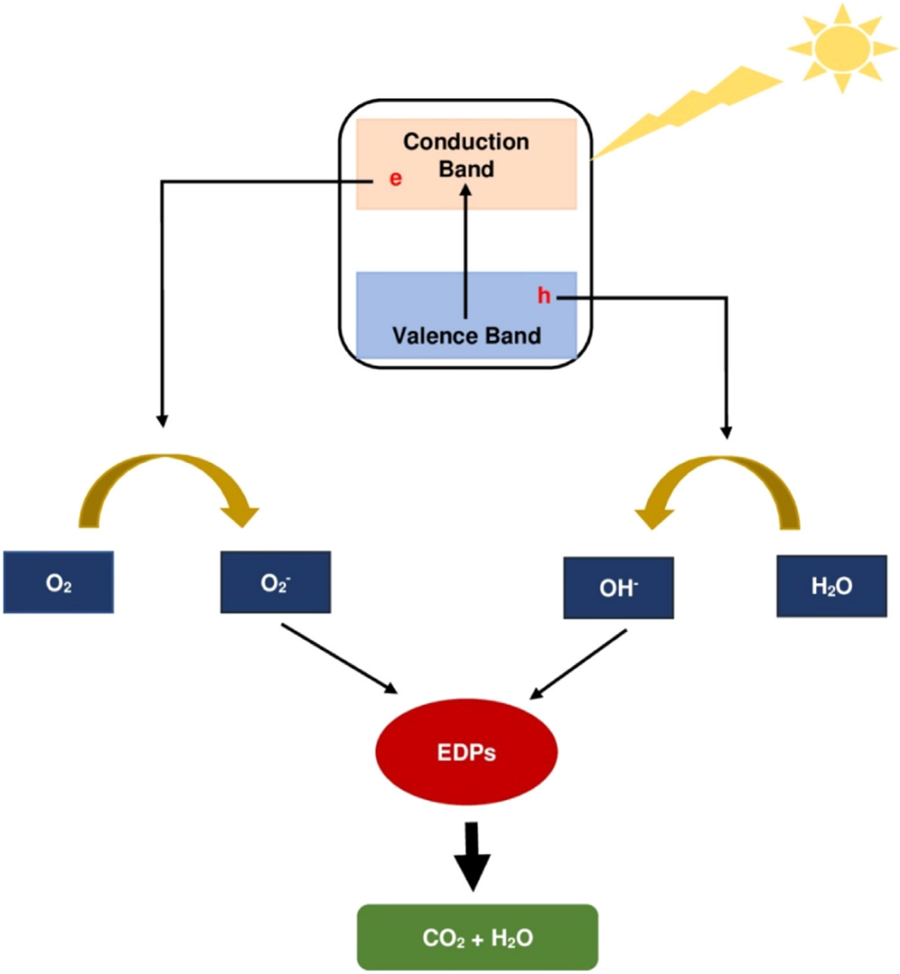

FIG. 2.4 Mechanism of photocatalytic degradation of EDPs.

photocatalysts are heterogeneous and semiconductive oxide materials such as TiO_2 which is the most intensively explored photocatalyst. To increase the surface area for the catalytic mechanisms, the photocatalysts may be employed in form of nanopowder form which increases the efficiency of degradation (Vela et al., 2018). Besides TiO_2, ZnO is also considered as suitable photocatalyst due to its affordability, high stability and band gap energy similar to TiO_2 (Gao et al., 2020). However, the frequent recombination of electrons and holes is the major limitation associated with using ZnO as photocatalyst. In order to prevent the electrons and holes to recombine quickly, the ZnO photocatalysts are often doped with other semiconducting or transitional metal ions such as CeO_2, TiO_2, WO_3 (Pant et al., 2012; Gao et al., 2020).

To improve the efficiency of photocatalytic degradation, the nanocomposites of oxide materials are used as photocatalyst. The nanosized photocatalysts enhance the rate of photo degradation by higher adsorption of photons due to increased surface area. These nanocomposite photocatalyst can be prepared by combining the oxide materials such as ZnO/WO_3, ZnO/SiC, Au–TiO_2, and ZnO/TiO_2 through sol–gel or coprecipitation method (Sornalingam et al., 2018; Meenakshi et al., 2018). These nanosized photocatalysts have been employed for removal of EDPs such as bisphenol A and diethyl phthalate.

Photocatalytic degradation is considered to be effective for persistent contaminants present in the wastewater. Hence, the application of photocatalytic degradation is expected to grow in the future for removal of EDPs from refinery wastewater. Further, the emerging involvement of nanotechnology in development of new and more efficient photocatalysts is also contributing to the potential of this method for EDPs removal.

2.3.3 Biological methods

2.3.3.1 Bioadsorbents

Bioadsorbents are the green alternatives for chemical adsorbents for removal of EDPs from refinery wastewater. Biological materials present in the nature are used as adsorbents which have the inherent ability to selectively absorb certain chemicals. These biological materials may be the natural polymers and their derivatives such as chitin, chitosan, egg shells, agro-waste or the living biomass such as algae (Crini et al., 2019; Escudero et al., 2019). Chitin, an abundant natural polymer may be extracted from the seafood waste accumulated in the food and hospitality industry to be used as adsorbent for pollutant removal. The deacetylation of chitin results in generation of chitosan which is preferred to be used as absorbent in comparison to chitin due to its better physiochemical properties in terms of selectivity and reactivity (Sudha et al., 2017). Levan is another natural polymer produced by bacteria which has been investigated for removal of bisphenol A (Hacıosmanoğlu et al., 2019). Similarly, cyclodextrins biopolymers have been explored for removal of EDPs such as parabens. The hydrophobic nature of cyclodextrins enables it to capture the lipophilic molecules like parabens. Yusoff et al. (2018) functionalized the cyclodextrin adsorbent with magnetic nanoparticles and witnessed efficient removal of benzyl paraben to approximately 92%.

The lignocellulosic agriculture residues which are frequently disposed of as waste materials may also be employed as absorbent for EDP removal. These waste materials comprised of wasted tea and coffee, cotton, rice husk, nut shells etc. These residues can be used directly or indirectly by their transformation into biochar. Sudhakar et al. (2016) explored rice husk for the adsorption of Bisphenol A and reported 73.2% adsorption. Similarly, tea leaves and coffee waste were also employed for the adsorption of bisphenol A and sulfamethoxazole (Ahsan et al., 2018a, 2018b). The adsorption uptake of EDPs showcased by these waste materials was comparable to the commercially available activated carbon adsorbent. Seafood waste such as fish scales have also been employed as the absorbing material for pollutants present in wastewater like nonylphenols (Thongkon, 2017). These reports suggested that the agro and food residues may be considered as the cost-effective alternatives for commercial absorbents.

Beside the above-mentioned direct approaches, the waste materials may also be employed for the production of biochar which is considered as an excellent bioadsorbent for the removal of EDPs from wastewater. Due to its porous structure and higher surface area, biochar possesses remarkable adsorption characteristics which can be utilized for the efficient removal of pollutants from refinery wastewater. Biochar is produced by the process of pyrolysis in which organic matters such as the agro-waste residues are thermally decomposed in absence of oxygen. In terms of porosity and adsorption efficiency, biochar is comparable to the activated carbon. Hence, biochar presents more economical and environment friendly method for removing the pollutants by also addressing the challenge of waste management. The abundant availability of waste materials including agro-industrial waste, municipal waste and algal biomass may be utilized as feedstock for biochar production. Biochar produced from marine algae *Ulva prolifera* has been reported to remove 90% bisphenol A in duration of 4 h. Similarly, rice straw and bamboo-based biochar have also been investigated for removal of EDPs such as bisphenol A, estradiol and sulfamethoxazole (Pan et al., 2017; Heo et al., 2019). The functionalization of biochar with other metal oxide may further enhance the adsorption properties through the additional surface area facilitated by the metal oxides. Functionalization of bamboo biochar with copper zinc ferrous oxide ($CuZnFe_2O_4$) revealed higher adsorption uptake as compared to unfunctionalized bamboo biochar (Heo et al., 2019). Moreover, the magnetic properties of metal oxides assisted in easy separation of adsorption and the adsorbent which boosted the reusability of the biochar as adsorbent. Biochar can also be activated by physical (steam) or chemical activation agent (acids, bases, and salt solutions) which improve the porosity of the biochar for efficient adsorption of pollutants (Alves et al., 2019; Kosheleva et al., 2019; Zhou et al., 2019).

Overall, bioadsorbents provide an economical route for EDPs removal from wastewater. Though, the inherent selectiveness of these adsorbents for the contaminants is the limiting factor. Hence, more natural adsorbents are required to be explored that are capable to eliminate a wider range of EDPs from the refinery wastewater. Moreover, the functionalization and surface modification of bioadsorbents is also gaining the attention of researchers. The incorporation of metal nanoparticles can also be explored in this direction to improve the removal efficiency through increased surface area for adsorption.

2.3.3.2 *Biological degradation*

Biodegradation method for EDPs removal comprised of degradation of pollutants by using micro-organisms (bacteria and/or fungi) or the enzymes produced by theses micro-organisms. Several micro-organisms have been reported to be used for degradation of organic EDPs present in the wastewater. Due to the ability to secrete the cellulolytic and lignolytic enzymes, several fungal strains including *Aspergillus niger, Umbelopsis isabelina, Aspergillus niger, Pleurotus ostreatus, Chrysosporium tropicum* (Janicki et al., 2016; Obukohwo et al., 2020) have been investigated for the fungal degradation of EDPs present in the refinery wastewater. Fungal biodegradation of EDPs can be accomplished in two ways, either using the dispersed fungal mycelium or using fungal pellets which are densely packed mass of entangled hyphae (Kasonga et al., 2021). Lignolytic fungi possessing the ability to secrete the lignin degrading enzymes are specifically favored for the degradation of polycyclic aromatic hydrocarbons. White rot fungi such as *Pleurotus ostreatus* and *Trametes versicolor* have been reported to efficiently remove the EDPs such as bisphenol A and estradiols (Gao et al., 2020).

Similarly, bacterial species such as *Sphingomonas* sp., *Aeromonas* sp., *Stenotrophomonas* sp., *Bacillus flexus*, *Camelimonas* sp., *Bacillus lichis* sp., and *Enterococcus faecalis* have also been explored for bacterial degradation of EDPs (Gao et al., 2020). *Pseudomonas aeruginosa* have been investigated for removal of EDPs from the wastewater collected from a petroleum refinery. The study reported efficient removal of carbazole, dibenzothiophene, and fluorene by *P. aeruginosa* bacterium isolated from oily sludge of oil refinery (Ghosh and Mukherji, 2020).

Besides bacteria and fungi, algae have also been considered to be employed for the biodegradation of EDPs. The algal species such as *Chlorella fusca*, *Chlorella vulgaris*, *Chlamydomonas*, *Cyclotella caspia* have the capability to absorb and then degrade the EDPs through the process of glycosylation (Ji et al., 2014; Gao et al., 2020). Table 2.4 summarizes the microbial strain used for biological degradation of targeted EDPs.

Table 2.4 Microbial strains and consortium used for biological degradation of EDPs.

S. No.	Type of biodegradation	Species	Target EDPs	References
1.	Bacterial	Rhizophore bacteria	Phenols	Toyama et al., 2013
2.	Bacterial	*Pseudomonas aeruginosa*	Carbazole, dibenzothiophene and fluorene	Ghosh and Mukherji, 2020
3.	Bacterial	Consortium comprising *Bacillus, Pseudomonas, Ochrobactrum, Marinobacter, Rhodococcus, Stenotrophomonas* and *Martelella*	Polycyclic aromatic hydrocarbons viz. pyrene, benzo pyrene, benzo fluoranthene	Al-Mur et al., 2021
4.	Fungal	*Pycnoporus sanguineus*	Nonylphenol	Ramírez-Cavazos et al., 2014
5.	Fungal	*Umbelopsis isabellina*	Phenolic EDPs	Janicki et al., 2016
6.	Fungal	*Pleurotus ostreatus*	Bisphenol A	Kresinová et al., 2018
7.	Fungal	Fungal consortium consisting *Aspergillus flavus, Chrysosporium tropicum, Rhizopus oryzae*, and *Aspergillus niger*	Phenols and heavy metals	Obukohwo et al., 2020
8.	Microalgae	*Chlamydomonas mexicana*	Bisphenol A	Ji et al., 2014
9.	Microalgae	*Chlorella vulgaris*	Bisphenol A	Ji et al., 2014

Microbial degradation offers a natural method for removing the EDPs. However, the performance of the process is highly dependent on the growth of micro-organisms which in turn affected by several parameters. The concentration of the pollutants is one such parameter that affects the degradation efficiency of microbes. While the very high concentration of the pollutants exhibits the toxic effect on microbial growth, the very low organic pollutant concentration tends to reduce the supply of carbon source to microbes (Yan et al., 2019). The pH, temperature and salinity are other crucial parameters which need to be monitored and controlled for efficient degradation of pollutants by micro-organisms (Yan et al., 2019). Hence, the microbes isolated from the extreme environments are preferred for the microbial degradation due to their high tolerance for environmental factors (Fernández et al., 2017).

2.3.3.3 Membrane bioreactors

Membrane bioreactors employ the hybrid methodology for removing EDPs from wastewater through combining the microbial degradation and physical removal of pollutants by membranes. Due to the hybrid system, the recalcitrant compounds which escape the microbial degradation process are physically separated from the wastewater through low pressure membranes (Kamaz et al., 2019). The removal of EDPs by membrane bioreactors relies on the combined action of microbial degradation, bioadsorption, and physical retention. While bioadsorption and physical retention primarily work for the separation of the nonpolar pollutants, the microbial degradation is the main mechanism behind removal of polar pollutants. Size of the pollutants and the working parameters of the bioreactors viz. temperature, pH, concentration, etc. are the controlling factors in this process that affect the efficiency of EDPs removal.

2.4 Conclusions and perspectives

EDPs present in the refinery wastewater have become an emerging concern from the perspective of human health. Even exposure to small quantity of EDPs may develop in an instant health concern or some latent disorder which become evident in the later stage of life. Due to the necessity of water reuse, it is imperative to understand the characteristics of EDPs and find the appropriate treatment methodology to ensure the release of properly treated effluent. Among the treatment methodologies discussed in the chapter, photocatalysis, natural bioadsorbents, and biodegradation seems to be appropriate methods in terms of environmental and economical perspectives. Though the choice of appropriate photocatalyst and the micro-organism are crucial to obtain high efficiency from photocatalysis and biological degradation respectively. Using nanocomposite as photocatalyst may be explored more to obtain highly efficient photocatalytic process. For the refinery wastewater having organic EDPs as major pollutants, the microbial biodegradation may be more fitting due to its approach to utilize inherent natural phenomena. However, the biodegradation process requires infrastructure as well as the maintenance of operating parameters. To counter these expenses, it will be economical to find the group of microbes with high tolerance for environmental fluctuations as well as the ability to work in synergy to degrade a wider range of EDPs.

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Conflict of interest

No conflict of interest is declared by authors.

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3

Fate, effects, origins, and biodegradation of bisphenol A in wastewater

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3.1 Introduction

BPA is released into the environment either through sewage treatment effluent (Körner et al., 2000), landfill leachate (via hydrolysis of BPA from plastics (Wintgens et al., 2003)), or natural degradation of polycarbonate plastics. Sewage effluent and landfill leachate are point sources of BPA in the environment, fragments of epoxy resins, and polycarbonate plastic debris entering the watershed through runoff are nonpoint sources. Industrial releases of BPA to the environment are likely to come from wastewaters and washing residue produced during production and processing of products, fugitive dust freed during handling, and minor volatilization losses during manufacturing. BPA may enter the environment through possible physical and chemical breakdown during disposal and recycling operations within wastewater treatment plants (WWTPs) and also by release from manufacturing industries.

Bisphenol A (BPA) is a high priority organic compound for assessment of human health risk as it is considered to present greatest potential for human exposure (GPE) and has been classified by other agencies on the basis of reproductive toxicity. BPA has been identified as EDC by the US Environmental Protection Agency (EPA), World Wide Fund for Nature (WWF) (Meiping et al., 2003) and is becoming a social issue of increasing interest (Bautista-Toledo et al., 2005; Clara et al., 2004). According to EPA, "BPA is an exogenous agent that interfaces with synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction or behavior." Such concerns have heightened the need for novel and advanced remediation techniques to effectively remove BPA from a variety of contaminated environmental media including water, WW, WWS, sediments, and soils.

One of the main sources of BPA is untreated urban wastewater and WWTP effluents (Körner et al., 2000). Most current WWTPs are not designed to treat emerging contaminants including BPA. As a result, high portion of emerging contaminants including BPA and their metabolites

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can escape elimination in WWTPs and enter the aquatic environment via sewage effluents. Various studies have been already carried out to remove BPA in wastewater (Mohapatra et al., 2010b). The behavior and removal of BPA within WWTP depends on its physicochemical properties and on WWTP configuration and operation. Major removal pathways of BPA in sludge include: (i) adsorption to the sludge, (ii) biological degradation and transformation (Langford and Lester, 2003; Mohapatra et al., 2010a). Recently, considerable interest has been shown in the identification, trace concentration analysis and degradation of BPA in aqueous environment due to advances in analytical techniques (Mohapatra et al., 2011b, 2011a).

3.2 Bisphenol A in wastewater

Wastewater is a significant issue that has negative impacts on the atmosphere and public health (Onaizi, 2021). The accumulation and concentration of plastic particles have gradually risen in the ocean, with the latest negative effects on marine life of organic plastic waste leaching. At extremely low doses, some of these substances, known as endocrine disrupting compounds (EDCs), have the ability to serve severe health effects in animals and humans. The United States Environmental Protection Agency (EPA) and the World Wide Fund for Nature (WWF) have designated BPA as an EDC (Bautista-Toledo et al., 2005). BPA is a hazardous water pollutant found in wide range of products, including plastics, sheets, optical lamps, pipe linings, paints, to name a few (Corrales et al., 2015; Husain and Qayyum, 2013). When exposed to trace amount of certain natural and synthetic chemicals, pharmaceuticals, and personal care products may have harmful effects on the atmosphere and health. The US Geological Survey discovered 13 organic drainage pollutants in water samples with ranging from 0.0120 to 0.480 g/L in concentration as well as prescription and personal care chemicals with concentrations ranging from 0.0038 to 0.0577 g/L (Zimmerman, 2005). Sewer tank discharge is the principal source of these contaminants in the water cycle.

Several endocrine disruptive substances with the massive potential were known to be found in wastewater treatment plant (WWTPs) effluent in trace levels (e.g., μg/L or ng/L) (Luo et al., 2014; Terzić et al., 2008). Furthermore, some of these PPCP products, owing to their chemical and recalcitrant properties, proceed through traditional wastewater treatment systems without being transformed, as a consequence of which they are discharged directly into collecting waters (Kasprzyk-Hordern et al., 2008). Compounds such as BPA are widely used in manufacturing processes as key raw materials in the manufacture of many items such as engineering plastics (e.g., epoxy resin and polycarbonate plastics), electrical equipment, food cans, bottles, and dental sealants (Huang et al., 2012). BPA is seen as a strong concern with undesirable reproductive and carcinogenic effects in mice 25 ng/kg per day and 1 μg/kg, respectively (Newbold et al., 2009). Membrane bioreactors, sludge activation, ozonation, photocatalysis, and batch sequencing are among the treatment systems being tested for the removal of EDCs from wastewater. Most of these processes entail a large financial commitment as well as high environmental costs for operation and maintenance, making them impossible to introduce in developed countries. Some research focuses on environmentally friendly wastewater disposal by reducing energy use and lowering greenhouse gas emissions (Yan et al., 2017).

The identification and accumulation of BPA in wastewater and wastewater load are important steps for determining the endocrine function of treatment effluents discharged into the atmosphere. BPA is commonly used for adhesives, powder color, paper covers, and thermal clothing. Due to the everyday consumption of these products, BPA concentrations in wastewater were seen to be high. BPA was determined using the LC–MS/MS approach in samples from the Urban Community of Quebec wastewater treatment plant in Quebec (Canada). BPA was observed in substantial amount (0.07–1.68 g/L in wastewater and 0.105–0.312 g^{-1} in wastewater treatment plants). Although the treatment plant is successful (76%) in extracting pollutants out of the process stream, the treated effluent also has an environmental impact of 0.41 g/L. A rheological analysis was used to determine BPA separation within the treatment plant. It is the basis for deciding which parts of the process stream need additional care of BPA degradation and for the different methods of treatment. The primary and secondary sludge solids (0.36 and 0.24 g^{-1}, respectively) were separated by centrifugation with more BPA than their liquids (0.28 and 0.16 g/L, respectively). BPA was contained in large quantities within the WWTP and divided into primarily the solid sludge fraction (Kd values for main, secondary sludge as well as mixed sludge were 0.014, 0.015, and 0.013, respectively) (Mohapatra et al., 2011c).

Due to their dispersal and high volume in the WW and WWS in North American countries, BPA was detected as an organic compound with a greater human exposure tendency. In the United States, the plastics polycarbonate and epoxy resin are synthesized each year as a rough product, making it a high volume compound in production (Schwartz, 2005). In some industry-related warehouses, including those for paper or allied products (maximum 0.14930 mg/L; minimum 0.00873 mg/L) chemicals and chemical products (maximum 0.09128 mg/L; minimum 0.00149 mg/L), and commercial lavatories BPA are found for municipal waste processing products within Canada and the United States, and in some industries high rates were found (maximum 0.09127 mg/L; minimum 0.00150 mg/L) (Lee and Peart, 2002). The prevalence of BPA in every environmental media, along with the observed presence in and around the world in Canada, indicated: (i) The substance was detectable and widely dispersed in the population in WW and WWS, (ii) The input rate in the atmosphere, as taken into account, outweighed the rate of decay, which led to the high degree of detection, often even above the initial level, particularly in matrixes that were not released directly, and (iii) The substance is robust and does not readily degrade in metrices such as WW and WWS (Mohapatra et al., 2010b).

In addition to the correlation of BPA emissions and characteristics of different types of plastics industries, the environmental contamination of plastics sectors was studied. Sixty-six river water samples, six marine animal samples, and 64 soil surface samples from three cities have been obtained in Southeast China, each with a separate plastics industry. The largest volume of BPA in water (244–5680 ng/L), marine creatures (11.12–478.43 ng/g), and surface soil (38.70–2960.87 ng/g) in Yuyao city, where the most popular plastic products are manufactured from plastic raw materials. Despite the fact that Taizhou is noted for its massive production of plastic products, the levels of BPA in the region were modest and comparable to those seen elsewhere. BPA concentrations in Wenzhou, which is comparatively underdeveloped, have been lowest in the plastics industry. The plastics industry that uses BPA as an intermediary for raw plastics processing including polycarbonate and epoxy resins plastics, according to their reports, the leading cause of environmental BPA pollution (Lin et al., 2017).

3.2.1 Fate and origin of bisphenol A in wastewater

BPA, which has been linked to endocrinological damage, is used in the primary manufacturing of polycarbonate plastics and epoxy resins used in the plastics industry. Because of the large-scale manufacture and wide-ranging uses BPA is released from end-of-life treatment into the atmosphere by air, land and water. Owing to its use in food and beverage cans and containers, the world's population were vulnerable to BPA. When subjected to thermal or acidic conditions, BPA leaches from plastic. Concerns about BPA have increased in recent years; however, there is still considerable controversy about the possible adverse consequences of BPA. Since the majority of existing wastewater treatment plants (WWTPs) are not equipped to handle emerging pollutants like BPA, they can contaminate the marine ecosystem (Pookpoosa et al., 2014).

BPA is an organic compound that was first synthesized in 1891 and consists of two equivalent phenol groups. Many of the negative effects of BPA on human wellbeing were found accidently over two decades ago. BPA was discovered to be leached from autoclaved polycarbonate flasks in 1993, resulting in increased proliferation of breast cancer cells (Vandenberg et al., 2007a). BPA exposure to broken polycarbonate cages caused meiosis in the control oocyte female mouse to be disrupted (Hunt et al., 2003).

BPA enters the atmosphere via sewage treatment effluent (Körner et al., 2000), landfill leachate (via BPA hydrolysis from plastics (Wintgens et al., 2003)) or natural degradation of polycarbonate plastics. Point sources of BPA in the atmosphere include sewage effluent and landfill leachate; nonpoint sources include epoxy resin particles and polycarbonate plastic debris entering the watershed through runoff. Industrial releases of BPA into the atmosphere would probably result from wastewater and waste products released during the production and processing, fugitive dust liberated during handling and low manufacturing volatilization losses (Wintgens et al., 2003). During the disposal and recycling process of waste water treatment plants (WWTPs) and also via release from production, BPA can reach the atmosphere through the possibility of a physical and chemical breakdown. Untreated municipal waste water and WWTP effluents are one of the major causes of BPA (Körner et al., 2000). The majority of existing WWTPs are not equipped to handle emerging pollutants such as BPA. As a result, a significant amount of emerging pollutants, such as BPA and its metabolites, will avoid removal in WWTPs and reach the aquatic environment through sewage effluents. Different tests to eliminate BPA in wastewater have also been carried out (Mohapatra et al., 2010b). The behavior and elimination of BPA in WWTP is dependent on the nature of the BPA and the configuration and execution of WWTP. Major routes of sludge reduction of BPA include: (i) sludge adsorption, (ii) biological transition and decay (Langford and Lester, 2003; Mohapatra et al., 2010a). The recent development of analysis techniques has shown great interest in the detection, trace concentrations analysis, and degradation of BPA in aqueous environments (Jin et al., 2004; Mohapatra et al., 2011b, 2011a). BPA amounts of waste sludge could be released into the soil if sludge biosolids are applied on farm fields (Canada, 2008). The draft evaluation report submitted by Health Canada's Gazette found that, in particular at the critical stage of development of the mental stage of the following decades, and through more than one mode of action, BPA can cause harm to aquatic species with persistent exposure at levels below those normally seen in brief exposures. Therefore, it is of great importance for the detection and quantification of BPA in waste water (WW) and wastewater sludge (WWS) to evaluate the endocrine function in WWTPs released into the atmosphere and to classify procedures that are more successful in mitigating pollutant environmental impacts. Most experiments have further established that BPA exists in WW and WWS (Fuerhacker, 2003; Kang et al., 2007; Lee et al., 2002; Pothitou and Voutsa, 2008) and have only achieved a mass equilibrium by focusing on all samples and not partitioning solid and liquid fractions, which are a vital body for the destiny of BPA in WWTP's. In addition, the presence and rheology of BPA in the WWTPs have been attributed to the physical–chemical–biological processing of BPA. Apparently viscosity and particle size rheology affect removal of BPA from WWS as viscosity and particle dimensions' decrease during various treatment processes of WWTPs improve the degree and thus degradation of adsorption and desorption of BPA. The reduction in particulate size will also increase access to biodegradation of the pollutant via the biological process of microbial enzymes to BPA. The biodegradation of waste water waste was actually enhanced by a smaller particle size and viscosities (Verma et al., 2005).

Due to its moderate water solubility and low vapor pressure, BPA has been found in influent and effluent (Meesters and Schröder, 2002), as well as WWS in WWTPs (Fürhacker et al., 2000; Körner et al., 2000), and is released into the atmosphere by sewage treatment effluent, landfill leachate (via BPA hydrolysis from plastics (Wintgens et al., 2003)), or natural degradation of polycarbonate plastics. BPA is also used as a reactive agent in manufacturing color developing layers of temperature-sensitive material. Therefore, paper factory effluents (either paper fabrication or recycling) and paper recycling materials such as toilet papers are also a major source of BPAs in WW and WWS (Gehring, 2004; Rigol et al., 2002). BPA was also discovered in groundwater from agricultural and commercial wells as a result of its leaching (Latorre et al., 2003). The contaminant may also be passed to food from various sources: (i) Piping, gaskets, and containers food packaging by interaction with plastics, resins, lacquers, surfactants, and paints (ii) Migrations of material, envelopes, and ink from wrapping and bottling.

Based on particular treatment conditions, the release of BPA to water streams is reduced by the increased installation of WTTPs (Céspedes et al., 2008). WWS landfills/dumps leaching, industrial use, and incineration operation reintroduce the compound into the environment. When treated or dewatered WWS is used as fertilizer or soil conditioner, the compound may join the food chain in its natural or transformed form.

3.3 Effects of bisphenol A on humans

BPA, also known as 2,2-bis(4-hydroxyphenyl) propane, is an estrogen-like endocrine disruptor. Krishnan's group discovered the estrogenic function of BPA by chance (Krishnan et al., 1993). They find that autoclaved polycarbonate bottles have been leached from BPA, increasing the rates of MCF-7 breast cancer cell proliferation. BPA is one of the world's largest volumes of chemicals generated with more than 6 billion pounds annually (Burridge, 2003). In normal conditions of use, BPA was found to be leaching from food and beverage containers and some dental dentures and composites. Studies have shown BPA in serum, milk, amniotic fluid, follicular fluid, placental tissue, and umbilical cord blood can be tested in humans. Total BPA (free and conjugated) levels in human blood and other fluids are higher in certain cases than concentrations recorded to promote a variety of molecular endpoints in cell culture in vitro (Wetherill et al., 2007), and tend to be within an order of magnitude of BPA levels in animal studies (Richter et al., 2007).

BPA enters the human body through the diet, household dust inhalation, and dermal contact (Vandenberg et al., 2012). In 2002, a total of 2.8 million tons, and an estimated 5.5 million tons, of BPA were released in 2011 (Market and Report, 2008). BPA has been shown to bind to estrogen receivers and have estrogenic effects in laboratory trials. Although BPA has been shown to be lower in relation to 17 beta estradiol (E2) for nuclear estrogen receptors, their estrogen potential is equivalent to E2 for responses mediated by non-nuclear estrogen receptors (Viñas et al., 2012). Furthermore, BPA has the potential to function as an antiestrogen, inhibiting the estrogenic reaction by competing with endogenous E2 (Bonefeld-Jørgensen et al., 2007; Richter et al., 2007). BPA may also bind to androgen receptors specifically, making it potentially antiandrogenic by inhibiting endogenous androgen action (Sohoni and Sumpter, 1998; Wetherill et al., 2007). BPA has been demonstrated to bind to thyroid receptors and has both agonistic and antithyroid effects (Moriyama et al., 2002; Wetherill et al., 2007). BPA also interacts with other organs and physiological systems including central nervous system growth, pancreas, and immune system (Wetherill et al., 2007).

A host of women's disorders, such as obesity, endometrial hyperplasia, repeated miscarriages, pathological karyotype, and polycystic ovarian syndrome have been linked with BPA levels in the bloodstream. Two researchers discovered that people with PCOS had higher serum BPA levels than women without PCOS, and that BPA levels were positively associated with circulating androgen levels (Takeuchi et al., 2004; Takeuchi and Tsutsumi, 2002). Three tests have found increased susceptibility to BPA for chromosomal adverse health effects. In one study, women with fetuses with an irregular karyotype were seen to have higher maternal serum BPA compared with women with a typical karyotype (Yamada et al., 2002). This research did not account for maternal age, which is a significant possible confounder. An additional epidemiology report indicated that the connection between serum BPA and a recurring error was more than threefold higher in 45 women with three or more successive first-quarter errors compared to 32 women without fertility issues without paralysis (Sugiura-Ogasawara et al., 2005). Furthermore, among 35 women who were pregnant, there was some proof of lower BPA among those who had a healthy pregnancy as opposed to those who miscarried again. It is important to remember, though, that the exposure distribution for women who had recurring error was very distorted, with only a small number of women having elevated exposure levels and that the median levels of exposures in the two groups were similar. Finally in peripheral lymphocytes, the sister chromatid exchange was linked to the urinary BPAs in adults (Yang et al., 2006).

BPA has been found in the environment, including the air, soil, water, landfill leachate, and the human body. Any forms of food packaging (e.g., polycarbonate containers and epoxy coating of metal cans) and recycled containers have been found to leach the chemical into foods and drinks (Von Goetz et al., 2010). People can also be exposed to BPA by touch with the skin, dentures, and exposures inhaled. Human serum, milk, saliva, urine, and amniotic fluid have all been found to contain BPA (Vandenberg et al., 2009, 2010, 2012).

The widespread presence of BPA in the atmosphere and the human body has raised questions about possible negative health consequences. The molecular composition of BPA enables it to fit into a binding pocket of the estrogen receptor (ER). At higher doses, BPA behaves as an androgen receptor (AR) antagonist, interacts with the thyroid receptor (Vandenberg et al., 2009) and stimulates the gamma of the peroxisome proliferator activated receptor (PPARc) (Kwintkiewicz et al., 2010; Wang et al., 2013). BPA has been linked to numerous health problems such as infertility, weight gain, personality changes, early-start puberty, prostatic and mammalian tumors, cardiovascular effects, obesity, and diabetes (Birnbaum et al., 2012).

3.3.1 Cancer outcomes

The pervasive involvement of BPA and an increase in the prevalence of cancers linked to the endocrine, such as breast, uterine, and prostate cancers have led to studies evaluating how BPA plays a part in human carcinogenesis. In 2008, Lang et al. (2008) identified the levels of urinary BPA in samples obtained by the National Health and Nutrition Examination Survey (NHANES) of US adults who had already conducted a health survey in 2008. There was no connection found between high BPA levels and the occurrence of cancer in general. Since breast cancer is most often vulnerable to estrogen (ER-positive cancer), numerous studies have examined the possible effect of BPA on human and animal models specifically on breast cancer. Early-life BPA sensitivity has been linked to developmental changes in mice, which have been linked to an increased risk of cancer later in life. Yang et al. (2009) studied overall serum BPA from people with and without breast cancer in an analysis of the links between BPA and cancer in humans. BPA levels were shown to be nonsignificantly higher in cancer patients (Yang et al., 2009). Another research did not identify a connection between BPA and breast cancer diagnoses in adular work-related exposure (measured by survey) (Aschengrau et al., 1998). According to these findings, there is no correlation between BPA and breast cancer. Indeed, there is enough evidence from rat (Ayyanan et al., 2011; Durando et al., 2007; Markey et al., 2001, 2003; Muñoz-de-Toro et al., 2005; Soto et al., 2008; Vandenberg et al., 2007b) and primate (Tharp et al., 2012) research that prenatal BPA exposure disrupts mammary tissue and increases the tissue's resistance to chemical carcinogens.

3.3.2 Male sexual function

Li et al. (2010b, 2010a) conducted two outstanding cohort studies on self-reported male sexual function in workers. Men who worked in BPA and epoxy resin manufacturing firms in China, as well as men who were not exposed, were observed. BPA exposure was calculated by analyzing the factory's historical data, conducting spot air sampling, and performing personal air monitoring. The self-reported sexual activity (e.g., erectile function, orgasmic function, sexual appetite, and general sexual life satisfaction) of exposed employees was slightly lower than controls. Diminished sexual activity was associated with dose-related BPA exposure (Li et al., 2010a). A portion of the same workforce provided urine samples for complete BPA testing. Higher urinary BPA was substantially associated with lower sexual function recorded. It is noteworthy that, in certain metrics (sexual appetite, overall sex life satisfaction), the control group exposed environmental but not occupationally still demonstrated substantial negative associations that could decrease exposure to BP A in the overall population that had a lower exposure to BPA than occupational employees (Li et al., 2010b).

3.3.3 Female reproductive outcome

BPA toxicity has also been linked to female reproductive anomalies in humans, including effects on the ovary, uterus, and oocyte production. Takeuchi and Tsutsumi (2002) and Takeuchi et al. (2004) discovered that women with PCOS had considerably higher average BPA exposures. Kandaraki et al. (2011) also analyzed women with and without PCOS and discovered that overall serum BPA levels in the PCOS population were slightly higher than in the controls. They also discovered a connection between BPA and higher levels of androgen in the blood. BPA exposure was associated with a drop in peak serum estradiol levels prior to oocyte recovery, which could adversely affect embryo production in three trials of women under in-vitro fertilization (IVF) (Bloom et al., 2011; Ehrlich et al., 2012; Mok-Lin et al., 2010). The findings of a case control analysis of 69 women indicate the presence of endometriosis at serum BPA standards (Cobellis et al., 2009), however the study was constrained by the small sample size and the choice of serum BPA measuring methods.

3.3.4 Neurodevelopment outcome

Several new findings have shown altered behavior in children who were subjected to BPA in utero or before puberty, suggesting brain damage during crucial developmental windows. The brain organizing of the neuroendocrine system, which coordinates the sex-specific physiology and behavior of the vertebrates, is based on steroid hormones. As a consequence, the symptoms of endocrine disruption can be permanent and result in a typical conduct (Patisaul and Adewale, 2009; Wolstenholme et al., 2011; Wright et al., 2010). The association between childhood BPA sensitivity and cognitive capabilities was investigated by two epidemiological trials. In the New England Infant Amalgam Trial, Maserejian and colleagues investigated childhood BPA toxicity from bisphenol-A-diglycidyldimethacrylate (bis-GMA) comprising composite tooth fillings and cognition (Maserejian et al., 2012). There was no indication of a connection between total surface-years of bis-GMA composite filling exposure and cognitive, memory, or visual-spatial skills, according to the researchers (Maserejian et al., 2012). A Korean study found that the concentrations of existing urinary BPA in children aged 8–11 are linked to higher academic difficulties identified by the teacher (Hong et al., 2013).

3.4 Biodegradation of bisphenol A in wastewater

The systematic use of BPA-containing materials has resulted in extensive BPA pollution in numerous marine ecosystems, including urban drainage dam (Kotowska et al., 2014; Luo et al., 2014), river water and sediment(Esteban et al., 2014; Selvaraj et al., 2014; Shi et al., 2014;

Wang et al., 2013), lake water and sediment (Matsumura et al., 2009), groundwater (Luo et al., 2014), and drinking water (Esteban et al., 2014). BPA has become increasingly ubiquitous in marine ecosystems, because of its estrogenic consequences on both humans and other animals (Chouhan et al., 2014; Zhang et al., 2013). Microbial degradation is essential in the degradation of BPA in natural habitats. Aerobic BPA degraders from many bacterial genera, such as *Pseudomonas* (Chang et al., 2011; Kang and Kondo, 2002), *Bacillus* (Chang et al., 2011), *Novosphingobium* (Toyama et al., 2012), *Sphingomonas* (Sakai et al., 2007), and *Streptomyces* (Kang et al., 2004), have been isolated from normal aquatic environments. Furthermore, anaerobic oxidation of sediment habitats can play a more important role in cleaning up BPA waste because it is mostly anaerobic.

The biological destruction of BPA by microorganisms is a sustainable and economical method for the environmental removal of BPA (Eltoukhy et al., 2020; Fu et al., 2019). Bacteria capable of degrading a variety of xenobiotics, including BPA, have been isolated and studied. The first BPA-degrading bacterium, *Sphingomonas* sp. strain MV1, was isolated from a plastic manufacturing facility's sludge (Lobos et al., 1992). BPA degrader *Sphingomonas bisphenolicum* strain AO1 was isolated and BPA degradation was investigated in the cytochrome P450 (CYP) (Sasaki et al., 2005a, 2005b, 2008). Determination of BPA *Sphingobium* sp. BiD32 was isolated from active sludge, and BPA degradation was assumed to include p-hydroxybenzoate hydroxylase BPA degrader (Zhou et al., 2015). Moreover, several bacteria with BPA biodegradation capacity, such as *Achromobacter xylosoxidans* strain B-16, *Cupriavidus basilensis* strain JF1, *Cupriavidus basilensis* strain SBUG 290, and *Novosphingobium* sp. TYA-1, were isolated and investigated (Toyama et al., 2009; Zhang et al., 2007).

Huang et al. (2017) performed an analysis in which sediment was spiked with BPA solution in order to investigate the relationship between indigenous bacterial species and BPA biodegradation in sediment. The results revealed that BPA could be adsorbed to the sediment and then quickly biodegraded. On the first day, the biodegradation performance of BPA in treatments containing 10 and 50 mg/L BPA was 64.3% and 61.8%, respectively. BPA greatly influenced the densities, habitats, and diversities of bacteria, according to quantitative polymerase chain reaction and denaturing gradient gel electrophoresis analysis. The bacterial community's reaction to BPA favored BPA biodegradation by encouraging the growth of BPA-reducing bacteria while inhibiting other competitors. *Pseudomonas* and *Sphingomonas* played a key role in the degradation of BPA, according to the sequence data. More than 73% of the initial bacterial population is represented, and they were both promoted by BPA compared to controls.

In detoxifying waste water containing BPA, bacteria play a major role. Since the effluent levels of BPA are over 90% less than influential, this contamination can be attributed to the marine setting (Kang et al., 2006). The triggered sludge method is the most often used technology for biowater treatment. Bacteria play a key role in the purification process, when all nutrients and xenobiotics are the product of a highly dependent on the metabolism and interactions of the microbial population (Hashimoto et al., 2014). The triggered sludge environment is similar to soil in terms of species diversity (Ye and Zhang, 2013). *Betaproteobacteria* is found to be the most abundant class of *proteobacteria* phylum, followed by *gamma proteobacteria* (Kwon et al., 2010; Snaidr et al., 1997). Otherwise, *Alpha proteobacteria* and *Actinobacteria* were the top two groups in the triggered study, according to Ye and Zhang (2013). Based on the chemical compounds in the waste water, the dynamics of the bacterial population varied. In light and dark incubations, bacterial consortia from activated sludges were shown to be capable of fully degrading BPA to intermediates, which were then further degraded to harmless end products (Eio et al., 2014). Both BPA- and non-BPA-degraders are used in these consortia, and they work together. Microorganisms that are incapable of degrading BPA may aid in the removal of this chemical by increasing the activity of BPA-degraders or by cometabolism (Zhao et al., 2014).

Bacterial consortia used in wastewater treatment plants are made up of a diverse group of bacteria. Bacterial consortia are more effective in the utilization of organic compounds and potentially toxic biodegradation intermediates (Hanson et al., 1999), and are resistant to substrate inhibition (Marrot et al., 2006). As a result, a number of bacteria with various degradation pathways can degrade BPA to intermediates that can then be used by other bacteria. For these purposes, the intermediate BPA biodegradation formed by bacterial consortia should be analyzed in order to assess their potential for degradation.

3.5 Conclusions and perspectives

The study reports the boon and bane of BPA in all kinds of waste waters. There are severe cacogenic problems that are associated with BPA in waste water, when the humans come in contact with it. BPA being a very menace compound in terms of living organisms, but it was introduced majorly by humans in various industries through the waste water effluents. The maximum concentrations are induced mainly through domestic waste waters. There were various studies reported in this review on bioremediations and biodegradation of BPA in waste waters, but the still the problems pursuits in the world due to the improper guidelines followed by the humans in terms of desirable limits of the chemical compounds. The major perspective of the study involves systematic approaches in selecting the suitable treatment techniques for degradation of BPA in waste water.

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4

Phytoremediation of endocrine disrupting pollutants in industrial wastewater

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4.1 Introduction

It is important to note a harmful environment condition has been observed in recent years, such as: (1) clear climate change, (2) depletion of fossil fuel reserves, (3) growing amounts of liquid and solid waste caused by strong industrial activity and great demographic growth in urban areas, and (4) a sharp increase in energy demand and a pressing need to find alternative energy. In fact, nowadays, all the governments of the world agree on the need to put in place policies that allow the development of new technologies that will provide us with a sustainable and clean environment (Rajhi, 2012). In particular, the production of biomass and solid and liquid wastes attract special attention as it can transform a large amount of organic wastes into energy resources (Rajhi et al., 2016). The microbial/biological conversion of industrial and urban waste residues into clean renewable energy therefore attracts interest insofar as the cost advantage of production by biological means could be maximized from organic and/or mineral waste. Industrial wastewater is a general term used to represent poor quality water that contains more amounts of pollutants and microbes (Rajhi et al., 2016). They can cause serious environmental and health problems, especially the chemical endocrine disruptors. The treatment of industrial water is an important measure to reduce the pollutant and other contaminants present in this water (Mulbry et al., 2008). Several methods, in this case, chemical treatment, and conventional biological methods are used to remove nutrients, organic pollutants, and heavy metals including chemical endocrine disruptors EDCs from industrial wastewater (Haq and Raj, 2019). Compared to treatment methods conventional, phytoremediation can be suggested as an alternative to remove pollutants from industrial wastewater. The use of plants, microalgae, or macroalgae (algae) for the treatment of wastewater was called phytoremediation (Li et al., 2013). The treatment of industrial water by phytoremediation complies with a clean environment notion and offers the advantage of a cost-effective means of removing pollutants. The

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main objective of this chapter is to develop and discuss the different technological processes of phytoremediation (economically profitable) used to remedy industrial water, in particular water containing endocrine chemical disruptors.

4.2 Phytoremediation

Phytoremediation is a technology using the metabolism of plants and algae/microalgae associated with them to accumulate, transform, degrade, concentrate, stabilize, or volatilize pollutants (organic and inorganic molecules, metals, and radio elements) contained in soils or contaminated water. It is a set of in situ techniques (which can be installed directly on the contaminated site) focusing on plants to extract, degrade, or immobilize the contaminants in the soil, sediment, sludge as well as in water from surface or underground and in the air. Phytoremediation is a very effective economic bioremediation strategy powered by solar energy (Masojidek et al., 2004). Fig. 4.1 shows a simplified process of the different phytoremediation techniques applied by plants.

4.2.1 Description of process

The various phytoremediation techniques are based on the following different principles of action namely, the extraction, the stabilization, the degradation, the volatilization, or filtration.

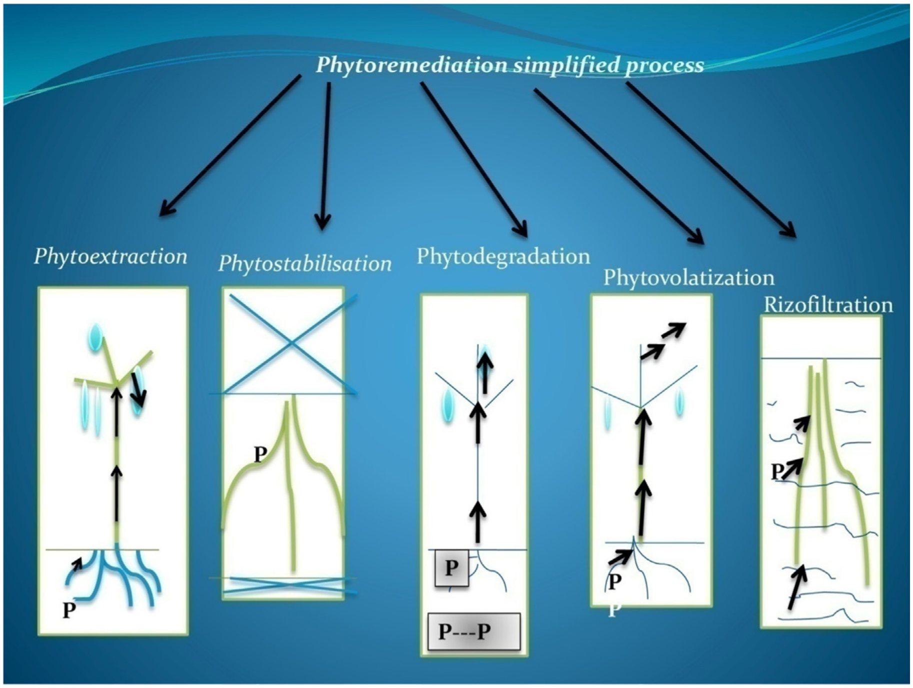

FIG. 4.1 A simplified process of the different phytoremediation techniques, namely, phytoextraction, phytostabilization, phytodegradation, phytovolatilization, and rhizofiltration.

4.2.1.1 Phytoextraction

The phytoextraction or phytoaccumulation, in this process the plant removes contaminants from the soil, such as bioavailable trace metal and metalloid elements, as well as certain types of organic contaminants and accumulates them in their aerial parts that can subsequently be harvest. This is the most used method. Plants can acidify the rhizosphere or even secrete ligands capable of chelating metal ions. Sometimes mycorrhizal fungi form symbiosis with plant roots to aid the metals uptake when the soil concentrations are low, and conversely, can help plant to phytotoxic levels of resistance (Peer et al., 2005). For example, mycorrhizae are directly involved in the sequestration and uptake of zinc (essential element) and cadmium (nonessential element) by plants exposed to toxic concentrations, thus increasing the potential for phytoremediation. Once in the plant, the contaminants can remain in the roots, but to facilitate extraction, ideally as much as possible is translocated with the sap, in the xylem vessels, to the aerial parts of the plant. This takes place when there is a negative pressure in the xylem, created by the transpiration of the leaves, which accelerates under the effect of heat, wind, low ambient humidity, or strong light (Peer et al., 2005). Then a biomass harvesting process must be applied to permanently remove contaminants from the site. Sometimes the thermal energy during this combustion can be recovered. Thus, composting can generate a valuable by-product which must be well controlled. In the case of phytoextraction of precious metals (phytomining), the metal can be recovered after low temperature combustion or a chemical extraction process. These processes can represent an economically important potential (Giasson et al., 2004).

4.2.1.2 Phytostabilization

The plant reduces the mobility and bioavailability of contaminants in the soil or the rhizosphere, by chemical immobilization (precipitation, stabilization, absorption, or trapping) or prevention of lateral or in-depth movements via erosion or leaching. Plant stabilization thus prevents the dispersion of contaminants in surface and groundwater. A vegetated land cover minimizes wind or water erosion, as well as direct contact between animals and pollutants. The plant can minimize the formation of contaminated leachate and limit the migration of dissolved contaminants into groundwater. However, during phytostabilization, there may be a conversion of pollutants into less bioavailable forms, for example, when these precipitate in the rhizosphere (Giasson et al., 2005).

4.2.1.3 Phytodegradation

In phytodegradation/phytotransformation, the plants take up and break down organic pollutants in their tissues or secrete degradation-related enzymes in the rhizosphere. Decontamination is carried out in the rhizosphere by microorganisms whose growth and activity are stimulated by plants. The degradation of organic compounds can be completed (generating inorganic elements such as CO_2, H_2O/Cl_2), but it can also be incomplete, leading to the formation of stable intermediates (called metabolites) which can be stored in the plant. The degradation of organic products can take place in the roots or in the aerial parts of plants, thanks to enzymes such as dehydrogenases, oxygenase, and reductase. This type of remediation can be used, among other things, to remedy contamination problems with petroleum hydrocarbons (Pilon-Smits, 2005).

4.2.1.4 Phytovolatilization

The organic pollutants and certain inorganic compounds are extracted from the soil by plants, transported in their vascular system, and then exposed to the atmosphere through transpiration. It is an attractive technology because the pollutants are thus fully volatilized (in the form of gas) (Olson et al., 2004). However, the risk of the transfer of pollutants to the atmosphere must be well characterized before undertaking phytovolatilization. Phytovolatilization is used for chlorinated solvents such as trichlorethylene, herbicides, insecticides, hydrocarbons, and certain metalloids such as mercury, arsenic, and selenium (Glass, 1999). Volatile organic compounds can simply be released into the atmosphere by plants. On the other hand, components such as selenium must be transformed in the plant before being volatilized (this transformation simultaneously decreases their toxicity). Mycorrhizal fungi can facilitate the absorption of mercury and selenium, two elements that have a gas phase. It is well known that microbes can transform and volatilize arsenic and mercury (Giasson et al., 2005).

4.2.1.5 Rhizofiltration

This technique can treat municipal/industrial wastewater, surface run-off or water that infiltrates the soil in agricultural areas, leachate from mines and landfills, or contamination of water, underground water (Giasson et al., 2005). The contaminants targeted include metallic trace elements, radionuclides, selenium, nutrients, certain organic compounds such as pesticides, or acid mine drainage. The rhizofiltration can use aquatic plants or terrestrial plants, and sometimes a combination of species with complementary properties. The rhizofiltration often relies on flow-through systems that maximize contact between water and roots, and thus minimize treatment time (Glass, 1999). The rhizofiltration can take the form of an artificial pond or a hydroponic system. Rhizofiltration can also limit the horizontal diffusion of contaminants into groundwater if plants are positioned to provide a hydraulic barrier, so that the plants suck water from the soil and limit the movement of pollutants through the water. Rhizofiltration can be exploited, for example, in riparian strip systems (Giasson et al., 2005).

4.2.2 Phytoremediation by plants

The phytoremediation by plants could also be called “rhizoremediation”: this process is mainly carried out by the roots. However, the aerial parts of the plant play an important role, insofar as they capture solar energy and ensure the flow of pollutants through transpiration, but it is in the root environment that most of the processes take place (Newman et al., 1997). The root system can develop a very large surface (several square meters) which constitutes the place of interactions with the soil. If we look at what is happening at the end of a root (the apex), a lot of organic compounds, called exudates, are released there. They serve as substrates for the microorganisms present, so that around the root there is particularly intense biological activity. Therefore, the root behaves like a well of water, solutes, and oxygen, and like a source of carbon dioxide and organic compounds, which stimulate the growth and development of microorganisms, which will then multiply around the root and constitute what is called the rhizosphere (Zayed et al., 1998). Phytoremediation brings different modes of action (*see more details in* Section 4.2.1). Phytostabilization by plants: this is the first effect observed when a surface is cultivated. It is thus protected against degradation phenomena such as erosion, which limits the transport of particles laden with pollutants by water and wind. This process is widely used by civil engineering to stabilize structures, such as, for example, road embankments. Beyond the mechanical effects, plants also help stabilize pollutants (Zayed et al., 1998). Rhizo-attenuation by plants: this process takes place in the rhizosphere, resulting primarily from the stimulation of biological activity, which can contribute to the degradation of organic pollutants, with the ultimate production of carbon dioxide, but also of intermediate products. In addition, the roots help the organic pollutants' transformation. Phytoextraction by plants: this is the principle of the vacuum cleaner. The plant takes up pollutants through its roots. They are transferred to the aerial parts where they are sequestered in the leaves. Phytovolatilization is the extension of phytoextraction, since the plant is able to metabolize pollutants. The latter, like organic pollutants of the very volatile chlorinated solvent type, can then be volatilized. Plants can also transform trace elements such as selenium, mercury or arsenic, which then take on volatile chemical forms (Morel et al., 1999). In fact, phytovolatilization can present pertinent methods for the EDCs industrial wastewater phytoremediation using plants.

4.2.2.1 Characteristics of hyperaccumulator plants

Over 400 currently are known as hyperaccumulator species, the most numerous of which are nickel hyperaccumulator (Quiroz et al., 2016). Thus, there is a close relationship between the plant's ability to take up metal and the amount of metal available in the soil (Montargès et al., 2008). The choice of plants depends on various criteria, generally related to the preparation and maintenance of the site during phytoremediation. In contaminated environments, plants that can tolerate a certain pollution threshold must be favored in the process of natural selection. These tolerance mechanisms are varied and include plant/microbe interactions, rhizosphere processes, plant uptake, translocation, degradation, and completion (or chelation) during transport and storage to minimize toxicity (Montargès et al., 2008).

4.2.2.2 Phytoremediation by macro- and microalgae

Microalgae classification and uses

Microalgae are photosynthetic unicellular organisms (2–200 μm) which can grow in an autotrophic or heterotrophic manner. In general, they are highly efficient in fixing CO_2 and in using solar energy to produce biomass, with efficiency up to four times greater than that of plants (Blossfeld et al., 2010). The importance of microalgae lies in their role as primary producers in the food chain. Microalgae are the basis of food webs, and their large number of species and versatility allow them to be used in different industrial fields with great potential for success. They are present in all climates with water such as lakes, seas, and rivers, although we can also find them in soil and in the majority of terrestrial climates; even the most extreme. This makes it possible to find them widely distributed in the biosphere, adapted to numerous conditions. Microalgae are, in general, photoautotrophic organisms; that is, they get energy from light from the sun and develop from inorganic matter. However, some species are able to grow using organic matter as a source of energy or carbon (Xu et al., 2006). There are over 30,000 species of microalgae, of which only 100 have been studied in detail and about 10 are commercially exploited. Although there are currently many studies showing that shortly after 493 species of microalgae could be used in various industrial applications (Xu et al., 2006). In relation to the environment, microalgae can be used in environmental bioremediation, as in the case of urban/industrial wastewater treatment. In addition, these organisms help to fix CO_2 by what they could reduce the emissions of this gas, which is a big responsible for the greenhouse effect (Kaniemi et al., 2011).

Cultivation of microalgae

Photosynthesis is a specific metabolic process of autotrophic organisms which are able to synthesize organic substances from other inorganic. In fact, light energy is converted into stable chemical energy (Rajhi et al., 2020). Chemical energy is stored in the form of adenosine triphosphate (ATP) molecules. These ATP molecules are subsequently used to synthesize other, more stable organic molecules. Photosynthesis is essential for the life of our planet since, from light and inorganic matter, organic matter is synthesized, allowing carbon dioxide (CO_2) to be fixed and oxygen (O_2) to be released (Fig. 4.2).

The external factors that affect photosynthesis are temperature, light intensity, and the concentration of CO_2 and O_2. It is important to know the perfect conditions and tolerance limits for each species of microalgae. In mass culture of microalgae, the yield depends on the concentration of cells in the culture and the degree to which the cells can develop its growth potential. Indeed, to obtain a culture of microalgae with a growing active, it is necessary to put a viable inoculate, a minimum supply of nutrients and microelements and adequate chemical and physical conditions such as light, aeration, temperature, and salinity (Cañizares et al., 1994). Different factors can affect the microalgae production. For their development, microalgae need CO_2, nitrogen, phosphorus, potassium, magnesium, and other nutrients such as metals, which

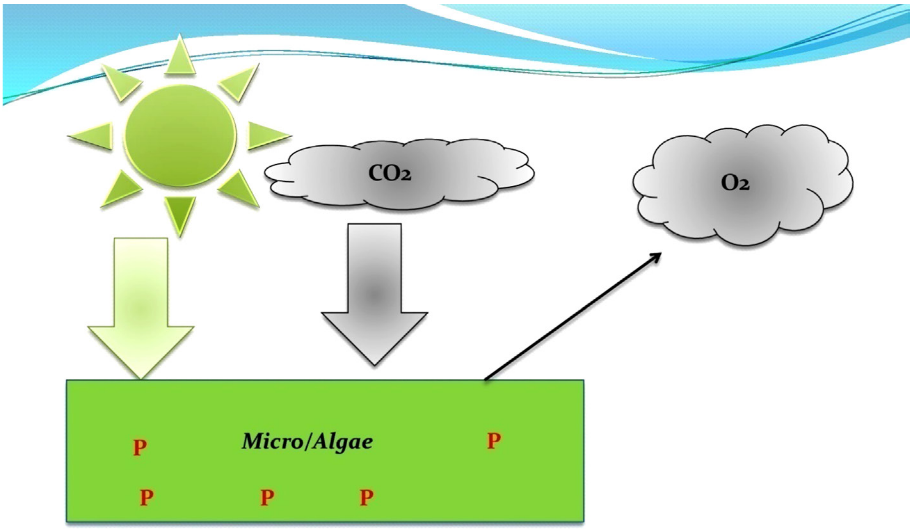

FIG. 4.2 The photosynthesis process carried out by microalgae.

are essential because they play the role of cofactor of enzymes essential for microalgae metabolism. Other important factors for the production of microalgae are temperature, light intensity, salinity, nutrients, and pH, which vary widely from species to species and which must be taken into account for the microalgae production, such as,

- Lighting: Microalgae only use light in the range 300–700 nm, a region of the spectrum known as photosynthetically active radiation.
- Temperature: most species grow between 10°C and 35°C, with an optimum temperature between 16°C and 24°C.
- Aeration: is an important factor for the homogenization of nutrients and to avoid the sedimentation of microalgae. Proper agitation promotes a homogeneous distribution of cells, metabolites, heat, and gas transfer across the gas–liquid interface. However, excessive agitation can cause hydrodynamic stress leading to a decrease in the rate of growth.
- The tolerance to salinity depends on the species considered (of freshwater or saltwater origin).

Within the chemical requirements necessary for a good growth of microalgae culture are found, specific macronutrients and micronutrients. The basic nutrients are carbon, nitrates, and phosphates. The decrease in the source of nutrients is a limiting factor for algae culture. Some metals are used in very small quantities but, they are essential for growth and play various roles in the different cellular mechanisms namely, potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{2+}) and Fe^{3+}) (Prescott et al., 2002). Certain other micronutrients, such as manganese, zinc, cobalt, molybdate, nickel, and copper, are needed in small amounts for cells and generally serve as cofactors of reactions and to maintain protein structures (Brenan and Owende, 2010). However, in some microalgae, more macronutrients and micronutrients require other substances for their development like vitamins, since they are not able to synthesize all of them. In addition, they require other elements in small quantities which are essential for their growth namely, manganese, zinc, cobalt, cadmium, copper, molybdenum, and nickel, which are part of the enzymes necessary for the electron transport, CO_2 fixation and transport, DNA transcription, nitrogen fixation and transport (Rajhi et al., 2020). Likewise, the level of O_2 and CO_2 supplied to the crop can be converted into a limiting factor. By improving circulation, by means of the proper addition of CO_2 or sodium bicarbonate can cause the prolongation of the exponential growth of microalgae (Rajhi et al., 2020).

Different methods that have been developed to obtain a pure microalgae culture, which free from pollutants. Starting from a contamination-free monoculture, this is diluted in a large volume under perfect growth conditions, until obtaining the quantity and quality necessary to be able to initiate a massive culture in the laboratory or on a large industrial scale. The production of photoautotrophic microalgae is the only one that can be achieved on a large scale, so that it can appear economically profitable and technically viable (Prescott et al., 2002). In addition, microalgae have been cultivated in various forms, namely, in artificial lagoons, in cement ponds, in plastic bags or in complex closed, automated and controlled systems such as photobioreactors. Cultivation systems are classified according to their configurations and the type of operation in open and closed cultures.

4.2.3 Phytoremediation of waste

4.2.3.1 Phytoremediation of contaminated soil

The toxic substances responsible for this pollution are either organic molecules such as pesticides, or metals present in large quantities (Morel et al., 1999). Phytoremediation, therefore, appeared to be decontamination alternative, admittedly slower, but also much more economical and more respectful of the microflora, an essential component of good soil quality. There are several strategies for phytoremediation of soils contaminated by metals (Brenan and Owende, 2010). The most used are the following, namely: Phytovolatilization: In this technique, plants have the capacity to absorb certain elements such as mercury or selenium and to add methyl groups (–CH) to them. These methyl elements are volatile and are therefore released into the atmosphere (Baker et al., 1997). Phytoextraction: It consists of the use of plants capable of removing metals from the soil and accumulating them in the aerial parts to harvest the latter and incinerate them. The resulting ash, easier to handle, can be stored or else reused by metallurgy. This ability to absorb and accumulate has also given rise to the concept of "phytomining" (Baker et al., 1997). Process: It is accepted that 16 mineral elements (C, H, and O being excluded) are essential for plants: six elements constitute the major nutrients, necessary in high quantities (macroelements): N, K, P, Ca, Mg, S, and 10 others constitute minor nutrients, generally consumed in small quantities (trace elements): Fe, Mn, B, Zn, Cu, Mo, Cl, Na, Ni, and Co, of which the last four are essential only for certain plant species. Other elements such as, for example, Pb, Cd, and Hg called "nonessential" because although they are present in plants, they do not participate in any known physiological or biochemical function (Banuelos et al., 1997). Exceed the gaseous nitrogen present in the soil atmosphere and usable in this form by legumes, the elements are taken up by the roots of plants mainly in the form of solutes in the soil solution. The elemental resource on the surface of the root is continually being renewed, both by mass flow and by diffusion. Absorption is the physiological process that involves crossing the plasma membrane of the root cells and thus allows entry of an element into the plant from the soil solution. However, in soils, for most elements, this process is not the limiting step in mineral nutrition (Banuelos et al., 1997).

The acquisition of elements is a broader concept which covers absorption, but also all the processes resulting from the action of the plant and allowing the different solid constituents of the soil to replenish the soil solution with elements, as well as transfer processes to the root surfaces (Marschner, 1995). This volume of soil varies according to the nature of the plants, in particular the extension of the root system and its surface properties, the elements considered and the physicochemical properties of the soil (Hinsinger, 1998). For poorly mobile elements, the rhizosphere is limited to the first millimeter (s) of soil located around the roots (Marschner, 1995). Root activity modifies the physicochemical parameters of the soil in the rhizosphere, and consequently the speciation of metallic elements (Alloway, 1995). The flux of ions present in large quantities in the soil solution, such as calcium or magnesium, is often greater than demand. These ions can then accumulate in the rhizosphere and lead in calcareous soils to the formation of precipitates of calcium carbonates around the roots (Alloway, 1995). Conversely, elements present in small amounts in the soil solution, as is typically the case with trace elements, are transferred in amounts comparable to the removal of the plant (Alloway, 1995). The mechanisms of uptake and accumulation of metallic elements in plants can occur at different levels, from absorption by the roots to accumulation in the leaves. These plants develop a specific physiological response that allows hyperaccumulator and prevention of metal toxicity. It is estimated that for the majority of metals and metalloids, the sample is taken in ionic forms: cationic (Zn^{2+}, Pb^{2+}, Cd^{2+}) or anionic ($HAsO4^{2-}$). In particular cases, inorganic and/or organic complexes seem to play a role in the removal of metals (Hinsinger, 2001).

In terms of microorganism–soil interactions, microbial transformations likely to influence the fate of metallic elements can be classified into four categories: (i) mineralization of organic matter; (ii) immobilization of inorganic compounds by the microflora; (iii) oxidation; (iv) reduction. We must add processes that are still poorly understood, such as the solubilization of minerals by complexes of microbial origin, the microbial precipitation of solubilized minerals, the accumulation on the microbial surfaces of certain elements (Mn, Fe, P, etc.). The influence of microorganisms on the plant includes, among others, the following actions: (i) nitrogen supply resulting from nitrogen fixation by rhizosphere bacteria (such as Rhizobium, Frankia, Azospirillum, etc.); (ii) synthesis of phytohormones (auxins, gibberellins, cytokinins, etc.); (iii) solubilization of nutrients through chelating agents; (iv) antagonism toward pathogens (Lasat et al., 1998). The surfaces of the roots support active bacterial biofilms and fungal extensions, which significantly increase the contact surface with the soil and the metabolic capacities of the plant. During evolution, plants have developed mechanisms to adapt and multiply under hostile conditions. Some plants have adopted root mechanisms that immobilize metals at the roots and reduce their transfer to the leaves, where the metals are toxic. Other plants have developed complex mechanisms to tolerate, absorb, and accumulate significant amounts of metals in their tissues. Likewise, metals are trapped at the root level, reducing the risk of leaching into groundwater or even entrainment by wind or hydraulic erosion. This technique is often supplemented by the addition of organic or mineral amendments. Phytostabilization is well suited to rehabilitate large areas contaminated and exposed by the excessive phytotoxicity of the substrate (Babalola and Glick, 2012). However, this technique does not allow the substrate to be decontaminated, and the long-term risk would be a remobilization of the pollutants and their propagation in the environment, following changes in the physicochemical conditions of the environment (Babalola and Glick, 2012).

4.2.3.2 Phytoremediation of EDCs from contaminated water

Algae and more particularly micro- and macroalgae represent a significant diversity (and therefore a very large potential) with a high conversion rate (production of matter) based on a metabolism that can be fermentative (heterotrophic) or photosynthetic (autotrophic). The algal cells are devoid of lignin, which facilitates their recovery through methanization. It is photosynthetic algae (assimilation of CO_2, N, and P) that can be used in water treatment, which implies a pretreatment of water to remove suspended matter and degradable carbon and thus promote good diffusion of the water. Light radiation is necessary for photosynthesis. Therefore, microalgae need nutrients present in the medium for their growth. It turned out that these algae had a very important treatment potential: indeed, they could remove many nutrients from water, with greater efficiency than activated sludge (Mejare and Bulow, 2001). The treatment of water

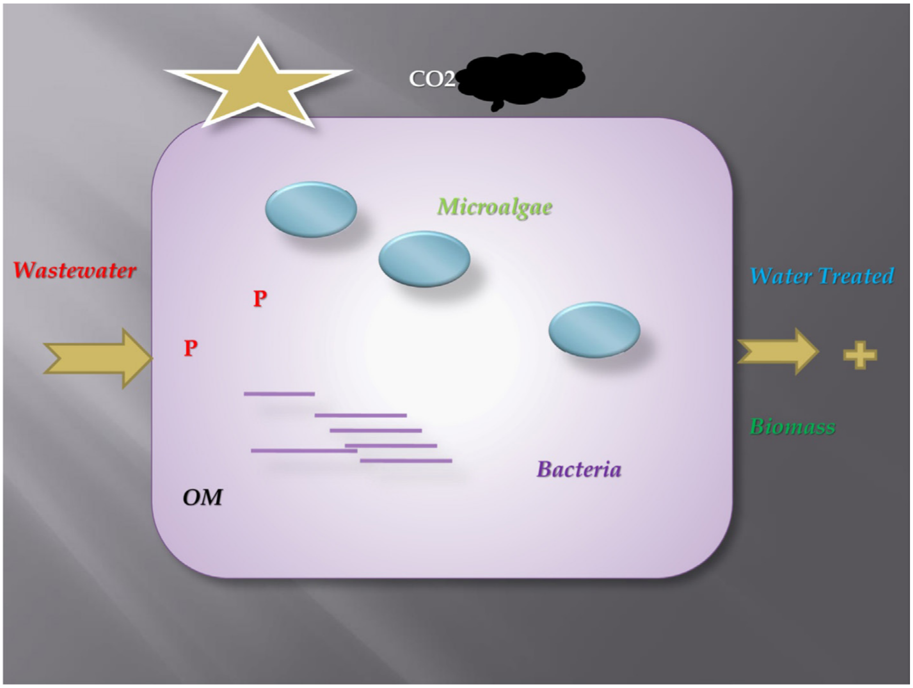

FIG. 4.3 Simplified process of wastewater phytoremediation.

rich in organic matter requires coupling the action of bacteria to that of microalgae. The oxygen produced by the photosynthesis of microalgae is used by bacteria to oxidize organic matter (by respiration). The CO_2, nitrogen, and phosphorus released by bacteria present in wastewater are used by the metabolism of microalgae (Fig. 4.3). In the case of water low in organic matter and rich in inorganic elements such as nitrogen and phosphorus, microalgae must be supplemented with CO_2.

4.2.4 Phytoremediation as a compulsory treatment of industrial wastewater

4.2.4.1 Phytoremediation of EDCs from industrial wastewater (case of plants)

Two phytoremediation subsets depending on the nature of the sites and the desired goal, can be distinguished. The first covers the protection and restoration of ecosystems with regard to diffuse pollution. The second concerns polluted sites and soils of often industrial origin, and covers the concept of phytoremediation taken in a narrow sense, knowing that some authors also use it to designate the first case (Tam and Wong, 1989). By drawing a parallel with brownfields, it is possible to find these two types of pollution there, which makes the decontamination phases more delicate. Indeed, the industrial era has generated very significant anthropogenic releases of trace elements, but also of complex molecules in the atmosphere, water, and of course in existing soils. A final concept is important to define when dealing with the field of pollution and contamination in general: the diffuse and the local. These two concepts are applicable to both pollution and contamination. The location of toxic elements on a plot will vary depending on a number of factors (the structure and texture of the soil, the nature of the old industrial activity, etc.) (Charnet, 2009). The most frequent cases in the human environment remain places which have undergone massive inputs of toxic elements. For example, we will find mining and industrial operations, whether they are still in operation or abandoned. Major elements 12 elements (99.4% of the earth's crust) and trace elements 68 elements (0.6% of the earth's crust). Thus, by analyzing the behavior of a pollutant in a soil as a function of its physical, chemical, and biological, it will be possible to know in which compartment(s) it is located, therefore whether it is more or less bioavailable (Charnet, 2009). Recall that there are mainly: phytoextraction, rhizofiltration, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization.

Rhizofiltration, the most relevant of the techniques mentioned above, which comes within the field of water pollution control. However, it should be noted that the plants capable of carrying out phytoextraction do not all store pollutants in these two places (some of them store them in the leaves or/and in their wood) (Peer et al., 2005). In addition, it is an important notion to understand for the general field of phytoremediation, plants of each subtechnique cannot store all trace elements. For example, some have specialized in soils with high lead concentrations, but will not tolerate cadmium. One of the peculiarities of phytoextraction remains that the stored metals are intended to be extracted from the plants used. Plants are producers of organic matter (and if we want to respect the principles of phytoremediation), it is important to ensure that certain parts of these plants (such as leaves) are not disseminated in other places, and to limit their possible contact with a population. Indeed, with regard to brownfields, it is common to come across dwellings near contaminated plots (Pereira and Sonnet, 2007).

Although natural lagooning, beds and filters planted with reeds are all techniques that copy, reproduce, and improve the functioning of a given area. Macrophyte lagoons, for example, reproduce natural wetlands with a slice of open water, while trying to enhance the interests of natural ecosystems. This process is generally used to improve treatment (on biological oxygen demand BOD5 parameters). This method applied for urban water but can also be applied with industrial water. Phytoremediation is carried out using successive, watertight basins filled with gravel, and planted with various aquatic species, called macrophytes (reeds, rushes, irises, phragmites, cattail, and loosestrife). These macrophytes play a role in structuring and aerating the bed, while serving as a support for the bacteria which do most of the work. The gravel of increasing granulometry by evolving toward the depth (80 cm to 1 m), allow the mechanical filtration of wastewater. Plants fix bacteria colonies on the basis of their stems and rhizomes, which improves the performance of purifying organisms. In addition, they absorb by their roots a part (approximately 10%) of the mineral salts-nitrates and phosphates-resulting from the decomposition of the organic matter present in the waste water. Most macrophytes are able to assimilate heavy metals, which are always present in wastewater and harmful to the environment. Several plant species can be used but reeds (of the *Phragmites australis* type), by their resistance to the conditions encountered (long period of submergence of the filter, dry periods, high organic matter content), and the rapid growth of hairy roots and rhizomes, are most often used in temperate climates. Several criteria are involved such as: accessibility, topography, geology, and nature of the treated site (Allouche et al, 2006).

4.2.4.2 Phytoremediation of EDCs from industrial wastewater (case of algae)

The biofuels' industry has specific and complex chemical issues. Chemical components are very often found in their discharges. The interest of microalgae is therefore to find an effective water treatment with added value for industry. The industrial wastewater used had a complex composition. In order to be able to provide the industry with a rapid answer on the feasibility of cultivating microalgae in industrial wastewater, it was chosen to test several aspects of growth (Allouche et al., 2006).

It therefore seems possible to believe that the carbon present in the water waste can be used by algae for their growth. On another note, it is possible to think that certain compounds limit the potential of using pure strains not preacclimatized in this wastewater. The available studies regularly suggest the use of reacclimatized microorganisms, which could indeed have made it possible to increase the proportion of wastewater in the culture medium. Indeed, if already acclimatized microorganisms could have been used, this would possibly have made it possible to operate in 100% wastewater, since they would have been resistant to the high concentrations of contaminants present. It seemed interesting to try to determine which contaminants present in these waters made it impossible to use wastewater concentrations above 50% (Rubín et al., 2006).

4.2.5 Economics of sustainable development

Intensive growth has resulted in increasing predation on the natural resources offered to us by the planet and harmful effects on the environment. Human productive activity has always been accompanied by negative externalities exerting harmful effects on the environment and disastrous consequences on human health due to the high levels of concentrations of pollutants from industrial production. The industrialization policies implemented for several decades all over the world have been an important step in the anthropization of the planet and the biosphere through the use of fossil energy reserves and its environmental consequences. This mode of development can be generalized to all countries when we realize that the growth model of industrial countries has resulted in significant climatic disturbances (global warming, various pollution, depletion of natural resources) and by an unprecedented degradation of the environment. Today, sustainable development has become one of the major challenges of contemporary economies, due to the ecological limits that economic growth faces. The establishment of adequate environmental policies that will be in perfect harmony with recent developments in the economics of sustainable development in which the environmental costs of growth are taken into account and whose supporters advocate the sustainability of economic development that preserves the environment and safeguard the interests of future generations and improve the well-being of individuals, has become the essential route for national and international political decision-makers in the search for economic, ecological, political, and social solutions for the preservation of the environment.

4.2.5.1 Environment and the restoration of the rights to life for future generations

Several questions arise at this level, namely: is economic growth compatible with the preservation of the environment? Can the damage to growth on the natural and human environment be repaired? Can we expect economic growth and scientific and technical progress to solve all our problems? Is the market capable of regulating and correcting human behavior in the direction of sustainable development? What policy can the state pursue in favor of sustainable development? Should it just regulate? Should it encourage economic agents by adopting a tax or subsidy system in favor of "green growth"? Can we set up a "polluting rights" market to limit greenhouse gas emissions? What instruments do the public authorities have to effectively carry out climate and environmental policies? Awareness of the environmental risks of economic growth and therefore of the value of integrating environmental standards into economic production cycles has paved the way for a new model of governance in the management of the environmental constraint that weighs on growth and socioeconomic dynamics of development, by providing an approach to method integrating economic, ecological and social dimensions.[1]

The phytoremediation technique is in perfect harmony with recent developments, in the economics of sustainable development in which the environmental costs of growth are taken into account and whose supporters advocate green growth ("green business"[2]) and sustainability.

Economic development can preserve the environment and the safeguards interests of future generations, in addition to improve the well-being of individuals. This technique can therefore be considered as a contribution in the way of research on the processes of biological remediation of industrial waste, while highlighting the international standards of respect for the environment which aim at the preservation of the environment and the reduction of environmental costs linked to production in the industrial sector.

4.2.5.2 Sustainable development and the negative effects of the economic system on the environment

Economic development is a qualitative process of transformation of economic, social, cultural, demographic, and mental structures that accompanies and promotes the economic growth of a country. We insist here on the structural (industrialization, urbanization, wage employment, institutionalization, etc.) and qualitative (transformation of mentalities, behaviors, etc.) aspects of long-term development. Development translates into the advancement of the well-being of the population. Human well-being is a qualitative and subjective notion that expresses the satisfaction that an individual derives from life.[3]

[1] This trend in the economics of sustainable development shows to what extent the health-environment field must integrate multiple, different and complementary approaches and points of view, in this case the economic, ecological and social dimensions, in the search for a new model. Governance in the management of the environmental constraint weighing on growth and the socio-economic dynamics development.

[2] Green business can be defined as the set of economic activities that make it possible to produce goods and services that help to avoid, reduce or eliminate harmful effects on the environment. Areas such as the management of scarce resources, renewable energies, climate change, risk prevention or even waste management are found in this economy.

[3] It should be noted that economic development is the expression of a strong and sustained expansion of material production (growth in gross domestic product (GDP) or national income) associated with a reduction in monetary poverty, progress in health and education and the universalization of real freedoms. Development is a qualitative phenomenon taking into account the economic and social dimensions, it is measured using the human development index (HDI).

4.2.6 Development and sustainability of usage of phytoremediation as a compulsory treatment of industrial wastewater

4.2.6.1 Concept of sustainable development

Sustainable development brings together two concepts, namely: development, and sustainability. According to the Brundtland Report of 1987, sustainable development, is "development which meets the needs of present generations without compromising the ability of future generations to meet theirs." It is about having a mode of growth that allows the next generation to have at least as much well-being as our own generation, in particular not made destroying the ecosystem, part of which is nonrenewable. In other words, development is sustainable if the capacity of society to produce well-being remains constant.[4]

The Brundtland report thus advocates a new model of governance in the management of the environmental constraint that weighs on growth and the socioeconomic dynamics of development, by providing an approach method integrating the economic, ecological, and social dimensions. The idea is that an economy must both meet the needs of the present generations (equity in the sharing of wealth at the global level and fight against poverty and hunger) and thus allow their well-being but also allow the generations to future generations can meet their needs and achieve a level of well-being at least equal to the present generations (taking the environment into account in economic calculations). Two implications therefore emerge from the "Brundtland" commission: (i) taking into account the concept of need, and more particularly the essential needs of the most deprived, to whom the highest priority should be given. (ii) Resources are limited: "the idea of the limitations that the state of our techniques and our social organization impose on the capacity of the environment to meet current and future needs." According to the theses of the economics of sustainable development, growth, and development have several limits: (i) their impacts on the environment deplete natural resources and mankind's natural heritage, (ii) at the social level, we note a persistence of inequalities and the social divide remains in many countries, (iii) not all countries benefit from growth: persistence of inequalities between developed and developing countries. When there are social and environmental constraints and possible intergenerational conflicts weighing on growth and development, it is necessary to be able to reconcile the economic, social, and ecological dynamics of growth and to put in place the basic elements of a new development model, namely, "development which meets the needs of the present without compromising the ability of future generations to meet theirs" and which advocates solidarity between generations (reduction of greenhouse gas emissions), and between people (fair trade), participation of all in the preservation of the environment, precautionary principle (risk prevention). Growth is said to be sustainable when it is consistent with sustainable development. Sustainable development

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[4] At the initiative of the United Nations Environment Program (UNEP) created in 1972, the World Commission for Environment and Development (WCED) known as the "Brundtland" Commission (named after Gro Harlem Brundtland, Norwegian Prime Minister) published a report, entitled "Our Common Future", published in 1987, calling for sustainable or sustainable development. The emphasis in the Brundtland Report is on two concepts: the concept of needs, and more particularly "the basic needs of the most deprived to which the highest priority should be given": and the concept "of the limitations that the state of our techniques and our social organization impose on the capacity of the environment to respond to current and future needs."

is not only about preserving the environment; it must make compatible the creation of wealth, the satisfaction of basic needs and the preservation of the environment for future generations.

4.2.6.2 Three pillars of sustainable development

Due to the importance of the risk of environmental degradation, in recent years we have witnessed an awareness of the interest of sustainable development or sustainable development which tries to respond to two aspects relating to environmental degradation linked to the increasing rate of the level of economic activity and therefore of economic growth, namely: - sustainable development as a response to the environmental costs of growth (i.e., economic development which seeks to reconcile the economic, social, and environmental dimensions of development); - and sustainable development that meets the needs of the present without compromising the ability of future generations to meet theirs. Given that natural resources are irreplaceable and that a preserved environment should be left to future generations. The three pillars of sustainable development are : (i) The economic pillar: economic development—more equitable place of developing countries in the world economy; (ii) The environmental pillar: taking into account the environmental dimension of growth—Respect for biodiversity and ecosystems, reduction of polluting emissions, nondestruction of natural capital; (iii) The social pillar: fight against inequalities and poverty (social consequences of economic activity, problem of inequalities, working and living conditions) (Fig. 4.4).

The concept of sustainable development therefore combines three dimensions: economic (creating wealth, improving material living conditions), social (meeting health, education, housing, employment, prevention of exclusion, intergenerational equity), and environmental (preserve the diversity of species and natural and energy resources). Economists will have to make their contribution in order to present a solution that makes it possible to reconcile the economic, social, and ecological dynamics of growth. It is about answering the question of knowing how countries should proceed in order to be able to increase the well-being of the world population, fight against social inequalities, and safeguard the dynamics of the biosphere (Vivien, 2008). This debate must be organized around the two concepts introduced by the Brundtland report, namely: the concept of needs and that of limitations. Two theoretical projects have thus emerged: The first focuses on meeting needs, and examines the links that may exist between growth and development. The second focuses on the environmental constraint weighing on the socioeconomic dynamics of growth.

4.2.6.3 Premises of the concept of sustainable development

Since 1972 and the publication, under the aegis of the Club of Rome, of the “Stop Growth” report, known as the “Meadows” report, several events have fostered awareness of the existence of limits to economic growth. The oil shocks of the 1970s revealed the fragility of this natural resource. The same goes for fears about the loss of biodiversity, the extinction of certain animal species or deforestation. Major industrial accidents like that of the Bhopal factory in India in 1984, Chernobyl in 1986, Fukushima in 2011, the numerous oil spills show the damage of intensive production on the environment. The consequences of global warming (melting ice,

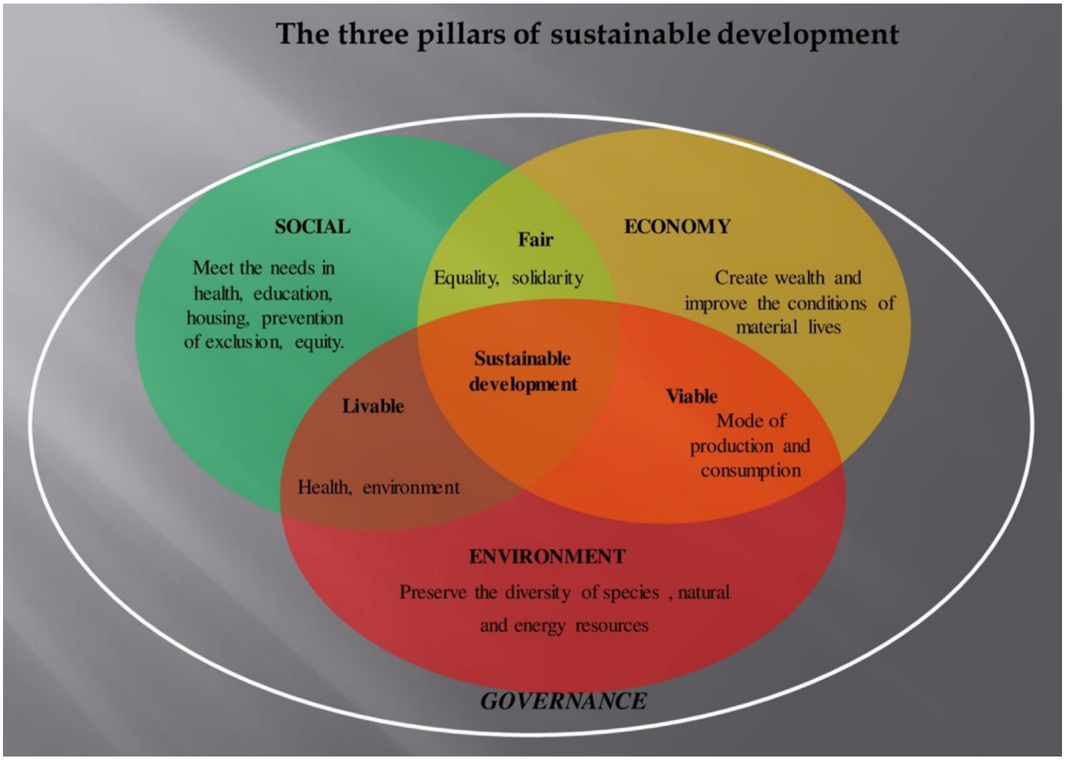


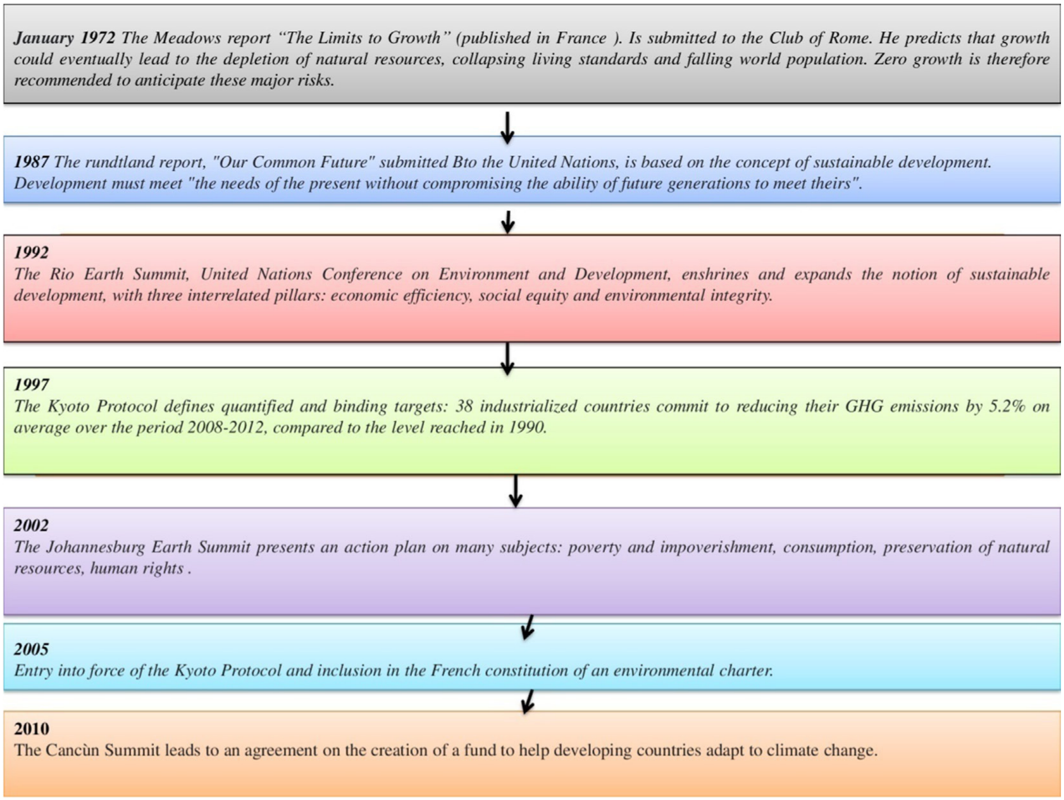
FIG. 4.4 The three pillars of sustainable development.

progression of arid zones, destructive climatic catastrophes, etc.) seem to go in the same direction. The premises of the concept of sustainable development will be popularized and will be the subject of proposals for actions for governments in "Agenda 21," adopted by the 178 countries participating in the first Earth Summit in Rio in 1992. These proposals will be confirmed in 2000 by the United Nations under the name of "Millennium Development Goals."

Sustainable development is now the objective to be followed for international institutions (UNEP, World Bank, etc.), public authorities and economic agents, in particular companies, which intend to reconcile the three P's, people, planet, profit, as part of so-called "social and environmental responsibility" (CSR) approaches (Fig. 4.5).

4.2.6.4 Is economic growth compatible with the preservation of the environment?

The economic analysis of sustainable development, which is based on the preservation of development possibilities for future generations, looks at the level and evolution of the stocks of each type of capital (accumulation and destruction) as well as the decisive question of the degree of substitution between these different capitals as well as how to overcome the ecological limits encountered by economic growth (depletion of energy resources and fish stocks, deforestation, increase in the concentration of greenhouse gases, etc.). To this has been put forward the need



January 1972 *The Meadows report "The Limits to Growth" (published in France). Is submitted to the Club of Rome. He predicts that growth could eventually lead to the depletion of natural resources, collapsing living standards and falling world population. Zero growth is therefore recommended to anticipate these major risks.*

1987 *The rundtland report, "Our Common Future" submitted Bto the United Nations, is based on the concept of sustainable development. Development must meet "the needs of the present without compromising the ability of future generations to meet theirs".*

1992
The Rio Earth Summit, United Nations Conference on Environment and Development, enshrines and expands the notion of sustainable development, with three interrelated pillars: economic efficiency, social equity and environmental integrity.

1997
The Kyoto Protocol defines quantified and binding targets: 38 industrialized countries commit to reducing their GHG emissions by 5.2% on average over the period 2008-2012, compared to the level reached in 1990.

2002
The Johannesburg Earth Summit presents an action plan on many subjects: poverty and impoverishment, consumption, preservation of natural resources, human rights .

2005
Entry into force of the Kyoto Protocol and inclusion in the French constitution of an environmental charter.

2010
The Cancùn Summit leads to an agreement on the creation of a fund to help developing countries adapt to climate change.

FIG. 4.5 Chronological benchmarks of the concept of "sustainable development."

to put in place a climate policy that will make it possible to analyze the instruments available to the public authorities to carry out environmental policies in the face of negative externalities suffered by the environment and market failures.

Beyond economic growth, development results from the interaction of several types of capital

- The economic analysis of sustainable, or sustainable development, emphasizes the preservation of possibilities for future development. By relying on the classic analysis of production in which the product flows result from the mobilization of factors of production (capital and labor), it broadens the notion of productive capital and adopts a patrimonial approach in which various factors are taken into account: Capital stocks.

We can, thus, make a clear distinction between the natural, physical, human, and social and institutional capital. Development therefore results from the accumulation of these four types of capital:

- Natural capital brings together the various resources of nature likely to generate a productive service (wealth of the sea, the soil, the subsoil, etc.). It corresponds to natural resources (such as water, soil, coal, oil, fauna, flora, etc.), ecosystems and biodiversity which provide populations with material well-being or not. It can take the form of a stock of renewable or exhaustible resources, which make it possible to produce well-being by its exploitation for productive purposes. A direct source of well-being, it represents the essential support of our life. Some natural resources are nonrenewable; others are renewable (regenerate on their own) as long as they are not overexploited (e.g., Fishery resources).

- Physical capital is a good produced in the past by man and used as a means of production (building, machine, material, etc.). It is the set of means of production, including fixed capital (capital goods) and circulating capital (intermediate goods). This stock of durable goods available to a community is used to produce goods and services capable of meeting the needs of the population and improving their well-being. The progressive wear of this capital is taken into account through the concept of depreciation.
- Human capital can also be accumulated by humans and includes the physical and intellectual capacities of an individual or a group of individuals; it can be accumulated through training, initial or professional. It brings together all of: individual wealth made up of know-how, interpersonal skills and knowledge (acquired during initial or continuing training, learning, social, and professional experiences) which provide advantages (particularly in terms of well-being) both individually and collectively. According to G. Becker, labor power is capital: it is possible to invest in human capital in order to improve its productivity. It is possible to integrate the level of health into it.
- Social and institutional capital: set of social networks, standards, values, and institutions that increase trust between actors in a given society. This increased confidence brings individual interests and collective interests together, and thus promotes the well-being of populations. Institutions are the set of human frameworks and constraints that structure political, economic, and social interactions. Legislative apparatus, other norms, formal or informal, values, can contribute to the well-being of populations as well as to economic growth. Institutional capital brings together these institutions. Political, institutional, and legal arrangements correspond to institutional capital. These institutions have the following functions: protection (of property, contracts, resources, etc.), surveillance (of competition), regulation (respect for economic balances), coverage (insurance and social protection), and arbitration (of social conflicts). The contribution of these different types of capital to the formation of production growth can be measured conventionally and thus participate in improving the well-being of the population. However, some capital can also contribute in ways that are more difficult to measure. If we take the example of a natural resource such as forest, it can constitute a measurable productive capital (exploitation of trees, firewood, …) but also absorb part of the production of greenhouse gases (unmeasured productive service), be suitable for hiking (service productive most often nonmarket) or even arouse the pure well-being or the wonder of those who cross it.

Sustainable or sustainable development and the debate on the substitutability of capital: sustainability, growth, and environment

The notion of sustainability, economic growth, and its link with environmental constraints has become an inescapable necessity that should be realized in the economy of sustainable development. This approach to the sustainability of development makes it possible to ask crucial questions. Is the current global level of production sustainable? Isn't the environmental constraint on the growth of wealth so restrictive that it calls into question its viability? To these questions, only one answer emanates from neoclassical economists; the solution is growth. Their argument is based on a theorization leading to an environmental Kuznets curve. The underlying idea is fairly well translated by Beckerman (1992). "There is clear evidence that although economic growth normally causes environmental degradation in the early stages, in the end the best—and probably the only—path to regain a decent environment in most countries is to get rich."

Application of the Kuznets curve to the environmental paradigm: (Kuznets curve: from inequalities toward the environment)

The environmental Kuznets curve (inverted U) is a possible representation of this notion of sustainability of economic growth and its link with environmental constraint and as an element referring to the hypothesis of substitutability between capitals. Like social inequalities, polluting emissions would initially increase as average income increases. Second, new "cleaner" technologies would reverse the trend. If we consider the environmental Kuznets curve as a satisfactory representation of the relationship between economic growth and the environment, then not only is growth not contradictory with the preservation of the environment, but, correctly oriented, it is a condition of this preservation.

Social inequalities with regard to growth

The Kuznets curve Economic theory has long questioned the link between production distribution and social inequalities. The relationship discovered by Kuznets in 1955 (Kuznets, 1955) highlights the relationship between social inequalities and per capita GDP.[5]

Although, this approach to social inequalities is still debated, neoclassical theory considers it to be the most relevant approach to apply; given that the latter advocates perpetual growth which guarantees the reign of the market, the only possible regulator of the economy

The Kuznets curve is always taken as a benchmark to insist on the fact that only growth, in a market functioning without hindrance, political or social, should allow regulation of the factor of inequality. The Kuznets curve represents economic inequality in a country as a function of its level of development, which is assumed to be increasing over time (Fig. 4.6).

- In the early stages of development, when investment in infrastructure and natural capital is the primary mechanism for growth, inequalities encourage growth by sharing resources in favor of those who save and invest the most. This economic phenomenon is called the "Kuznets curse."

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[5] The Kuznets curve (from Simon Kuznets's work on economic development in the 1950s) describes an inverted U-shaped relationship between a country's level of development and income inequality.

FIG. 4.6 Kuznets curve: relationship between social inequalities and GDP per capita.

- Conversely, in more advanced economies, the increase in human capital takes the place of the increase in physical capital as the source of growth. Inequalities therefore slow down economic growth by limiting the general level of education, because not all can directly finance their training.

Kuznets offered two reasons to explain this historical phenomenon:

- Workers have moved from agriculture to industry;
- Rural workers have become urban. In both of these explanations, inequalities decrease after 50% of the workforce has been employed in a higher income sector. The Kuznets curve, which advocates according to which inequalities are reduced “mechanically” with the economic growth of a country, has been widely discussed both from an empirical, theoretical and methodological point of view:
- Kuznets uses cross data from different countries but over the same period. This prevents the use of data over time to observe individual progress in the country’s economic development.
- Its data focused mainly on middle-income countries in Latin America where inequalities have been quite high for a long time. If we control this variable, the inverted U shape of the Kuznets curve disappears.
- Kuznets’ work insists on the fact that inequalities can tend toward reduction only through social and political mechanisms, and therefore with an interventionist tendency. On the other hand, this work, not taking into account these exogenous data, shows that the model highlights a purely mechanical phenomenon. There is a certain contradiction here between the model and the argument.
- Finally, the inverted U-shape of its curve does not seem to be due so much to the progress of the economic development of each country as to historical differences between these countries (“growth paths”).
- From a theoretical point of view, some authors question the strict causality assumed by the Kuznets curve between the level of growth and income inequalities (Piketty, 2006).

> One might believe, in view of this relationship, that the increase over time of a country's inequalities is a "natural" phenomenon which resolves itself over time, endogenously. However, Piketty affirms, on French and American data, that the reduction of inequalities is not mechanically associated with the growth of the GDP per capita. Historically, it has mainly been linked to unexpected events affecting capital (war, inflation, catastrophes) and by taxes (in particular on income). The issue is therefore to know whether it is necessary to put in place redistribution mechanisms (through taxes) to reduce income inequalities, rather than expecting them to be reduced.

Kuznets and the environmental approach

In order to resolve the environmental problems linked to growth (in this case the question of the sustainability of economic growth and its link with the environmental constraint), economists argue on a theory leading to an environmental Kuznets curve (EKC) (Fig. 4.7).

Since 1991, Grossman and Krueger[6] have proposed to transpose this idea in the environment field; however, it was not until 1993 that the expression environmental Kuznets curve appeared, by Panayotou (1993)[7] (Grossman and Krueger 1994). The EKC implies that during the early stages of economic development, agents care little about the environment. When the level of income is sufficient to meet basic needs, a threshold level (the turning point) is reached where concern for the environment increases and the trend is reversed. Beyond this threshold, economic growth is accompanied by an improvement in environmental conditions and particularly a reduction in pollution. There is therefore an inverted U-shaped relationship between pollution and economic development.

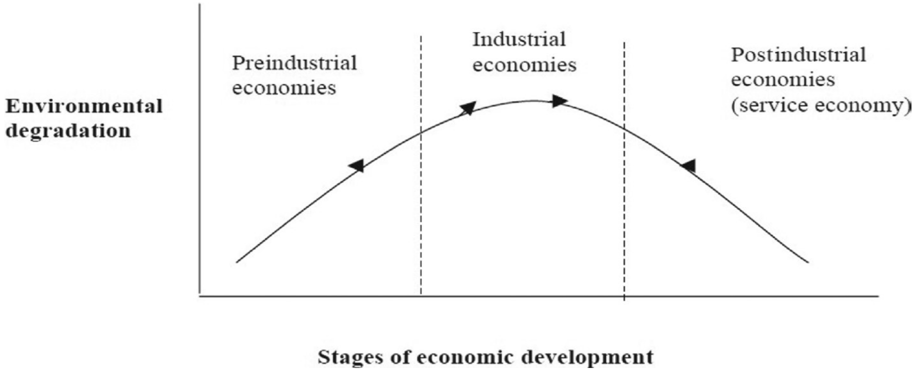

FIG. 4.7 The environmental Kuznets curve: growth is not the problem, but the solution.

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[6] Grossman, G.M. and Krueger, A.B. (1991) « Environmental impacts of a North American Free Trade Agreement » NBER Working paper, 3914. November.

[7] Panayotou T. (1993) « Empirical Tests and Policy Analysis of Environmental Degradation at Different Stages of Economic Development » *Working Paper* WP238, Technology and Employment Program, International Labour Office, Geneva.

The Kuznets environmental curve assumes that pollution increases with growth at low levels of development, and then tends to decrease once a certain threshold is reached. As the growth of production and per capita income increases, pollution decreases during the development phase for rich countries. The basic essential elements explaining this phenomenon are well recognized by economists: during the first phase of development, the growth of production requires more exploitation of resources and generates more waste and polluting products. The idea is that beyond a certain development threshold, a company will move toward cleaner activities; therefore the ratio of emissions to the increase in per capita GDP is falling. In other words, as the GDP increases (growth), the rejection rate tends to stagnate. Once this stage is over, a company has the capacity to invest part of its wealth in the research and development of means of production that are more respectful of the environment; which tends to lower emissions while increasing GDP. These effects would be expressed by principles of social evolution and political demands.

According to Grossman and Krueger (1994), many health indicators such as water or air pollution show an inverted U-curve at the start of economic development: we care little about the environment and the increase in pollution that goes hand in hand with industrialization. When primary needs are met, a threshold is reached where concern for the environment increases and the trend is reversed. Society then has the means and the will to reduce the level of pollution and the use of resources to create a unit of GDP (of wealth) which tends to decrease. Nonetheless, it has been established that the Kuznets environmental curve can be applied to certain pollutants of localized range and can in no way be generalized to the whole ecosystem. According to a study by André Meunié of Bordeaux IV University in 2004[8] "not only is this curve detected for a few pollutants with localized effects, but even in this case, numerous methodological criticisms weaken its scope." This relationship is found to be true for some localized pollutants (such as sulfur dioxide or nitrogen dioxide), but there is less evidence for other pollutants with more global effects on the environment.[9]

Further, studies on the scope of the Kuznets environmental curve indicate that the type of environmental quality indicator significantly affects the presence of an "inverted U" relationship and the predicted value of the "point of income inflection." The results indicate the presence of an EKC (environmental Kuznets curve) type relationship for landscape degradation, water pollution, agricultural waste, municipal waste and several air pollution measures. Whereas, in the case of CO_2 emissions, the Kuznets environmental curve literature provides no basis for predicting that continued economic growth will necessarily lead to a significant reduction in CO_2 emissions. Although some empirical studies indicate that economic growth may be associated with improvement in some environmental indicators, this does not imply that economic growth is sufficient to improve the state of the environment in general. These findings show that the empirical scope of the Kuznets environmental curve may be limited to

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[8] Meunié, A. (2004) « Controverses autour de la courbe environnementale de Kuznets », document de travail du Centre d'Economie du Développement (CED), Université de Bordeaux IV.

[9] We are therefore afraid to think of the possibility of considering a multiplicity of Kuznets environmental curves according to the types of pollutants and according to the location (soil, water, and air).

certain pollutants of localized scope and in no way can be generalized to the entire ecosystem. In general, Kuznets environmental curves can be highlighted in some data concerning some local environmental issues (such as air pollution) but this is not the case in other cases (such as soil renewal or the biodiversity). We must also add that the effects of climate change such as the disappearance of species and the loss of biodiversity are irreversible.

4.2.6.5 Sustainable development: strong sustainability and/or low sustainability

Sustainable or sustainable development integrates three dimensions: the economic dimension (growth in wealth must be possible), the social dimension (this wealth must be equitably shared in the world and between generations), the environmental dimension (resources and the planet must be preserved). Economic analysis is based on the possibilities for development and improved well-being for future generations; in accordance with the heritage approach adopted, it bases the sustainability criteria on the evolution of stocks of the four types of capital, mentioned above. A debate remains on the substitutability of these four types of capital and therefore on the means to ensure the sustainability of our development. Two conceptions of sustainability linked to sustainable development should therefore be distinguished: low sustainability in which capital is substitutable and strong sustainability in which capital is not substitutable. Those in favor of “weak sustainability” believe that nature is productive capital like any other. Therefore, it can be considered substitutable. If it becomes scarce, its price will become higher and economic agents will strive to find productive technologies that will make more use of other factors of production that have become relatively cheaper. Technical progress can then push back the limits of economic growth. The freedom of agents, which pushes them to seek the optimal technology to produce, may therefore be sufficient to ensure the sustainability of production growth and our development. Humans have been able to save and even reintroduce animal species, rebuild endangered natural environments. A polluted river can be cleaned up, a destroyed forest replanted, biodiversity restored. It suffices to maintain a capacity to produce economic well-being at least equal to that of the present generations. To ensure this, the level of total capital (natural and built) must be kept constant. As the economist Robert Solow specifies, for its development to be sustainable, a company must maintain its productive capacity indefinitely, that is to say, in a more technical way, that its total capital per capita would not decrease over time intergenerational. Those in favor of “strong sustainability” do not share this optimism. They consider that damage to natural capital is, to some extent at least, irreversible: the damage caused to the environment remains partly irreparable and certain exhaustible resources are irreplaceable. In this hypothesis, it cannot be enough to keep the global capital constant. Natural capital must be the subject of specific conservation. The factors of production are not all substitutable. Technological innovations alone cannot push the limits of economic growth. Indeed, following a very intense production cycle, the evolution of “natural capital” can be compromised by the rise in environmental costs, which have become quite significant. These high environmental costs are linked to:

- Excessive drain on nonreproducible natural resources,
- Excessive drain on natural resources or their degradation, which leads to an erosion of biodiversity,

- Fairly significant damage linked to pollution (negative externality), while the expenditure for nature protection is very negligible (the expenditure for the treatment of polluted water, for example, is quite low or even nonexistent),
- The massive use of fossil energy (oil and coal) which contributes to the increase in greenhouse gases and therefore to global warming,
- Atmospheric pollution linked to industrial economic activity and lifestyle, which exerts a negative externality, and increases greenhouse gases, responsible for warming and climate change. In the pessimistic version of the concept of sustainability (strong sustainability), damage to natural capital is, at least to a certain extent, irreversible. Some damage is irreparable, some resources are not renewable, and others are over exploited. Natural capital must therefore be the subject of specific conservation and other capitals cannot be substituted for it, capitals are complementary, that is to say the use of one type of capital necessarily implies that of other capitals. In the optimistic version of the concept of sustainability (low sustainability), nature is a productive capital like the others, natural capital is therefore substitutable, in particular by human capital and physical capital. If it becomes scarce its price will increase, agents economic players will be encouraged to find technologies that save this factor or use other factors (e.g., oil) (Table 4.1).

Table 4.1 The sustainability criteria of sustainable development (adopted from Viven, 2008).

	Low sustainability	Strong sustainability
Design of natural capital	Natural capital can be substituted for other forms of capital.	Natural capital must be maintained as it is.
Substitutability between natural capital and built capital (physical, human, institutional capital)	Capital is substitutable. It is the sum of natural and built capital that must be kept constant from generation to generation.	Capital is not substitutable, it is complementary.
Role of technical progress in preserving the environment	Technical progress makes it possible to preserve the environment (pollution control techniques, energy savings, less polluting techniques, etc.).	Technical progress does not make it possible to preserve the environment since capital is not substitutable.
Examples confirming each thesis	Environmental Kuznets curve, discovery of new oil deposits, pollution control, reintroduction of animal species, etc.	Kuznets curve questioned, deforestation (Amazonia), overexploitation of fishery resources, increased waste.
Policy to be implemented	Investments in education, Research and Development (R-D) which allow technical progress preserving natural capital.	Determination of quantitative thresholds for harvesting from nature (fishing quotas) and discharge into the environment (warming). Prohibition of certain discharges (CFCs) or of certain withdrawals (prohibition of trade in wild animals, trade in ivory.

The essential idea that emerges from this table summarizing the sustainability criteria of sustainable development (Vivien, 2005), is that we must pass on to future generations the same stock of global capital composed of four types of substitutable capital (natural, human, physical, and institutional). It is above all a question of passing on or preserving the same stock of natural capital to future generations. As a result, natural capital can be substituted for other forms of capital (human, social, technical which incorporates new technology). In this case, it is up to the state (institutional capital) to promote substitution between different types of capital, for example, by supporting technological changes that save nature, and by educating individuals on the benefits of sustainable development.

4.3 What environmental policies to be implemented by the governments?

Environmental degradation and climate change resulting from industrialization (release of pollutants into nature) can be analyzed as pollution which, in economic analysis, corresponds to a negative externality. In such situations, individual economic agents only take into account in their decisions the private costs and benefits of their actions, thus neglecting the costs incurred by humans. Since there is an externality, there is necessarily a market failure in a laissez-faire situation: in the presence of a negative externality, the private cost is lower than the social cost, so that the action at the origin of the externality tends to be excessively chosen over the look at what is socially desirable. In the event of obvious market failures, it will be imperative to intervene by the public authority, which must conduct a climate policy with a view to reducing the effects of pollutants on the environment. It is also desirable that global agreements force countries to conduct the measures. Necessary efforts and to reconcile their environmental policies to limit the damage caused to the environment, which is not without posing serious difficulties. Several instruments for carrying out climate policies by the public authorities with a view to reducing greenhouse gas emissions since these are responsible for global warming/disruption, given that air pollution linked to economic activity and to life exerts negative externalities. There are two types of economic instruments for managing the climate issue: some are based on coercion, others on incentive. Negative externalities can in fact be combated by regulation, that is to say coercion, and/or by the implementation of instruments aimed at internalizing them: it is then a question of ensuring that the private costs borne by the producers of externalities include social costs, that is to say the damage suffered by other agents. Two instruments can be mobilized for this internalization of social costs: environmental taxes, which correct the prices of existing markets and "emission rights" markets (polluting rights market), which allow a decentralized development of a price of emissions. These two instruments are derived from the respective works of Pigou (1920) and Coase (1960).

The taxation of economic activities and the market for rights to pollute are economic tools where we will encourage economic agents to modify their behavior (consumption or production). It should be noted, however, that each instrument has advantages for some and disadvantages for others (producer, worker, consumer, State). Many standards areas can be applied to engines and limit emissions of pollutant emissions from vehicles, etc. However, although this regulation has advantages insofar as the prohibition of a particular manufacturing process or a product in a territory is not costly, since workers and consumers are protected from the effects of harmful products for the environment and also for their health, the fact remains that these regulations can lead to an increase in manufacturing costs, which are becoming important for economic agents. For example, the business will have to use a replacement product, and so will the consumer because of this rise in costs. Likewise, it is necessary to ensure that the rule is respected (surveillance and controls to be carried out by the public authorities). In addition, the ban often only applies to domestic productions and not to foreign productions. The risk is that production will take place in another territory where the standards are not as restrictive. The effect is then only just out of place.

4.3.1 Taxation of economic activities

The Ecotax implies that those who are at the origin of the pollution will have to pay a tax in order to compensate for the damage caused by their economic activity to the environment. For example, the polluter pays principle is applied (that is to say that we will seek to penalize polluters and reward virtuous economic agents. Examples: Ecological bonus-malus on cars, carbon tax, etc. These taxes constitute an additional cost for the polluter which is added to the private market cost, which modifies its calculation of optimal production. In the short term, the producer is thus encouraged to produce less, and therefore to reduce polluting emissions. In the medium and long term, he could also be encouraged to use less polluting production technologies to minimize his payment of the tax. The incentive to reduce the volume of production or to invest in eliminating or reducing harmful emissions will be greater the higher the level of the tax. Logically, the level of this tax should also reflect the extent of the damage. The ecotax nevertheless has some advantages and disadvantages which should be specified:

- Its use constitutes additional tax revenue for the public authorities. These revenues make it possible to finance the clean-up policies undertaken in certain countries and to repair, at least partially, the damage caused. They can also use a portion of these revenues to reduce the tax burden on other factors, including labor, in which case employment will be boosted.
- Each company is free to make its own trade-off (economic calculation) between the cost of the tax and the cost of investing in pollution control or finding substitutes, which is a more flexible solution than regulation. For the disadvantages, we denote:
- That the ecotax increases the selling price for consumers and production costs for businesses. Its acceptability is more problematic.
- That there are difficulties in establishing a tax at the international level insofar as this raises a risk of circumvention of the tax by relocation or those foreign productions can escape the tax.
- That we cannot know in advance the volume of reductions in polluting emissions (this will depend on the sensitivity of economic agents to the price signal that is the tax). Determining the optimal level of the tax becomes delicate and problematic.
- That the tax can prove to be unfair, and its negative economic effects are accentuated on the most disadvantaged social strata if the latter do not have any alternatives (ex: increase in the price of gasoline for workers who are dependent of the car).

4.3.2 The emission allowances market or the polluting rights market

The polluting rights exchange market is the fact that the State creates a market where polluting rights will be exchanged. Each company is allocated a quota (maximum level) of pollution. If the company exceeds this level, then it must purchase other rights. It must do so with companies that does not use all the rights to pollute. It is therefore a market where rights to pollute are exchanged. The price of the right to pollute depends on the quantity offered and demanded on the market. The total volume of authorized issues is set by the public authorities, which distribute these "emission allowances" to issuing agents, under terms—free or auction—which have no impact on incentives. These allowances are then exchangeable on the market thus created, which determines a price by simply comparing the supply, the volume of which is set by the public authorities, and the demand from issuers. The polluting emission therefore entails an additional private cost for the producer. The advantages associated with this instrument of the polluting rights market can be enumerated as follows:

- Flexibility for businesses (invests or not, buys or sells, etc.).
- Rewards the most virtuous companies and penalizes the most emitting companies.
- Unlike the eco-tax, the state controls the level of pollution and can decide to reduce the level of pollution by allocating fewer quotas. Respecting international commitments becomes easier. For the disadvantages, it is noted that this instrument represents:
- A very heavy and expensive control system. In addition, the efficiency of the market depends on the efficiency of the supervisory authority (compliance with quotas) and trade regulation.
- A system which cannot be generalized to all economic agents. It can only concern industrial sites whose size makes it possible to minimize transaction costs. It is difficult to extend it to small businesses.
- A risk of speculation on the market that could destabilize companies in an economic sector dependent on this market. It should be noted, however, that these instruments must be combined carefully in order to derive maximum benefit from them and increase their use in efficiency for the preservation of the environment and human health.

4.4 Conclusions and perspectives

Intensive growth has resulted in an increasingly important predation on the natural resources that the planet offers us. Productive activity has always been accompanied by negative externalities exerting harmful effects on the environment and dangerous consequences on human health due to the high levels of concentrations of pollutants from industrial production. The industrialization policies implemented for several decades all over the world have been an important step in the authorization of the planet and the biosphere through the use of fossil energy reserves and its disastrous environmental consequences. This mode of development can be generalized to all countries when we realize that the growth model of industrial countries has resulted in significant climatic disturbances (global warming, various pollution, depletion of natural resources) and by an unprecedented degradation of the environment. The economics of sustainable development is nowadays one of the major challenges of contemporary economies, due to the ecological limits encountered by economic growth. The establishment of adequate environmental policies (climate policies, regulations, taxes, etc.) in which the environmental costs of growth and the negative externalities resulting from industrialization and consequently the sustainability of economic development which will be taken into account. Preserves the environment and safeguards the interests of future generations and improves the well-being of individuals, has become an essential necessity for national and international political decision-makers in the search for economic, ecological, political and social solutions for the preservation of the environment and the restoration of the rights to life for future generations.

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5

Elimination of alkylphenols from wastewater using various treatment technologies

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5.1 Introduction

The growing population along with rapid advancements in industrial and domestic activities has enhanced the possibilities of introducing phenolic compounds into water bodies. Among these, alkylphenols (APs) are the one that are frequently utilized in industrial and agricultural sectors that cause their accumulation in almost all water bodies and ground water table by effluent discharge from industries and wastewater treatment plant. APs are used to synthesize polyethoxylated derivatives, mainly octylphenol polyethoxylates and nonylphenol polyethoxylates, which are essential in many applications. For example, industrial grade nonylphenol (NPs) is produced on a large scale from phenol and is used for the production of alkylphenol polyethoxylates. These nonionic surfactants are commonly utilized in household detergents, dispersants, industrial and public place cleaners (Priac et al., 2017). Direct entry of these molecules into the environment is through the industrial wastewater while municipal wastewater treatment plants also play an indirect role in the transfer. Because of this APs have become one of the emerging pollutants in wastewater and industrial effluents that can have toxic and adverse effects on living organisms. Even exposure of very less dosage can led to permanent character changes and alterations in tissue development in human beings (Colborn et al., 1993). Additionally, these emerging compounds have endocrine disrupting properties due to their similarity with the natural hormones. Kim et al. (2004) reported that all isomers do not have equal effects, the para position of OH-phenol group and the branched aliphatic side chain appears to have the determinant effect. Branched NPs showed greater endocrine activity as compared to the linear NPs (Bärlocher et al., 2011). Additionally, not only parent molecule but also, its degradation products can create potential ecotoxicity in aquatic environment because of their prevalence in surface water and sediments (Soares et al., 2008; Rizzo, 2011).

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Alkylphenols ethoxylates (APEOs) mainly include two groups—octylphenol ethoxylates (OPEOs) and nonylphenol ethoxylates (NPEOs) that are widely produced to meet the industrial demand of cosmetics, plastics, lubricants, surfactant, and detergents (Ying et al., 2002). NPEOs cover up to 80% of alkylphenol ethoxylates (APEOs) whereas remaining 20% is occupied by OPEOs. Continuous demand, degradation, and discharge of NPEOs are responsible for the ubiquitous occurrence of nonylphenols in the atmosphere and their degraded metabolites seem to be more persistent in environment (White et al., 1994). From the toxic point of view, NPs are highly toxic to aquatic organisms and also harmful for human health as they belong to endocrine disrupting pollutants (EDPs) that affect the endocrine system of living organisms and cause hormonal imbalance in body. It has been reported that they have badly affected the reproductive and endocrine system of humans (Priac et al., 2017). Numerous studies and articles reported the occurrence of APs produced from the APEOs degradation and entry into the sewage sludge, sediments, water, landfill, incineration, atmosphere through discharge of effluent from household septic systems, sewage treatment plants and wastewater treatment plants (Corvini et al., 2006; David et al., 2009; Soares et al., 2008). Various treatment technologies have been reported to completely remove APs from water prior to use but very few have shown efficient treatability. Present chapter prominently focuses on adsorption-based treatment, membrane-based treatment, biotechnology-based methods and advance oxidation processes for the elimination of APs. These methods have been reported in a series of research findings considering appropriate elimination of even trace concentrations of APs. Additionally, the chapter also summarizes brief insights of APs derivatives and physicochemical properties.

5.2 Alkylphenols

APs belongs to the class of aromatic compounds, obtained through the depolymerization of plant-based material lignin. Generally, it is present in solid form at 258°C. The properties of APs depend on several factors viz. configuration, purity, position on the ring, and the length of alkyl chain (Ahmad et al., 2021). APs are nonionic surfactants and produced in large amounts to meet the high demand of industrial applications and also used in household cleaners, institutional, and personal care products. Nowadays, developed countries have been facing major problems during sewage treatment due to incomplete elimination of APs and found persistence of its biodegraded intermediates in secondary effluents and various rivers receiving such effluent discharge.

Alkylphenol ethoxylates ($AP\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)n\text{-}CH_2\text{-}CH_2\text{-}OH$) have been produced by the reaction of ethylene oxide with branched chain of APs. From the structural chemistry point of view, APs and APEOs are synthetic compounds having numerous complex mixtures of oligomers, homologous and structural isomers. The ethoxylates chain consists of 1–50 ethoxy units and their application varies according to the length of ethoxy units. For example, ethoxylate chain having 9 or 10 units have been used in cleaning purpose while ethoxy units ranges from 1 to 100 manufactured for commercial products.

The two main structural isomers nonylphenol (NP) and octylphenol (OP) are the important commercial isomers used in large quantities in various industries and other sectors. The nonylphenol is a phenol ring having nine ethoxy units either in linear or branched form at different location such as ortho, meta, and para of the ring (Reed, 1978). Ethoxylates (NP and OP) having merely branched alkyl substituted chains are commercially relevant and found in the manufactured products. Synthesis of linear AP isomers occurred but they are commercially not usable. Therefore, only branched isomers are referred as NPE and OPE (Melcer et al., 2006).

5.2.1 Alkylphenols: derivatives and physico-chemical properties

A range of AP derivatives have been derived commercially worldwide.

4-tert-Amylphenol—Also known as 4-(1,1-dimethylpropyl) or p-tert-amylphenol (PTAP); is produced commercially by alkylating phenol with isoamylene by acidic catalysis.

4-tert-Butylphenol- or 4-(1,1-dimethylethyl) or p-tert-butylphenol (PTBP) phenol is produced by alkylating phenol and isobutylene under acid catalysis.

2-sec-Butylphenol—Also called as 2-(1-methylpropyl) or o-sec-butylphenol (OSBP) phenol is generated from alkylation of phenol and butene using acid or aluminum catalysts.

4-Cumylphenol- or 4-(1-methyl-1-phenylethyl) or p-cumylphenol (PCP) phenol is obtained by alkylating phenol and α-methyl-styrene under acid catalysis.

4-Dodecylphenol (p-dodecylphenol, PDDP))—is a product of phenol and dodecene under acid environment.

2-Methylphenol (o-cresol)—synthetically obtained by gas-phase phenol alkylation into methanol using altered alumina as catalyst. Alternatively, it can also be recuperated from natural petroleum streams.

3-Methylphenol (m-cresol)—is a synthetic product of toluene. Chlorotoluene which is a product of toluene chlorination is undergo hydrolysis in a methylphenol blend and subjected to distillation for generation of a both 3 and 4-methylphenol.

4-Methylphenol (p-cresol)—is produced by caustic melting of p-toluenesulfonic acid.

4-Nonylphenol (p-nonylphenol, PNP)—is generated by performing alkylation of phenol and nonene.

4-tert-Octylphenol—Also known as 4-(1,1,3,3-tetramethylbutyl) or p-tert-octylphenol (PTOP) phenol is produced by alkylating phenol and di-isobutylene under acid catalysis.

Dialkylated phenols- or 2,4-bis(1,1-dimethylpropyl) or 2,4-di-tert-amylphenol (2,4-DTAP) phenol is obtained by alkylating phenol and isoamylene (2:1 ratio) under acid catalysis.

Lorenc et al. (2003) stated that the physical properties of APs are dependent on the position of alkyl substituent on the ring. They are in solid state at 25°C, and appears to be colorless, pale yellow, or white. Configuration, size, and the purity of the alkyl group affect the form of APs. p-Alkylphenol has greater boiling and melting point as compared to the ortho-isomers. For tetrabutyl, melting point of p-alkylphenol goes higher then it decreases. APs tend to supercool, especially when di- and trisubstituted. APs undergo various chemical transformations, which involve hydroxyl or aromatic nuclei, turning them into value-added products (Lorenc et al., 2003).

The hydroxyl group—Electron pairs that are not shared on hydroxyl oxygen look for electron-deficient centers. Reactivity of the hydroxyl group can be improved despite the attraction of circulating current by employing a basic catalyst to remove the acidic protons from hydroxyl group.

The reaction involve the ring—Aromatic nucleus of APs is involved in various aromatic electrophilic substitutions. Hydroxyl group not only activates the aromatic nucleus but also directs the incoming electrophilic reagent (Lorenc et al., 2003).

5.2.2 Alkylphenols: applications

APs are having diverse applications in industrial and agricultural sectors and also used for household purpose. They can be utilized as surfactant, detergents, dispersants, wetting agents solubilizers and emulsifiers. For more than 50 years, APEOs have been used as important surfactants (Priac et al., 2017). First, it is introduced in the United Kingdom for industrial and household purpose in 1944. Then the use in the form of domestic detergent was phased out in 1976 in the United Kingdom (DOE, 1992).

For the commercial purpose, the nonylphenol (NP) is the most demanding AP and primarily used as a raw material for the production of nonylphenol ethoxylates (NPEOs). NPEOs has various applications in several industries viz. textile, leather, petroleum, paper, etc. OP and OPEOs are also significant compounds at commercial levels and involved as a chemical intermediate in the formation of phenolic resins (Priac et al., 2017). Due to the global relocation activities, number of leather industries has been increased in developing countries viz. India, Pakistan, Bangladesh, etc. There are various chemicals required for the tanning process, in which raw animal skin transformed into usable and durable leather material, which is further processed for consumer products (Saxena et al., 2020). Along with all required chemicals, NPEOs contribute large fraction (almost 90%) of all APEOs used in leather industry for tanning process (USEPA, 2010).

5.2.3 Toxicity

In recent years, APs have been evolved as an emerging pollutant and attracted scientific interests. APs become a great concern for our health and environment due to persistence nature and toxicity. The nature of toxicity depends on the length of hydrophobic chains of APEOs. Human beings are directly affected by intake of contaminated food and drinking water as well as through consumer goods. As a result of high usage, disposal and disintegration of NPEOs, NPs present ubiquitously in the environment. By the biodegradation of APEOs, the major product formed in the environment is 4-octylphenol and 4-nonylphenol (Stenholm et al., 2020). The metabolites produced following the degradation of NPEOs and OPEOs viz. NPs and Ops are generally more stable, persistent and toxic as compared to the parent compounds. For instance, the values of LC_{50} of APEOs is more than 1.5 mg/L whereas NPs having LC_{50} values around 0.1 mg/L. In addition, these metabolites start accumulating in aquatic and other organisms with a bioconcentration factor in a range of ten to several fold (Scrimshaw and Lester, 2002). They act as endocrine disrupting compounds (EDCs) that affect endocrine activity by mimicking the natural hormone and alter their function. EDCs constitute a major group of AP and its derivatives, having adverse health effects on animals and humans by obstructing the hormonal system (Priac et al., 2017). All isomers of APs are not equally effective, branched NPs having higher endocrine activity and appear to be more determinant than linear NPs molecule (Kim et al., 2004).

In 1996, European Commission defined EDCs as an exogenous substance that can have toxic effects on living organisms and their progenies by inhibiting the normal action of endocrine system (Can et al., 2014). Endocrine system is considered to be very crucial for the proper functioning of other systems which is responsible for maintenance, growth, reproduction and homeostasis (Birkett and Lester, 2002). EDCs also led to the reduced sperm count in men, children obesity, breast and testicular cancer, reproductive abnormalities, enlargement of prostate in male mice and appearance of feminization features in fishes and alligators (Auriol et al., 2006; Janesick and Blumberg, 2011; Miyagawa et al., 2011). Indeed, these compounds also exhibit estrogenic effects by disturbing the binding of estradiol hormone to their receptor and evidence of the same have been reported in rats and fishes with a concentration ranging from 1 to 10 ug/L (Sumpter et al., 1996).

Humans are often exposed by using packaged food and drinking supplement as those packaging containers and wrappers having constituents of NPs and OPs. There are various routes of exposure to humans, that is, detergents, personal care products and presence of spermicides in contraceptives. Their presence has also been detected in urine, blood, and human milk (Talmage, 1994). Our environment is adversely affected by inappropriate disposal of solid waste having APs and its derivatives and also the discharge of wastewater into river and oceans. They disrupt the aquatic organisms and reach to other organism through food chain. These NPEO compounds having two short chain (NPE_1O and NPE_2O) and NP metabolites are the major environmental concern.

5.2.4 Alkylphenols: sources

The main entry source for APs into various environmental compartments is by direct urban and industrial input (Fig. 5.1). Spent solutions and left residue containing APEs are generally

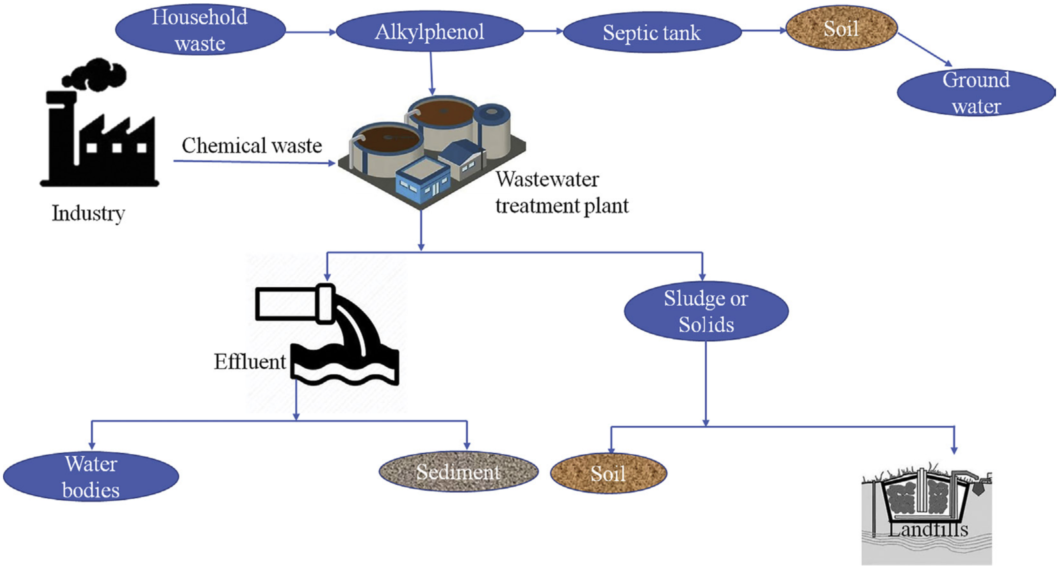

FIG. 5.1 Alkylphenols in environment: sources and accumulation.

discharged into various sewage treatment plants (STPs) viz. industrial or municipal sewage treatment plants or household septic systems. These compounds introduced into the environment in the form of EDCs produced by anthropogenic sources. Due to the frequent use and primary biodegradation of APEs in waste-water treatment plants, they produce another more persistent shorter chain APEs and their metabolites, that is, OP, NP, and AP mono- to triethoxylates (NPE1, NPE2, and NPE3) (Giger et al., 1984). Substantial quantities of NPEOs reach to treatment plants where they are degraded by microbes into several by-products including NP. After going through the wastewater treatment plant, the effluents become the major source of NPs that generally discharged into several water bodies like rivers, estuaries, lakes, coastal lagoons, oceans, surface water, other portable and drinking water. Numerous studies showed that the occurrence of NPs in aquatic ecosystem due to incomplete removal from treatment plants (Johnson et al., 2005).

The distribution of APs and their degradation product NP, OP, etc. varied widely and their concentration ranges from below than the limit of detection (LOD) to 343 ug/L in various water streams (Ying et al., 2002). Sometimes NP concentration ranges up to >600 ug/L in rivers and lakes. For instance, in the proximity of urban discharges and STPs, Spanish rivers have been detected by NP concentration up to 644 ug/L. (Solé et al., 2000).

5.3 Techniques for the elimination of alkylphenols from wastewater

Removal of APs from wastewater has become global problem due to the lack of appropriate methods for elimination of contaminants present on the industrial or urban scale. Effluents are one of the prime sources of APs and APEOs due to partial degradation or absence of complete removal. Low concentration of APs in wastewater makes it further complicated to trace and treat. Each WWTP has different design and efficacy which resulted into discharged effluents with varied concentrations of APs (Ying et al., 2002). More concentration of these substances has been found in industrial wastewater and therefore slightly increased occurrence of contaminants in comparison to WWTP as well as drinking water including rivers, lakes and other water reservoirs. However, the important techniques proposed for wastewater treatment are adsorption, membrane, biotechnology and advanced oxidation-based processes (Tables 5.1 and 5.2). A combination of these methods could also be applied to get usable quality of water and/or clear water that can further be utilized for other purposes.

5.3.1 Adsorption-based treatment

Adsorption is considered as one of the effective technologies for removing phenols from water, owing to its relatively simple design and ease of operation. It does not produce toxic waste as well. The used adsorbent can be reused as a fuel source for energy production (Aksu and Yener, 2001). It involves amassing of pollutants on the adsorbent surface. An ideal adsorbent should be a porous material with considerable surface area that impart the ability to selectively

Table 5.1 Technologies used in different treatment approaches for APS and their efficiency.

Name of methods	Technology	Alkylphenols studied	Effectiveness	References
Adsorption-based treatment	Cyclodextrin-based gel	APEOs	85%	Yamada et al. (2009)
	Alginate-immobilized *C. vulgaris* beads	NPs	>95%	
	Chitosan beads	4-NP and 4-n-OP	97–100%	
Membrane-based treatment	Membrane filtration	NPEOs	91–97%	Li et al. (2000)
	MBR coupled with GAC and ultrafiltration	NPs	80%	Wintgens et al. (2003)
Biotechnological-based method	Packed bed bioreactor	NPs	99.5%	Soares et al. (2003)
	Fixed cell bioreactor	NPEOs	77–99%	Bertin et al. (2007)
	Biofiltration	APs	49–95%	and Di Gioia et al. (2008)
	Packed bed bioreactor on silica gel	NPs	80–97%	Gilbert et al. (2012)
				Di Gioia et al. (2008)
Advanced oxidation processes	Ozonation	NPs and Ops	96%	Zhang et al. (2008)
	ozonation coupled with GAC	OPEs and APEOs	–	Derco et al. (2017)
	Electron irradiation followed by ozonation	NPEOs	–	Petrovic et al. (2004)
	UV-enhanced ozonation	NPEs	–	Tehrani-Bagha et al. (2012)
	TiO_2 photocatalysis	NPs	92%	Ike et al. (2002)
	UV–TiO_2 photocatalysis	NPs	75–80%	
	Fenton reaction, photo-Fenton reaction, photocatalysis with TiO_2, and ozonation	NPs	100%	

Table 5.2 Characteristics of different technologies used for elimination of Aps.

Treatment methods	Characteristics	References
Adsorption-based methods	Adsorption of AP and 4-NP on granular activated carbon Efficiently reduced chemical oxygen demand (COD) and total organic carbon (TOC) Followed by biological step that enhance removal efficiency by 80% of NP Obtained excellent quality of treated effluent/solution Effective treatment for mainly water and waste water applications	Choi et al. (2005) Gao et al. (2011a)
Membrane-oriented processes	Nanofiltration and reverse osmosis No chemicals required Operate at high concentration of biomass to gain better quality of permeate Membrane-assisted biological treatment improve NP removal efficiency, NPEOs 4-t-OP and 4-OP	Jung et al. (2007) Wintgens et al. (2003) Cases et al. (2011) Li et al. (2000)
Biotechnology-based method	Use of microbial culture for natural degradation of 4-t-OP Degradation of 4-NP and NPEOs up to 80–97% Ecofriendly and economical approach as compared to other method Efficient treatment for mainly water applications	Chang et al. (2020) Bertin et al. (2007)
Advanced oxidation process	Through oxidation by using UV/TiO_2-photoctalysis for NP and 4-OP Complete mineralization of AP to CO_2 and H_2O Graphene enhance the photocatalysis efficiency Efficient emerging process at laboratory level No or few need of chemicals and less production of sludge Mainly for wastewater treatment applications Through ozonation—degradation of NP, 4-NP, NPEO Efficient process, disinfection but require high energy for generation of ozone on site Biodegradability of effluent increases Best for water and waste water treatment applications	Basheer (2013), Gültekin and Ince (2007) Petrovic et al. (2004)

accumulate water contaminants. Bhatnagar and Minocha (2006) illustrated that the efficiency of the adsorption process relies on various factors.

- Adsorbent—functional groups, surface area, pore distribution, and ash content.
- Solution—pH, temperature, polarity, adsorbate concentration, and presence of competing solutes.
- Adsorbate—water solubility, size, molecular weight, polarity, and hydrophobicity.

The removal of APs through adsorption-based treatment has been performed employing various synthetic as well as natural adsorbents including algae (Gao et al., 2011a; Peng et al., 2012), alginate (Gao et al., 2011b), biosorbents viz. chitosan (Yamada et al., 2009), biomass such as bagasse ash (Mukherjee et al., 2007; Lang et al., 2009; Gao et al., 2011a), carbon (Choi et al., 2005; Xing et al., 2009; Liu et al., 2009; Yu et al., 2009a, 2009b), clays (Barhoumi et al., 2003; Espantaleon et al., 2003), cyclodextrins (Aoki et al., 2003; Bonenfant et al., 2010; Sancey and Crini, 2012), hypercrosslinked resins (Yang and Ren, 2010; Fan et al., 2012), silica gels (Nikolenko et al., 2002), magnetic particles (Kurinobu et al., 2007; Niu et al., 2012).

Removal efficiency of several types of activated carbon produced from different base materials viz. coconut, coal and wood has been compared by Choi et al. (2005). All APs were efficiently adsorbed onto the activated carbon, obtained from coconut shells. APs having alkyl chains of different length consisting 5–9 carbon atoms required different activation times for adsorption on microporous carbon (Iwasaki et al., 2001). This showed that the ability of adsorption depends on the activation time and it increases with increasing activation time. The adsorbed amount depends on the number of carbon atoms. APs either exist in linear form (heptyl > hexyl > pentyl) or branched form of alkyl chains (nonyl > octyl) (Iwasaki et al., 2001). Choi et al. (2005) also reported that the adsorption capacity of NP is influenced by the volume of pore size, type of carbon, surface area, and surface charge density. They found that NP having high K_{ow} shows more hydrophobicity and adsorbed effectively than others compound having low K_{ow}. The log K_{ow} of APs and their metabolites ranges between 4.00 and 6.19 that indicate hydrophobic nature of these substances (Ying et al., 2002).

Yu et al. (2009a) found granular activated carbon was highly effective for removal of EDCs having high K_{ow} such as nonylphenol. Because of the presence of larger pore volume, coal-based carbon become better adsorption material for NP as compared to other types. Xing et al. (2009) reported that the varying pore size of ordered mesoporous carbon of silica is directly linked with adsorption capacity of NPEO. The isotherms of NPEO has been studied by using Langmuir adsorption model shown that the material having pore size >1.5 nm become a crucial factor for its adsorption rate. Cyclodextrins are the derivate of starch, produced naturally and form adsorbing gel material for the removal of nonionic surfactant such as APEOs by formation of inclusion complexes with the aqueous solution (Bonenfant et al., 2010). Niu et al. (2012) prepared nanoparticles with a core/shell structure surrounded by paramagnetic nanoparticles (CMNP) by a simple method using inorganic iron salts and glucose solution as precursors to remove 4-n-NP and 4-OP. Organic solvents were not used in the synthesis step. The material was efficiently adsorbed to remove APs from water.

5.3.2 Membrane-based treatment

Membranes are a particular type of barrier that can separate species from gases or liquids through various mechanisms viz. diffusion and sorption. Optional separation occurs due to the translucency of the membrane. In the membrane-based integrated separation methods, water generally passes through membrane, whereas airborne pollutants, which are relatively large in size and molecular weight, hold on to the media or membrane prior to removal.

Membrane separation is used for several kinds of identical or similar separation processes. Propulsion for separation might be done through the application of high pressure, generation of concentration gradients and electrical potentials (Peter-Varbanets et al., 2009). These processes are categorized into reverse osmosis, nanofiltration, microfiltration, and ultrafiltration (Esfahani et al., 2014).

Reverse osmosis: Membrane having pore diameter between 0.0001 and 0.0001 μm is utilized to filter polymer chain solutions, production of ultrapurified water, and desalination of sea water and brackish water.

Nanofiltration: This type of membrane has a pore size range of 1–10 nm, used for the desalination of brackish water and removal of trace pollutants and metal ions.

Microfiltration: It is commonly employed for filtration of colloidal solutions containing bacteria or suspended particles using a membrane with pore size of 0.1–1.0 μm.

Ultrafiltration: This type of membrane has a pore size range of 0.01–0.1 μm and can be used to filter large molecules, such as protein and polymers, from solutions.

Membrane-based treatment utilizes membrane-based bioreactor (MBR) for the effective elimination of organic and inorganic contaminants along with biological entities bacteria, viruses, and several pathogens from wastewater. It is an integrated system through which waste material degraded in a biological manner by using membrane filtration (Cicek et al., 1998). It is highly reliable and cost effective for the removal of many pollutants viz. nitrates, herbicides, pesticides and EDCs. Since the last three decades, this technology has grown toward large scale processes from simple laboratory methods, with advanced technical and significant commercial impact. Nowadays, it is evolved as an efficient technology in order to get better quality of water, it is simple to automate and producing less amount of sludge during WWTP in comparison to other conventional processes viz. flocculation, coagulation, sedimentation filtration, and chemical oxidation. There are various advantages of MBR which includes effective control of biological activity, smaller plant size, release of high quality effluent that is free of bacteria and pathogens without chemical disinfection and a higher organic load ratio. MBR has the significant ability to recycle the wastewater and make it reusable. Drinking water is probably the main cause of adoption of MBR because more stringent regulations on drinking water recently make conventional treatments unsuitable for handling of contaminants. The application of MBR includes wastewater reclamation in buildings, industrial wastewater treatment, and landfill treatment (Cicek, 2003). However, recent studies have shown the utilization of this technology for the treatment of APs by using physical (nanofiltration) and biological processes (membrane bioreactors). Membrane bioreactors have the potential to operate at higher biomass concentration gaining an excellent permeate quality, amount of total suspended solids produced <5 mg/L (Sombatsompop et al., 2006) and removal of higher biological oxygen demand (BOD) due to separation of membrane by utilizing micro- or ultrafiltration processes. Li et al. (2000) reported about 91–97% elimination of NPEOs and its precursors through the employment of different types of membrane filtration, while only 86% removal of NPEOs is achieved by conventional WWTP.

Researchers have conducted studies and reported that membrane-based techniques act as an effective barrier for EDCs including APs (Gallenkemper et al., 2003; Wintgens et al., 2003, 2004; Lyko et al., 2005). Wintgens et al. (2003, 2004) conducted experiments using various elimination techniques, that is, MBR, reverse osmosis (RO), nanofiltration (NF), activated carbon-based adsorption. Surveys were conducted from landfill leachate, WWTPs where high input of NPs were detected and it was reported that the MBR is able to remove >80% of NPs load (Wintgens et al., 2003).

Many researchers have suggested reverse osmosis and nanofiltration for elimination of APs (Kiso et al., 2001; Agenson et al., 2003; Jung et al., 2007). Kiso et al. (2001) examined the behavior of 10 types of APs adsorbed on the membrane polymers (polyamides). The results showed that a desalting membrane containing a reverse osmosis membrane was needed for the effective removal of APs. As expected, adsorption was controlled primarily by hydrophobic interactions. Effect of MBR for removal of NPs and NPEOs with WWTP has been studied (Camacho-Munoz et al., 2012). The system studied worked on a flat sheet and hollow fiber membrane. Addition of RO module reported to enhance the removal efficiency.

5.3.3 Biotechnology-based methods

Biotechnology-based methods presents another interesting bio-based approaches to eliminate the APs from wastewater. This method is primarily categorized in to microbial and enzymatic methods. Microbial methods involve employment of bacteria, yeast and mold to break down phenol into carbon dioxide and water (Anku et al., 2017). These phenol removal methods are feasible because some microorganisms are known to utilize APs as source of carbon or nutrients (Kanekar et al., 1998). It has the advantage of relatively low operating costs. Elimination of APs by microorganisms is carried out either via aerobic or anaerobic process and is initiated by hydroxylation of the aromatic ring (introduction of hydroxyl groups) (Xiaojian et al., 1991). Hydroxylation via aerobic mode has catechol as the final product. In the first step, one molecular oxygen is reduced to water in the presence of a hydrogen donor and another oxygen atom is swallowed followed by hydroxylation to produce catechins using dioxygenase (Anku et al., 2017). Then, depending on the type of microorganisms, specific enzymes are used to cleave the aromatic ring of catechol and via multiple steps resulted in the conversion of phenolic compounds into carbon dioxide and water.

The enzymatic degradation method uses biocatalysts that can effectively and selectively remove pollutants in water (Demarche et al., 2012). In addition, compared with other types of reactions, enzymatic reactions occur much faster (Bailey and Ollis, 1986). As an advantage over the microbial pollutant degradation system, the enzymatic pollutant removal system can occur under conditions that are unfavorable or toxic to bacteria. Bevilaqua et al. (2002) and Ikehata et al. (2002) have reported that membrane-based treatment received extensive attention because of its high pollutant removal efficiency, ability to operate at wide temperature and pressure range and generation of a safe final product. A series of studies using enzymes to remove phenolic compounds from wastewater have been reported. Cabana et al. (2007) proposed cross-linked laccase aggregates to eliminate NPs, triclosan, and bisphenol A. This immobilization involves the precipitation of the enzyme and the chemical cross-linking of the protein using two functional compounds. The researchers reported fluidized continuous bed reactor as an effective method for removal of NPs from the aqueous waste.

Biotechnology-based elimination of APs uses encapsulated biofilm reactors to maintain high biomass concentration and activity during processing, minimizing both cell start-up and wash-up (Soares et al., 2003, 2006). In addition, the bioreactors have a very high and variable load capacity. Soares et al. (2003) examined an encapsulated bioreactor to eliminate NPs with *Sphingomonas* sp. First, the NP saturated medium was continuously injected into the bioreactor for simulation of groundwater pollution. About 99.5% degradation of nonylphenol was observed with 7.5-fold lesser wastewater toxicity. Gilbert et al. (2012) designed an experiment by combining biological and physical processes, a biofiltration treatment plant which have been provided APs contamination in raw effluent and finally resulted in the elimination of APs from 45% to 95%.

5.3.4 Advanced oxidation processes

The advanced oxidation processes (AOPs) involve the elimination of micropollutants by the attack of hydroxyl radical species that leads to chemical degradation of pollutant into various by products (Brillas et al., 2010; Oden and Sari-Erkan, 2018). Electrochemical and chemical oxidation are two types of AOPs. Electrochemical oxidation is based on the utilization of electricity for degradation of micropollutants with the help of oxidizing agents. Chemical oxidation resulted in the degradation of pollutants by using different chemicals followed by oxidation reactions for complete destruction of pollutant in wastewater. Chemical oxidation techniques carried out through several powerful oxidants such as ozone, referred as ozonation process. It has the ability to work both in the presence of catalyst such as metal oxides or in the absence of catalyst. Beltran et al. (1994) have reported that UV ozone is mainly used for treating wastewater with small volumes. Ozonation is not only used as clarifying and disinfecting process in large number of wastewater treatment plant but also used for oxidation purpose with aim to complete mineralization of organic matter (Gültekin and Ince, 2007) since, ozone acts as a strong oxidant and prefer to attack on electron density rich site that increases the rate of oxidation kinetics. The ozonation has been done directly by molecular oxygen or indirectly by hydroxy radicals produced from decomposition of ozone in alkaline medium. However, ozonation is mainly used for treatment of industrial effluents and for the purpose of making drinking water free from contamination. Ozonation has the potential to biologically transform the industrial compounds which is applied to treat extensive amount of effluent without or little formation of any by-product (Tunay and Kabdasli, 2010). In order to increase the oxidation capacity, ozonation can be carried out along with other oxidants like H_2O_2 or in the presence of catalyst such as Fe^{2+}, TiO_2, etc., or in combination of other methods viz. membrane filtration, UV irradiation (Neyens and Baeyens, 2003). AOPs are mainly responsible for oxidation of organic contaminants by production of hydroxy free radical from various oxidants such as H_2O_2, ozone and nowadays persulfate is also used as an alternative oxidant (Liang et al., 2009).

Zhang et al. (2008) have conducted ozonation study of Aps, that is, NP and OP in aqueous solution. A series of batch experiments have been conducted to examine the effect of initial pH, ozone dose, and APs concentration on the degradation. Both APs had been completely decomposed following 6 min at pH 9.0. However, the degradation efficiency has reached up to 96%, with ozone dose of 0.38 mg/min. Derco et al. (2017) have reported higher APs elimination rate and treatment efficiency with ozonation in industrial wastewater. In addition, Derco et al. also stated that coupling of ozonation with granular activated carbon could result into higher removal efficiency of octylphenol ethoxylate. The transformation of alkyl phenol ethoxylates and their removal from WWTP have been documented via AOPs using ozonation. Petrovic et al. (2004) studied NPEOs degradation in wastewater by means of ozonation, followed by electron irradiation with and without added ozone. It was observed that ozonation and AOPs could degrade not only the NPEO but also the polyethylene glycol is formed as a by-product from the degradation of the NPEOs, to the concentration remaining below the detection limit. Bertanza et al. (2010) reported elimination of NPs through ozonation process from a treatment plant (Verona, Italy). Bertanza and his coworkers also concluded ozonation as an cost effective and practicable alternative for tertiary treatment.

5.4 Conclusions and perspectives

A considerable amount of research has been conducted for degradation and removal of APs, however, scarce information is available related to the effectiveness of method at field. This is because existing WWTPs are not designed for these new pollutants nor have any suitable method at industrial and urban scale. Hence, employment of adsorption-based treatment, membrane-based treatment, biotechnology-based methods and advanced oxidation processes has been suggested at conventional WWTPs, so that APs could be eliminated at source and will not go further to the different environmental matrices especially in water bodies. Complete treatment along with AOPs, activated carbon, and ozonation has achieved at significant levels. Biotechnological processes employing immobilized microorganisms and/or catalysts could also represent a proficient substitute to the conventional methods. A series of literature showed that the advanced research is needed to develop and improve coupled oxidation–bioadsorption, oxidation–biodegradation treatment for efficient elimination, decomposition, and biodegradation of APs. Future research must take this aspect into account. Still, an interdisciplinary approach has to be developed in which microbiologists, biologist, chemists, engineers and polymer experts could collaborate to develop an innovative elimination approach for APs in wastewater.

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6

Biodegradation and removal of phthalate esters from wastewater

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6.1 Introduction

Due to the high negative impacts on public health and the environment, pollution due to emerging toxins along with hazardous organic compounds leads to the world's most pressing challenges (Khan et al., 2015; Patino et al., 2015). Phthalate esters (PAEs) are constituted by a group of industrial chemicals produced in large quantities yearly around the world (Kong et al., 2016). Dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-n-butyl phthalate (DBP), commonly employed in cosmetic products, personal care products, and pharmaceutical compounds are characterized by low molecular weights. Butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate are among the high molecular weight PAEs (DOP) used to increase the performance of polymers as plasticizers, notably in polyvinyl chloride production (Kong et al., 2016). The organic and synthetic chemicals known as phthalic acid esters (PAEs) or phthalates have been classified, for example, promising contaminants, typically synthetic chemical, refractory, and hazardous contaminants (Ahmadi et al., 2015; Benjamin et al., 2015). PAEs are also thought to pose a risk to human health, including endocrine disruption (Tsa et al., 2016), reproductive toxicities (Liu et al., 2015), organ damages, cancer, birth defects (Ahmadi et al., 2015; Huang et al., 2015), and type 2 diabetes (Shapiro et al., 2015). Some PAEs, for example bis (2-ethylhexyl) phthalate which are commonly utilized in the manufacturing and processing of plastic goods (e.g., plasticizers), have previously been designated as of importance water contaminants by the US EPA. The United States EPA and the Chinese Environment Monitoring Center are two organizations that work together to protect the environment (Planello et al., 2011).

Photochemical oxidation, biodegradation, and advanced oxidation are the most commonly used methods for degrading DMP (Wang et al., 2017; Huang et al., 2017). The extremely significant pathway for the breaking down of DEHP and other hazardous PAEs is microbial degradation because their photodegradation and hydrolysis rates are so sluggish (Wolfe and Steen, 1980). Biological treatments were used first, followed by physiochemical treatments in hybrid systems. A combination of membrane filtrations (RO/NF) and membrane bioreactors

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(MBR) successfully eliminated a variety of ECs, including medicines and EDCs. Bioelectrical reactors (BERs) use the stimulating effect of low voltage to impact metabolite formation and biotransform organic molecules (Thrash and Coates, 2008). Furthermore, the application of minimum voltage-current might affect the population formation of anaerobic microorganisms, stimulate dehydrogenase secretion, and increase dehydrogenase activity (Ding et al., 2016). The biosorptive removal of pharmaceuticals in some hybrid systems of the CWs and waste stabilization ponds have shown substantial promise (Dhangar and Kumar, 2020). The CWs are effective at removing PAEs in previous research (Zhao et al., 2004). Under a hydraulic load of 420 mm/day, researchers evaluated the removal efficiency of dibutyl phthalate in the greenhouse having small stage vertical flow wetland systems sets.

6.1.1 Phthalate esters in the environment

Phthalates are synthesized in vast quantities for use in several plastic products. PAEs are primarily used as plasticizers in the manufacture of polyvinyl chloride (PVC), while terephthalic acid (TA) esters are used to make polyester fibers and polyethylene terephthalate. Isophthalic acid esters (IAEs), which are manufactured in lesser quantities in comparison to the other two esters are used to produce rope, resin, and other products (Liang et al., 2008). PAEs generally have low water-solubility, volatility, and temperature tolerance (Alatriste-Mondragon et al., 2003). PAEs have comparatively higher octanol–water partition coefficient logarithmic values, which increase their probability of accumulation in the environment and organisms (Chi et al., 2016). PAEs tend to get released into the environment quite easily by evaporation from finishing products, leaching, or by manufacturing processes (Benjamin et al., 2015) as PAEs are linked to the polymeric matrix merely by van der Waals forces (Clara et al., 2010). PAEs are also presumed to be a category of persistent organic contaminants (POPs) because of their long half-life in the atmosphere and high bioaccumulation propensity (Wang et al., 2017).

6.1.2 Atmosphere and water/wastewater

The US EPA has explicitly listed six PAE compounds as priority pollutants that include di-n-octyl phthalate (DNOP), dibutyl (DBP), dimethyl (DMP), di (2-Ethylhexyl) (DEHP), butyl benzyl (BBP). Plastic additives are made of phthalates primarily to enhance the resin's mechanical properties, especially its softness and flexibility (Cartwright et al., 2000). Phthalates have a variety of properties that are dependent on the composition and form of alcohol used to make up the alkyl chain (Wittassek et al., 2011). Since the 1930s, phthalate esters have been commonly used in the plastics industry (Roslev et al., 2007; Abdel daiem et al., 2012; Peng et al., 2013). If plasticizers are not added, the plastic articles tend to become brittle and inflexible, rendering them useless for any of their supposed purposes (CEFIC, 1989). The DEHP [(bis-(2-ethylhexyl) phthalate)] is the most prominent phthalate, which constitutes about 80% of the phthalates that are manufactured in China and the European Union (EU) (Huang et al., 2008; Meng et al., 2014). Another most widely used phthalate in several countries is dibutyl phthalate (DBP) (Wang et al., 1995; Fang et al., 2010). Phthalate ester concentrations in freshwater often differ greatly between urban and rural samples (Teil et al., 2014).

6.1.3 Soils and sediments

The majority of current literature emphasizes the presence of phthalate esters in agricultural fields and phthalate esters may be polluting arable soils as an outcome of agricultural use of polyvinylchloride plastic film (Hu et al., 2003). Phosphate esters are abundant in waste sludge, which is used as a soil amendment (Net et al., 2015; Vikelsøe et al., 2002). The phthalate esters in agricultural soils could end up in crops and vegetables, posing a risk to human health (Ma et al., 2013). Rain transfers phthalate esters from the environment to fresh water on land, as a result of their deposition in water, they are widely distributed in rivers, sediments, and reservoirs. Freshwater is the most common mechanism of environmental dissemination of phthalate esters produced by the hydrological cycle (Teil et al., 2014). DEHP is the most common congener in sediments followed by DBP due to industrialization and urbanization. Since phthalate esters are the most abundantly developed and used, DEHP and DBP together constitute the two most common congeners. The development of congeners and the biodegradability of PAEs in the environment are related. The phthalate esters concentrations in sediments vary significantly between urban and rural samples (Teil et al., 2014).

6.2 Phthalate ester's effect on human, animal, and environment health

It can be observed that there has been a paradigm shift from conventional "priority pollutants" to "emerging contaminants (ECs)" or "new generation contaminants" over the last decades from the existing research scenario (Garcia-Rodríguez et al., 2014; Grassi et al., 2012; Dolar et al., 2012; Ahmed et al., 2015). The high risk to marine organisms associated with DEHP toxicity results in dwindling aquatic species, which pose a serious challenge to human health by entering through the food chain and food web (Fig. 6.1). Phthalate esters (PEs) or phthalates are a significant constituent of ECs and are becoming ubiquitous at a very rapid pace (Singh et al., 2017). Owing to their endocrine-disrupting effects and potential public health consequences, they have piqued people's interest in the last decade (Nikonorow et al., 1973; Vitali et al., 1997; Latini et al., 2003). Inhalation and dermal contact with phthalate esters in the air may result in serious damage. They may even get accumulated in humans across the food chain by soil and water. The phthalate esters which are a class of endocrine disrupting pollutants (EDPs) (Horn et al., 2004) are accused of interfering with biological processes in humans and wildlife, posing a teratogenic risk, mutagenicity, and carcinogenicity even at very low doses (Becker et al., 2004; Caldwell, 2012).

6.3 Phthalate esters biodegradation and its biodegradation mechanism

The PAE biodegradation by microorganisms has been established as the primary method of removing PAEs from the ecosystem (Ebenau-Jehle et al., 2020; Gao and Wen, 2016; Liang et al., 2008; Vamsee-Krishna and Phale, 2008; Boll et al., 2020). The microorganisms begin to degrade

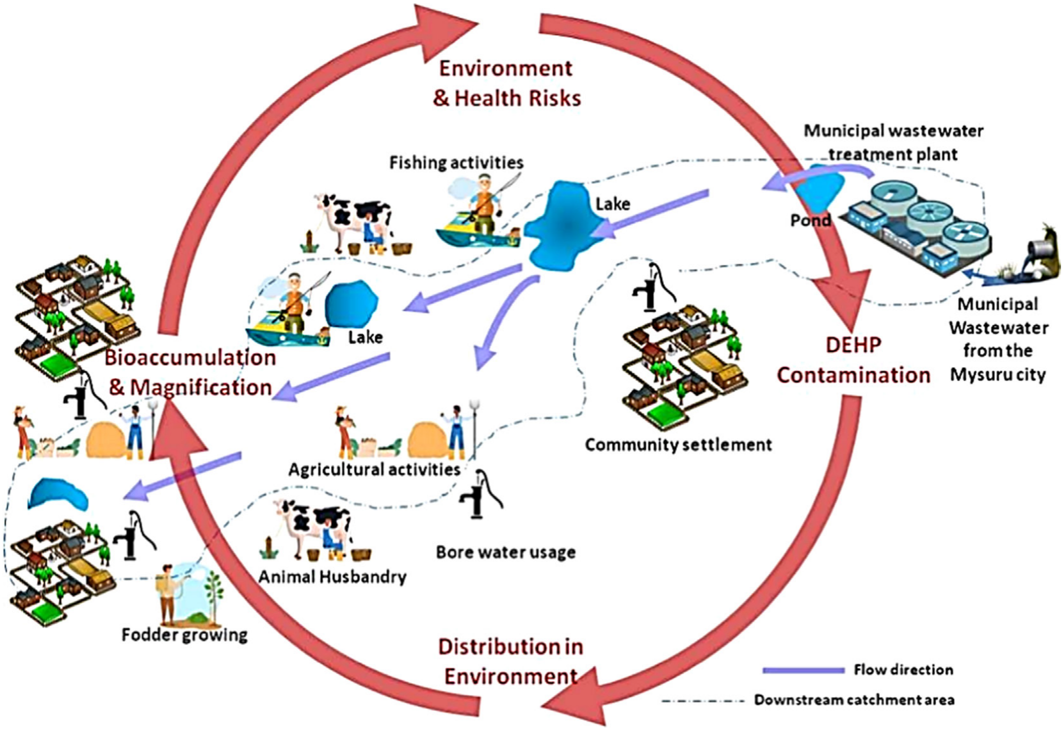


FIG. 6.1 DEHP pollution in aqueous ecosystems by urban wastewater and related practices poses a high risk to public health across the food chain (Shivaraju et al., 2020).

xenobiotic phthalic acid esters by hydrolyzing them to their respective alcohols and ortho-phthalate (hereafter, phthalate) (Fig. 6.2). PAEs hydrolysis into alcohols and o-phthalic acid is the common PAE biodegradation pathway. Both anaerobic and aerobic microorganisms have been documented to degrade o-phthalic acid but in radically different ways. Deoxygenase-dependent reactions are extensively used in the aerobic degradation of phthalates while the oxygen-sensitive main enzyme phthaloyl-CoA decarboxylase is used in anaerobic degradation (Ebenau-Jehle et al., 2020). In facultatively anaerobic bacteria, aerobic phthalate degradation occurs through a hybrid degradation pathway that was formerly unknown involving oxygen-sensitive and oxygen-dependent main enzymes. For facultatively anaerobic microbes having a transition between anoxic and oxic environments regularly, such a technique is critical (Ebenau-Jehle et al., 2020).

The most critical mechanism that fares well in breaking down the DEHP and other toxic PAEs is microbial degradation since their photo-degradation and hydrolysis rates are slower in normal environmental situations (Wolfe and Steen, 1980). The previous research has shown that phthalates break down biologically by the microorganisms such as phthalate-degrading bacterial organisms, both in aerobic and anaerobic conditions (Table 6.1). The microorganisms that degrade phthalates have been isolated from diverse environmental samples, including *Arthrobacter, Enterococcus, Bacillus, Rhodococcus, Gordonia, Acinetobacter, Agromyces,*

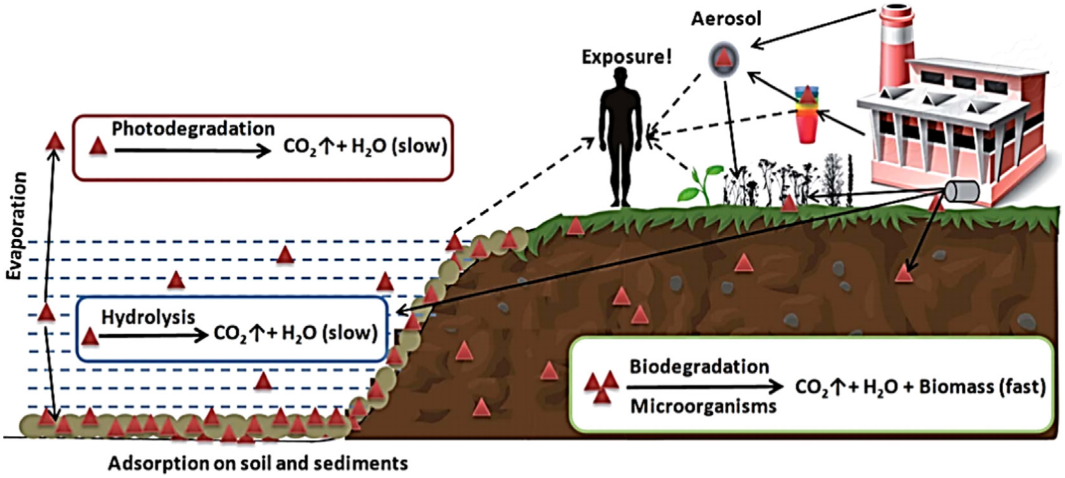


FIG. 6.2 The presence of phthalate esters and their biodegradation (Prasad, 2021).

Brevibacterium, Microbacterium, and *Pseudomonas* (Liang et al., 2008; Gao and Wen, 2016; Chang et al., 2004; Jianlong et al., 1997). Different types of pathways, for example, de-esterification and dealkylation, operate in aerobic and anaerobic environments. The initial degradation of phthalate diesters to phthalate monoesters is caused by beta-oxidation and trans-esterification (Liang et al., 2008). The ester linkage binding the alkyl chain and the aromatic ring gets sequentially hydrolyzed in primary biodegradation, containing first the monoester and then PA (Johnson et al., 1984). This mechanism has been found in at least 10 bacterial genera and is normal to both aerobic and anaerobic degradation (Eaton and Ribbons, 1982). The mineralization of the PA occurs as a result of secondary biodegradation in a variety of forms Elder and Kelly (1994).

6.3.1 Aerobic biodegradation

Table 6.1 enlists some microbial isolates well-known for their phthalate-degrading ability and are strictly aerobic. Taxonomic groups include *Proteobacteria, Actinobacteria, Firmicutes, Chlorobi*, and *Deinococcusthermus*. In addition to bacteria, phthalate esters may also be degraded by a variety of fungal species. Previous research has compiled a list of phthalate-degrading fungal species (Liang et al., 2008; Luo et al., 2009; Chatterjee and Karlovsky, 2010; Ahuactzin-Pérez et al., 2014). The eumycota is largely made up of *Deuteromycotina* and *Basidiomycotina*. *Aspergillus parasiticus, Fusarium subglutinans*, and *Penicillium funiculosum* are three mycelial fungi that can completely utilize intact DEHP, either bound or unbound (Pradeep and Benjamin, 2012). The complete decomposition of phthalate esters has been documented for a mixture of microbes. Under favorable conditions, di-n-octyl phthalate (DOP) might be entirely reduced under 48 h (Gao and Wen, 2016) by the mutual consequences of *Gordonia* sp. strain JDC-2 and a strain of *Arthrobacter* sp. JDC-32 (Wu et al., 2010).

Table 6.1 Aerobic and anaerobic phthalate-degrading bacterial species (Gao and Wen, 2016).

Isolation	Species	PHEs (mg/L)	Performance	References
Aerobic phthalate-degrading species				
Samples of sewage outfall	*Camelimonas* sp. M11 soil	DBP = 20 mM	56% after 72 h	Chen et al. (2015)
Contaminated river sludge	*Acinetobacter* sp.HS-B1	BBP = 500	28% after 24 h	Yang et al. (2013)
	Arthrobacter sp. HS-B2		59% after 24 h	
Municipal waste-contaminated soil	*Gordonia* sp. Dop5	DOP = 750	100% within 40 h	Sarkar et al. (2013)
Mangrove sediment	*Arthrobacter* sp. ZH2	DBP = 500	No residues within 48 h	Wang et al. (2012)
Sewage sludge	*Rhodococcus* sp. JDC-11	DBP b 1000	100%, pH = 8.0 after 28 h	Jin et al. (2010)
Marine sediment	*Burkholderiacepacia* DA2	DMP = 400	100% after 9 days	Gu et al. (2009)
Anaerobic phthalate-degrading species				
-	*Clostridium* sp.,	-	-	Nozawa and Maruyama (1988) Qiu et al. (2006)
	Pseudomonas sp.,			Nozawa and Maruyama (1988) Qiu et al. (2006)
-	*Bacillus* sp.,	-	-	Nozawa and Maruyama (1988) Qiu et al. (2006)
-	*Pelotomaculum* sp.,	-	-	Nozawa and Maruyama (1988) Qiu et al. (2006)
-	Methanogenic consortia	-	-	Vamsee-Krishna and Phale (2008)
River sediments	Sulfate-Reducing Bacteria	-	-	Chang et al. (2005)
River sediments	Eubacteria	-	-	Chang et al. (2005)
-		DEP), (DBP) (DEHP),	100% 49, 28 and 84 days	Chang et al. (2005)
-	Strain JTT.	-	100%	Qiu et al. (2006)
-	-	-	100% 17–156 days	Kleerebezem et al. (1999b)

BBP, butyl benzyl phthalate; DBP, di-n-butyl phthalate; DEP, diethyl phthalate; DEHP, bis (2-ethylhexyl) phthalate; DMP, dimethyl phthalate; DOP, di-n-octyl phthalate.

6.3.2 Anaerobic biodegradation

The phthalate ester de-esterification is known to be the main degradation process in anaerobic systems, much as it is in aerobic conditions (Shelton et al., 1984). When phthalate esters are anaerobically mineralized, phthalic acid and monoester phthalates are typical core intermediates (Liang et al., 2007). The anoxic metabolic process of PA is the rate-limiting stage in anaerobic PAE breakdown (Kleerebezem et al., 1999a). Decarboxylation may also be employed to transform phthalic acid into benzoate (Nozawa and Maruyama, 1988). However, in this degradation pathway, there is no experimental support regarding the precise role of decarboxylation (Kleerebezem et al., 1999c). Benzoate decomposition involves cleavage of the ring structure, which produces carbon dioxide, hydrogen, and acetate (Kleerebezem et al., 1999c).

6.4 Treatments technologies and phthalate esters removal from water/wastewater

Photochemical oxidation, advanced oxidation, the most prevalent ways for removing DMP are decomposition and biodegradation (Wang et al., 2017; Huang et al., 2017). Due to its minimal energy consumption and secondary emissions, a microbial degradation is an excellent option (Dong-lei et al., 2007). Because of its low water solubility and poor bioavailability, DMP accumulates quickly in anaerobic conditions (Yuan et al., 2002; Barnabe et al., 2008). As a result, research into the anaerobic biodegradation of DMP would be extremely useful for in situ bioremediation. PAEs are known to have full anaerobic degradation cycles, for instance, Diethyl phthalate, dioctyl phthalate, and dibutyl phthalate each took 49, 84, and 28 days to break down (Chang et al., 2005).

6.4.1 Activated sludge and activated carbon technology

In this operation, based on the type of secondary sludge, flocculent suspension of microbes and aeration of the combination are ensured for prolonged intervals. The *Nitrosococcusmobilis* and *Nitrospira* sp., are ammonia and nitrite oxidizing bacteria found in activated sludge. Suspended solids and colloidal matter combine to form microbial aggregation (Suresh and Abraham, 2018). PAEs have been found in the wastewater treatment process regularly in recent decades, owing to their mutagenic, carcinogenic, and xeno-estrogenic effects on organisms, numerous studies have dealt with their fates in wastewater treatment systems.

In wastewater treatment, for the oxidation of phthalate esters, activated sludge systems have been used successfully for a long time. In the activated sludge treatment, oxygen and nitrate reduction are common biodegradation processes. The biodegradation of six PAEs in sewage has been demonstrated to be about 60–70% (Fauser et al., 2003). The activated sludge could biodegrade a DEHP concentration of 58.70 ± 5.70%, as corroborated by respirometric experiments (Stasinakis et al., 2008). In aerobically activated sludge wastewater treatment plants, the DBP, DEHP, DMP, DEP, and BBP elimination efficiencies ranged from 73% to 87% (Huang et al., 2008). The anoxic–oxic (AO) and anaerobic–anoxic–oxic (A2O) methods, which are adapted versions of the activated sludge technique also showed maximum elimination performance for PAEs during the wastewater treatment process. Anaerobic–oxic (AO) technology is a type of anaerobic technology that combines anaerobic hydrolysis with an aerobic activated sludge process. In comparison to AO, A2O technology includes an anaerobic zone that provides superior nitrogen and phosphorus reduction. The elimination performance for phthalates after the anaerobic treatment stage was 64–69% in a pilot AO system and as high as 75–80% followed by the phase of aerobic treatment (Balabanic and Klemencic, 2011). To examine the course of DBP and DEHP in the system, a laboratory-scale A2O-activated sludge system was developed, and the following properties may be used to classify the fates of influent phthalate esters: Activated sludge degraded 72.66% of DBP and 71% of DEHP, while the system collected 24.40% of DBP and 26% of DEHP. DBP and DEHP levels of 2.44% and 2%, respectively, were discharged into the effluent in the waste sludge while 0.50% DBP and 1% DEHP were retained respectively (Huang et al., 2008, 2010).

Activated carbon (AC) is a well-known kind of carbon technology for eliminating a variety of organic contaminants. AC is most frequently encountered in crushed or granular form in sealed bed filters. In several water treatment facilities in the UN and Canada, granular activated carbon is being used. In traditional filters, anthracite media can be replaced by granular activated carbon. As a result, adsorption and filtration are obtained together. Alternatively, GAC may also be utilized as an adsorption bed after conventional filtration (Snyder et al., 2007). Several scientists have verified the effectiveness of AC in eliminating trace organic compounds from water (Matsui et al., 2002; Asada et al., 2004; Westerhoff et al., 2005; Zhou et al., 2007). In addition, in the laboratory, AC has demonstrated elimination capacity for several endocrine disrupting pollutants (EDPs) in both artificial and natural wastewater in many studies, in the pilot and full-scale plants (Choi et al., 2005; Fukuhara et al., 2006). In a study the chemical compositions of around 70 EDPs were used to estimate their AC absorbability, after that, their isolation from wastewater was proven to be successful by adsorption by AC (Abe, 1999). Using symbolic endocrine substances for example estrone (E1) and 17-estradiol (E2), the removal output on absorption was also evaluated. In comparison to simulated EDP wastewater and actual wastewater, there was a significant gap in EDP removal by AC adsorption.

6.4.2 Membrane bioreactor technology

Physical/chemical systems are a popular wastewater treatment process. To address the changing consumer demands, new technologies are being developed. To treat pharmaceutical wastewater, the MBR is used in conjunction with biological methods. While membrane bioreactor (MBR)structures are used, the preservation of biomass is ensured, as a consequence of which high-quality effluent is generated. The membrane bioreactor (MBR) is a biochemical wastewater treatment device that incorporates both biological and chemical processes: (1) a suspended growth bioreactor for biochemical reactions with (2) a membrane separator for solids and liquid separation. Submerged MBR, also known as incorporated MBR, is the other kind of membrane used in bioreactors. The reactor also includes microfiltration, ultra-filtration, nanofiltration, and a reverse osmosis membrane. The target is segregated by the surface membrane pore size, which has a compact structure, small scale, and low power consumption. The most important membranes used in the MBR treatment process are ultrafiltration and microfiltration membranes (Suresh and Abraham, 2018).

Membrane separation processes are divided into two categories: pressure-driven and electricity-driven. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis constitute pressure-driven separation methods where in hydraulic pressure is used to propel water molecules through the respective membranes (Adams et al., 2002; Walha et al., 2007). In the electrically regulated membrane process, ions are transferred across the membrane using an electric current, leaving behind filtered water. Membrane treatment, when used at the end of a traditional wastewater treatment ability, is a feasible option for obtaining optimal effluent removal efficiency. The membranes are broadly used in potable water treatment to eliminate dissolved solids, color, and hardness. Several forms of EDPs found in wastewaters have been removed according to scientific literature (Bodzek, 2015). Phytoestrogens (70–93%), PAH (85–99%), and surfactants (92–99%) are the most common EDPs and can all be easily removed from industrial wastewaters using the RO and NF methods. The UF procedure can be used to remove surfactants from wastewater. Plant health products in surface and groundwaters, such as pesticides, herbicides, and insecticides, can be eliminated effectively from water using NF or combined MF-NF AC adsorption systems (powdered or granulated) (Bodzek, 2015; Mavrov et al., 1992). These processes also regulate the phthalate concentration in various domains of the environment, principally in water since high phthalate retention was noted in both the RO and NF processes (initial concentration 40 g/L) (Bodzek et al., 2004). For DEP, DBP, and DEHP, the retention rates found were extremely high and were in the range of 89.7% (UF)–99.9% (UF) (RO and NF). The NF may be used to separate phenolic xenoestrogens from water such as APs, NPs, BPA, and BPF (Bodzek, 2013). Recently, a rise in artificial hormone concentrations such as α-ethinylestradiol, diethylstilbestrol and mestranol has been observed from vast quantities of discarded pharmaceuticals from households and drainage, as well as hospital waste and chemical plants. It was observed that membrane methods could be used to eliminate these types of toxins from water (Bodzek and Dudziak, 2006). As the toxins have a low molecular weight, RO or NF must be used. The retention coefficients of the RO membranes were found to be higher than those of NF and UF membranes, indicating that RO membranes fully suppress particular hormones (Bodzek and Dudziak, 2006).

6.4.3 Constructed wetlands

The USEPA, China's and Japan's equivalents, and several European countries classify PAEs as priority management toxins and EDPs. PAE hydrolysis, photolysis, and volatilization have all been shown to be sluggish, though biodegradation is critical for PAE degradation (Kurane et al., 1977; Wolfe et al., 1980; Giam et al., 1984; Kurane, 1986; Chauret et al., 1996; Wang, 1996; Jianlong et al., 1997). Constructed wetlands (CWs), a form of green and sustainable technology, have become increasingly popular for treating various wastewaters in recent years due to their low energy usage and ease of operation (Wu et al., 2014). The CWs are mainly made up of water, plants, substrates, microorganisms and the contaminants such as suspended particulates, organic materials, heavy metals, and pathogens get eliminated by integrating physical, chemical, and biological processes (Kumar and Singh, 2019; Wu et al., 2015). Various studies showing the degradation of phthalate using CWs are presented in Table 6.2. Multiple pathways influence

Table 6.2 Phthalate elimination during various wastewater treatment systems (Gao and Wen, 2016).

Treatment systems	Origin	PAEs (μg/L)	Performance	Time	References
Bioreactor	Latosol	DEHP	100%	120 days	Ferreira et al. (2015)
Activated sludge	Wastewaters	DEHP33	93.90%	365 days	Tran et al. (2015)
Moving bed biofilm reactor	Synthetic wastewater	DEP300,000	94.96%	SRT = 18.20 days	Ahmadi et al. (2015)
Flat sheet-MBR	Wastewater	DEHP37.5	29%	365 days	Camacho-Munoz et al. (2012)
Hollow fiber-MBR			37%		
HF/RO-MBR			70%		
Anaerobic + aerobic + UF + RO filtration	Papermill Wastewaters	DMP	100%	–	Balabanič et al. (2012)
		DEP	100%		
Anaerobic + MBR + RO filtration		DBP	100%		
		BBP	100%		
		DEHP	100%		
MBR	Municipal solid waste leachate	DMP20.80	78%	300 days	Boonyaroj et al. (2012)
		DEP12.50	81%		
		DBP35.40	87%		
		BBP21.50	77%		
		DEHP65	96%		
		DOP8	82%		
UASB-CW	Urban wastewater	DEHP4.40; 8.50	>90%; >90%	21 days	Reyes-Contreras et al. (2011)
		DiBP0.40; 0.50	>70%; >80%		
		DEP1.80; 2.70	>70%; >70%		
		DBP0.40; 0.20	>90%; >80%		
CWs	Heavy eutrophic urban lake	DBP 9840.0 In. 1.19 out	99.99	–	Liang et al. (2009)
		DBP 19860.0 In.0.21 out	99.99		
VFCW + HFCW + SF-CW	Urban wastewater	EDCs (Bisphenol A)	99.0 %	–	Ávila et al. (2015)
BES	–	DMP	≤84.0%	–	Feng et al. (2014)
MFC	–	PA	47.8%	21 days	Marash et al. (2013)
Aerobic digestion Anaerobic–	Wastewater sludge	DEHP31.4 mg/kg	72%	20 days	Pham et al. (2011)
anoxic–oxic (A2O)	Synthetic wastewater	DBP171.40–257.10	>95%	SRT = 15–25 days	Huang et al. (2010)
Vertical flow CW	Heavy eutrophic urban lake	DBP19860	100%	90 days	Liang et al. (2009)
Fixed film bioreactor	water	DMP105 –5 ∗ 105	81.4%–100%	HRT = 6–48 h	Pirsaheb et al. (2009)
	Synthetic wastewater				

BBP, butyl benzyl phthalate; BES, bioelectrochemical system; CWs, Constructed wetlands; DBP, di-n-butyl phthalate; DEP, diethyl phthalate; DEHP, bis (2-ethylhexyl) phthalate; DMP, dimethyl phthalate; DOP, (di-n-octyl phthalate; In, inlet; MBR, membrane bioreactor; MFC, microbial fuel cell; Out, outlet; UASB-CW, up-flow anaerobic sludge blanket.

the elimination of toxins in the CWs such as sedimentation, adsorption, microbial degradation, absorption and transport by plants (Watson et al., 1989).

The potential of the CWs systems to treat polycyclic aromatic hydrocarbons (PAHs) (Machate et al., 1997), benzoic acid (Walter et al., 1996), and microcystins (Zhenbin et al., 2000) in recent years has grown significantly. However, the effectiveness of constructed wetland structures in treating the PAEs is yet to be determined. In CWs soil, microorganisms and enzymatic activities are expected to play a dominant role in PAE elimination (Liang et al., 2009). Removal of PAEs in the CWs is dependent on the microbial and enzymatic activity as wetland plants transport and convert phthalate esters into less potent compounds (Liang et al., 2009). These processes are more effective at higher temperatures, hence they are an essential removal mechanism (Gao and Wen, 2016).

The temporary physical isolation of PAEs from the inflow is aided by adsorption by the soil matrix. Interception, biodegradation, plant adsorption, plant absorption, and transformation are all part of this complicated process (Watson et al., 1989). The CWs are categorized into three clusters based on the way of water flow: surface flow, subsurface flow, and vertical flow. Since they may efficiently eliminate trace organic pollutants from a variety of diverse plant processes, microbes and soil mediums (Haarstad et al., 2012). The CWs microcosm has drawn global attention and developed applications for wastewater treatment in current years (Haarstad et al., 2012), with a 99.9% removal output, of phenanthrene (Machate et al., 1997), PPCPs (pharmaceutical and personal care products) with an elimination performance of 90% (Matamoros et al., 2008). The potential of the CW systems for the treatment of polycyclic aromatic hydrocarbons (PAHs) (Machate et al., 1997), benzoic acid (Walter et al., 1996), and microcystins (Zhenbin et al., 2000) was considered in recent years.

The CWs are effective at eliminating the PAEs in earlier research. The removal of PAEs in the CWs was aided by substrate adsorption and the degradation of microorganisms. In current years, the CWs have been extensively tested for treating phthalate esters-polluted wastewater. Flow in two directions: vertical and reverse-vertical DBP elimination rates of up to 100% may be achieved by using the CWs to eliminate DBP from wastewater (Liang et al., 2009). Another research has found that DBP was effectively eliminated by vertical and reverse-vertical CWs from contaminated water at a rate of 99.9% (Zhao et al., 2004). DBP degradation is influenced in sterile wetland soil, implying that microbes play an important part in the process (Zhou et al., 2005).

6.4.4 Bioelectrochemical system

Bioelectrochemical systems, which incorporate biological and electrochemical methods to extract refractory compounds, have been developed and used in recent years (Kong et al., 2014; Liang et al., 2013; Pant et al., 2010; Zhang et al., 2016). An anaerobic biofilm carrier and an electrochemical device make up the bioelectrical reactors (BERs) as shown in Fig. 6.3. Table 6.2 lists the number of research studies that indicate how BESs can degrade phthalates. The plastics industry's exponential expansion has put a strain on everyday wastewater disposal. The low concentration of chronic organic contaminants of plastic additives containing phthalic acid esters (PAEs), which have been found in wastewater, soil and the human body (Al-Saleh et al., 2017). The simplest

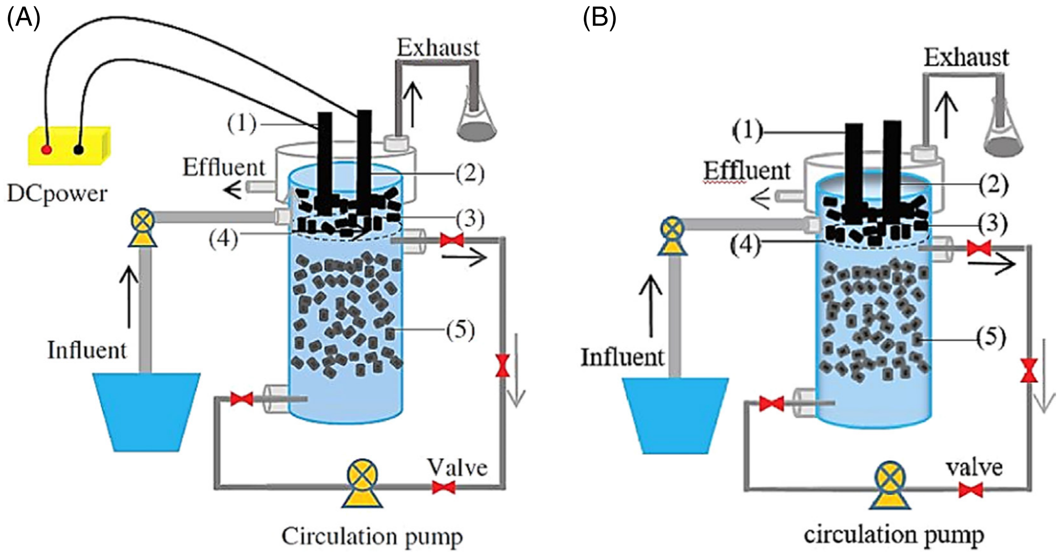


FIG. 6.3 Anaerobic reactor schema with (A) and without (B) applied V. 1, anode; 2, cathode (graphite rod); 3, 3D particle electrode; 4, perforated baffle; and 5, biofilm carrier (Zhou et al., 2019).

chemical structure of all PAEs is dimethyl phthalate (DMP). The DMP is a natural endocrine disrupter that quickly accumulates in the body and poses a significant threat to human health by the food chain (Jianlong et al., 2004; Chen et al., 2015). The DMP can lower testosterone levels and interfere with human reproduction. Finding a modern, highly effective means to degrade low-concentration organic wastes of this sort is critical. The bioelectrical reactors (BERs) use the stimulation effect of low voltage to influence metabolite synthesis and biotransform organic compounds (Thrash and Coates, 2008). At the same time, a low-voltage current can have an impact on the population structure of anaerobic microorganisms, induce dehydrogenase secretion and increase dehydrogenase production (Lim et al., 2020). Bioelectrical reactors (BERs) use the stimulation effect of low voltage to influence metabolite synthesis and biologically convert organic compounds (Thrash and Coates, 2008).

Feng et al. discovered that the rate of e-transfer increased and biodegradation half-life of p-fluoronitrobenzene (pFNB) decreased from 13.33 to 3.83 h upon raising the applied voltage up to 1.4 V (Feng et al., 2014). In the studies, it has been found that due to the microelectrical stimulus on bacterial metabolism with the application of little voltage (0.2 V), the deteriorated performance of 2,4,6-trichlorophenol and p-chloroaniline improved (Xu et al., 2018a, 2018b). As a result, it's critical to investigate the impact of BERs on DMP anaerobic degradation. Organic pollutant biodegradation has been improved upon by using 3D particle electrodes with a wide area of the surface, a high proportion of biomass, and a current performance maximum (Wei et al., 2010).

In the BES technology, chemical reactions are triggered by the interaction between electrodes and chemicals in the electrochemical phase and are currently being employed in treating sewage and wastewater. Electrodeposition, electrocoagulation (EC), electro flotation (EF), and electrooxidation have received the most attention. At the laboratory scale, anodic reduction (oxidation) of EDPs, viz. 17-estradiol (E2) and bisphenol A (BPA), has been investigated using a boron-doped diamond electrode (BDDE). The electrochemical methods for E2 and BPA reduction resulting from applied voltammetry cycles were evaluated using cyclic voltammetry experiments (Yoshihara and Murugananthan, 2009).

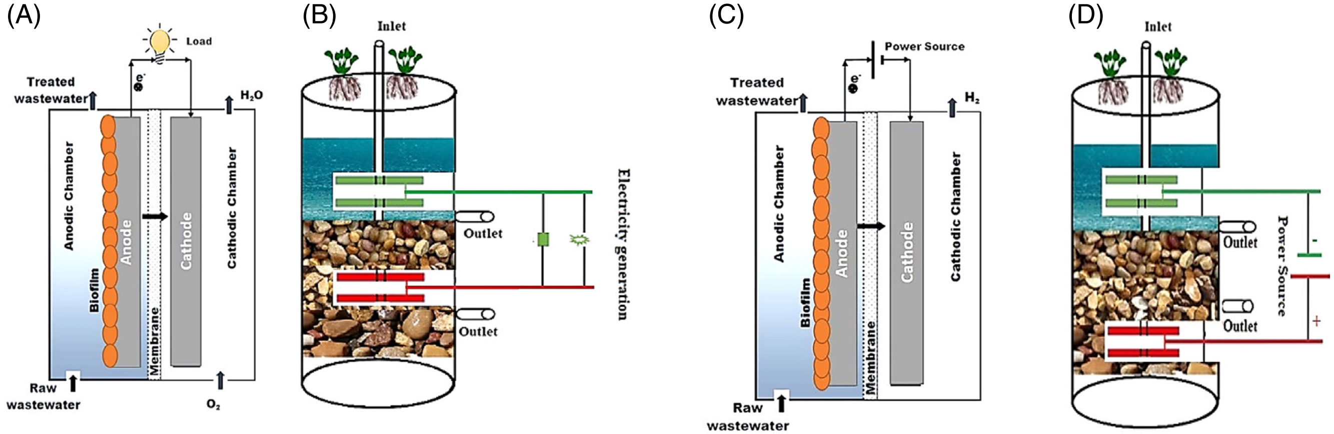
The electrooxidation reactions appear to be regulated by the applied current density at three separate times as has been measured and discussed. The EDCs can be quantified using oxidation through electrolysis by providing high anodic potential, resulting in CO_2 production (Yoshihara and Murugananthan, 2009). On a comparable basis, the BDDE anode outperformed Pt and amorphous graphite under equal experimental conditions (Yoshihara and Murugananthan, 2009) (Fig. 6.4).

6.4.5 Microbial fuel cell system

The microbial fuel cells (MFCs) utilize microbes as catalysts in electrodes to perform oxidation and/or reduction reactions. MFCs have proven to be promising in terms of several applications like azo dye degradation and energy generation (Cao et al., 2010; Xu et al., 2016; Yadav et al., 2012; Li et al., 2016). MFCs can be characterized as systems that convert organic matter into energy using living microbes (Logan et al., 2006). They can produce energy from organic wastes and wastewater by using naturally occurring microbiomes (Watanabe, 2008). In the last few years, the microbial fuel cell has garnered a lot of consideration and has emerged to be promising in the management of environmental issues. Various studies showing the degradation of phthalates using MFC have been presented in Table 6.2. MFC may be used as an alternative to facilitate bioremediation for the effective elimination of variability of polluting agents. Typically, MFC uses microbes for converting chemical energy to electrical energy. MFC uses bacteria to degrade organic and inorganic matter, resulting in pollutant bioremediation as well as bioelectricity generation (Logan et al., 2006). Toxic pollutant removal technologies currently in operation consume a lot of electricity, additives, and capital with little return on investment. As a result of these issues, new facilities have been redesigned and operated to focus on removing toxins and recovering capital, reducing electricity use and improving energy recovery. The energy savings, less active sludge generation, the ability to run at any temperature and the output of energy are all benefits of MFCs, making them an ideal tool for environmental remediation as opposed to traditional approaches (Watanabe, 2008).

6.4.6 Integrated microbial fuel cell and bioelectrochemical system constructed wetlands

The optimal operating parameters have been investigated to improve the capabilities of bioelectrochemical reactors (BERs) in eliminating refractory substances, such as reactor materials (Kong et al., 2014), voltage application (Mu et al., 2009), cosubstrates (Sun et al., 2016), and hydraulic retention time (Sun et al., 2015). Energy use is still a concern in bioelectrochemical reactors (BERs), but it is lower than in conventional physicochemical technologies. An MFC-BER coupled device with a microbial fuel cell could be used to efficiently reduce azo dyes



Microbial fuel cell
Escapa et al (2014)

Integrated Constructed wetlands with Microbial fuel cell

Bioelectrochemical system
Escapa et al (2014)

Integrated Constructed wetlands with Bioelectrochemical system

FIG. 6.4 Combination of constructed wetland with microbial fuel cell and bioelectrochemical system (Kumar et al., 2021, Escapa et al., 2014).

without needing extra energy input (Yadav et al., 2012; Li et al., 2016). In a previous analysis, it was discovered that when the applied voltage in the bioelectrochemical reactors was more than 0.7 V, energy processing was successful (Liu et al., 2015). The electrochemical technique has been effectively used to treat wastewater containing nitrogen, arsenic, heavy metals, and other contaminants (Merzouk et al., 2009; Grafias et al., 2010; Lacasa et al., 2012; Demir et al., 2015). Bioelectrochemical systems (BESs) incorporate biology and electrochemistry to transform the chemical energy present in the organic fraction of wastes such as manure and lignocellulosic biomass to electrical energy or biohydrogen (Pant et al., 2012). The microbial electrochemistry, a relatively new science, has recently been hyphenated with engineered wetlands for achieving intensification of yield, including some state-of-the-art designs that incorporate both CW and microbial electrochemical technology (MET) (Ramírez-Vargas et al., 2018; Yadav et al., 2012; Doherty et al., 2015). The microbial electrolysis cells (MEC) are similar to the MFCs in that they use a potentiostat or a power source to polarize the electrodes (Aguirre-Sierra et al., 2016; Srivastava et al., 2018). In terms of application in various fields, the BES-CW integration is still in its infancy; hence, new hybrid developments with successfully combined configurations are required.

Genetic engineering can increase the catabolic potential of the microorganisms used in phthalate esters bioremediation. By combining catabolic pathways from diverse backgrounds in the same host cell, genetic engineering allows researchers to create new degradation pathways. As a result, it is possible to create fungi and bacteria with several catabolic pathways (Chatterjee and Karlovsky, 2010). Even so, the bioremediation requirements and the selection pressure imposed through xenobiotics on natural microbes are not always in sync. For instance, xenobiotics containing low levels of net energy that are detrimental to microbes, are unlikely to be targeted by new receptors than nontoxic, high-energy producing xenobiotics because of their importance to human and animal health. These catabolic mechanisms would therefore be critical in the immediate future for the elimination of harmful anthropogenic chemicals like DEHP from the setting (Chatterjee and Karlovsky 2010).

6.5 Conclusions and perspectives

The phthalate esters can be found in measurable levels in a variety of habitats around the world. The most commonly encountered phthalate ester pollutant in various environmental matrices is DEHP. Because of their potential biological magnifications, the ecological and health implications of these pollutants by wastewater at comparatively lower concentrations do need more attention. The biodegradation pathways for phthalates are often divided into two stages: primary biodegradation from PDEs to PMEs and then to PA, and ultimate biodegradation from PA to CO_2. Activated sludge technology, for example, is not designed to remove these micropollutants in conventional wastewater treatment. Although available treatment technologies, such as Constructed wetlands, The previous study intermittent-aerated CWs for treating low-carbon wastewaters, high DMP removal performances (88.5–97.9%) were achieved. PAEs were removed by CWs through two key processes: biodegradation and adsorption onto surfaces, integration of microbial fuel cell (energy recovery), and microbial electrolysis cell with constructed wetlands methods as promising alternatives are efficient for efficient removal of EDPs. Electrolysis at a high anodic potential resulted in quantitative oxidation of EDCs, resulting in CO_2 production. The bioelectrical reactors performed well in a prior investigation with operating parameters of 50 h HRT, 400 mg/L DMP, and 1.3 V applied voltage. We summarized recent progress and applications in eliminating organic pollutants from wastewater in this chapter. The biodegradation and absorption will eliminate phthalate esters from wastewater during certain wastewater treatment procedures (e.g., biodegradation, activated sludge operation, MBRs, CWs, MFC, BESs, and MFC-BESs-CWs) as well as in the future. This chapter suggests that constructed wetlands and bioelectrochemical system for Phthalate esters (PAEs) contaminated places is a cost-effective strategy.

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7

Bioremediation of androgenic and mutagenic pollutants from industrial wastewater

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7.1 Introduction

The major sources contributing hazardous pollutants to the environment are industrial wastewater several unknown pollutants (Sharma et al., 2021a, 2021b). The major causes of aquatic and soil contamination are most agriculture industries, for example, distilleries, tanneries, and pulp paper industries wastewater. Wastewater with very complicated organic and inorganic contaminants is released from the paper mills. Hydrogen sulfide, methyl mercaptan, chlorine dioxide, and primary gaseous pollutants, together with nausea and headache, are reported as chronic, respiratory and skin, eye, and heart disease abnormalities. The main toxic substances contain Fe, Cu, Ni, Zn, and Mg, which have been notified of catfish's neurotoxicity (*Ictalurus punctatus*). Their bioaccumulation was reported highest in the gills, followed by liver, ovary, and muscles. The primary identified organic and inorganic contaminants are palmitic acid, straight-chain alkane named octacosane, a phytosterol called β-sitosterol, trimethyl-silicic acid, and other, 1-tetradecane, guaiacol (2-methoxy phenol), 3,4,5-trichlorocatechol, 3,4,5,6-tetrachlorocatechol, organochloride of phenol like chlorophenols, chlorocatecholes, aromatic compounds like terpenes, and methanol. Many of them are identified as chemical perturbance of the endocrine reported for aquatic flora and animals (Singh and Chandra, 2019). *Salmonella typhimurium*, *Vibrio fischeri*, fungi, and fish showed significant growth inhibition and decreased bioluminescence in in-vitro

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experiments. The independent studies on eastern mosquitofish (*Gambusia holbrooki*) and rainbow trunks fish (*Oncorhynchus mykiss*).

Several studies have found Rainbow trunks fish and eastern mosquito fish (*Gambusia holbrooki*) have smaller gonads, alterations in secondary sexual character, delayed development, and no sex hormonal agents. The presence of organic and inorganic pollutants in wastewater causes chromosomal abnormalities that are genotoxic in *Allium cepa* (Dutta et al., 2018). Therefore, the text concluded that contaminants found produce unpleasant breath and induce hermaphroditism in fish, hepatotoxicity, and carcinogenic damage. Furthermore, coliform bacteria development in rivers and other water resources has been detected due to waste contamination. Most industrial waste contaminants lead to masculinization and a decrease in the number of fish glands. Due to its hydrophobicity and capacity to enter cell membranes, the low-molecular-weight (LMW) compounds of waste generated during the process has been described as the main source of teratogenicity and bioaccumulation (Savant et al., 2006).

The resin acids accumulate in fish livers and bile, causing liver and red cell disruption such as rapid red-colored cell disintegration and abnormal iron metabolism (Kostamo et al., 2004). It also reduces reproductive hormone levels and may disrupt the formation of cells (Christianson et al., 2008). Wood sterols, for example, are related to a class of steroid hormones that can impede human growth and reproduction (Mattsson et al., 2001). The concentrations of these substances are minimal, and the hormonal balance of aquatic organisms has not been disrupted. Furthermore, even slight amounts of resin acids in an organism's liver and bile might cause long-term problems (Rissanen et al., 2003). During the 1990s, endocrine environmental chemicals became a major concern when they were discovered to have a wide-ranging impact on the aquatic ecosystem (Wangmo et al., 2018; Andersen et al., 2002; Blair et al., 2000; Houtman et al., 2006). Low natural steroid hormone levels already generate biological repercussions, as well as agonistic or antagonistic activity in steroid hormone receptors in synthetic and nonsteroidal substances (Houtman et al., 2009; Itzel et al., 2018; Liscio et al., 2014). Progestogens are female sex hormones that are active in the menstrual period, pregnancy survival, and embryogenesis. Progesterone (P4) is the primary endogenous agent in humans. Both humans and animals spontaneously secrete endogenous progestin like other steroid hormones. As active ingredients for contraception prescription in high quantities, synthetic progestogens are employed (Okubo et al., 2004; Rostkowski et al., 2011; Schriks et al., 2010; Sumpter, 2005). Therefore, endogenous and synthetic progestogens infiltrate the aquatic environment and interfere with the breeding of females in water species (Sauer et al., 2020; Sharma et al., 2020a, 2020b, 2021a; Sumpter, 2005). The low ng/L content in wastewater and surface water has been found in progestogenic hormones and progestatic activity in in vitro reporter gene bioassays (Chang et al., 2011; Golovko et al., 2018; Hashmi et al., 2020; Houtman et al., 2018). The activity of these chemicals to alter human-animal health is widely reported (Sauer et al., 2018). This chapter includes an updated summary of EDCs formation, features, toxicity, and options for elimination, including physical, chemical, and biological processes.

7.2 Characterization of androgenic and mutagenic pollutants

Groundwater absorbs enormous amounts of industrial, agricultural, and household polluted wastewater (Ohe et al., 2004). Mutagenicity and endocrine interference are both major endpoints for assessing water quality in drinking water production and for toxicological and environmental testing of drinking water sources (Sharma and Rath, 2021). The urban or industrial wastewater, on post-combustion, dispose of Mutagens and EDCs such as sex hormones, glucocorticoids (GCs), and their metabolites in the agricultural rivers (polycyclic aromatic hydrocarbons) (Blankvoort et al., 2005; Durhan et al., 2006; Houtman et al., 2006; Luvizutto et al., 2015). Furthermore, in wastewater treatment transformation, UV/peroxide oxidation and water ozonation phase contribute to the degradation and by-product of steroidal hormones (Carballa et al., 2004; Mestankova et al., 2014). In efforts to keep track of their release into the environment and ensure their removal during the purification process, the capacity to establish the presence and identity of mutagens and EDCs in the potable, subsurface, subsoil, and wastewater water is essential. Betulinol is a steroid (Sharma et al., 2021c, 2021e). Wood-based estrogenic chemicals may cause reproductive failure in fish if discharged through industrial wastewater into the aquatic ecosystem (Christianson et al., 2008). There is some evidence that wood extractives, particularly betulinol, may have endocrine effects on fish throughout their developmental or maturation stages, as well as during their exposure period. Betulinol has also been shown to help rainbow trout (*Oncorhynchus mykiss*) develop faster when exposed to wastewater and other wood extractives (Mattsson et al., 2001). Betulinol is estrogenic compared to -sitosterol and -sitostanol, although not as much as estradiol (Figs. 7.1–7.3).

Only a tiny percentage of extractive chemicals, like sterols, get adsorbed to the sludge within the primary clarifier, and activated sludge is the major treatment for their removal (Kostamo et al., 2004). In the water phase, sterols are more likely to exist than in wastewater treatment particles. After the initial treatment, sterols are often adsorbed to a primary sludge, while some are already eliminated due to microbial activity (Sharma and Singh, 2021). Sterols are more resistant to transformation than the breakdown in biological treatment (Rostkowski et al., 2011). Moreover, betulinol with wood sterols may be desorbed sediments in the water (Latorre et al., 2005). High levels of betulinol and wood sterols can be dissolved and hazardous for aquatic species in the case of widespread erosion (Rissanen et al., 2003). The potential adverse effects

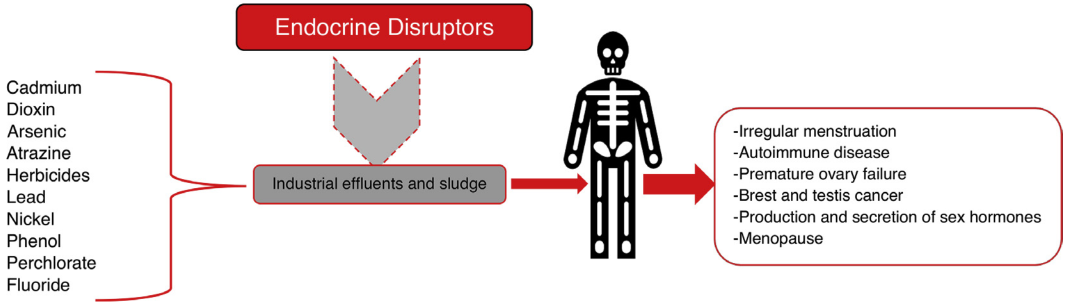

FIG. 7.1 Types of endocrine-disrupting pollutants and their effects on humans.

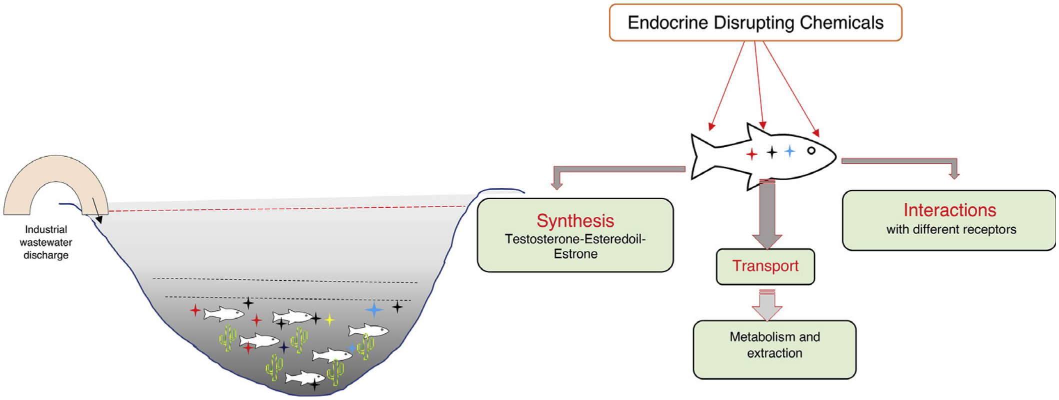

FIG. 7.2 Endocrine-disrupting pollutants effects on fishes.

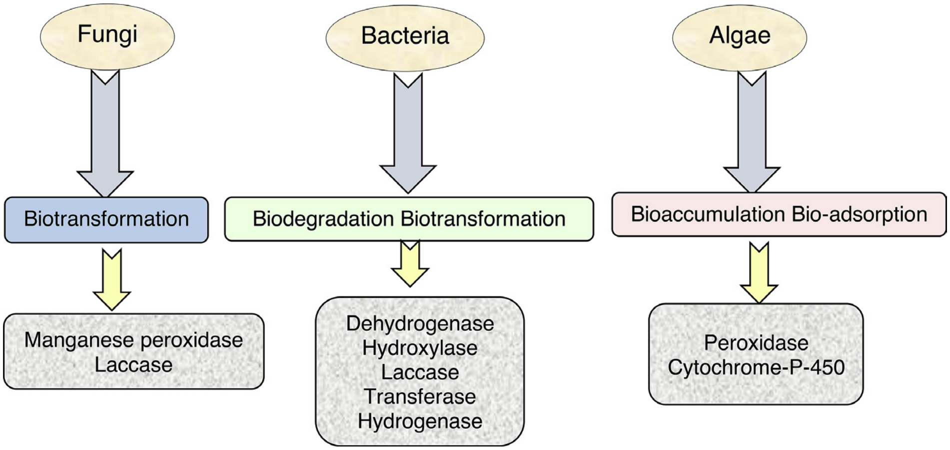

FIG. 7.3 Bioremediation of endocrine-disrupting pollutants using different microbial mechanisms.

drinking streams is biocides (Latorre et al., 2005; Oller et al., 2011). Due to their great solubility, their growth in the environment is relatively easy. Several biocides are resistant chemical and photocatalysis breakdown under regular environmental conditions. Many of these effects are carcinogenic, neurotoxic, and have long-term consequences for fertility and cell development, especially in the early stages of life. The surface water of streams and ditches next to lakes, farmland, and reservoirs contains biocides (Liess and Ohe, 2005; Skark et al., 2004).

7.3 Toxicity assessment of androgenic and mutagenic compounds

The examination of the mutagenicity in surface water only shows the potential risk of the toxins and their features (Ohe et al., 2004). In particular, groups of strains of *Salmonella* are sensitive and may be utilized to identify genotoxicants in environments (Shiozawa et al., 2000).

Ecological mixes comprise possibly carcinogenic, unidentified, and unregulated toxicants. Sewage treatment techniques do not effectively remove all hazardous chemicals, and the procedure can enhance the mutagenicity of wastewater due to derivatives created during water treatment activities. Exposure analysis is among the steps in which environmental effects are assessed, that is to say, potential exposure to EDCs residues from food, water, air, and soil from animals, plants, and water resources can be quantified by a profile of exposure (Cohen Hubal et al., 2010). In addition, ecological findings have presented a broad picture of the fate and degradation of primary EDCs compounds. Data from silicic simulations, in vitro tests, in vivo testings, and field investigations have been used to establish a quantified environmental destiny profile for EDCs exposure evaluation by the United States Environmental Protection Agency (https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk).

Heavy metals like Cu, Hg, Fe, As, Zn, Mn, Cd, Pb, and Cr, including organic regulators, can adversely affect reproductive hormones (Farkas et al., 2000; Handy, 2003; Lwanga et al., 2003; Nawaz et al., 2010). Furthermore, living organisms can be highly hazardous to their own native/compound or nanoparticular forms, based on exposure and ability stage (Deepa et al., 2019; Denier et al., 2009). Several of those investigations utilized mature or juvenile fish to assess the risks to human health owing to bioaccumulation as indicators of toxic metals in several aquatic environments (Vives et al., 2006). Current research has found Hg, Cd, Fe, Cu, Pb, Zn, and methyl mercury (Me-Hg) endocrine-disrupting activity on the axis of HHG in different fish (Cao et al., 2019; Gárriz et al., 2019; Olivares-Rubio et al., 2015; Tilton et al., 2003). This research on zebrafish found an adverse effect on many brains and sex steroid receptor genes of metallic compounds, $BaCl_2$ (Kwon et al., 2016). The section discusses the toxicity of androgenic and mutagenic pollutants in wastewater.

7.4 Endocrine-disrupting pollutants effects on the reproductive system

One of the main issues in this context is the contamination of wastewater with potentially EDCs substances. Several studies showed a decrease in female spawning and decreased motility, spawning, and fertilization in teleost aside from physical deformities and ovarian disorders (Wu et al., 2003). Decreasing the rate of hatching in zebrafish was seen when a pesticide was exposed to toxaphene. The p,p\-DDE exposure impacted the expression of reproductive genes and histologic anomalies in mature oocytes, particularly largemouth bass and zebrafish (Garcia-Reyero et al., 2006; Monteiro et al., 2015). Long-term exposure to carbaryl harmed fathead's survival, development, and reproduction and resulted in larval fatalities. Furthermore, the lake trout, *Salvelinus namaycush*; the rainbow trout*, O. mykiss; Atlantic salmon*, *S. salar*; zebrafish, and *Danio rerio*, have all shown early-life-stage mortality (Hansson and Hahn, 2008; King-Heiden et al., 2012). A perchlorate report showed that the success of zebrafish spawning had been reduced significantly (Mukhi and Patino, 2007).

7.5 Microbial remediation of androgenic and mutagenic pollutants

The rising population and industrialization are causing major freshwater pollution by a range of micropollutants, mainly EDCs. Wastewater treatment plants ever can extract EDCs fully, and it is then discharged directly into the environment and released in wastewater effluent. The growing interest inefficient and ecologically friendly wastewater treatment technologies have sparked concerns about the EDC's present management tactics. One intriguing strategy for EDCs treatment is to boost the effectiveness of treatment facilities with microbial populations, microalgae, or fungi (Roccuzzo et al., 2021). The application of next-generation sequencing (NGS) to microbial phylogenetic research has aided in interpreting microbial functional roles in the transformation and degradation of contaminated environments (Bai et al., 2014; Feng et al., 2018). Traditional treatment facilities are based on a wastewater treatment microbiome to break down EDCs (Itzel et al., 2018). In these systems, primary filtered wastewater is routed to a reactor with a mixed microbial population that is aerated to provide oxygen to aerobic EDCs binding and decomposing bacteria. This method also makes it easier for contaminants to bind to organic materials and then be separated from the treated waste quickly and efficiently (Scholz and Lee, 2006). Extracellular polymeric substances (EPS) generation and properties depend on the creation and preservation of flocs. The EPS may aid in the uptake of nutrients from the environment as well as the adsorption of organic pollutants by interacting with relative, polysaccharides, lipids, and nuclear acids (Flemming and Wingender, 2010).

Wastewater treatment systems do not achieve ultimate removal efficiencies and 100% EDCs breakdown (Aissani et al., 2018; Eio et al., 2014; Servos et al., 2005). Temperature, hydraulic retention period, and bucking age are only a few of the operational elements that affect EDCs (Balabanic et al., 2012; Liu et al., 2009). The efficiency of the elimination of these micropollutants might be improved by using sophisticated oxidation, activated carbon sorption, nanofilter, photocatalysis, physical, and chemical treatment technologies (Aissani et al., 2018; Ayuba et al., 2019; Bartolomeu et al., 2018; Fernando et al., 2019; Khan et al., 2020; Mohammadi et al., 2020; Polloni-Silva et al., 2017). This is successful, but it is rarely used in large systems due to the high chemical and operational costs and the generation of complicated waste sludge, which makes it impractical to treat large amounts of wastewater (Liu et al., 2009; Nawaz and Ahsan, 2014). Metal–organic framing (MOF) is a new type of adsorption framework that has been proposed in wastewater to remove micropollutants (Dehghan et al., 2019). Furthermore, many key challenges need to be tackled, including prices, adsorption capabilities, structural stability, dispersibility, and soluble (Khan et al., 2020). However, since the impacts of present environmental management policies have increased in knowledge and concern, there is a drive for developing effective and environmentally acceptable technologies for EDCs processing. One intriguing approach in this area is that conventional wastewater systems with particular microbial communities that include microalgae, fungi, etc., can be improved to remedy endocrine activity with natural environmental circumstances (Sharma and Singh, 2021).

Several enzymes and secondary metabolites are used in biotechnology to create various technically helpful bacteria that help reduce pollution impacts (Sharma et al., 2021d). Bacteria, cyanobacteria, microalgae, and fungi can effectively degrade endocrine-disrupting contaminants by sorption, aggregation, as well as other intra and extracellular enzyme activities (Hashemian et al., 2019; Liu et al., 2009; Sharma et al., 2021d; Wang et al., 2017; Xiong et al., 2018; Yu et al., 2013). Microalgae or mixed populations of microalgae have also been more effective than single microbes in the bioremediation of contaminants and the simulcasting of minerals (Xiong et al., 2018). Furthermore, when used in conjunction with commonly activated lobster systems, microalgae-bacterial mutualistic communities can reduce high electrical energy needs. Microalgae can supply oxygen to aerobic bacteria via photosynthesis while consuming carbon dioxide released from the microorganism's respiration (Ariza, 2018). On the other hand, EDCs enzymes appear to have different properties depending on whether they derive from microalgae, bacteria, or fungi (Illanes, 2008; Jia et al., 2016). Pollution from low levels of bioactive chemicals, particularly interference with steroid hormone systems, affects the quality of the surface waters (Luvizutto et al., 2015). Such substances arise from various uses in industry, residences, and farming are frequently dumped inside the freshwater by wastewater treatment plant effluents (Di Marcantonio et al., 2020; Houtman, 2010; Kasprzyk et al., 2009).

7.6 Conclusions and perspectives

Androgenic and mutagenic pollutants released by industrial wastewater/effluent into aquatic ecosystems, mostly from treatment and diffusion, and impact many aquatic biota, such as fish. Furthermore, ongoing efforts should be made to develop suitable consortia that work in various conditions and assist in the recovery of valuable products from wastewater. Although these realities, strict discharge rules must be applied on the one hand, and researchers and the scientific community must create cutting-edge technology. As described, further work can be done to generate biohydrogen and bioelectricity from industrial waste. This will enhance the industrial economy by generating green energy. Bioremediation strategies were used to remove androgenic and mutagenic chemicals from industrial wastewater in the majority of the studies. The commercial viability of bioremediation as a cost-effective and efficient approach must be investigated. Microbes' genomes can be utilized to enhance modified microbial strains with improved biodegradation properties. This chapter includes a careful evaluation of reports of EDCs on fish behavior with a focus on reproductive potential. Microbial-aided remediation demonstrates novel strategies for reducing pollutant and toxicant levels in the environment.

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8

Toxic effects of the endocrine disrupter on plants

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8.1 Introduction

The extensive application of modern technology, accelerating growth of urbanization, and simultaneous progress in the industrial sector has resulted in comfort and flexibility in our daily life but elevated successive degradation to the environment. The disposal of hazardous toxic chemicals with wastewaters and solid wastes originating from different industrial and domestic activities cause such devastating consequences on natural resources that reduce the normal living quality of a particular residential zone further lead to major health problems. A survey of the World Health Organization (WHO) has reported that environmental exposure to different noxious chemicals results in approximately 13 million deaths per annum mostly in developing and less developed countries. The manifestation of different chemicals and biological elements is responsible for such genetic and epigenetic systems that hamper normal psychological development and body growth (Erkekoglu and Kocer-Gumusel, 2016).

Among these toxic chemicals, endocrine disruptors (EDs) are getting more attention among scientific communities for their adverse effect on human physiopathology. According to WHO, “An endocrine disruptor is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations” (Combarnous, 2017). Furthermore, the US Environmental Protection Agency (USEPA) describes an endocrine disruptor as an exogenous substance that may inhibit the synthesis, exertion, transference, metabolism, receptor binding, or reducing of endocrine hormones, thus altering the endocrine and homeostasis system (Lauretta et al., 2019). Endocrine disruptors mostly appear in various day-to-day commodities including drugs and medicines, food packaging, plastic bottles, cleansing agents (detergents/surfactants), toys, cosmetics and toiletries, flame retardants, and pesticides that act as interference with normal hormonal systems, often mimic endocrine hormones and produce negative influences on the

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developmental, neurological, immune, reproductive system in mammal breeds (Yang et al., 2015). Therefore, several scholarly articles and review papers have been documented on the characterization of EDs including their action mechanism, hazardous impacts on human health, and precaution strategies to raise global public health awareness (Kahn et al., 2020; Yilmaz et al., 2020).

Lauretta et al. (2019) classified endocrine disruptors as industrial (dioxins, polychlorinated biphenyl (PCB), alkylphenols, bisphenol A (BPA)), agricultural (pesticides, herbicides, phytoestrogens, methoxychlor, dichloro-diphenyl-trichloroethane (DDT), nonylphenol (NP)), residential (phthalates), and drug agents (17-β estradiol, parabane) based on their sources. However, some heavy metals such as mercury, lead, cadmium, and arsenic may be act as EDs. The consumption of contaminated food and potable water, direct contact with contaminated consumer products are the two topmost vital reasons that stand for EDs exposure to living organisms (Strauss III and Barbieri, 2013). Various plant parts such as stems, roots, leaves are often consumed as a daily diet because they are considered as a good source to fulfill the basic need of different proteins, vitamins, and other essential nutrients of the human body. Scholars showed that toxic symptoms (chlorosis, necrosis, germination reduction, etc.) are higher in those plants that are grown around industrial zones, dumping yards, and around wastewater treatment plant (WWTP) owing to a higher bioconcentration rate of toxic matters in their edible/reproductive organs than most other plants grown elsewhere (Clemens, 2019; Xaba et al., 2018). As a result, profound knowledge on the EDs toxicity in plants is also important since such plant species can be a common trail to introduce EDs in the human food chain, though very scanty information is available in the existing literature (De Bruin et al., 2019; García-Cortés et al., 2018; Kim et al., 2019).

In this context, this chapter elucidates a brief review on the EDs toxicity in the plant life cycle including the exposure route, different toxic symptoms in various plant cell organs based on the findings of previously published research articles. Additionally, the chapter may help the readers to accomplish a clear concept of plant toxicity and motivate other researchers to flourish the chance of future research on this burning concept.

8.2 Presence of endocrine disruptors in plant environment

Mainly, plants are subjected to come in contact with EDs via multiple routes. Industrial wastewaters originated from various industries such as paper and pulp, tannery, distillery, fabric manufacturing, etc. are considered as the key route to release EDs into the environmental milieus (Haq and Raj, 2019). Besides, effluents from WWTP, agricultural runoff containing residual pesticides and fertilizers, livestock wastes and feedstock are also responsible for significant EDs load into natural watercourses (Gonsioroski et al., 2020). Some EDs (NP, BPA) are present in soil through the disposal of sediment, biosolids, and sewage sludge (Novo et al., 2018) (Fig. 8.1). The presence of EDs in air occurs from house building materials, furnishing agents, unconventional oil and gases (UOG), flame retardants, and multiple industrial solvents for their volatile characteristics (NP, Phthalates, Alkylphenols, fragrance agents) (Bolden et al., 2018; Rudel and Perovich, 2009).

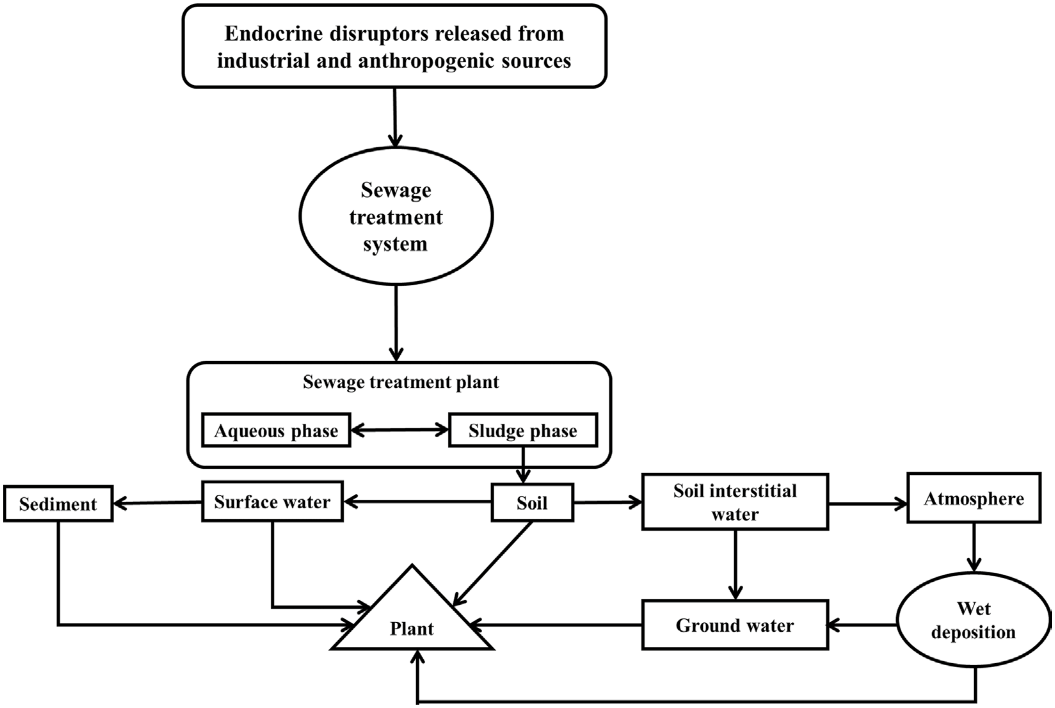

FIG. 8.1 Sources of different endocrine disruptors and their exposure routes to plants, reprinted from Haq and Raj (Haq and Raj, 2019) after modification with permission from Springer Nature.

8.2.1 Soil

The disposition of endocrine-disrupting chemicals in the terrestrial environment occurs from solid wastes of different manufacturing industries, accidental spills, landfilling materials (sediments, WWTP sludge) as biosolids, pesticide/herbicide spraying, and wastewater (both sewage and industries) irrigation process (De Bruin et al., 2019). EDs can easily get absorbed by condensed organic particulates present in soil matrix due to their low solubility, hydrophobicity, and other physicochemical characteristics, and later accumulates into the living cells (both microorganisms and fauna [snake, earthworms, and insects]) (Sun et al., 2010). The translocation of EDs from wastewaters or sediments to soil depends on factors like organic carbon–water partition coefficient (K_{OC}) or soil–water partition coefficient ($K_{soil\text{–}water}$) (Kwak et al., 2017).

Previous studies have shown that the storing of EDs into the soil (more or less than the threshold limit) as residues from various manmade activities results in soil ecotoxicity and these EDs are further uptaken with other nutrients by the plants grown on that soil (Loffredo et al., 2021; Qhanya et al., 2017; Zhang et al., 2018). An eco-epidemiological survey on market available 175 crop protection compounds (CPCs) (herbicides (48%), insecticides (29%), and fungicides (23%)) was piloted by the General Direction of Agricultural services in Uruguay to witness the spatial distribution of EDs in soil and their translocation in some common crops including wheat, rice, barley, sugarcane, corn, soybean, and other fruit and vegetable plants which concluded that the selective crop species was acknowledged as the initial hotspot associated with the introduction of EDs into biota (Eguren and Rivas-Rivera, 2018). While conducting a comprehensive study at Khyber Pakhtunkhwa, Pakistan, researchers assessed the total concentration of 30 endocrine-disrupting pesticides including ß-hexachlorocyclohexane, endosulfan sulfate, ß-endosulfan, dieldrin, heptachlor epoxide, etc. ranged 192–2148 μg/kg in the respective soil samples (120), recorded the concentration of these EDs in six different plant species such as lettuce, radish, turnip, garlic, spinach, and onion at a range between 14.7 μg/kg and 28.9 μg/kg, and however they found no possibility of lifetime cancer risk related to their ingestion ($<10^{-6}$) (Ali et al., 2019).

Although there may or may not have potential health risks associated with the vegetative plants grown in EDs containing soils for the tolerable EDs concentration, the practice to use legacy chemicals as crop protecting agents(CPAs) in agricultural sites should be controlled strictly for future environmental sustainability.

8.2.2 Air

EDs are distributed in atmospheric conditions as volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), or by attachment with other particulate matters by evaporation, and their presence is found in both indoor and outdoor air (Darbre, 2018). Researchers showed that endocrine disruptors like phthalates, NP, BPA, parabane, etc. can be vaporized to the atmosphere from different emission passages viz. industrial processes, geological location, usages of excess chemical appliances, personal care products (deodorant, antiperspirant, perfumes, etc.), incineration of solid wastes, WWTP, domestic heating, and cooking by solid fuel (Annamalai and Namasivayam, 2015; Darbre, 2018). The emission of EDs in air depends on three equilibrium coefficients such as air–water, water–octanol, and octanol–air (Jayshree and Vasudevan, 2018). Once endocrine disruptors reach the air, they can probably return to the plant environment through wet deposition (rain, storm falls, and snow) (De Bruin et al., 2019). Plant breeds come in contact with EDs-loaded air while consuming carbon dioxide during the carboxylation process in photosynthesis.

8.2.3 Water

Wastewaters originated from both industrial activities and household chores, sewage sludge, landfilling sediments, agricultural runoffs containing residual pesticides, animal excretion, and graywater from laundries and domestic cleaning has been considered as the possible sources to spawn EDs-load into surface water and aquifers (Caballero-Gallardo et al., 2016; Wee and Aris, 2019). Farounbi and Ngqwala measured the concentration of ten endocrine disruptors including 4-NP, 2,4-dicholorophenol (DCP), BPA, estrone, triclosan, 17ß-estradiol, 4-tert-octylphenol, imidazole, atrazine, and triazole in four river waters and WWTPs of the Eastern Cape province in South Africa and found that the concentration of NP was 6.72 μg/L in wastewaters of King Williams Town and 2.55 μg/L in the Bloukrans river's midstream (1–10 μg/L = polluted), also DCP was estimated 2.20 μg/L and 0.737 μg/L in the water samples collected from Alice wastewater influent and Bloukrans river's midstream, respectively. While BPA was found

0.477 μg/L (permissible limit = 0.01 μg/L) in Bloukrans river's downstream which depicted noticeable threat of EDs load in surface water (Farounbi and Ngqwala, 2020). In Austria, a survey was conducted in 2017 and 2018 on water samples collected from surface water (*n* = 12) and groundwater (*n* = 22) including bathing water (*n* = 5) and river water (*n* = 7) to assess the concentration of common EDs such as BPA, alkylphenol, triclosan, estrogens, phthalates, perfluoroalkyl substances, and polybrominated diphenylethers (PBDPEs), and the findings of the survey showed that BPA was found in most of the water samples of them two samples exceed threshold limit (0.01 μg/L) set by the European Commission (Brueller et al., 2018). Besides, the sewer flow (already contains industrial and domestic wastages) exceeds its capacity while mixing with both rainwater and stormwater during the rainy season and finally discharged into natural water streams as a combined sewer overflow (Pironti et al., 2021). Owing to the emerging scarcity of fresh water in around the world, governing authorities are encouraging wastewater irrigation in vegetable cultivation among farmers around municipalities to meet the demand for vegetable protein in human's daily diet (Singh, 2021). Although reclaimed water after wastewater treatment fulfills the demand for irrigation water in crop harvesting at country town sides, the consequences of wastewater irrigation for perennial period and immersion of plants under flood and stormwater causes deposition of EDs into soil and the chemicals translocate into plant parts through bioaccumulation that leads toward toxic symptoms during prolonged exposure (De Bruin et al., 2019).

8.2.4 Harvesting materials

Most of the CPCs are chemically classified as endocrine disruptors. Among 105 CPCs around 46% are enlisted as insecticides, 21% include herbicides, and 31% are fungicides (Mnif et al., 2011). The most common EDs that are found in CPCs are NP (pesticides and fertilizers), alachlor (herbicides), endosulfan (insecticides and acaricides), DDT, and metabolites (insecticides), iprodione (fungicides), etc. (McKinlay et al., 2008). These chemical compounds are assumed to be persistent in environmental elements which can lead toward consecutive environmental degradation and highly accumulative in sediments and organs of living biota depending on their solubility and mobility through the food chain that consequences vigorous diseases in both human and other living organisms (i.e., plants, microbes, and other vertebrates) in the long-term exposure (Fatma et al., 2018). Among CPAs, pesticides show several toxic symptoms in plants resulting in chlorophyll reduction (which inhibits photosynthesis rate) and protein content (causing cleavages in peptide chain), augments oxidative stress that decreases enzymatic activities (Sharma et al., 2019). Moreover, a combined toxic effect is observed due to synergism and antagonism between pesticides and heavy metals that occurred from sediments and sludge causing biomolecular cleavages in plant cells, concealment of roots, leaf twisting, and cell tissue damage (Table 8.1). Besides, some herbicides (mostly systemic herbicides) imitate plant hormones (phytoestrogens), necrosis, genetic and chromosomal malfunctions, chlorosis, and stuns plants regular growth rate at long-term storage in plants reproductive organs and finally lead on the verge of fatality (Alengebawy et al., 2021). Furthermore, insecticides are responsible for resuming pollination in flowers apart from killing pollinator insects like honeybees and butterflies (Bakshi et al., 2020). Scientists opine that if the toxic effect of EDs

Table 8.1 Individual and conjugal (with heavy metals) toxic effects of pesticides and other CPAs in plants slightly modified from Alengebawy et al. (Alengebawy et al., 2021), which is licensed under CC BY 4.0 and permission was taken from the corresponding author.

Individual toxic effects

Crop protecting agents	Plant toxicity
Insecticides	Dilution in grain protecting matters, congestion in stomatal transportation, alteration in photosynthesis
Herbicides	Decrease biochemical and physiological activities in plant body, reduces plant immunity and raises susceptibility toward various diseases
Fungicides	Reduces chlorophyll, carotenoids and other pigment contents, suppression in electron transportation, destruction of plastids, stomatal closure

Conjugal toxic effects

Pesticides	Heavy metals	Conjugal effect type	Plant toxicity
Acetochlor Bensulfuronmethyl	Cd	Synergism	Degrade soluble protein, influence in nitrate reduction, suppress root and shoot growth
Acetochlor	Pb	Synergism and antagonism*	Inhibit root elongation
Glyphosate	Cu	Synergism and antagonism*	Change the cell membrane and tissue structure, peroxidize cellular lipids, higher generation of reactive oxygen species (ROS)
Glyphosate	Zn	Antagonism	Prevents phytotoxicity of destructive weeds

**Depending on the concentration of pesticides and heavy metals.*

containing CPCs on living organisms continues onward, it will cause a diminishing of biodiversity that includes scarcity of safer foods and crisis of famine diseases, which will be a potential obstacle in our gradual prosperity (Hashimi et al., 2020).

8.3 Assessment of endocrine disruptors on vegetative plant parts

It must be kept in mind that endocrine disruptors can show a negative impact on the ecosystem and living cells at a very lower concentration hence their detection level should be very much precise and measured with higher accuracy. The analytical methods to analyze EDs in a specimen upon subsequent screening require selective analytical instruments and standard methods with a very low detection limit (LD) and quantification (LQ) (Hrouzková and Matisová, 2012). The general procedure to measure EDs concentration in a plant material involves sample extraction after pretreatment, purification/separation, and detection, since EDs are diversified in chemical characteristics and molecular configuration, multiple analytical methods are employed to measure their concentration with a possible degree of accuracy. The pretreatment process of specimens is indulged in proper drying of plant material and extraction upon selecting a proper solvent (methylene chloride, hexane, isooctane, acetonitrile, and sometimes with a mixture of solvents). The solid samples are completely digested and extracted homogenously by following standard extraction techniques such as ultrasonication, steam distillation, soxhlet extraction, liquid–liquid extraction, and solid-phase extraction (De Bruin et al., 2019).

After extraction, the analytes are subsequently taken for EDs detection following various analytical equipment, and chromatographic methods have been reported as the most favorable approach of all (Hrouzková and Matisová, 2012). Over times, chromatographic techniques like high performance liquid chromatography (HPLC), liquid chromatography (LC), and gas chromatography (GC) are coupled with mass spectroscopy (MS) or tandem MS, fluorescence detector, and biosensor-based methods are the most frequently used techniques with satisfactory detection levels in analyzing EDs (nonylphenol, α- and β-endosulfan and three main metabolites (sulfate, ether, and lactone)) in food items, CPAs, environmental matrices, human adipose tissue and in plants like soft wheat (*Tríticum aestívum*), fern (*Polystichum setiferum*), tomatoes (*Solanum lycopersicum*L.), mung bean (*Vigna radiata*), and rice (*Oryza sativa*) (Eltzov et al., 2009; Esteban et al., 2016; Jiang et al., 2019; Kim et al., 2019; Kuzikova et al., 2019; Vidal et al., 2006). Besides, enzyme-linked immune sorbent assay (ELISA) has been reported as a more efficient method than chromatographic methods for measuring BPA in canned vegetables because of achieving lower limit of detection (LD) compared to conventional methods (De Meulenaer et al., 2002). In recent advances, technologies like LC–MS, ultraperformance LC coupled with tandem MS, highly superficial fluid chromatography tandem MS have been developed for EDs detection to augment signal intensity and decrease detection time (De Bruin et al., 2019; Hrouzková and Matisová, 2012).

8.4 Toxicological impact of endocrine disruptors on crops and vegetables

8.4.1 Phytotoxicity

The term “phytotoxicity” refers to any visual damage that interrupts normal plant growth. It can appear in several ways owing to the adverse effect of a particular agent (phytotoxin) and mostly five types of damages are commonly observed such as leaf burning, necrosis, chlorosis, leaf distortion, and abnormal plant growth. The phototoxic syndromes occur mostly from spraying of pest controlling chemicals in ornamental plants in commercial nurseries and also in other harvesting and aquatic plants that come in contact with such agents in agricultural sites and agricultural leachates (Mizell III and Short, 2015; Short, 1981). Short (1981) observed that soil soaked with pest controlling agents can harm root tissues during water absorption, cause slow plant evolution, and damage foliage leaves faster than old ones. De Bruin et al. (2019) showed that EDs like nonylphenol (NP) inhibits normal plant growth, decreases biomass content, and reduces germinal activities, interrupts ATP production during respiration, and damages cellular organs (mitochondria, chloroplasts, and chromoplast degradation). They also documented the capability of NP in mimicking natural allelochemicals (phytohormones) and disappearing effect on mitochondria in plant cells of *Oryza sativa* L. (rice) and *Lemna minor* L. (duckweed/khudipana) in their review paper. The phytotoxicity of BPA induces into broad bean (*Vicia faba* L.), tomato (*Lycopersicon esculentum* Mill.), durum wheat (*Triticum durum* Desf.), and lettuce (*Lactuca sativa* L.) after 21 days of accumulation under hydroponic conditions that causes noticeable morphological anomalies and reduction in dry weight and length of roots and shoots of the plants, and showed clastogenic effect and xenobiotic side effects on soil. After accumulation from soil to plant BPA completely transforms into glycosylated (a highly polar and nonextractable compound) that excludes its detection in plant material (Ferrara et al., 2006). Besides, inorganic endocrine disruptors like heavy metal ions, alums, and amalgams show phytotoxicity such as cell elongation, root growth inhibition, reduces turgor pressure during osmosis, DNA degradation, decreases enzyme secretion from cell walls, homeostasis, and photosynthesis reduction due to protonic corrosive nature even at lower ionic strength or lower cationic concentration (Ernst, 1996; Santos et al., 2014). Because of phytotoxicity plant roots lose a significant amount of hair and root cells become thicker (due to less growth), which adversely affects water absorption and nutrient uptake rates, finally causes death to plants and accelerates the decay of plant-diversity (De Bruin et al., 2019).

8.4.2 Genotoxicity

Genotoxicity is designated as one of the most significant endpoints to evaluate the toxic effect on living organisms, analyze chemical toxicity of a particular chemical agent associated with their environmental and public health risk assessment (Martínez-Paz et al., 2013). Both estrogenic and antiandrogenic EDs are responsible for genotoxic symptoms in plant organs including epigenetic mechanisms like hormonal disturbance, peroxisome accretion, DNA methylation, histone modification, RNA interruption, dysfunction of cellular metabolism, chromosomal aberrations, cell death (apoptosis, autophagy), etc. The biological influence of phthalates is getting major concerns due to their epigenetic effect which can be transferred to future generations by bringing about alterations in genome sequences. Also, the biotransformation of BPA is reported in vertebrates, invertebrates, plants that cause DNA deformation, protein degradation, chromosomal aberration, and alters in metabolic degradation in different microbial strains (bacteria, algae, and fungi) (Erkekoglu and Kocer-Gumusel, 2016). Triclosan (TCS) shows severe chronic impact than temporal (acute) influences on aquatic plants (*Lemna minor, L. gibba*), crops (*T. aestivum, O. sativa L., C. sativas*), cyanobacteria and green algae (*Chlamydomonas* sp., *D. tertiolecta, S. subspicatus*), and its high sensitivity toward microorganisms that may create disturbance in ecological balance. Studies showed that residual sediments and sludge from WWTPs are the main source of TCP for its introduction to soil, in which it becomes persistent under anaerobic conditions, and finally transported to plant tissue through bioaccumulation (Bedoux et al., 2012). Wastewaters generated from pharmaceutical industries containing residual drug agents and antibiotics elucidate reproductive toxicity in *Daphnia magna* (phytoplankton) including a reduction in age, antagonism, decrease in offspring number, and cause synergistic effect in future generations (Hamid et al., 2021). Besides, the residual organic by-products endured in tannery wastewaters after secondary treatment showed chromosomal aberration in agricultural crop *Allium cepa* (onion) during four stages of cell division, nuclear abnormalities, chromosomal loss, colchicine mitosis, and less mitotic index (Yadav et al., 2019). Veterinary drug agents (e.g., hormones, growth promoters, antifungals, and miscellaneous medicines) such as ionophores, sulfonamides, halofuginone, enrofloxacin, levofloxacin, trimethoprim, etc. can cause seed germination, toxoplasmosis, reduce photosynthesis and respiration, decreases cellular growth and development, reduce water and nutrient uptake capacity in several plant species including edible crops, vegetables, and forage crops such as *Cucumis sativus* (cucumber), *Oryza sativa* L. (rice), *Lemna minor* (duckweed), *Daucus carota* (carrot), *Triticum aestivum* (wheat), *Medicago sativa* (alfalfa), *Brassica campestris* (field mustard), and many more aquatic weeds (Bártíková et al., 2016). The uptake and transform of these xenobiotic endocrine disruptors hamper cellular growth that causes reduction in biodiversity and chemicals may enter into food chain resulting in fatal diseases in long-term exposure (Caballero-Gallardo et al., 2016).

8.4.3 Metabolic fate

While coming in contact with xenobiotic endocrine disruptors like NP, BPA, TCS, ROS is produced upon biotransformation of EDs materials that trigger an antioxidative defense system. The metabolic fate/biotransformation of EDs follows three sequential procedures that are: (1) transformation of the original compound into reactive intermediates upon hydrolysis/oxidation, (2) conjugation, and (3) compartmentalization. In the case of NP, enzyme (e.g., catalase, peroxidase, and superoxide dismutase) assisted reaction yields to hydrophilic and xenobiotic intermediate molecules that are neutralized by hydrophilic compounds like glucose, malonate/glutathione by forming water-soluble matters. These water-soluble compounds are distinguished by oxygen and hydrogen peroxide (HP) coming from cytosol to vacuole and apoplast during compartmentalization to produce water-insoluble particulates that are deposited into plant cell walls. Storage of such water-insoluble particulates may cause cellular deformation and cell damage on successive exposure to HP (De Bruin et al., 2019). Metabolic routes of accumulated BPA in different plants elucidate conjugation with carbohydrates (glycosylation), producing bonded residues and finally yields to polar polymeric compounds. Although conjugation with glycosylation of reactive intermediate is considered as the key metabolic pathway of BPA in plant breeds, the reactive intermediates of BPA may vary from plant to plant. BPA is converted into BPA-mono-*O*-ß-D-glucopyranoside as the reactive intermediate in *Nicotianatabacum* (tobacco) cell suspensions and *Ipomoea aquatic* (water spinach), 2,2-bis(4-β-d-glucopyranosyloxyphenyl)propane, 2-(4-β-d-glucopyranosyloxy-3-hydroxyphenyl)-2-(4-β-d-glucopyranosyloxyphenyl)propane, and 2-(4-β-d-glucopyranosyloxy-3-hydroxyphenyl)-2-(3-β-d-glucopyranosyloxy-4 hydroxyphenyl)propane in *Eucalyptus perriniana* (spinning gum) cell suspension cultures (Hamada et al., 2002; Im and Löffler, 2016). These intermediates turn into polymeric compounds that reduce protonic free radicals that damage cellular organs like mitochondria, cytochrome, and nucleus in presence of peroxidizing enzymes like peroxidase (soybean, horseradish), polyphenol peroxidase (potato), and alters depending on the plant species (Im and Löffler, 2016).

8.5 Conclusions and perspectives

Endocrine disruptors have a different regulatory and monitoring status than most other emerging contaminants due to their detrimental effect on both terrestrial and marine environment and living biota depending on their originating sources and geological locations of countries around the world. Because of hydrophobicity and volatility/semivolatility, most of the EDs have a tendency to get stored in soil/water and finally accumulate in plant body with other organic enriched matters (nutrients), which shows toxic effect in prolonged duration. In this chapter, the authors tried to highlight the tentative pathways of some common EDs to introduce them into the plant environment, including their detection methods and toxic symptoms based on the available literature.

In plants, endocrine disruptors are responsible for deducting seed germination, interfering in ATP generation during cellular respiration, decreasing photosynthesis, reducing chloroplasts and other cellular components, and changing cellular structure and membrane degradation. On the contrary, the transportation and deposition of some EDs in some vegetative plant parts like tomatoes, onions, radish, and some other fruits compromise the assurance of safer foods in our daily diet chart because of a higher bioaccumulation factor that possesses a potential threat to human health risk if such vegetables/fruits are introduced to our daily dietary. According to some early research, it is evident that wastewater irrigation is a typical exposure route of EDs to plant’s edible parts. Therefore, specific research is required to understand the transportation mechanism of EDs to plant species along with their toxic impact and further risks for humans owing to their consumption as food items. Also, proper monitoring of wastewater irrigation (both gray and black water) in urban and town side areas should be taken under consideration to avoid possible health risks and environmental deterioration by providing a standard regulatory aspect and guidelines by the concerned authorities.

The deleterious influence of EDs yields a higher threat to all living beings and environmental resources and the scenario is getting worse day by day due to versatile applications of various EDs chemicals in different industries in their production phases, and also in the agricultural sector because of the escalation of CPAs usage in the cultivation of numerous crops and plants. As a result, the standardization of restricted chemical levels should be developed and their application can be limited to reduce their emissions, which is now at the center point of interest in recent wastewater management. Finally, extensive research should be encouraged to investigate the links between environmental milieus responsible for distributing EDs while understanding the mechanism of toxicity during binding with hormone receptors, and find possible methods to reduce toxic symptoms both in plants and animals for the betterment of bioconservation and environmental protection.

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9

Emerging contaminants in municipal wastewater: Occurrence, characteristics, and bioremediation

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9.1 Introduction

Municipal wastewater treatment plants are considered to be a hotspot of a huge range of pollutants belonging to different chemical classes like pharmaceuticals, pesticides, personal care products (PCP), human or synthetic estrogens, hormones, polychlorinated biphenyls (PCB), alkylphenols, etc. which might disrupt the hormonal systems and can cause adverse effects in endocrine functions when present even in ng/L to μg/L level (Cruz-Morató et al., 2014). In 1996 the European Commission has termed those toxic exogenous substances as endocrine disrupting pollutants (EDPs) which could affect the health of an organism, its progeny, or its endocrine system, (European Commission, 1996; Cases et al., 2011).

EDPs were detected in the early 1970s which got more attention after the 1990s due to their detrimental impacts on humans, animals, and the environment. There are several possible routes of exposure of EDPs in freshwater bodies like sewer overflow or leakage, discharge of treated and untreated municipal sewage or industrial wastewater, and agricultural runoff (Kasonga et al., 2021). Natural hormones are excreted from the human body via body fluids into the surface water as a less bioactive compound of conjugated sulfates or glucuronides. However, in municipal sewage, sulfatase and glucuronidase enzymes are present in fecal bacteria like *Escherichia coli* which might help to activate the estrogens via deconjugation reactions, (Johnson and Sumpter, 2001). The free estrogens in water are reported to cause cancer, pubertal changes, neurotoxicity, and adversely affect the reproductive and immune systems along with kidney, breast, and prostate damages (Kasonga et al., 2021). Leet et al. (2015), observed in a study that synthetic estrogen ethinylestradiol caused feminization in 84% of the male fish in the larval stage. On another hand, progestin levonorgestrel which is largely used in contraceptive pills had a serious impact on masculinization in fish, including reduced fish growth and reproduction capacity (Runnalls et al., 2015). Bisphenol A (BPA) is a chemical used to manufacture plastic bottles hence found

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in mineral and surface water (FDA, 2012), and has been included in "Unregulated Contaminant Monitoring Regulation" by USEPA (2012), for its toxic estrogenic potential.

Due to the occurrence and toxicity of EDPs as trace elements in water, their mitigation is an emerging environmental concern. Application of advanced oxidation, activated carbons, membrane filtration, adsorption, and biodegradation techniques to remove EDPs from municipal wastewater has been largely investigated by researchers (Kasonga et al., 2021). However, the physicochemical methods involve the requirement of chemicals, expensive technologies, high maintenance, and operational energy cost, but biological remediations are comparatively cheaper and environment friendly than the above-mentioned processes. For biological treatment, microorganisms like fungi, bacteria, algae, and protozoa are observed to be effective in removing EDPs (Qasim and Zhu, 2018). Fungi are considered to be the most efficient organism degrading pharmaceutical compounds and EDPs due to the presence of organics degrader enzymes, (Liu et al., 2016). As the activated sludge process is inefficient in completely removing estrogens and alkylphenols, conventional municipal wastewater treatment plants are the major source of releasing EDPs as micropollutants in the aquatic ecosystem. Previous literature discussed several activated sludge processes (Petrie et al., 2014), biofilm reactors and their hybrid bioreactors (Luo et al., 2014), along with membrane bioreactors (Clouzot et al., 2010), for EDPs removal from municipal wastewater. But trace amount and dependency on environmental factors were the major drawbacks for complete biodegradation of EDPs.

Hence, the latest and comprehensive biotechnological approaches were further explored to improve EDPs removal efficiency from wastewater. Self-aggregating aerobic granular sludge has been in core attention of environmentalists due to its high-density granular biomass, a wide variety of microbial population, toxicity tolerance providing 60–90% efficiency in removal of EDPs like antibiotics, PCPs, bisphenol A, natural and synthetic hormones with simultaneous removal of COD (chemical oxygen demand), nitrogen, and phosphorus (He et al., 2019; Cydzik-Kwiatkowska et al., 2020; Castellanos et al., 2021). Constructed wetlands (CWs) are another low-cost, eco-friendly, and user-friendly option for bioremediation of EDPs reported for 90% removal of ethinylestradiol, bisphenol A, and other phenolic micropollutants present in municipal wastewater (Yang et al., 2011; Dai et al., 2017; Wirasnita et al., 2018). However, the requirement of sophisticated detection and characterization techniques for EDPs is still challenging but the future development in EDPs remediation indicates the use of fungal granular bioreactors and advanced hybrid bioreactors (Johnson and Sumpter, 2001).

This chapter gives an outline on occurrence, distribution, classification, toxicological characterization of EDPs along with their hormonal interaction and emerging bioremediation technologies for EDPs removal from municipal wastewater, and discusses existing challenges and potential future research prospects.

9.2 Occurrence and distribution of EDPs in municipal wastewater

Since the last decade, researchers have largely focused on the occurrence and traces of EDPs in treated wastewaters of European nations and other high-income countries. Whereas, in low-income or middle-income nations, studies related to these are few. One main reason behind this is the poor and merely nonexistent connectivity of wastewater networking systems in developing nations. This makes it difficult to track the source and conveyance of contaminants into the water bodies (Williams et al., 2019).

EDPs are generally capable of causing adverse health effects by alteration of hormonal balance which leads to metabolic, neuronal, and reproductive system dysfunction (Adeel et al., 2017). According to the European food safety authority (ECHA, 2012), EDPs are:

"A substance or mixture that alters the functions of the endocrine system and, consequently causes adverse effects on health of an intact organism, or its progeny or (sub) population."

Different types of plasticizers, steroid hormones, surfactants, and personal care products are included in the category of EDPs. The existence of EDPs has been reported in the surface water, drinking water and in the effluents of wastewater treatment plants of several countries including India, South Africa, China, Canada, USA, Malaysia, Italy, Mexico, Singapore, etc., which establishes the fact of global occurrence and ubiquitous nature of these pollutants. The predominance of EDPs in municipal wastewaters is found because the conventional municipal wastewater treatment plants are not designed to target these recalcitrant pollutants. Table 9.1 summarizes the maximum detected levels of different EDPs present in the wastewater treatment plant effluents from three different continents of the globe. The major target of municipal water and wastewater treatment units are organic matters (mainly biodegradable), solids, pathogens,

Table 9.1 Maximum detected concentration of EDCs in different continents.

EDC	Europe (μg/L)	Reference	Asia (μg/L)	References	North America (μg/L)	References
Amoxicillin	0.19	Dinh et al. (2017)	1.67	Matsuo et al. (2011)	<LoQ	Palmer et al. (2008)
Azithromycin	0.784	Sidhu et al. (2013)	0.980	Mohapatra et al. (2016)	n.r.	NA
Ciprofloxacin	5.692	Rosal et al. (2010)	0.524	Tewari et al. (2013)	0.620	Brown et al. (2006)
Erythromycin	0.29	Rosal et al. (2010)	0.186	Tran et al. (2016)	n.r.	NA
Micronazole	0.035	Casas et al. (2015)	<LoQ	Yang et al. (2017)	0.027	Guerra et al. (2014)
Triclosan	0.430	Kosma et al. (2014)	0.264	Anumol et al. (2016)	0.360	Guerra et al. (2014)
Triclocarban	n.r.	NA	5.860	Subedi et al. (2015)	0.617	Hedgespeth et al. (2012)
Diclofenac	5.164	Kosma et al. (2014)	0.069	Yang et al. (2017)	0.359	Metcalfe et al. (2003)
Salicyclic acid	10.1	Papageorgi-ou et al. (2016)	1.426	Tran and Gin (2017)	0.320	Lee et al. (2005)
Carbamazepine	4.596	Kahle et al. (2009)	0.9	Subedi et al. (2015)	0.551	Palmer et al. (2008)
Estrone	0.095	Migowska et al. (2012)	0.051	Tran and Gin (2017)	0.056	Subedi et al. (2015)
Caffeine	13.9	Papageorgi-ou et al. (2016)	51.7	Tewari et al. (2013)	37.2	Palmer et al. (2008)
DEET	n.r.	NA	0.324	Sui et al. (2010)	1.663	Mohapatra et al. (2016)
Bisphenol A	1.840	Terzić et al. (2008)	0.123	Yang et al. (2017)	0.45	Mohapatra et al. (2016)

n.r., not reported; NA, not applied.

nutrients (Carvalho et al., 2016), which also results in the occurrence of EDPs in the drinking water as well (Kasonga et al., 2021). Jiang et al. (2020), reported in their study, that the average removal of EDPs by conventional municipal wastewater treatment systems ranges between 20% and 80%. However, the removal efficiency largely depends on the operational condition of the treatment plant. In the effluents of domestic wastewater (WW) treatment plants, the traceable range of EDPs has been reported as 0.1 ng/L to 94.6 μg/L in the soluble form and 0.01 ng/L to 0.01 μg/L in the particulate form (Pothitou and Voutsa, 2008). This mainly impacts the ecology of the inland lotic and lentic systems as well as around 100,000 aquatic organisms including numerous fish species. The distribution of the EDPs in several water matrices generally depends on the physico-chemical attributes like the ability of dissolution in water systems, the potential of terrestrial or aquatic bioaccumulation, leaching into the ground waters, etc. The soluble fraction of the EDPs even has a high probability to reach the food and drinking water chain, possessing potential risk to public health. Fig. 9.1 depicts the origin and circulation of EDPs in the municipal water and wastewater matrix. Due to various anthropogenic activities, EDPs are disposed into the natural environment. The steroidal EDPs such as bisphenol-A, estrone, etc. are generally originated from human and animal defecation. Other than this, some natural and engineered hormones also reach the wastewater treatment plants along with their metabolites. Some medication techniques like hormone replacement therapy and oral hormonal doses also increase the level of steroidal EDPs in municipal wastewater.

9.2.1 Global existence of endocrine disrupting contaminants in water and wastewater

EDPs have been traced globally in surface and groundwater, and also in tap waters post-treatment and in domestic wastewater treatment plant effluents, which has raised concern within scientists and researchers over the world. Bayen et al. (2013), conducted studies on the occurrence of EDPs in the marine environment of Singapore. In the study, several EDPs were

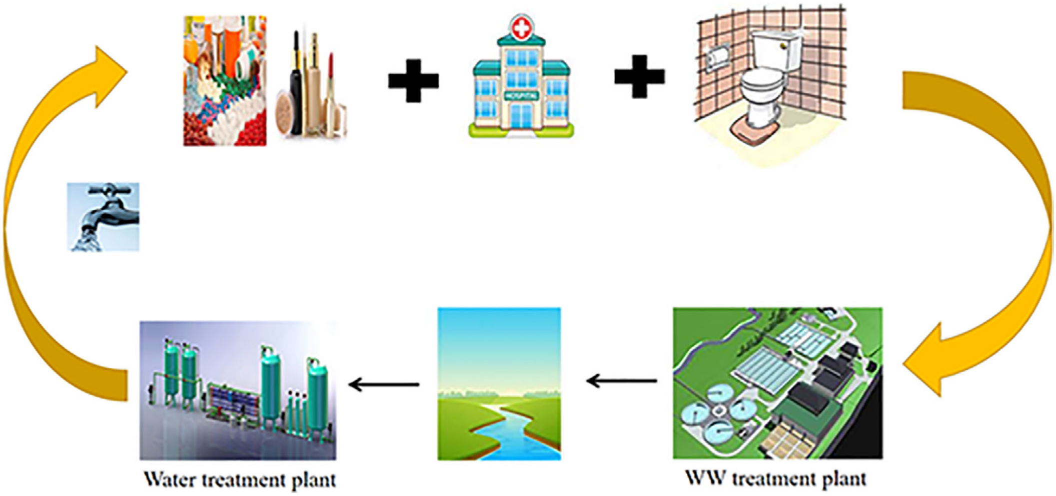

FIG. 9.1 Origin and circulation of EDCs in municipal water and wastewater matrices.

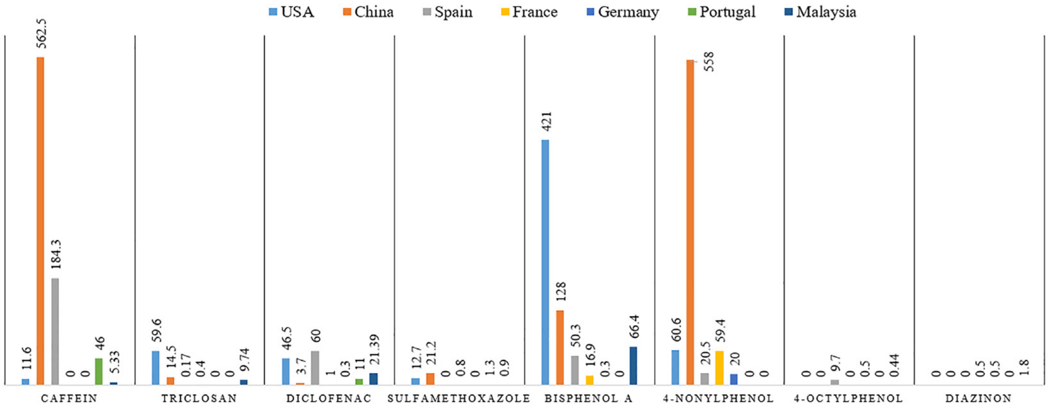

FIG. 9.2 Maximum detected EDCs in ng/L in tap waters of several countries (data obtained from Anumol et al., 2016).

found in variant concentrations, such as carbamazepine (0.28–10.9 ng/L), triclosan (0.55–10.5 ng/L), ibuprofen (2.2–9.1 ng/L), etc. Bai et al. (2018), reported the occurrence of multiple waste indicators, pharmaceutical, and pesticide compounds in the watershed of the Denver, Colorado metropolitan area in a study conducted by the US Environmental Protection Agency. In a recent study, López et al. (2021), determined the existence of five EDPs in the wastewater treatment plant effluent in Monterrey, Mexico. Most persistent EDPs were 17β-estradiol, 17α-ethinylestradiol, bisphenol-A, 4-nonylphenol, and 4-tert-octylphenol in the range of 0.2–26.8 ng/L, all are capable of altering the endocrine functions. Wee et al. (2021), analyzed EDPs in the tap water from different housing types in Putrajaya, Malaysia. Their study revealed the presence of 16 EDPs in the tap waters which was comprised of plasticizers (2), hormones (5), pesticides (1), and pharmaceuticals (8). Fig. 9.2 illustrates the global occurrence of maximum detected EDPs in tap water in different nations. Figs. 9.3 and 9.4 illustrate the classifications of EDPs by previous researchers, present in domestic and industrial wastewater.

In India, however, data on the occurrence of EDPs in different types of water are seriously lacking and very few documented studies are available. Anumol et al. (2016), reported the presence of iohexol (2.1–8.7 μg/L), sucralose (0.79–1.87 μg/L), acesulfame (0.45–0.89 μg/L), caffeine (0.11–5.4 μg/L), atenonol (0.08–1.6 μg/L), and diclofenac (1.1–2.3 μg/L) in three wastewater treatment plant effluents in Chennai, India. Other than these, carbamazepine, triclosan, testosterone, triclocarban, etc. were also detected. Tewary et al. (2013), conducted another study to monitor the presence of bisphenol A, phthalates, and other EDPs in the estuarine systems of Mumbai, India. Among phthalates, di-n-butyl phthalates had the highest concentration (0.13–0.4 mg/kg of soil sediments). The average bisphenol A concentration was found to be 16.3–35.79 μg/kg. Among synthetic EDPs, 4-para-nonylphenol (average concentration 356.6 μg/kg), and 4-tert-octylphenol (average concentration 176 μg/kg) were also detected. In another study by Mohapatra et al. (2016), presence of pharmaceutical EDPs was reported in the effluents of two different wastewater treatment plant effluents in the metropolitan region of western India. The average pharmaceutical concentrations were found to be 537 ± 5 and 353 ± 9 μg/L, respectively.

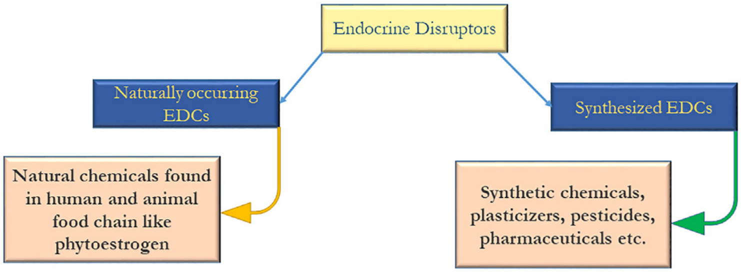

FIG. 9.3 Classification of EDCs (adopted from Diamanti et al., 2009).

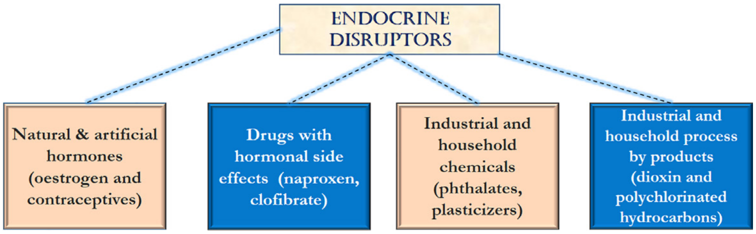

FIG. 9.4 Classification of EDCs (adopted from Caliman and Gavrilescu, 2009).

Seasonal variation of these contaminants in the influent and effluent of the treatment plant was also found to be considerable.

9.2.1.1 The fate of EDPs in municipal wastewater treatment systems

Generally, the domestic wastewater treatment units are equipped with primary, secondary, and occasionally tertiary treatment units/processes. The main objective of the primary treatment unit is to remove suspended and settleable solids, oil, grease, etc. Several reports have suggested the inaccuracy of such treatment in removing the vast majority of hydrophilic EDPs. However, the hydrophobic EDPs are partially removed from the soluble phase by sorbing onto the primary sludge (Ternes et al., 2004; Martin et al., 2012). The removal efficiency ranges between 10% and 27% depending on the nature of the pollutants (Tsui et al., 2014).

The objective of the secondary treatment stage is to remove organics and nutrients depending on aerobic or anaerobic, attached, or suspended biological processes. In this stage, the EDPs are generally partially mineralized and various transformation products are formed. To date, many studies have confirmed that incomplete biodegradation of EDPs occurs in biological treatment processes via cometabolism rather than metabolism, mainly due to two reasons, (i) toxic nature of the EDPs and (ii) presence in trace levels (ng/L to μg/L) in wastewater which is insufficient for the maintenance and production of the biomass (Tran et al., 2018). The volatilization process is also associated with the removal of some volatile EDPs by transferring from soluble to the gaseous phase. This basically depends on the physicochemical properties of the EDPs and also the operating condition of the treatment plant (Tran et al., 2013).

9.2.2 Hormonal interaction and toxicity of EDPs

9.2.2.1 Interaction with hormone receptors

The action of all the hormones depends on their binding to specific receptors. If the binding is performed with improper receptors, it may cause considerable negative effects on health and development (Wadzinski et al., 2014). Inappropriate hormone binding by the EDPs can result in adverse effects. Several EDPs can activate the hormones associated with nuclear or estrogen receptors. EDPs that inappropriately bind to and/or activate hormone receptors can produce adverse biological effects. There are numerous examples of chemicals that cause adverse effects after binding to nuclear hormone receptors. For example, DDT and PCB can increase the fertility rate in humans and also, can activate hormone systems related to the thyroid (You et al., 2006).

9.2.2.2 Blocking of hormone receptors

EDPs sometimes play the role of antagonist and block the function of endogenous hormones. For example, BPA can block or alter the receptive function of oxytocin, estrogen, and vasopressin and β estrogen receptor (ERβ) and DDT can disrupt the internalization of cell receptors and hamper the genomic factor regulation (Gore et al., 2015). Pesticides belong to the organochlorine class (methoxychlor, carbamate), work as antiandrogens, and can block the binding of testosterone with androgen receptors (Gray et al., 2001).

9.2.2.3 Alteration of receptor expression

The action of any hormone depends on the response or expression pattern of the hormone receptor toward the hormone signal. Sometimes the receptor may determine both the hormone concentration and the hormone effect (Mongan et al., 2015). Some EDPs are capable of modulating the receptor expressions and internalization. For example, phthalates can decrease the expression of reproductive hormone receptors like mineralocorticoid (Ge et al., 2005). Further, BPA can alter the expression of oxytocin in the brain nuclei, and DDT is capable of preventing the internalization of thyroid-stimulating hormone receptors (Picchietti et al., 2009).

9.2.2.4 Alteration of hormone synthesis

The synthesis of hormones is generally regulated by endocrine feedback mechanisms (both intracellular and distant). This phenomenon is common with TSHs. In the case of steroid hormone synthesis; the transformation of cohormone to hormone occurs almost simultaneously (Gevers et al., 2016). EDPs like phthalates can reduce the synthesis of testosterone and may generate acute testosterone deficiency syndrome. Perchlorate is also an EDP that can hamper the iodine uptake and block the synthesis of thyroid hormone (Mylchreest et al., 2002).

9.2.2.5 Change in hormone metabolism and inactivation

The inactivation mechanism of different hormones is dissimilar. Protein hormones like gonadotropins are generally inactivated due to breakdown by enzymes (proteases) in the blood. On the contrary, the steroid and thyroid hormones are inactivated by increasing their water solubility by enzymes, which facilitates their removal from the bloodstream (Bernal et al., 2015).

Some EDPs (chlorophenols, poly-chlorobenzenes) have the tendency to modify the hormone inactivation and metabolic degradation that ultimately affects the hormone concentration and the activity (Kester et al., 2000).

9.2.3 Toxicological characteristics

EDPs are responsible for generating toxic effects on an organism or its progeny by interfering with the endocrine systems. Some notable toxic effects of EDPs are developmental toxicity, neurotoxicity, mutagenicity, and carcinogenicity.

9.2.3.1 Developmental toxicity

Several hormones have a different role to play during the development phase of any human life. During this phase, it is highly possible that an external chemical (EDP) which can mimic and modify endogenous messenger, can create an adverse effect on the system. Such a chemical is DDT which may result in the low weight of an infant if the mother is exposed to DDT during her pregnancy. Other than humans, developmental toxicity has been experienced in multiple species due to DDT exposure. This also results in reproductive toxicity and homeostasis (Ottinger et al., 2001). Choi et al. (2004) reported from a survey that out of 48 selected EDPs, 81% showed positive developmental toxicity results.

9.2.3.2 Neurotoxicity

Exposure to EDPs leads to adverse effects on the nervous system. Compared to the nervous system of an adult, a developing nervous system is more vulnerable to the actions of this EDP. The main reasons behind this are differential affinity, different metabolic enzymes, absence of protective blood–brain barrier, etc. (Garry, 2004; Tilson, 1998). Several EDPs like dioxins and PCBs can hamper neurological development, by creating interference to the neuroendocrine functions (Kavlock et al., 1996). All of these ultimately lead to changes in learning performance, disruption of sensory functions, and altered cognitive behavior (Legradi et al., 2018).

9.2.3.3 Carcinogenic toxicity

Laden et al. (1999) have presented the association of polychlorinated biphenyls with breast and uterine cancer. Davis et al. (1993) documented the enhanced risk of breast cancer in women, who are exposed to EDPs like DDT, polyaromatic hydrocarbon (PAHs), etc. Some other detrimental effects of EDPs are increased prostate cancer, enhanced rate of breast cancer, etc. From these observations, a substantial body of evidence has been accumulated indicating that the incidence of testicular cancer in men has risen significantly. In a literature review by Choi et al. (2004), about 42% of randomly chosen EDPs were found to be capable of producing carcinogenic effects in the human body. Fig. 9.5 illustrates the characteristics of EDPs and their hormonal interactions.

9.2.3.4 Immunotoxicity

Generally, the human immune system is capable of responding to low levels of external chemicals by maintaining the antidisease resistance of the host. However, EDPs are capable

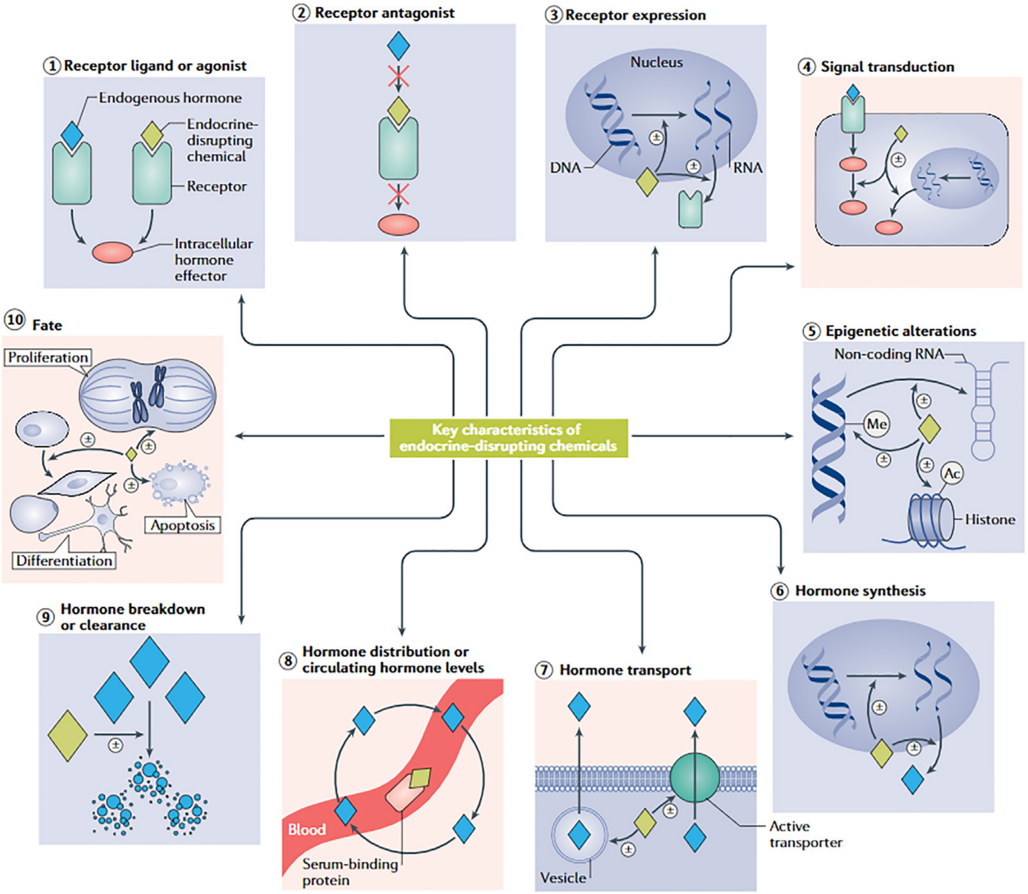

FIG. 9.5 Characteristics and hormonal interactions of EDCs (adopted from La Merrill et al., 2020).

of generating, functional immune system disorders in the human body. The research group of Belles-Isles reported their observation of cord blood lymphocytes in infants as they were exposed to EDPs like organochlorides and methylmercury (Belles-Isles et al., 2002). Among other EDPs, PCBs and DDT can be associated with reduction of immune functions and increased probability of infection and toxicity development (Svensson et al., 1994).

9.3 Emerging bioremediation strategies for removal of EDPs from wastewater

Advancements in activated sludge processes have evolved different path-breaking bioremediation technologies to remove EDPs from municipal wastewater. Use of ligninolytic fungi, manganese-oxidizing granular sludge, modified constructed estuarine wetland, or wetlands amended with activated carbons or bioreactors operated with varying operational conditions were proven to be effective for the degradation of antibiotics, estrogens, and phenolic EDPs in wastewater (Cases et al., 2011; Cajthaml, 2015; He et al., 2019; Wirasnita et al., 2018). This section elaborates on the state of art in the field of biological treatments of EDPs from municipal wastewater.

9.3.1 Modified activated sludge treatment

In an earlier study, pharmaceutical compounds such as phenolic EDPs like BPA, nonylphenol, octylphenol, and three natural estrogens like estrone (E1), 17β-estradiol (E2), and estriol (E3) contaminated wastewater was seasonally collected from five municipal wastewater treatment plants of Tokyo (Nakada et al., 2006). It was observed that after the primary and secondary treatment in the activated sludge process about 99% removal occurred for aspirin, ibuprofen, and thymol having 600–733 ng/L of influent concentration. Whereas, amide-type pharmaceuticals and naproxen had below 50% removal due to low hydrophobicity. In the case of EDPs, E1, E2, and E3 removal were about to 86–100% due to the chemical conversion of E2 to E1. Though BPA has low hydrophobicity, aerobic biodegradation provided nearly 92% removal efficiency from municipal wastewater in a secondary treatment plant.

The impact of sludge ozonation was observed in the lab-scale activated sludge process to reduce excess sludge production along with the removal of EDPs, COD, and nutrients from wastewater (Nie et al., 2014). About 100 mg O_3 g/SS (suspended solid) of ozone dosing for 45 days period provided zero excess sludge production from the reactor. The sludge ozonation further influenced target EDPs (E1, E2, E3, BPA, and 4-nonylphenol) removal in two possible ways. First, the EDPs bound with sludge particles was eliminated by direct oxidation due to the ozonation process. Second, ozone treatment might have modified the sludge particle surfaces for adsorption and microbial population for biodegradation in the reactor which further enhanced EDPs removal from wastewater. COD removal was always above 90% and accumulation of total phosphorus (TN) in the sludge reduction process indicated declined phosphorus removal and the necessity of phosphorus recovery in the system.

9.3.2 Bioreactors in EDPs removal

Biological treatment of BPA contaminated wastewater was conducted in catalytic membrane bioreactors operated under isothermal or nonisothermal conditions (Diano et al., 2007). Nylon membranes had immobilized laccase derived from *Trametes versicolor* grafted with glycidyl methacrylate and a phenylenediamine as a spacer. Under nonisothermal conditions, the affinity between the catalytic membrane and laccase increased at an average temperature. The enzymatic activity proportionally increased with applied temperature and was decreased with increased BPA concentration. The maximum BPA degradation occurred at the lowest BPA concentration (below 4 mM BPA) having minimum water solubility of the compound.

Cases et al. (2011), established a pilot-scale membrane bioreactor (MBR) having a flat sheet and hollow fiber modules to degrade EDPs such as nonylphenols, alkylphenols, BPA, estrogens, and phthalates present in wastewater through stir bar sorptive extraction and thermal desorption which was detected in gas chromatography–mass spectrometry (GC–MS). Samples were collected from the primary settling tank, tertiary treatment, and from the flat sheet hollow fiber modules after 3 months of reactor operation. The excellent removal efficiency of diethyl phthalate (DEP), di-n-butyl phthalate (DBP), and butyl benzyl phthalate (BBP) was observed by MBR modules while compared to activated sludge process, and activated sludge achieved significant removal of bis (2-ethylhexyl) phthalate (BEHP). 4-Tert-octylphenol and BPA removal efficiency were almost the same in MBR and activated sludge process. However, DBP and nonylphenol removal were higher in membrane modules whereas, DEP and BBP removal was better in flat sheet MBR.

Hospital effluents are another source of toxic pharmaceutical compounds and EDPs arising environmental concerns. Though hospital effluents are being cotreated with municipal sewage in recent days, the treatment efficiency is not adequate to completely remove the trace contaminants. Cruz-Morató et al. (2014) demonstrated a novel alternative pretreatment of hospital wastewater in a fungal bioreactor capable of removing EDPs and pharmaceuticals. A batch scale fluidized bed reactor was operated with *Trametes versicolor* fungus pellets under sterile and nonsterile conditions to treat the micropollutants. In nonsterile conditions, 46 out of the 51 EDPs and pharmaceutical compounds were either partially or completely removed. The sterile and nonsterile mode of fungal treatment provided about 83% and 53% pollutant removals from 8185–8426 μg of initial influent pharmaceuticals and EDPs load. The reduction of wastewater toxicity after the fungal reactor treatment was further confirmed by the Microtox test.

Edible mushroom *Pleurotus ostreatus* HK 35 exhibited above 90% biodegradation potential of EDPs such as BPA, E1, E2, E3, 17α-ethinylestradiol, triclosan, and 4-n-nonylphenol in laboratory conditions within 12 days of study (Balest et al., 2008), which was higher than the degradation efficiency of strain *P. ostreatus* 3004. Batch and trickle-bed reactors were employed for EDPs removal study in real and model communal wastewater by using a spent mushroom substrate collected from a farm. The fungus growth was not suppressed by the bacterial population in the wastewater and the spent substrate facilitated 95% of EDPs biodegradation by *P. ostreatus* HK 35 with minimizing the estrogenic activity of the compounds. The final study revealed that a pilot-scale trickle-bed reactor installed in a wastewater treatment plant could remove about 75% EDPs present in the wastewater within 10 days of the operational period (Křesinová et al., 2008).

9.3.3 Granular sludge reactors

A lab-scale study on sequencing batch biofilter granular reactor (SBBGR) was conducted to treat EDPs like BPA, estrone (E1), 4-tert-octylphenol (4t-OP), 17β-estradiol (E2), and 17α-ethynylestradiol (EE2) from municipal wastewater (Balest et al., 2008). The system provided around 90% COD removal at a high organic loading rate of 5.7 kg COD/m^3 due to the presence of a maximum 40 g/L biomass concentration and around 6 months of sludge retention. After 4 months of SBBGR operation, the removal efficiency of E1, E2, BPA, and 4t-OP were observed to be 60%, 69%, 93%, and 81%, respectively, which was significantly higher than the conventional activated sludge process.

He et al. (2019), cultivated manganese-oxidizing aerobic granular sludge (Mn-AGS) which provided 8–127 μg/h/g SS of removal rates for EDPs like BPA, EE2, tetracycline (TC), chloramphenicol (CAP), and imazethapyr (IM) from wastewater. Reduction of hydraulic retention time (HRT) from 18 to 9 h and addition of manganese-oxidizing bacteria *Pseudomonas putida* MnB1 could not affect Mn-AGS formation providing 22–28 mg Mn/g SS of biogenic manganese oxide accumulation in granular sludge after 55 days of reactor operation. The study indicated microbial degradation and chemical oxidation by biogenic manganese oxides to be the probable pathway for simultaneous removal of COD and EDPs from wastewater. However, the degradation rate of dichlorophenyl phosphine (DCPP) was observed to be lesser in Mn-AGS than conventional AGS due to microbial growth inhibition by biogenic manganese oxides.

Another study revealed the BPA removal potential of aerobic granular reactors (AGR). At the beginning of the AGR cycle at 2 mg/L BPA concentration, AGR achieved maximum respirometric activity providing complete biodegradation of BPA producing no by-product (Cydzik-Kwiatkowska et al., 2020). However, at 6 and 12 mg/L of BPA concentration microbial activity of BPA degraders was even higher than degradation efficiency in lower BPA concentration and 3-(benzyloxy benzoic acid) metabolite production was observed in the reactor. Gene coding results revealed that cometabolism took place in granules in higher BPA concentration whereas biodegradation was the only mode of BPA removal at lower BPA load in the AGR.

Biodegradation of natural and synthetic estrogens was also conducted by AGS in simulated domestic sewage (Castellanos et al., 2021). Alternating anaerobic and aerobic conditions in the reactor facilitated an initial anaerobic bioadsorption followed by aerobic biodegradation of EDPs providing 93% and 99% removals of EE2 and E2 from 20 μg/L of influent estrogen concentration. The AGS treatment also minimized the toxic estrogenic activities of the steroid hormones. Above 90% COD, ammonium, and phosphate removal occurred in the reactor where 80% of the organics were consumed in the anaerobic phase and nitrification and phosphate removal took place in the aerobic phase leaving only 2 mg/L of ammonium and phosphate in the effluent. Fig. 9.6 illustrates the lab-scale set-up of the aerobic granular reactor and probable E2 and EE2 degradation pathways in aerobic and anaerobic phases inside aerobic granules.

9.3.4 Application of algae in EDPs removal

Due to the low performance of municipal wastewater treatment plants and increasing human health risks of EDPs, further exploration in sustainable bioremediation techniques was essential. The role of fresh green alga *Nannochloris* sp. was studied by Bai and Acharya (2019), for the bioremoval of seven EDPs from wastewater. EDPs degradation by *Nannochloris* sp. was observed in two different types of wastewater effluents generated after ultrafiltration and ozonation treatment. After 7 days of algae treatment, the ultrafiltration effluent achieved about 60% removal rate for E2, EE2, and salicylic acid (SAL). However, removal of other EDPs was not observed in the ultrafiltration effluent. Photodegradation and biodegradation were observed as the basic mechanism of algal-mediated removal of E2, EE2, and SAL. In spite of adding algae in the effluent rapid photodegradation was observed for triclosan (TCS) removal providing 63–100% removal efficiency in 7 days and the further removal mechanism was explored to be

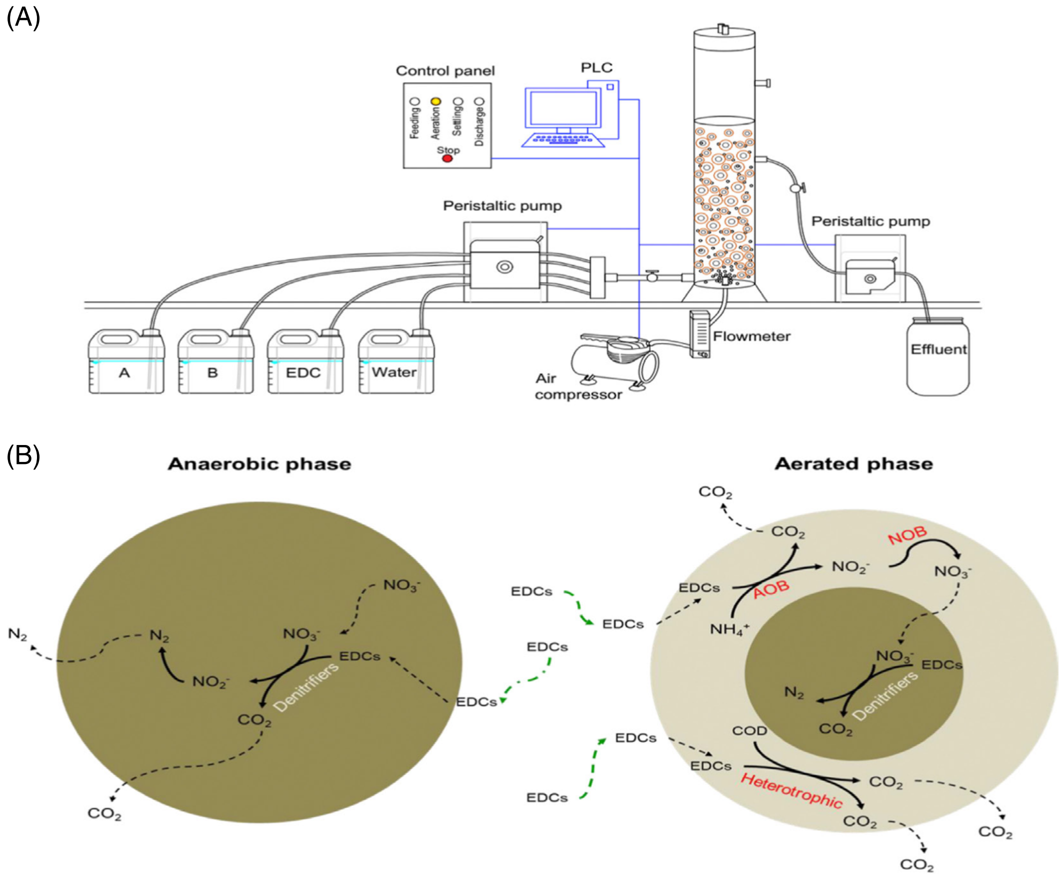

FIG. 9.6 (A) Lab-scale set-up of bubble column aerobic granular reactor equipped with a peristaltic pump, influent effluent vessels, air compressor, and programmable logic controller (PLC). A stands for a mixture of sodium acetate and trace metals, B stands for NH_4Cl and phosphate buffer mixture and EDC solution was a mixture of E2 and EE2. (B) Representation of EDC biodegradation pathways in anaerobic and aerated phase in aerobic granules: where conversion, diffusion, adsorption are indicated by an arrow, dot arrow, and green dot arrow, respectively (adopted from Castellanos et al., 2021).

bioadsorption and bioaccumulation by algae. Algal-mediated EDPs treatment efficiency was completely dependent on the chemical complexity of the compound and bioaccumulation of TCS in algae might further impose toxicity in the food web as the estrogenic activity of the compounds is not eliminated by algal treatment. Hence, the study indicated the use of modified sludge, bacterial and fungal bioreactors to be more appropriate and eco-friendly methods than algal treatment for EDPs removal from domestic wastewater.

9.3.5 Constructed wetlands

Constructed wetlands (CW) are engineered wastewater treatment processes mimicking the natural wetlands, simulating several biochemical reactions between microbial populations,

Table 9.2 Effects and mechanism of thyroid disrupting chemicals (adopted from Gore et al., 2014).

Thyroid disruptors	Mechanism	Effect
Perchlorate, thiocyanate, nitrate, bromates, phthalates	Blocking iodide uptake into cell	Reduction of T3 and T4 synthesis
Methimazole, amitrole, soy isoflavones, benzophenone 2	Blocking the function of thyroid follicles	Reduction of T3 and T4 synthesis
PCBs, pentachlorophenols, flame retardants, phthalates	Competitive binding to thyroid transport protein (TTR)	Affecting fetal T4 generation
Dioxin, PBDE, chlordane	Cell membrane transport alteration	enhanced biliary removal of T3 and T4
Acetochlor (herbicide), PCBs	increased hepatic metabolism	Increased rate of T3 and T4 biliary metabolism
PCBs, triclosan, pentachlorophenol, dioxin, difuran	Sulfation reduction	possible reduction of peripheral T3 formation
FD&C red dye #3, PCBs, octylmethoxycinnamate	Decrease in the deiodinase function	Reduced synthesis of peripheral T3
PCBs, bisphenol A, hexachlorobenzene, flame retardants	Alteration of thyroid receptor binding	Alteration in thyroid gene transcription.
DDT, PCBs	Inhibiting TSH receptor	Reduced productivity of T3 and T4

T3, triiodothyronine; T4, thyroxine.

adsorption in filtration media like sand, stone, gravels, and providing phytoremediation mechanisms to remove suspended solids, carbon, nutrients (N, P) and toxic pollutants from wastewater streams (Campos et al., 2019). CWs are considered to be an advantageous wastewater treatment system for their low-cost operation, low energy requirement, low maintenance, and low chance of production of secondary metabolites (Wirasnita et al., 2018). Moreover, CWs offer habitat for animals and birds and allow the incorporation of local landscape which is acceptable for a sustainable environment (Yang et al., 2011) (Table 9.2).

Since the last decades, several studies on CWs have been conducted on domestic or industrial wastewater treatments. Removal of EDPs such as estrogens, BPA, TCS, NP_1EO, and NP2EO in CWs is currently in the core interest of environmental researchers. Studies on removal mechanism and fate of EDPs have been carried out in CWs to check impacts of seasonal variation and lab scale to pilot scale implication. Effectiveness of individual vertical, horizontal, or subsurface flow wetlands or in series of wetlands and role of different types of vegetation (such as reeds or cattails) enhancing EDPs removal performances have also been explored in CWs. Bioremediation process of bisphenol A (BPA), bisphenol F (BPF), bisphenol S (BPS), and 4-tert-butylphenol (4tBP) in activated carbon attached CW is described in Fig. 9.7. Table 9.3 summarizes the current literature on studies about natural and engineered wetlands with operating conditions along with their EDPs removal efficiencies from domestic wastewater.

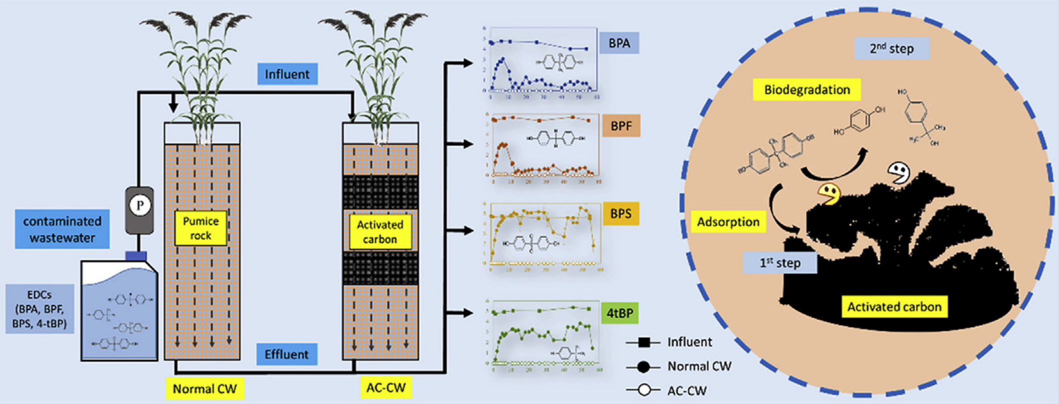

FIG. 9.7 Bioremediation process of bisphenol A (BPA), bisphenol F (BPF), bisphenol S (BPS), and 4-tert-butylphenol (4tBP) from wastewater in activated carbon attached constructed wetlands (AC-CW) in a nutshell. Schematics of fabricated normal and AC attached vertical flow wetlands along with removal profile of BPA, BPF, BPS, and 4tBP depicting EDCs were removed by two-step mechanism of adsorption (in activated carbon) and bacterial biodegradation (adopted from Wirasnita et al., 2018).

9.4 Challenges and future scope of bioremediation of EDPs: an economical perspective

One of the challenges in EDPs management in wastewater is the undefined source and point of EDPs exposure into the domestic wastewater stream. EDPs are not regularly monitored in surface water and their permissible limits of disposal are not properly framed. So it is the prime necessity of the government to define the maximum threshold limits of EDPs exposure and EDPs should also be incorporated among water quality standards to protect aquatic organisms, animals, and humans from their adverse health impacts (Bai & Acharya, 2019).

As EDPs sources are mostly determined from increasing anthropogenic activities, implementation of limitation of usage of EDPs in urban and industrial activities might be the most effective preventive measure reducing their chances of contamination in surface water.

As EDPs are usually found in trace amounts in wastewater, their monitoring and detection require sophisticated technologies such as GC–MS or liquid chromatography–mass spectrometry (LC–MS) and selective solid-phase extraction (SPE) with UPLC–MS/MS methods. Common wastewater treatment plants are proven to be inefficient in EDPs removal indicating the requirement of advanced technologies. Hence in developing countries like India EDPs remediation is a matter of economical concern which imposes a great challenge to the scientists for employing a cost-effective and eco-friendly EDPs removal process (Zhang et al., 2016).

There is still a knowledge gap in understanding the vulnerability of groundwater by EDPs pollution. Hence, further investigation and development of monitoring and easier detection technologies are required to trace EDPs in groundwater.

Table 9.3 Role of natural and constructed wetlands treating EDC contaminated in wastewaters.

Type of wetland	target EDCs with concentration	Operational strategies	Pollutant removal performance	References
Estuarine wetland of natural reed bed	4-nonylphenol (4-NP), bisphenol A (BPA), 4-t-octylphenol (4-t-OP), and 2,4-dichlorophenol (DCP) in 274 ng/L concentration	Four wetlands were employed of 1.00 km × 1.74 km area. Irrigation water converged in outlet ditch and discharged into the Bohai Sea	About 91.6% of EDC removed in 120 days of the irrigation period	Castellanos et al. (2021)
Estuarine and freshwater constructed wetland	nonylphenoldiethoxylates (NP_2EO), nonylphenolmonoethoxylates (NP_1EO), nonylphenol (NP), and octylphenol (OP)	Three freshwater wetlands along the Dahan river and three estuarine wetlands in Dapeng Bay National Scenic Area (DBNSA) were studied in Taiwan	Removal efficiency: 3.13–97.3% in DBNSA and 55.5–93.6% in Dahan River. Risk quotients: Dahan wetlands> DBNSA	Chen et al. (2014)
Constructed wetland	Estrone (E1), 17β-estradiol (E2), and estriol (E3) in 2.5–10 ng/L concentration	Wetland with 135 m × 5 m × 0.8 m dimension was equipped with settling and filtration pond, preaeration pond, aeration tanks, surface-flow wetlands, HRT: 27.5, 45.9, and 137.5 h	About 0–46% and 40–84% estrogen degradation occurred at 45.9 h and 137.5 h HRTs, respectively	Vymazal et al. (2015)
Constructed wetland	Estrogens, testosterone, and progesterone were present in 13–56, 7, and 10.5 ng/L in influent	Three horizontal subsurface flow wetlands having filtration bed filled with gravels of 8–16 mm depth were equipped with pretreatment units, HRT: 8.1–8.7 h	The E1 removal efficiency was 85%and other estrogen concentrations in wetland outflow did not exceed the quantification limit of 1–10 ng/L	Papaevangelou et al. (2016)
Pilot-scale constructed wetland	BPA, NP, NP_1EO, NP_2EO, and Triclosan (TCS) were found in 8–35 ng/L	Three horizontal subsurface flow (HSF) wetlands with 3 m × 0.75 m × 1 m dimensions and three vertical flow (VF) wetlands having 0.82 m diameter and 1.5 m height with gravel layers were planted with *Phragmitesaustralis* and *Typhalatifolia*	About 50–98% EDC removal in HSF-CW and about complete EDC removal occurred in VF-CW	La Merrill et al. (2020)

Stacked constructed wetland with biofilter	BPA, E2, EE2, E1, 4-t-OP, 4-NP, and TCS in 100–1500 ng/L of range	A stacked wetland was comprised of a VF-CW planted with *Thaliadealbata*, *Canna indica*, and *Typhaangustifolia*, and HFCW was planted with *Cyperusalternifolius*, *Arundodonax*, *Acorustatarinowii*, and *Desmodiumstyracifolium* operated in subunits containing gravels and slag for P removal	4-NP removal: 80% and 69%, 4-t-OP removal: 58% and 51%, E1: 48% and 44%, BPA: 45% and 32% in stacked CW and assembled biofilter system	Dai et al. (2017)
Activated carbon-amended constructed wetlands	bisphenol A, bisphenol F, bisphenol S, and 4- tert-butylphenol were applied in 5 mg/L in influent	Normal CW and AC-CW were set up in a 150 mm diameter × 650 mm height ratio. AC-CW was filled with AC granules and pumice rock and were planted with common reeds	About 98–100% EDC removal was achieved by AC-CW which was higher than normal CW by initial adsorption and bacterial biodegradation	Wirasnita et al. (2018)
subsurface constructed wetlands	Ethinylestradiol, bisphenol A, and levonorgestrel were present in 15–18 μg/L concentration	Four wetlands were constructed with gravel, *Cyperusisocladus*, *Eichhorniacrassipes*, and without macrophyte, respectively at 2 and 4 days HRTs	EE2 removal 9–95.6%, BPA removal: 29–91.2% and LNG removal: 39.1–100.0%	Zhang et al. (2016)

AC-CW, activated carbon-amended constructed wetlands; HSF-CW, horizontal subsurface flow wetland; VF-CW, vertical flow wetland.

EDPs are often found in higher concentrations in treatment plant effluents than their influents due to chemical reactions and the breakdown of precursor compounds. Hence, studies on the fate of EDP precursors should also be considered along with free EDPs behavior in domestic as well as drinking water treatment plant effluent.

Steroidal estrogens such as E1, E2, E3, and EE2 and xenoestrogens like BPA and NP are the six commonly known EDPs which are not generally detected in drinking water. But during the chlorination process in drinking water treatment plants occurrence of their chlorinated byproducts are reported. These chlorinated EDPs often exhibit more estrogenic toxicity than the original compound. However, literature on detailed information on the occurrence, distribution, and impacts of the chlorinated EDPs are mostly unavailable (Zhang et al., 2016).

At last, the major challenge in EDPs remediation is lesser-known facts about their detrimental health effects. More awareness regarding EDPs pollution should be regulated by the government to the citizens of developing nations. Carcinogenicity, neurotoxicological disorder, and pubertal damages are currently explored health impacts of EDPs. But more research is needed for a better understanding of the EDPs exposure route, probable pathways, acute or chronic health symptoms, and excretion from human and animal bodies. Hence, the establishment of an eco-friendly, user-friendly, and cost effective biological strategy for EDPs removal from water reclamation plants is the need of the hour toward a sustainable environment and circular economy in India.

The use of several bioreactors, granular sludge, engineered wetlands, and other comprehensive biotechnologies have been proved to be effective in EDPs bioremediation. But the increasing research interest toward fungal treatments of EDPs indicates the potential future research scopes (Kasonga et al., 2019a). The presence of enzymes like manganese peroxidase, laccase, and extracellular lignin peroxidase enabled a significant amount of EDPs removal by white-rot fungi in both water and soil matrices. Literature reported ligninolytic properties of fungi enabled the reduction of estrogenic activities of EDPs and their byproducts (Kasonga et al., 2019b), and (Johnson and Sumpter, 2001). In contrast, other studies reported the role of nonligninolytic enzymes, like intracellular cytochrome P-450 (Cyt-P450) mediated catalytic degradation of EDPs. The presence of Cyt-P450 monooxygenases in *Phanerochaete chrysosporium*was proved to be effective to degrade xenobiotics. Implementation of effective fungal degradation of EDPs can be achieved by using fungal bioreactors and fungal granules (Kasonga et al., 2019b).

9.4.1 Fungal bioreactors

Espinosa-Ortiz et al. (2016), and Syed and Yadav (2012), reported the use of dispersed fungal mycelium in EDPs bioremediation. Fungal ability to withstand adverse conditions like low nutrient concentration, low pH, and also to produce xenobiotics degrading enzymes are the advantages of fungal bioreactors. Application of stirred tank, fluidized bed, or airlift reactors along with hybrid reactors combining attached and pelleted fungal growth in a single reactor can also be used for EDPs remediation. Fungal granules were achieved by maintaining different pH, nutrient composition, varying dissolved oxygen, surfactants, and shear stress in bioreactors which provided enhanced EDPs removal from wastewater (Kasonga et al., 2019a, 2019b).

9.4.2 Formation of fungal granules

Cell aggregation for fungal granulation or dispersed fungal growth is especially favored by submerged cultures (Espinosa-Ortiz et al., 2016). Fungal granules or pellets are oval, spherical, or ellipsoidal in shape and sometimes appear as intertwined or densely packed hyphae. However, fungal granule formation requires optimum operating conditions such as fungal strain inoculum, optimum media composition, aeration, pH, salinity, rheology of growth media, and physicochemical properties of fungal inoculum. Granulation starts from swelling of spores causing germination followed by length-wise hyphal growth creating long branching which further helps in hyphae to hyphae aggregation producing fungal granules or pellets (Veiter et al., 2018).

Inoculum size, age, and amount are the key factors for successful fungal pellet formation and increasing granule diameter but granule formation depends on carbon source (glucose, sucrose), nutrients, and agitation speed. In submerged fungal bioreactors spore solution is used for fungal pellet formation whereas fungal mycelium fragments are required as a starter culture for the granulation process (Rodríguez-Couto, 2012).

Fungal granular reactors provide numerous advantages like bulk heat, mass and oxygen transfer, low power consumption, high settling velocity, high volumetric production, and improvement of media rheological properties by providing low-media viscosity and no adherence of fungal culture with reactor ensure quick separation process. However, autolysis of large pellets, nonuniformity in granule structure, low oxygen and nutrient transportation into the core granules, zone wise difference in growth, and metabolic patterns are the few limitations reported for fungal granulation by researchers (Espinosa-Ortiz et al., 2016). Literature suggested that the selection of any particular morphological growth of fungus (pellet or granules) enhanced EDPs removal properties in a fungal reactor. Hence, the future success in fungal remediation of EDPs depends on the appropriate approach toward a morphological modification of fungus to maintain uniformity in the stability and EDPs removal efficiency in the fungal reactor (Papagianni, 2004) and (Kasonga et al., 2021). A list of acronyms from the entire chapter is summarized in Table 9.4.

9.5 Conclusions and perspectives

EDPs remediation is one of the current international environmental concerns as they exist as micropollutants in treated and untreated domestic wastewater but exhibit long-term damages on the endocrine system which may further cause feminization of male fish, carcinoma, reproductive damages, and other diseases in humans and animals. Natural and synthetic estrogens and other phenolic EDPs were mostly removed by conventional processes like membrane separation or adsorption which were less eco-friendly and economic than biological methods. In the bacterial degradation of estrogens, E2 degradation usually follows E2 to E1 conversion pathway reducing estrogenic activities of the compounds. EDPs removal efficiency was further improved by 90% by using several membrane and fungal bioreactors. Use of compact, spherical, highly settleable, and microbial populated aerobic granular sludge enhanced 90–99% removal of E1, E2, EE2, BPA, TCS, and 4t-OP along with COD and other nutrients (N, P) removal from

Table 9.4 List of acronyms for the chapter.

List of acronyms	
EDPs	Endocrine disrupting pollutants
PCP	Personal care products
PCB	Polychlorinated biphenyls
COD	Chemical oxygen demand
CW	Constructed wetland
WW	Wastewater
DDT	Dichlorodiphenyltrichloroethane
BFR	Brominated flame retarder
ERβ	β-estrogen receptor
BPA	Bisphenol A
TSH	Thyroid stimulating hormone
PAH	Polyaromatic hydrocarbons
PPAR	Peroxisome proliferator-activated receptor
TP	Total phosphorus
MBR	Membrane bioreactor
GC–MS	Gas chromatography mass spectrometry
DEP	Diethyl phthalate
BBP	Butyl benzyl phthalate
BEHP	Bis-2-ethylhexyl phthalate
SBBGR	Sequencing batch biofilter granular reactor
AGS	Aerobic granular sludge
DCPP	Dichlorophenyl phosphine
AGR	Aerobic granular reactor
SAL	Salicyclic acid
TCS	Triclosan
NP1EO	Nonylphenol monoethoxylates
NP2EO	Nonylphenol diethoxylates
BPS	Bisphenol S
BPF	Bisphenol F
4tBP	4-Tert-butylphenol
LC–MS	Liquid chromatography mass spectrometry
NP	Nonylphenol
EE	Ethynylestradiol

wastewater. Constructed wetlands added a new dimension in emerging biological technique which was established on basic mechanisms of biodegradation, adsorption, and phytoremediation largely reported for EDPs removal from domestic wastewater.

However, the increasing worldwide population and high demand for pharmaceutical compounds are the reasons behind EDPs pollution in the environment. Limitation in research data on fate and health hazards of EDPs and their toxic byproducts, lack of regular monitoring, and requirement of sophisticated detection techniques are still the challenges for EDPs bioremediation which can be mitigated by regulating strict limitations on EDPs usage and by framing certain threshold disposal limits. Fungal pellets or granules appeared to be suitable seed cultures in EDPs biodegradation for their low energy cost, improvement in media rheology, nonsticky property, high mass transfer, and volumetric production which indicate potential future research scope by coupling physicochemical technique with fungal bioreactors for complete removal of trace EDPs from wastewater.

Declaration

Both authors have equal contribution to the paper and bear the same weightage.

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Microbial degradation of endocrine disruptors from industrial wastewater: Removal efficiency and metabolic mechanism

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10.1 Introduction

Estrogens are of high octanol–water partition coefficients and persistent nature, which can cause easy accumulation in animals and environments. These chemicals have been classified as group one carcinogens by the World Health Organization. Frequent occurrence of estrogens in surface water, groundwater, wastewater, seawater, and soil has induced emerging concerns since these endocrine disrupting pollutants (EDPs) readily cause disruption of sexual development in animals. Although traditionally conventional technologies are well designed for the treatment of organic substrates of high bioavailability, their performance in removal of such trace EDPs is relatively limited. Approaches such as adsorption, advanced oxidation processes, enzymatic catalysis, and microbial degradation have been developed for efficient treatment of such EDPs from various water matrixes (Vieira et al., 2021). Among these technologies, microbial biodegradation seems to have more engineering feasibilities since the generated biomass can be used to produce high-value-added by-products (Xiong et al., 2018). This chapter has focused on the recent trends in the bacteria- and microalgae-based biotechnologies for efficient treatment of estrogens. Several advanced processes for enhancement of estrogens' removal have been discussed.

10.2 Biodegradation and metabolic mechanisms of endocrine-disrupting estrogens

10.2.1 Biodegradation and metabolic mechanisms of estrogens by isolated bacteria

Isolation of estrogen-degrading bacteria (EDBs) from diverse environmental systems has been of great interests in the past decades (Ibero et al., 2020). Reported sources for isolation

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of EDBs are soils, activated sludge, sandy aquifers, and compost. These species belonging to the bacterial phyla of *Proteobacteria*, *Bacteroidetes*, *Firmicutes*, and *Actinobacteria* can efficiently degrade estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2) from wastewaters (Ibero et al., 2020; Chen et al., 2017; Liu et al., 2017). Five bacterial species belonging to the genus of *Rhodococcus* and *Sphingomonas* have been isolated from soil and were found to efficiently remove E1 and E2 with achieving 50–90% dissipation after 24–120 h of cultivation (Kurisu et al., 2010).The authors also demonstrated that bacterial degradation of E2 can be done through hydroxylation at C4 point and benzene ring meta-cleavage. Immobilized *Novosphingobium* sp. ARI-1 in calcium alginate achieved 80.43%, 94.76%, and 100% removal of E1, E2, and E3 from sewage after 7 days of cultivation (Liu et al., 2017). These results demonstrated free or immobilized bacteria is good candidate for bioremediation of estrogens.

Yu et al. (2007) isolated 14 bacterial species belonging to the genera of *Brevundimonas, Nocardioides, Aminobacter, Sphingomonas,* and *Flavobacterium* from activated sludge, and found that the strain *Sphingomonas* sp. KC8 was with the highest removal capacities of E2, which was demonstrated by the no residual E2 and E1 or estrogenic activities after 5 days of cultivation. Same group also found KC8 can degrade estrone through hydroxylation, bond cleavage, and oxidation with formation of a pyridinestrone acid, meta-cleavage product, and 4-hydroxyestrone (Chen et al., 2017). Later, three estrogen catabolic gene clusters in KC8 were found using functional genomics, and characterized two metabolic enzymes including 4-hydroxyestrone 4,5-dioxygenase and 17β-estradiol dehydrogenase in the bacterial strain KC8, which are the key enzymes in diverse proteobacteria to cause degradation of E1 (Chen et al., 2017). Degradation intermediates of E2 by *Novosphingobium tardaugens* NBRC16725 unraveled the potential metabolic genes including *edcA* and *edcB*. These genes encode 17b-hydroxysteroid dehydrogenase, CYP450 enzyme, and 4-hydroxyestrone-4,5-dioxygenase, which transformed E2 into E1, hydrolyzed E1 into 4-hydroxylation estrone, and finally caused ring A cleavage (Ibero et al., 2020). These results have demonstrated that bacteria can degrade estrogens through hydroxylation, hydrogenation, oxidation, and bond and/or ring cleavage by the catalytic enzymes such as hydrogenase, monooxygenase, dioxygenase, and dehydrogenase (Fig. 10.1).

Removal capacities of seven heterotrophic bacterial species including *Rhodococcus zopfii, Rhodococcus erythropolis, Rhodococcus equi, Rhodococcus rhodochrous, Pseudomonas putida, Pseudomonas aeruginosa*, and *Bacillus subtilis* toward EE2 have been evaluated (Larcher et al., 2013). The authors have found *R. rhodochrous* showed best performance for EE2 treatment and the other removed 21–61% of EE2 from wastewater. However, the removal efficiency of EE2 by the bacterial mixture decreased with a final elimination of 43% (Larcher et al., 2013). On the other side, the synergistic result (98%) in the removal of E2 by cocultured *Acinetobacter* sp. and *Pseudomonas* sp. has been observed, where individual strains showed 77% and 68% elimination of E2 (Li et al., 2018). Although single bacterial species can achieve high removal efficiency of estrogens, and even can use estrogens as sole carbon source, the bioaugmentation of such isolated strains in microbial communities showed contradictory treatment of estrogens from real wastewater. Furthermore, environmental factors including pH, temperature, and elemental positions have strong effects on the removal of estrogens. For example, the optimal

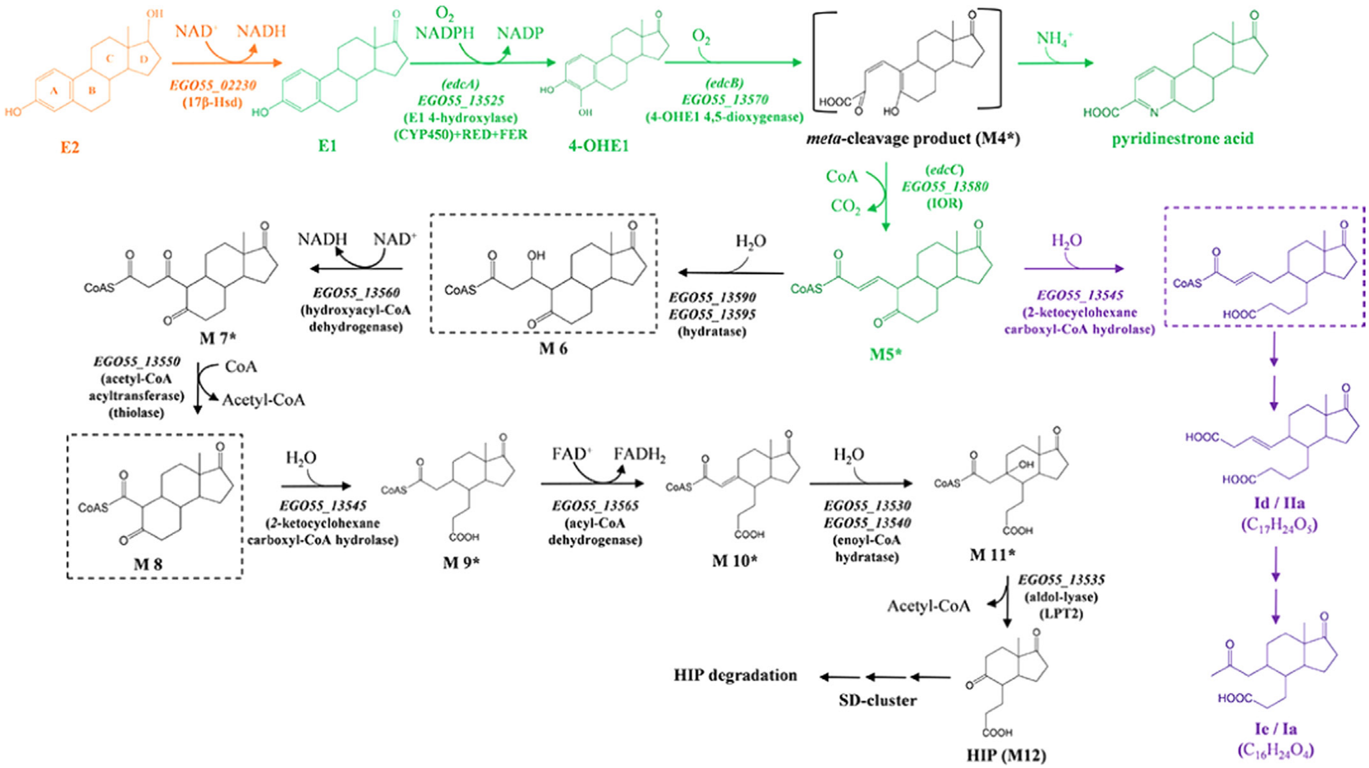

FIG. 10.1 Proposed metabolic mechanism of estrogens by a bacterial species, *N. tardaugens* NBRC 16725, and the corresponding genes (reproduced from Ibero et al., 2020 with reprint permission of Frontier publisher).

pH for removal of E2 by the *Acinetobacter* and *Pseudomonas* mixture ranged from 7 to 9, and found presence of organic substrates including acetate, glucose, and citrate inhibited the bacterial degradation of E2 (Li et al., 2018). Xiong et al. (2020a) investigated the effects of several environmental parameters including pH (3.0–11.0), salinity (4%), heavy metals (Cd^{2+} and Cu^{2+}), and surfactant on the removal of E2 by an isolated bacterial species, *Stenotrophomonas maltophilia* SJTH1. The authors have found these factors negligibly influenced the cell growth and E2 dissipation, and low doses of Cu^{2+} and Tween 80 promoted the removal of E2. Moreover, bioaugmentation of the *S. maltophilia* SJTH1 in clay soil achieved 80% elimination of E2 (Xiong et al., 2020a).

One more issue related to the bioremediation of estrogens by bacteria is that it seems like that some bacterial species can generate more hazardous intermediates from the biodegradation of estrogens (Wang et al., 2020a). Metabolic pathways of estrogens in a denitrifying bacterial species, *Denitratisoma* sp. strain DHT3 have been characterized, which showed that the bacterial species can anaerobically retroconvert estrogens into androgens by cobalamin-mediated methylation (Wang et al., 2020a). These results indicated the significance of the identification of bacterial degradation intermediates of estrogens, and there should be a comprehensive toxicity analysis of the formed by-products. Moreover, most (60%) of the isolated estrogens degradation bacterial species belong to the phylum of Proteobacteria, which contain many pathogenic species (Budeli et al., 2021). There should be a comprehensive ecological risk assessment for acclimation and bioaugmentation of such strains when considering as an effective remediation tool.

10.2.2 Biodegradation and metabolic mechanisms of estrogens by microalgae

Free and immobilized microalgae have been used to remove estrogens (Xiong et al., 2016, 2020b). Four freshwater microalgal species including *Chlorella vulgaris, Selenastrum capricornutum, Haematococcus pluvialis,* and *Scenedesmus quadricauda* were tested for the removal of E1, E2, and EE2 (Wang et al., 2019). EE2 is more persistent than E1 and E2 during the treatment, where 80–97% removal of E1 and 100% elimination of E2 have been reached with only 85% dissipation of EE2. Several metabolic pathways of estrogens by these microalgal species have been proposed, which indicated that microalgae can biotransform estrogens by hydroxylation, methylation, oxidation/reduction, and ring cleavage (Fig. 10.2). Two microalgal species *Chlamydomonas reinhardtii* and *Selenastrum capricornutum* were used to remove E2 and EE2 from anaerobic digester centrate, where *S. capricornutum* achieved 100% and 95% removal of E2 and EE2, respectively, and *C. reinhardtii* caused 100% and 76% dissipation of EE2 after 7 days of cultivation. The authors also found the presence of estrogens significantly inhibited the removal of other organic pollutants such as tris(2-butoxyethyl)phosphate (Hom-Diaz et al., 2015). It was found that 85% of 17α-E2 and E1, and 95% of 17β-E2 and E3 were removed by a green microalga, *Scenedesmus dimorphus* through sorption, direct-photolysis, and algae-mediated biotransformation, where microalgal transformation played major role (Zhang et al., 2014). A constructed photobioreactor containing *Chlorella*-dominated microalgal consortium to treat E2 polluted wastewater. The authors have found complete removal of E2 during indoor

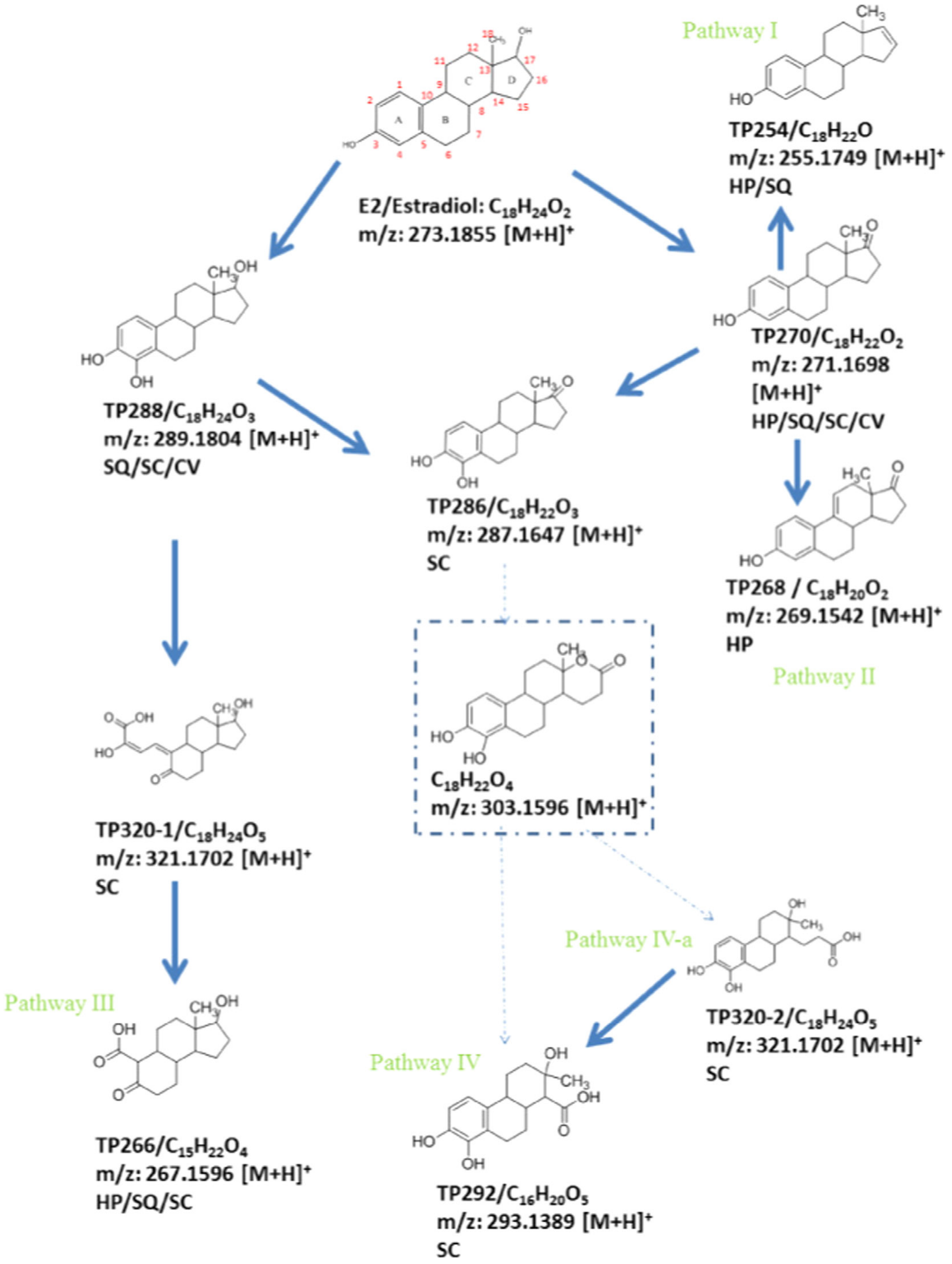

FIG. 10.2 Proposed metabolic pathways of E2 by microalgae (reproduced from Wang et al., 2019 with reprint permission of Elsevier).

and outdoor experiments, demonstrating that algae-based biotechnology is a promising tool for estrogens contaminated wastewaters (Parladé et al., 2018).

Immobilization of functional microalgal consortium dominated by *Chlorella* sp. and *Nitzschia acicularis* in alginate beads showed better removal of ammonia nitrogen (89%) and total phosphorus (96%) comparing to the efficiency in free living cells (64% and 90%). While, free living cell achieved faster removal of EE2 than the immobilized microalgae during 10 days of cultivation, which finally caused 97% elimination of EE2 (Solé et al., 2016). Aninoculum of 200 beads/mL of alginate immobilized microalgae performed 40–86%, 26–72%, and 85–99% removal of total nitrogen, total phosphorus, and E2. The authors also demonstrated that E2 was metabolized through decarboxylation, hydroxylation, glycosylation, O-methylation, and dehydrogenation. Interestingly, no detection of estrone and carcinogenic catechol estrogen quinones have been formed during this *Desmodesmus* sp.WR1-based technology (Wang et al., 2020b).

Free and immobilized microalgae-based biotechnologies have shown promising efficient for treatment of estrogens polluted wastewaters; however, most of current studies have focused on the performance of individual microalgal species. Biotransformation of EE2 by a freshwater green alga *Desmodesmus subspicatus* showed that mono- and dibrominated EE2 have been formed during microalgal degradation with presence of bromide (Maes et al., 2014). The brominated compounds are more readily accumulated and toxic than their parent compounds. Molecular mechanisms of microalgal degradation of estrogens remain unclear. Limited studies have conducted in a pilot-scale outdoors, and the effects of coexisting pollutants. Evolution of the microalgal communities during the treatment has been rarely reported. Therefore, there is still a big gap in terms of microalgae-based tools.

10.3 Effect of the coexisting contaminants on the biodegradation of estrogens

There are numerous contaminants (e.g., antibiotics, heavy metals) coexisting in natural systems, causing significant interaction on the fate of each other. For example, the removal of the mixture of 17β-estradiol (E2) and tetracyclines by a bacterial species, *Novosphingobium* sp. ES2-1 (Li et al., 2020a). The authors observed that no obvious effect of tetracycline and oxytetracycline with <0.1 mg/L on the removal of E2, and showed inhibition effect with dose of >10 mg/L. The strain ES2-1 finally achieved 52–100% removal of three estrogens (estrone, E2, and estriol) from natural water containing 0.2–3.85 μg/L tetracyclines (Li et al., 2020a). Higher concentrations of tetracyclines also influenced the metabolic pathways of E2 in *Novosphingobium* sp. since the abundance of pyridine derivatives of E2 has been elevated because of the antibiotics promoted the reactions of certain phenolic ring-opening products with ammonia (Fig. 10.3). He et al. (2019) used ^{14}C-labeled E2 to investigate the degradation and metabolic mechanism in swine manure with/without aminoglycosides, fluoroquinolones, chloramphenicols, tetracyclines, sulfonamides, and macrolides. The authors have found 94% removal of E2, of which 28% was mineralized, 9% was converted into E1, 9% was degraded into intermediates, and 48% was transformed into nonextractable by-products. Antibiotics have significant influence on

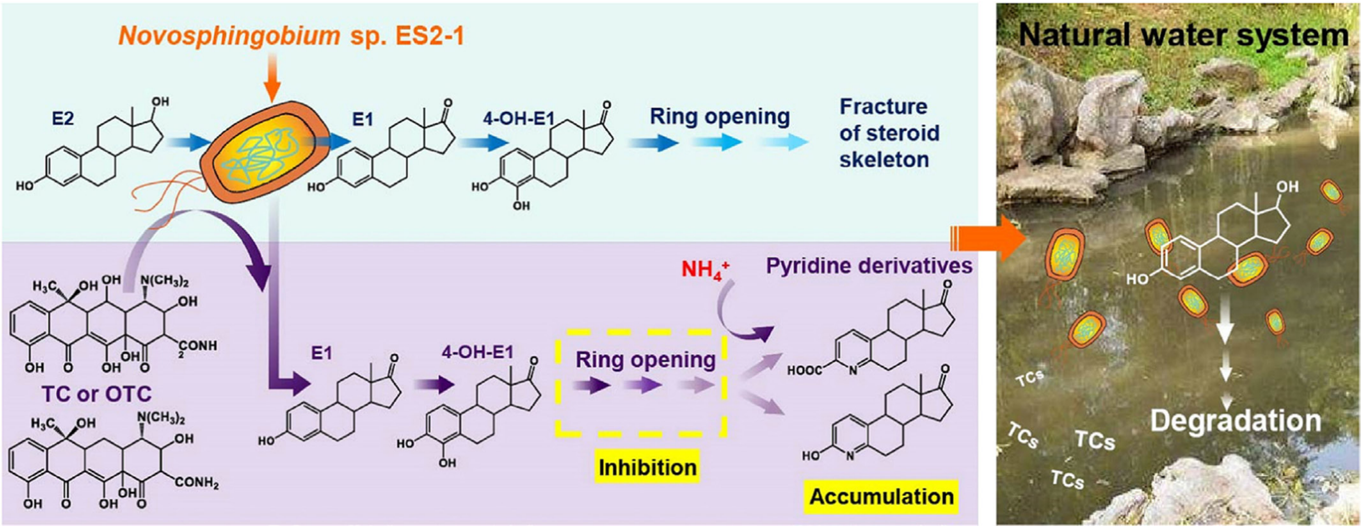

FIG. 10.3 Biotransformation pathways of estrogens in the presence of coexisting antibiotics (reproduced from Li et al., 2020a with reprint permission of Elsevier).

the removal of E2, where oxytetracycline hydrochloride, roxithromycin, and streptomycin sulfate inhibited E2 dissipation, and enrofloxacin and erythromycin promoted the removal of E2 (He et al., 2019). These results have indicated that cocontaminated antibiotics have significant influence on the bacterial removal of estrogens, and further investigation for a comprehensive understanding of the altered treatment efficiency should be supplied.

Co-contamination of heavy metals and estrogens has been frequently found in natural environments. Therefore, it is necessary to investigate the effect of such heavy metals on the bacterial and/or microalgal degradation of estrogens. The changes of removal efficiencies of E2 in existence of cadmium and copper, and found 6.25 mg/L Cd^{2+} negligibly influenced the elimination of E2, while same concentration Cu^{2+} promoted the removal of E2 (Xiong et al., 2020a). There is limited literature focusing on the effect of different heavy metals on the bacterial and microalgal removal estrogens, highlighting more evaluations should be given in coming future.

10.4 Improvement approaches for biodegradation of estrogens

10.4.1 Construction of microbial consortium

Establishment of microbial consortium with high estrogens degradation capacities has been of interest since this approach can act as a tertiary process for the treatment of such hazardous materials polluted wastewater. Microbial communities also rapidly adapt to the extreme conditions with evolution of more tolerant species, such feature enables engineers to find more reliable consortium. The microbiome of a submerged fixed-film reactor under the influence of 1 μg/L of EE2 has been identified using 16S rRNA gene amplicon sequencing or by bacterial isolation using culture-dependent approach. The authors have found a *Pseudomonas* and *Acinetobacter* consortium, which can utilize EE2 as sole carbon source (Vilela et al., 2020). A microalgae-bacteria consortium was established and can efficiently remove 50–93.75% of E2 during a year's operation, which found the environmental factors such as temperature and nutrients significantly influenced the treatment (Parladé et al., 2018). A bacterial consortium enriched from activated sludge showed completed removal of E1, E2, and EE2, where E2 was initially converted to E1 in the first 24 h, following degradation of E1 in coming 3–4 days, and EE2 was removed in 7–15 days as sole carbon source (Muller et al., 2010). Identification of the microbial communities has indicated that the bacterial consortium was consisted of *Denitrobacter* sp., *Pusillimonas* sp., *Brevundimonas diminuta*, and *Alcaligenes faecalis*. Similar to the isolation of capable bacterial species, construction of microbial consortium is also a promising approach to enhance the engineering feasibility of biodegradation of estrogens.

10.4.2 Development of cometabolic approach for enhanced degradation of estrogens

Additional carbon sources can drive the formation of the multiple substrate utilizing estrogen degraders during the adaptation strategy of the microbial communities (Xiong et al., 2017).

These cometabolic organic carbon sources also play essential roles in promising the activities of estrogen degraders. Effect of several carbon sources including glucose, sodium succinate and sodium acetate on biodegradation of E2 by a bacterial species, *Sphingomonas* sp. was investigated, and the authors found the removal efficiency of E2 was enhanced by 20% (Li et al., 2020b). An insight into the metabolomics of the bacterial strain indicated that metabolites belonging to membrane transport, carbohydrates, amino acid, and nucleotide were significantly influenced by E2. In the other study, the effects of organic carbon doses and loading rate on the bacterial degradation of E1 have been investigated, and found increased organic carbon concentrations elevated the removal efficiency of E1 (Tan et al., 2013). Additional acetonitrile reduced the lag phase and degradation period for EE2 by a bacterial consortium (Muller et al., 2010). Quantitative proteomic analysis has been applied to explain the enhanced biodegradation of E1 by a bacterial species, *Hydrogenophaga atypica* ZD1 with presence of nitrogen and carbon sources (Du et al., 2017). Addition of acetic acid and humic acid shortened the degradation duration of E1 from 168 h to 120 h, while, majority of significantly changed enzymes such as isocitrate dehydrogenase, malate dehydrogenase, lipoamide dehydrogenase, dihydrolipoyltranssuccinylase, branched-chain-amino-acid aminotransferase, and 4-hydroxyphenylpyruvate dioxygenase have been in the TCA cycle and tyrosine metabolism pathways (Fig. 10.4). In-depth mechanisms to explain the behind reason of cometabolism enhanced treatment efficiency are still limited.

10.5 Integrated processes for biodegradation of endocrine-disrupting estrogens

10.5.1 Integrated advanced oxidation processes and microbial degradation

Integrated advanced oxidation processes (AOPs) and microbial degradation technology have been suggested as the effective way for effective treatment of such biologically persistent wastewater (Oller et al., 2011). The hydroxyl radicals play major roles in photodegradation, and microbes are the main functional components. AOPs such as UV/TiO_2, photo-Fenton, oxidation by ferrate, and ClO_2 have shown effective treatment of estrogens (Fig. 10.5). On one side, in AOPs, the treatment efficiency of estrogens is significantly influenced by several factors including water categories, doses of dissolved organic matters, pH, and concentrations of contaminants. The removal percentage of estrogens will be decreased by the presence of organic substances. For example, the removal rate of E1 in sewage effluent was slower than that in deionized water (Trudeau et al., 2011). Coupling UV/H_2O_2 and O_3 decreased the treatment efficiencies of estrogens (Pereira et al., 2011). The ozone-mediated removal of estrogens increased with increasing pH with showing maximum dissipation at pH 10 (Deborde et al., 2005). On the other side, application of AOPs to degrade estrogens can also generate more hazardous intermediates. Larcher et al. (2012) demonstrated that EE2 was efficiently removed by ozonation, however, the treated effluent has a greater negative effect on testosterone secretion. Remaining

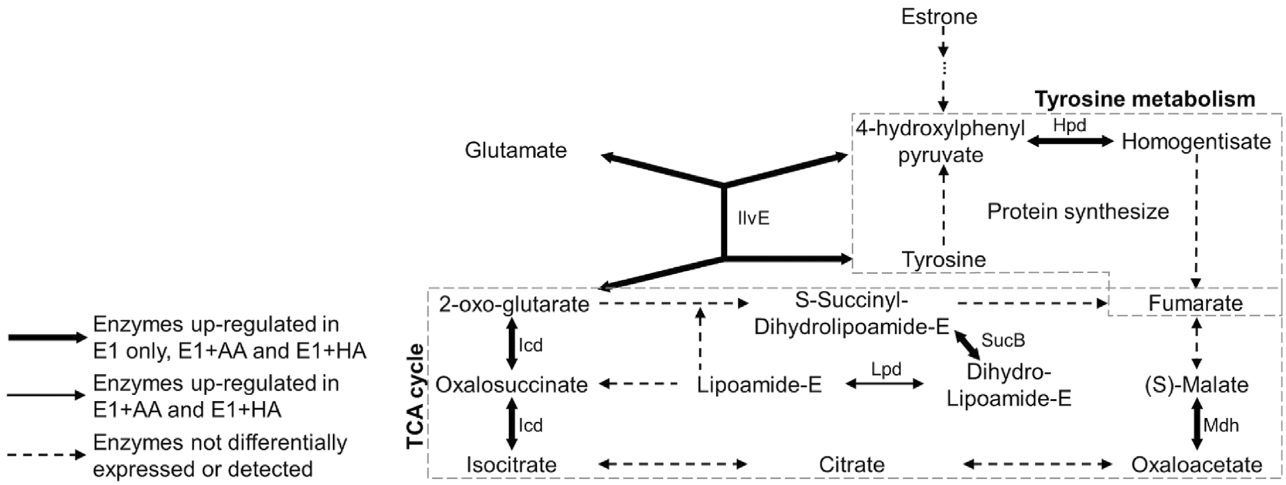

FIG. 10.4 **Changed metabolic pathways of** *Hydrogenophag aatypica* **by catabolism (reproduced from Du et al., 2017 with reprint permission of Elsevier).**

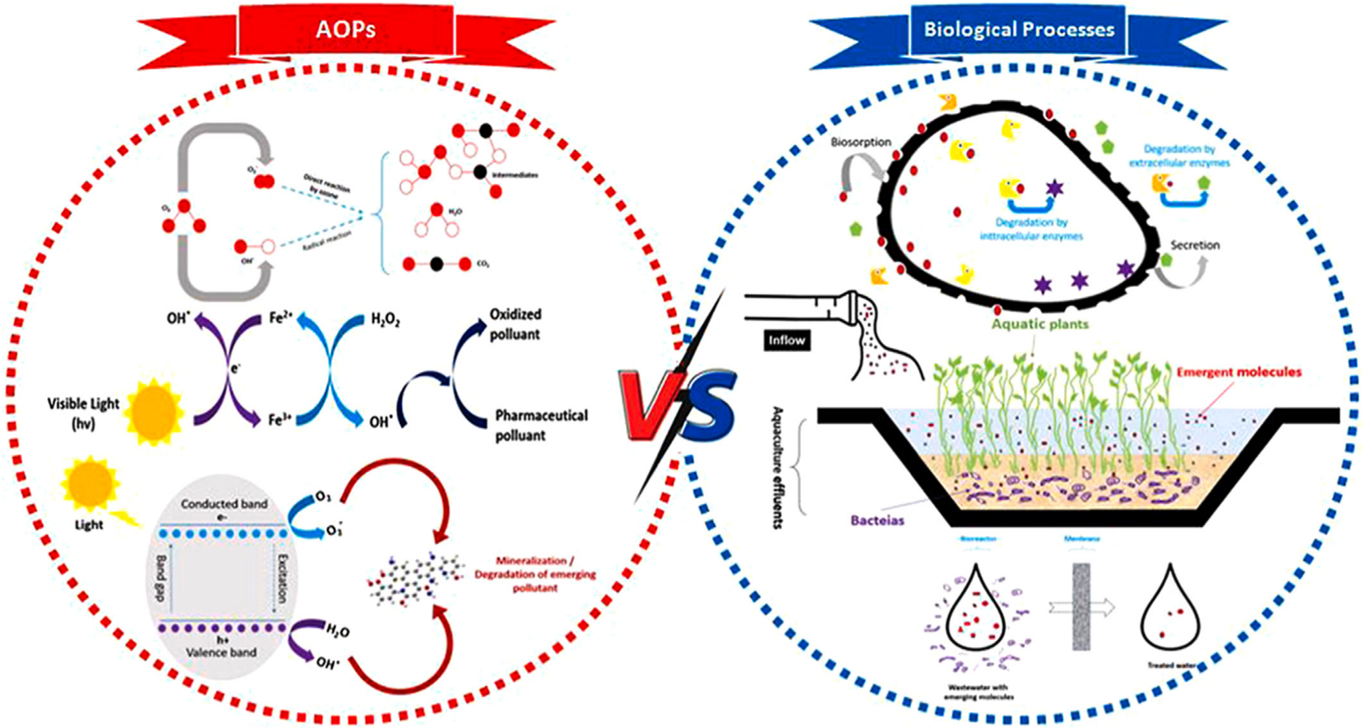

FIG. 10.5 Integrated advanced oxidation processes and biological processes for the treatment of estrogens from wastewater (reproduced from Taoufik et al., 2021 with reprint permission of Elsevier).

estrogenic effect of the AOPs treated estrogen-polluted wastewater and high operation cost has motivated people for better process. Biodegradation has shown good fitness. For example, aerated biological filter was attached to an electron beam, which helped to reduce the toxicity of treated water (He et al., 2014); Li et al. (2015) also demonstrated that the aerated biological filtration process decreased the concentrations of unknown by-products, which generated from ozonation. Moreover, integration of AOPs and microbial degradation has come from the truth of that the major destroying mechanisms of persistent organic pollutants in natural are biodegradation and photodegradation. It has been demonstrated that AOPs as a pretreatment method increased the bioavailability for following biological processes, and integrated Fenton/biological process caused 65% reduction of H_2O_2 absorption comparing to the individual Fenton process (Castillejo et al., 2018). Prado et al. (2017) found that integrating AOPs such as ozonation and ultrasound(O_3/US) and membrane bioreactor not only reduced 80% of the concentrations of residual intermediates, but also significantly slighted the fouling of biofilm. Although integration of AOPs and microbial degradation has been demonstrated as an efficient technology for removal of different pollutants from water, there are still lots of limitations. Current researches are not sufficient to support the application of this hybrid process. The existing investigations have mostly conducted in laboratory-scale, the engineering feasibility and economic perspectives have not been comprehensively evaluated (Taoufik et al., 2021).

10.5.2 Integrated constructed wetlands and microbial degradation

Constructed wetlands (CW) have been widely used for the remediation of estrogens from waters since this green technology is environmental-friendly, solar-activated, and cost-effective (Kurade et al., 2019, 2021; Xiong et al., 2019) (Fig. 10.6). Different types of CWs including vertical flow CW (VFCW), horizontal flow CW (HFCW), free water surface CW (FWSCW), and hybrid CW (HCW) have been investigated for their potential applications to remove estrogens (Xiong et al., 2021; Zhao et al., 2021). It has been demonstrated that the most effective CW to remove EE2 is *Eichhornia crassipes* planted CW (ECCW) comparing to the *Cyperusisocladus* planted CW, and CW without macrophyte. The ECCW system removed 35.8–54.7% of EE2 with gravel as support media, while, the removal efficiency was increased up to 95.6% in 2 days (Campos et al., 2019). The removal patterns of three HFCWs, which were planted with *Phragmites australis* and *Phalaris arundinacea* (CW1), and *Phragmites australis* (CW2, CW3) with gravel as support media during 10 years of operation in the Czech Republic, and the average removal of EE2 has ranged from 56.7% to 81.4% (Vymazal et al., 2015). A VFCW (depth of 7.5, 30, and 60 cm) showed 67.8%, 84.0%, and 75.3% removal of E1, E2, and EE2 (Song et al., 2009). A HCWs with two vertical flow type, one horizontal flow and one surface flow with cultivation of *P. australis* showed 20–80% removal of EE2 from wastewater (Ávila et al., 2014). Overall evaluation showed that different CWs can efficiently remove estrogens from wastewaters, however, Ilyas and Hullebusch (2020) found that the environmental risk of estrogens still remains after treatment by CWs. They have found that the risk quotients of estrogens (E1, E2, E3, and EE2) ranged from 10 to 1000,000, which were calculated with the concentrations of CW influent and effluent (Ilyas et al., 2020). These results suggest an integrated process is necessary to further

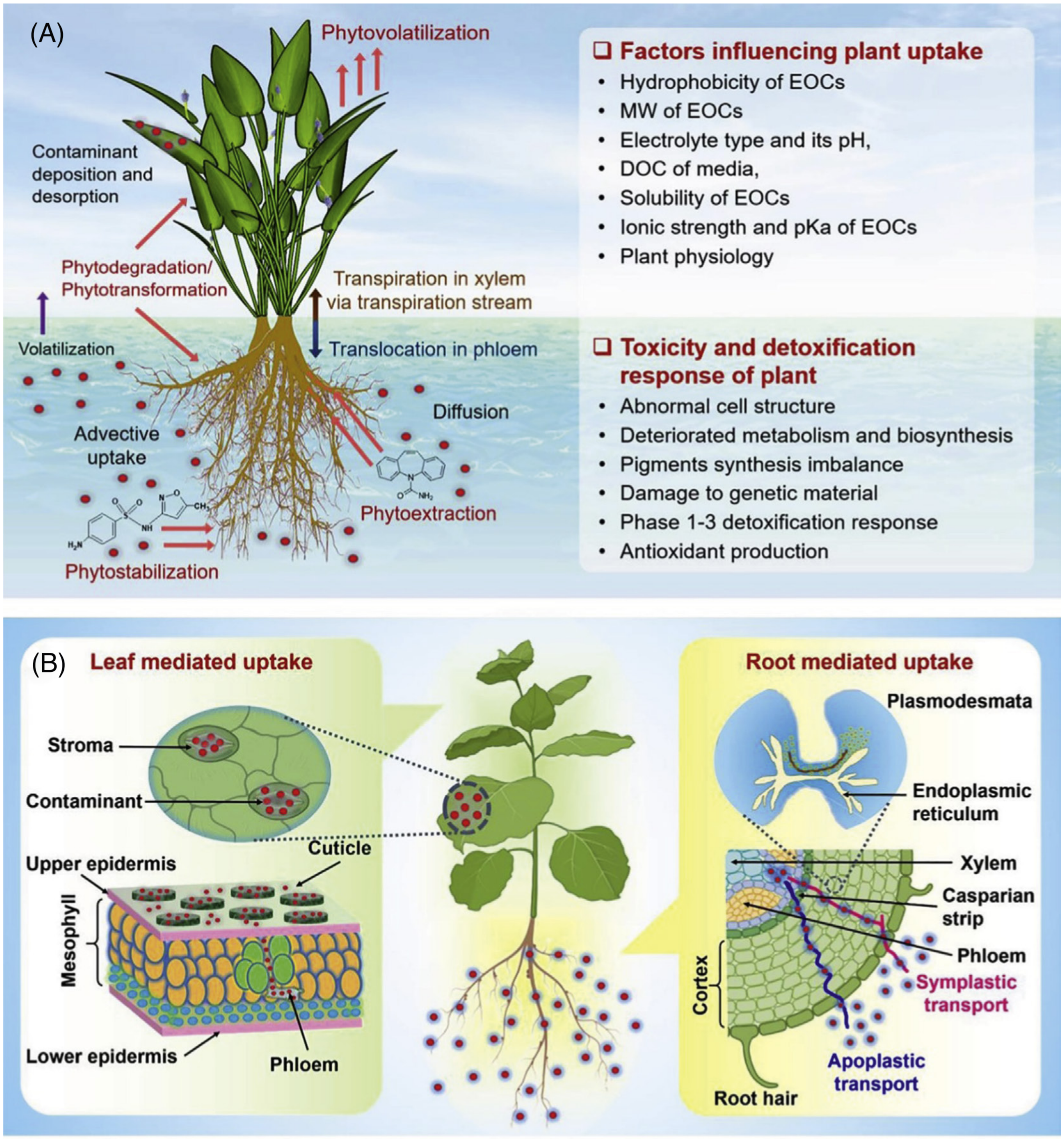

FIG. 10.6 Insights into the phytoremediation mechanisms of estrogens (reproduced from Kurade et al., 2021 with reprint permission of Elsevier).

reduce the environmental hazards of these emerging contaminants. An integrated high-rate algal ponds and VFCW achieved high removal of pollutants even at winter season (Zhao et al., 2016). Greater duckweed (*Spirodela polyrhiza*)-based FWCW achieved 32.2–100% removal of four xenobiotics (Liu et al., 2017). There are limited studies to show the removal efficiencies of estrogens in the hybrid process, indicating a big research gap in this field.

10.6 Conclusions and perspectives

Individual bacteria, microalgae, and their consortium-based biotechnologies for the degradation of various estrogens have been comprehensively reviewed in this chapter. Overall evaluation of these processes showed their high treatment efficiencies toward the removal of estrogens from wastewaters. While, EE2 has been suggested as the most persistent compound among the endocrine disrupting estrogens. Most of the bacterial degradation of estrogens has tried to isolate a capable species, and to identify the molecular mechanisms of estrogen biodegradation. Application of microalgae-based methods have focused on the free- and immobilized cells for removal of estrogens, as well as the generation of biomass for high-value by-products generation. Several hybrid processes including integrated AOPs and biological process and integrated CWs and biological processes have shown their priority for enhancement of the engineering feasibility. However, there are still rare studies in pilot-scale, indicating a design is necessary to achieve the application of such processes in treatment of estrogens from diverse environments.

Acknowledgment

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11

Bacterial degradation of emerging pollutants from paper industry wastewater

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11.1 Introduction

Numerous EDPs are released into the environment through industrial effluents and anthropogenic activity (Padmanabhan et al., 2021). As of now, lot of scientific literatures available which deeply focused on characterization of EDPs and their adverse effect on environment and human health. Besides industrial activity, other sources of EDPs included are by-products of fungicides, pesticides, plasticizers, plastics, phytoestrogens, pharmaceutical agents, polychlorinated biphenyls, polybrominated biphenyls, dioxins, and industrial/commercial products (Mattiske and Pask, 2021). According to guidelines of the US Environmental Protection Agency (EPA), EDPs are external compounds that may be interfering with or affect various types of vital processes of human physiology like, metabolism, secretion, transport, receptor binding affinity (Kabir et al., 2015; Kiyama and Wada-Kiyama, 2015). Criteria projected by the European Commission, for the process of EDPs, it seems clear that EDPs should display three promise actions: (1) pathologic and /or deleterious endocrine-mediated activity; (2) endocrine activity; (3) establishing lead to a cause-effect connection between endocrine activity and substance in exposed subjects (Slama et al., 2016). Later on, most of the EDPs are artificial substances that adversely interact with hormonal receptors/or regulation of genome expression about endocrine activity (Wan et al., 2021). Various processes such as DNA methylation and/or acetylation and histone modifications as a result of epigenetic changes, which was involved in endocrine disruption (Wan et al., 2021; Street et al., 2021).

EDPs can enter into the aquatic environment (river, streams, and surface waters) as a result of effluent discharge of industrial and municipal wastewater (Zhang et al., 2016). Naturally and synthetically, EDPs are emitted from various industrial activities that are directly threatening for living lifestyle and are not regulated as well. The physicochemical processes (adsorption,

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membrane filtration, advanced oxidation process, activated carbon treatment, electrochemical methods, etc.) are continuously operational. However, this approach is very costly and energy-consuming (Bila et al., 2007). Alternatively, bioremediation is the most environmentally friendly, cost-effective approach and highly public acceptance for the degradation of EDPs (Bharagava et al., 2018). Using among diverse microorganism potential such as bacteria and fungi for the breakdown of EDPs have been previously well-acknowledged information in various kinds of literature since last decade. This book chapter explores recent information relating to EDPs including the origin, allocation/shipping, and animal-linked health risk, and their corrective approaches for environmental/ecological wellbeing aspects.

11.2 Sources of endocrine-disrupting pollutants

People are exposed to various EDPs through a variety of sources, such as the consumption of food and beverages, the use of cosmetics and pesticides, and other industrial sources as detailed in the following sections.

11.2.1 Endocrine-disrupting pollutants from industrial wastewater

Industrial effluents emerged due to various chemical processes that have been considered as the core source of EDPs and phthalates compounds (Bharagava et al., 2018; Saxena and Bharagava, 2017). EDPs runoff from various industrial effluents such as pulp and paper industry, leather industry, and distillery industry, etc. Effluents released from pulp and paper are the greater source of the very diverse nature of EDPs (Chowdhary et al., 2017). Some EDPs, such as phthalates, are released from the paper production process using printing ink, glue, and softeners in additives and eventually become part of the pulp and paper effluents. EDPs such as alkylphenol polyethoxylates (APEs) and their related compounds have been reported to have an estrogenic effect under in vitro and in vivo conditions. By-product of APEs, used as cleaners, defoamers, and emulsifiers agents in the paper industry (Kumar et al., 2008).

11.2.2 Plastic material and food packaging containers

Plastic materials and food packaging containers contain bisphenol A and phthalate ester EDPs that migrate and accumulate in foods at small concentrations (Kumar et al., 2008).

11.2.3 Occupational exposure

If a person was working in the lead, mercury, manganese, and dibromochloropropane, carbon disulfide, and ethylene glycol-rich contaminated area can harm male reproductive organs (Kumar et al., 2008).

11.2.4 Endocrine-disrupting pollutants in drinking water and sewage

EDPs can be a major source such as drinking water of the sea, lakes, rivers, and sewage, for wildlife animals, and humans (Kumar et al., 2008).

11.2.5 Cosmetics and personal care products and their effects

The term “cosmetics” denotes the beautifying products of the body (Oumeish, 2001). Man has made many discoveries and developments since ancient times for the beautification of females. Over the centuries, many cosmetics have evolved and been influenced by the choice of ethnic traditions (Oumeish, 2001). Over the past decades, the variety of cosmetics and personal care products (PCPs) has grown in parallel with the quantity manufactured and consumed in both developed and developing countries. For example, in Spain has increased consecutively consumption of cosmetics and PCPs. Out of the total 1280 million units of these products, a total of 770 million units were exported during 2018. To date, consumption of cosmetics and perfumes by the United States is 78.6 billion euros, China 52 billion euros, Japan 32 billion euros, and Brazil 28 billion euros [https://www.stanpa.com/sector-en-cifras/mercado-cosmetico-ue/cosmetica-union-europea/]. It is therefore accepted that women use cosmetics and PCPs in greater quantities than men (Biesterbos et al., 2013), and therefore, potential adverse effects may primarily affect this population. EDPs from cosmetics and PCPs actively play a role in the development and advancement of countless gynecological diseases such as endometriosis and endometrial cancer. However, no studies have found yet the possible contribution of other EDPs which were released from cosmetics and PCPs such as parabens, camphene, and dimethicone for people at risk for endometriosis.

11.3 Types of endocrine-disrupting pollutants

EDPs are pollutants that hinder the binding activity of the receptor, leading to the synthesis, secretion, shipping, or elimination of naturally synthesized hormones in the body that are exclusively responsible for developmental, behavioral, fertility-related imbalances and remain uphold the maintenance of homeostasis. Nonylphenols and bisphenol A act as endocrine disrupters. Most of the biological processes in the body are regulated by an undisturbed endocrine system such as the development of the nervous system, reproductive growth, and their related function, metabolism, and blood sugar levels as well through conception through adulthood and into old age. EDPs are pollutants of natural (phytoestrogens) and anthropogenic chemicals (pesticides, alkylphenols, etc.). Some major EDPs are given below (Harrison and Hester, 1999; Diamanti-Kandarakis et al., 2009).

11.3.1 Polychlorinated biphenyls

These compounds are widely used as coolant fluids in capacitors, transformers, and electric motors. These chemicals were banned from 1975 because of environmental toxicity concerns and classified as persistent organic pollutants.

11.3.2 Alkylphenols

Some chemicals are classified as butylphenol, octylphenol, nonylphenol, and amylphenol. Those compounds are nonionic surfactants in detergents and paints.

11.3.3 Dioxins

Dioxins are polyhalogenated organic compounds that are considered significant pollutants to the environment. It bioaccumulates in humans and wildlife due to its lipophilic properties and may have detrimental effects on the developmental process. It also causes cancer.

11.3.4 Polyethoxylates

Nonylphenol and octylphenol are the breakdown products of herbicides, pesticides, and plastics found in industrial and sewage effluents.

11.3.5 Phthalate esters

It acts as plasticizers. These are usually for the construction of milk bottles and other plastic goods.

11.4 Mechanisms of action of endocrine-disrupting pollutants

EDPs work at different levels which interfere with a range of hormone-signaling sponsored pathways. For example, it acts on the synthesis, metabolism, or degradation of circulating hormone levels. They can interfere with the increase or decrease of the specific receptors for hormonal action and as to result, it affects their ability to respond to natural hormones. Many EDPs have been released as cosmetics and PCPs that have been evidenced to exert antiandrogenic and estrogenic reported in both in vivo and vitro studies (Kerdivel et al., 2013; Charles and Darbre, 2013). Estrogen receptor-α signaling pathways responsible that can induce oxidative stresses due to EDPs (Cho et al., 2018). Many EDPs to trigger inflammatory microenvironment are supported by previously reported evidence (Peinado et al., 2020). Both oxidative and inflammatory responses have been advocated as critical mechanisms in a variety of chronic diseases and beyond some gynecological situations such as endometriosis (Gupta et al., 2006; Lambrinoudaki et al., 2009).

11.5 Endocrine-disrupting pollutants: adverse impact on environment and health hazard

In recent years, human exposure to a diverse range of EDPs has raised mindfulness due to their association with human health, livestock, and wildlife as documented by several epidemiological and experimental studies (Fig. 11.1).

11.5.1 Endocrine-disrupting pollutants and mammals

Exposure to organochlorines responsible for deformity of reproductive and immune function was observed in the Baltic seals (Routti et al., 2010).

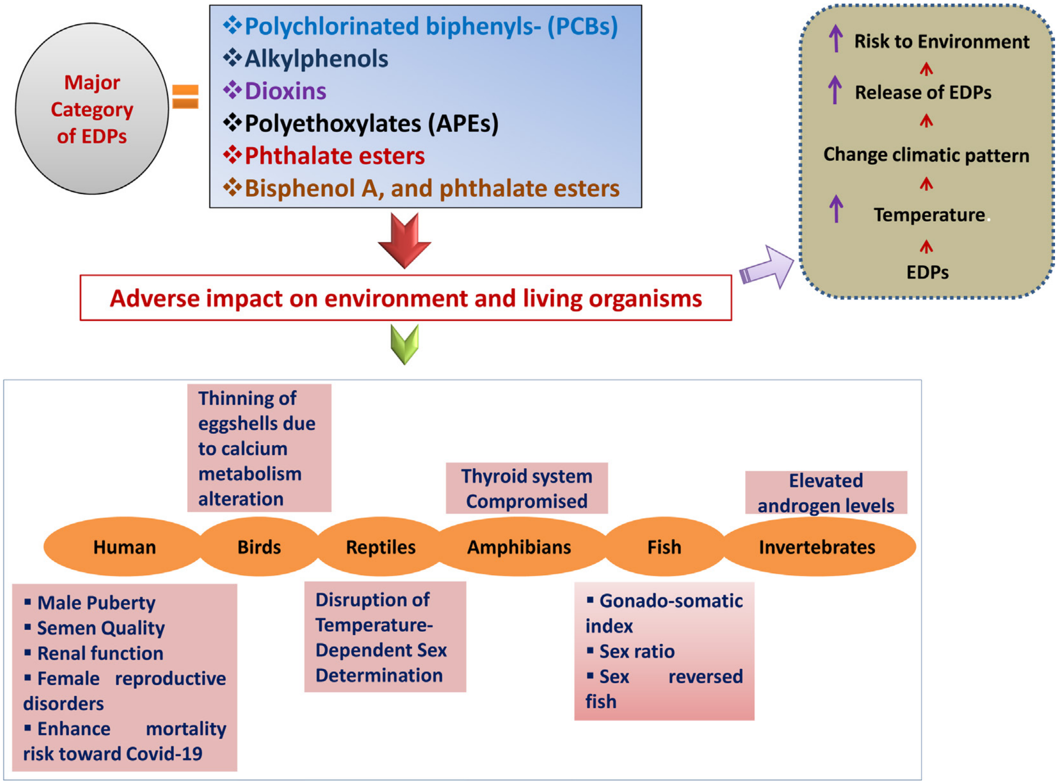

FIG. 11.1 Effect of endocrine-disrupting pollutants (EDPs) on the environment and all living organisms.

11.5.2 Birds

Dichlorodiphenyltrichloroethane (DDT) is a polychlorinated pesticide. It alters the calcium metabolism of birds, in such a way that results in thinning of eggshells by DDT and its metabolite DDE (1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene) (Brausch et al., 2012). Embryonic abnormalities in fish-eating birds have been directly linked to polychlorinated biphenyls (PCBs) exposure, but the actual reason behind this is uncertain (Hayes and Kruger, 2014).

11.5.3 Reptiles

Reptiles are considered as good biomodels for revealing the endocrine disrupter's mechanisms due to the different methods of sex determination of different types of reptile species, such as temperature-dependent sex determination. The experience of natural and manufactured chemicals (such as PCBs and organochlorines pesticides) to embryonic cells leads to temperature-dependent sex determination (Flint et al., 2012).

11.5.4 Amphibians

The impact of EDPs was shown on the thyroid gland of the amphibian animal model (*Xenopus laevis*) to be assessed, while the numerous categories of the reproductive requirement of comparative studies to test whether the common endocrine theories exist among several species such as anurans and urodeles (Kloas, 2002).

11.5.5 Fish

Effluent from the pulp and paper industry can have reproduction effects and contribute to endocrine function that alters reproductive development in fishes, for example, few quantifiable characteristics (Scholz and Klüver, 2009).

11.5.6 Invertebrates

The masculinization of marine gastropods exposed to tributyltin was responsible for its worldwide decline. Altered aromatase activity *via* the endocrine system could be responsible for the elevation of androgen levels (Matthiessen and Gibbs, 1998).

11.5.7 Human health

The adverse effects of EDPs on human health are still considered a controversial issue among the scientific community in the world (Annamalai and Namasivayam, 2015). Sometimes a minimal amount of chemicals can have a greater impact on health than a very high amount. Low concentrations of EDPs binding to receptors are sufficient to provoke biological responses. In contrast, higher concentrations at the same receptors inhibit the respective pathways due to receptors saturation (Boudia et al., 2014). Long-term exposure to low doses of certain chemicals can have adverse health effects.

11.5.8 Male reproductive disorders interconnected to endocrine-disrupting pollutants

Human sperm functionality is also affected by reactive oxidative stress generated throughout the metabolism of chemicals, perhaps an additional probable effect of EDPs that causes infertility (Sidorkiewicz et al., 2017).

11.5.9 Male puberty

A boy achieving earlier onset of puberty due to the progression of puberty interrupted by peripubertal exposure to bisphenol A (Wang et al., 2017a).

11.5.10 Semen quality

Several EDPs such as organophosphate pesticides (Melgarejo et al., 2015), bisphenol A (Meeker et al., 2010), perfluorinated compounds (Vested et al., 2013), phthalates (Bloom et al., 2015), and organochlorines (Mínguez-Alarcón et al., 2017) have been found to adversely affect semen quality.

11.5.11 Cryptorchidism

Several studies have found that prenatal or early childhood exposure to several chemicals such as PBDEs (polybrominated diphenyl ethers) (Goodyer et al., 2017), bisphenol A, parabens (Fernández et al., 2016), and PCBs (Koskenniemi et al., 2015) were associated with cryptorchidism.

11.5.12 Role in neurodevelopmental disorders

Adverse cognitive outcomes impart behavioral such as lower IQ, social communication characteristics in children were observed due to in utero exposure (Kim et al., 2018). Other EDCs such as organophosphates (Bouchard et al., 2011), PBDEs (Chen et al., 2014), perfluorinated compounds (Jeddy et al., 2017), and PCBs (Kim et al., 2018) were also adversely associated with varying degrees of behavioral problems and low IQ. Some evidence has shown that PBDEs and PCBs affect neuropsychological status in adults (Arguedas, 2013).

11.5.13 Female reproductive disorders related to endocrine-disrupting pollutants

Several known EDPs are causing detrimental effects on female reproductive hormones. Bisphenol A and phthalates, considered to be xeno-estrogens, both work in a receptor-dependent and receptor-self-regulating manner by directly binding to estrogen receptors, in turn, either increases aromatase activity leading to estrogen sensitivity. Increases, or indirectly leads to the release of gonadotropin-releasing hormone which in turn increases the production of intrinsic estrogen (Morgan et al., 2017; De Coster and Van Larebeke, 2012). The menstrual cycle affects fertility and oogenesis through EDPs, which is a disease similar to endometriosis (Hauser et al., 2016).

11.5.14 Female puberty

The onset of puberty involves composite neuroendocrine machinery and is also influenced by several other causes including ethnicity, genetics, nutrition, and other environmental factors (Özen and Darcan, 2011). Sex steroid receptors convey about the onset of early puberty through binding of estrogenic EDPs or xeno-estrogens. In childhood, the level of sex hormones in the blood is very low. However, androgen and estrogen receptors are expressed from a very early age (Paris et al., 2002). Therefore, even very smaller changes in the levels through external sources may bring about several pubertal changes (Pigneur et al., 2008). Phthalates, bisphenol A, and organohalogens were associated with the early onset of pubertal alterations in girls (Srilanchakon et al., 2017; Deng et al., 2012).

11.5.15 Renal function and endocrine-disrupting pollutants

Chronic kidney disease is increasing worldwide and has become a serious health concern, with a worldwide prevalence of approximately 13.4% (Hill et al.,2016). A previous study reported the exposure of di-(2-Ethylhexyl) phthalates through contaminated milk consumption was associated with microalbuminuria (Tsai et al., 2016). The urinary protein-to-creatinine ratio and estimated glomerular filtration rate, have also been reported in a children population exposed to EDPs (Malits et al., 2018). Among US children, the albumin to creatinine ratio is associated with urinary bisphenol A levels (Trasande et al., 2016), as well as Chinese adults (Li et al., 2012).

11.5.16 Impact of endocrine-disrupting pollutants on climate change

The escalating impact of climate change was rising due to EDPs pollutants. Brown et al. (2015) reported for the first time that climate change can replicate the harmful effects of pollution arising from EDPs on the aquatic environment. If the temperature increases the release of persistent organic pollutants into the wind are changed their rate division pattern between soil and air, and sediment, air, and water. Persistent organic pollutants persist and bioaccumulate in the environment *via* the food chain, and causing a detrimental impact on human health (Yoshida et al., 2009). The fate of persistent organic pollutants in ecosystems is regulated by biogeochemical processes and temperature. Climate change may also be responsible for increasing the redistribution and reemissions of persistent organic pollutants in different environmental set-ups via air–soil exchange. Persistent organic pollutants distribution is controlled mainly by the soil-air exchange.

11.5.17 Relationship between COVID-19 and endocrine-disrupting pollutants

The COVID-19 pandemics first emerged in 2020, spreading across the world during winter and spring. Patients who had faced a high risk of COVID-19 often suffer from chronic diseases, EDPs may also contribute to some chronic diseases during COVID-19 (Petrilli et al., 2020). In addition to male sex with older age, various comorbidities were associated with increased severity and mortality of COVID-19. Disorders such as heart disease, high blood pressure are increasingly associated with severe COVID-19 cases (Petrilli et al., 2020). Recently proposed, the underlying endocrine and metabolic dysfunction are suspected given by the vulnerability of hormonal modes (Zhou et al., 2020). EDPs such as bisphenol A, phthalates, organochlorines pesticides, and perfluorinated alkane substances represent the efficient triggers of aggravated infection (Drucker, 2020).

11.5.18 Obesogens and COVID-19

Obesogens are foreign chemical compounds that are hypothesized to disrupt the normal development and balance of lipid metabolism, alter lipid homeostasis which in some cases can lead to obesity, promote fat accumulation, and disrupt energy balance. COVID-19 Severe Acute Respiratory Syndrome-2 (SARS CoV-2), formerly recognized as HCoV-19, originated in the Chinese city of Wuhan in late 2019 and has caused unprecedented death globally. Previous animal studies have also shown early life exposure to particulate matter can lead to an increased risk of visceral obesity, insulin resistenstivity, and inflammatory reaction due to the result of endocrine disrupter (Zheng et al., 2013). As COVID-19 is similar to SARS in causing respiratory illness, exposure to NO_2 may increase the chances of mortality among COVID-19 patients; however, rigorous studies are needed to explore the confirmed relationship in the future.

11.6 Treatment technologies for endocrine-disrupting pollutants

Depending on the physicochemical characteristics of EDPs, EDPs can be removed from wastewater through wastewater treatment plants (WWTPs) using several methods such as absorption, adsorption, chemical degradation, biological degradation, transformation, and evaporation (Gadupudi et al., 2019; Ternes et al., 2002). Some of these methods are described below:

11.6.1 Adsorption technology

It refers to the phenomenon in which adsorption of mass transfer occurred due to the hydrophobic interactions and ionic interactions that exist between adsorbate and adsorbent (Sun et al., 2020). Adsorbents are activated carbon such as silica gel, activated alumina, etc. Powdered activated carbon, as a commonly used adsorbent, has become an effective method for the removal of micropollutants and drugs such as dimethyl carbonate, sulfamethazine, and trimethoprim from wastewater with a range of 81–98% (Adams et al., 2002). Nam et al. (2014) find that (1) the lower temperature reduced the adsorption of hydrophobic micropollutants, implying that the temperature may affect the adsorption; (2) the micropollutants absorbed by activated carbon showed signs of competitive behavior in surface water, and (3) the adsorption effect was promoted depending on the higher doses of adsorbent and longer adsorption time, but the method has some repercussions such as additional energy demand and cost (Nam et al., 2014). Therefore, to successfully remove EDPs in the environment, the capacity of existing adsorption technology needs to be optimized or enhanced.

11.6.2 Chemical advanced oxidation

In general, the chemical advanced oxidation (CAO) process involves such O_3, Cl_2, H_2O_2, ClO_2, permanganate (MnO_4^-), and their combinational forms, like UV/O_3, etc. for the removal of EDPs such as bisphenol A and 17-estradiol (E_2) (Wu et al., 2012). They were reported that the greater reaction occurred amid E_2 and O_3 than bisphenol A and O_3. In addition, UV and O_3 radiation is a more effective method of EDPs removal (Irmak et al., 2005). O_3-dependent oxidation is strongly influenced by the presence of triclosan, estrone, and estriol (Pauporte and Rathouský, 2007). CAO was not the most acceptable treatment process because of high investment expenditure (e.g., generators of O_3 and Cl_2) and become a limiting factor (Xiong et al., 2018). However other conventional water treatment approaches also have some disadvantages and limitations. It is not easy to adopt physical treatment methods such as adsorption in large-scale natural water bodies pollution treatment. The CAO approaches mainly need to emphasize the optimization of highly selective oxidants and operational parameters while ensuring the reduction of by-products in the oxidation process.

11.6.3 Bioremediation approaches for endocrine-disrupting pollutants removal

Bacteria, cyanobacteria, fungi, and microalgae are efficient degraders of EDPs by the process of accumulation, adsorption, and intra-extracellular enzymatic mechanisms, providing some additional advantages of being renewable, having better quality/well-treated effluents, and commercially produced valuable biomass which can be further used as manure, biofuel, etc. (Wang et al., 2017b; Hashemian et al., 2019). Furthermore, when the combined approach is applied to the activated sludge system, and the symbiotic association approach such as using microalgae–bacteria, there is a great potential that reduces the high electrical energy demand for the aeration process (Ariza, 2018). However, an enzyme is the most effective green tool for the degradation of EDPs, depending on whether they are driven from microalgal, bacterial, or fungal sources. They may differ in terms of positional specificity and substrate (Illanes, 2008). The most common procedures/approaches directly depend on the liquid culture medium or the free cell culture (Partovinia and Rasekh, 2018). *Enterobacter asburiae* strain LBQSKN4, *Pseudomonas* sp. LBQSKN5, and *Pseudomonas* sp. LBQSKN6, *P. nitroreducens* strain LBQSKN4, *P. putida* strain LBQSKN2 were isolated from soil samples that can degrade endocrine disruptor nonylphenols (Qhanya et al., 2017). Roh et al. (2009) showed mixed ammonia-oxidizing bacteria and *Nitrosomonas europaea* could degrade bisphenol A, triclosan, and ibuprofen through nitrifying activated sludge. Yu et al. (2013) isolated 17α-estradiol-degrading bacteria (strains KC1–14) from activated sludge taken from a wastewater treatment plant. Five bacterial species were isolated from the enrichment of cultures sediments of mud volcanoes of the Gulf of Cadiz were recognized as potential aerobic 17β-estradiol biodegraders (Fernández et al., 2016). Conventional WWTPs are mainly based on microbial communities containing activated sludge for the degradation of EDPs. However, activated sludge-based systems do not achieve complete degradation of EDPs due to fluctuating levels of EDPs and various operational parameters such as temperature, and sludge age (Gorgoglione and Torretta, 2018; Eio et al., 2014). Besides, the elimination effectiveness of these micropollutants can be increased by applying advanced treatment techniques such as oxidation process, nanofiltration, adsorption on activated carbon, and photocatalysis (Balabanič et al., 2012). These are skilled technology but are usually not operationalized as widespread, with some implications such as high operational and chemical cost. However, several key challenges can be addressed and need to be overcome at least (i.e., cost, structure stability, adsorption capacity, dispersibility, and solubility) before they can be implemented in full-scale wastewater treatment plants (Khan et al., 2020). Recently, there has been increased awareness and concern about the impact of existing environmental management strategies, and the impetus to develop sustainable and environmentally responsive EDPs technologies (Schug et al., 2016).

11.6.4 Enzyme perspective for removal of endocrine-disrupting pollutants

Considered as a basic biocatalyst, the enzyme has immense potential for degradation of EDPs coming from the ability of microorganisms, these enzymes such as laccase, manganese peroxidase (MnP) have been extensively studied (Hirano et al., 2000). Total 80% of bisphenol A was removed within 12 days using *Pleurotus ostratus*; MnP can potentially degrade bisphenol A and convert to phenol, and 4-isopropenylphenol can be effectively degraded/eliminated by laccases extracted from *Coriolopsis polyzona* (Cabana et al., 2007). Two thermostable laccases were reported to degrade nonylphenols (Ramírez-Cavazos et al., 2014).

11.7 Current issues and consequences of endocrine-disrupting pollutants

The amount of EDPs (ng/L to μg/L) is readily incorporated into the food chain, after which the food web becomes effectively hazardous to the lives of humans and animals by using sewage sludge in agricultural activities (Rajapaksha et al., 2014). The partial biodegradability of various EDPs with their derivatives poses a serious threat to ecosystem life (Kostich et al., 2014).

11.8 Conclusions and perspectives

In the current scenario, EDPs are a global concern because of their widespread existence, persistence, and bioaccumulation. Existing treatment technology is not capable of effectively removing EDPs from the environment. Bioremediation and photocatalytic degradation are highly acceptable, eco-friendly, low input cost, and promising future technology as compared to conventional water treatment technology. Previous studies reported that some bacteria, fungi, and microalgae degrade EDPs and help in environmental cleanup. Furthermore, combination approaches such as various biological and physical chemistry are offered as potential alternative methods for EDPs removal. A recently emerged genetically engineered bacterial strategy has been used as an alternative method to deal with EDPs. As the need to control the presence of incidental pollutants has become conscious and responsible, it is necessary to assess the harmful consequences of these pollutants on population fitness and/or health. In addition, there is a need to achieve strong comprehensive global policies and regulations and create a completely healthy environment around the world.

11.9 Author contributions

Rajesh Kumar: Literature search, Writing-original draft, and editing; Abhay Raj: Conceptualization, Supervision, final editing, manuscript cross-check, and approval of content used in this study to submit in the journal.

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12

Bioadsorption of endocrine disrupting pollutants from wastewater

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12.1 Introduction

Life on earth is impossible without "water." It is one of the most precious gifts of nature to living organisms. However, in the last few decades, this resource is constantly under threat because most water sources have reached the zenith of crisis due to its unchecked exploitation, population explosion, unplanned urbanization, and industrialization. With the elevating human population in the world, there is a burgeoning demand for water. Even in India, in the subsequent decade, the water requirement is expected to jump from 23.2 trillion liters to 47 trillion liters, that is, an increase by 20%, driven predominantly by industrial needs (Ministry of Water Resources, 2010). Domestic water requirement is projected to increase by 40% from 41 to 55 trillion liters, while the irrigation demand will increase from the current 517 trillion liters to 592 trillion liters in the next 10 years, that is, 14% growth (NCIWRD Report, 2010a, 2010b). The rapid urbanization and industrialization with tactless and inappropriate environmental planning often cause the release of industrial and domestic effluents and sewages into the aquatic bodies, altering the water quality. One of the emerging pollutants which are found in wastewater is endocrine disrupting pollutants (EDPs). Since most of the industries' effluent outlets are connected to nearby water bodies, therefore, water pollution due to the discharge of EDPs from industries such as pesticides and their metabolite, pharmaceuticals, cosmetics, veterinary products, plastics and food preservatives, electronics and building materials, and engineered nanomaterials (Qureshi et al., 2020; Gao et al., 2020). Today, EDPs has become one of the significant environmental concerns because along with its presence in industrial, medical and domestic wastewater, it is also prominently detected in aquatic systems and drinking water (Gadupudi et al., 2021). The existence and utilization of EDPs containing substances by humankind date long back, but the problems associated with EDPs have been identified recently.

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EDPs were brought into the limelight when some scientists in the early 1990s claimed that certain chemicals are responsible for disrupting the hormonal balance of humans and animals. Evidently, laboratory studies showed the problems of reproduction and development in certain fish and wildlife on exposure to specific chemical contaminants (Harding et al., 2006). The United States Environmental Protection Agency (US EPA) defines EDPs as "an exogenous agent that interferes with synthesis, secretion, transport, metabolism, binding action, or elimination of natural blood-borne hormones that are present in the body and are responsible for homeostasis, reproduction, and developmental process" (Diamanti-Kandarakis et al., 2009). Since 1940, with the bloom in chemical industries, a meteoric surge has been experienced in utilizing and discharging chemicals for different purposes into the environment (Gadupudi et al., 2021). Currently, the amplified discharge of chemicals in the environment is estimated to be approximately 400 million tons worldwide which will further magnify the chemical pollution (Katibi et al., 2021). Most of the synthesized products in use today are constituting of EDPs. Thus, it is not difficult to understand that a large amount of discharged chemicals imply toward the existence of a higher levels of EDPs in the environment. Although EDPs are detected in nanogram per liter (ng/L) to microgram per liter level (mg/L); however, their ability to affect the endocrine system at low doses (i.e., in the part-per-trillion to part-per-billion range) and their persistent nature can cause severe health-risk factors and considerable environmental pollution (Jung et al., 2015; Becker et al., 2017; Katibi et al., 2021). For example, perfluorooctanoic acid (PFOA), along with its long half-life (~4 years), can bioaccumulate and thus, US EPA has limited PFOA levels in drinking water to less than 0.4 mg/L.

EDPs consist of both synthetic and naturally occurring chemicals. The synthetic EDPs are derived from various industrial products and byproducts which include chemicals such as diethylstilbestrol, ethynylestradiol, dichlorodiphenyltrichloroethane (DDT), chlorpyrifos, dioxins, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), phthalates, perflurochemicals, alkylphenol, and bisphenol A (BPA) (Choi et al., 2006; Diamanti-Kandarakis et al., 2009). Metals (lead and cadmium) and organometallic chemicals (methylmercury) are also considered as EDPs (Gore et al., 2014). The naturally occurring EDPs include natural estrogen steroids (in humans and animals) and phytoestrogens. Gadupudi et al. (2019) categorized EDPs into natural steroidal estrogens, synthetic estrogens, phytoestrogens, and various industrial chemicals (xenoestrogens). Among these, native and artificial estrogens have substantial estrogenic effects than the other two categories. Li et al. (2013) grouped EDPs into two classes (i) estrogen and (ii) endocrine disrupting phenolic compound. The former class of chemicals are present in low concentration levels (nanogram per liter) in wastewater but with a high estrogenic activity which includes natural steroidal estrogen (17beta-estradiol or E2) and synthetic estrogen such as contraceptive (17alpha-ethinylestradiol or EE2).While, the latter is present in high concentrations (microgram per liter), having low estrogenic activity such as BPA and nonylphenol (NP) (Li et al., 2013; Gao et al., 2020). BPA, NP, E2, EE2 are some of the commonly found EDPs in wastewater and water bodies (Choi et al., 2006; Ifelebuegu et al., 2015; Jun et al., 2019).

Further, BPA is an inevitable endocrine disrupting pollutant (EDP) due to its use in the plastic industry. BPA can induce estrogenic activity at picogram level and is also lethal to humans at a dose higher than 1 mg/m^3 (Chang et al., 2012; Jun et al., 2019). It is estimated that the yearly global BPA production is approximately eight million tons. Moreover, a study revealed that the landfill leachate constituting plastic debris could have BPA content scaled up to 17.2 mg/L (Tursi et al., 2018). These facts of BPA build up a grave picture for ecological and human health.

Over the years, various types of physicochemical and biological waste water treatments such as coagulation, electrocoagulation, nanofiltration, photolytic and biodegradation, precipitation, ozonation, membrane separation, flocculation, filtration, oxidation (or) reduction and complex formations, aerobic and anaerobic degradation using various microorganisms, and reverse osmosis have been exploited to eliminate the EDPs from wastewater (Crini, 2006; Bello et al., 2017). Though some of these methods showed effective results, they still possess drawbacks such as the inability to scale up to large units, energy and chemical intensiveness, and high set-up and operational cost. Less adaptability to a wide range of EDP containing wastewaters, interference by secondary pollutants and other wastewater constituents, and accumulation of concentrated sludge are few more limitations to be tackled (Bello et al., 2017). Among the various techniques for removing EDPs from aqueous effluents, the “adsorption procedure” has emerged as an efficient method in recent times.

12.2 Impact of endocrine disrupting pollutants on the ecology and human health

EDPs released from various sources, whether natural or artificial, enters into the food chain via consumption of food and water, dermal contact, inhalation, and in case of a woman already exposed to EDP will transfer it to the baby (across the placenta or during lactation) (Gore et al., 2014). EDPs affect the endocrine system of animals and humans by disturbing the balance of normal hormonal functions (Qureshi et al., 2020; Katibi et al., 2021). These compounds disrupt the hormonal system by mimicking a hormone to bind at the specific hormone receptor causing inappropriate activation of a hormone receptor, or it nullifies the hormone receptor activation by blocking the receptor site so that specific hormone fails to bind at the receptor (Gore et al., 2014; Becker et al., 2017). The endocrine system disruption results in the increase risk of reproductive impairment, mental retardation, metabolic and immune diseases and disorders, and hormone-related cancer (Bergman et al., 2012; Jung et al., 2013; La Merill et al., 2020). The effects of EDP on the organisms can be acute or chronic depending upon the exposure time, concentration, and synergistic combination of two agents (Diamanti-Kandarakis et al., 2009; Bergman et al., 2012; Patterson et al., 2015). The EDPs, which are released into the freshwater and marine environment without any treatment, affect aquatic organisms' development. A study showed that exposure to estrogen-like EDP affected the reproductive performance of fish by feminizing the male fish in situ in an aquatic environment (Becker et al., 2017). EDPs can also decrease the production of fertile eggs in sand goby fish by ~90% (Gadupudi et al., 2021).

Ingre-Khans et al. (2017) revealed the impact of EDPs on the marine environment by studying the presence of a significant concentration of EDPs that reaches the Baltic Sea through the air, rivers and human activities. The study unveiled the transfer of persistent and fat-soluble chemicals across the marine food chain from small fishes (herring or roach) to the top predators in the sea. The high concentration of brominated flame retardants was also found to adversely affect birds such as American white-tailed sea eagles.

Many research works have documented the effect of EDPs on the reproduction process, development, histopathological variations, body organs of fishes, birds, mammals (Sosa-Ferrera et al., 2013; Gadupudi et al., 2021; Katibi et al., 2021). Apart from scientific articles (Monneret, 2017; Gadupudi et al., 2021), books such as “The Silent Spring” by Rachel Carlson also emphasized the impact of pesticides (DDT) on the population of birds.

Today, EDPs are a ubiquitous concern since all human settlement areas on the world map are in the clutches of EDP exposure. A study reported that 100% of humans have some chemical accumulation in their body based on tests conducted for detectable chemicals in the blood, body tissues, urine, placenta and umbilical cord. A lot of chemicals identified as EDPs are being studied for their effects, and some are even banned from being produced or used. However, many banned EDPs, still continue to exist in the environment due to their slow degradation property. Another suspected lurking danger is the countless unidentified endocrine disruptors that are yet to be tested. The discharge of EDPs into wastewater from various sources has raised unsettling concerns because of potential health risks related with the entry of toxic components into the food chains of living organisms. Therefore, removing EDPs from the effluents is paramount for the appropriate maintenance and regulation of the ecosystem. However, the discharged EDPs in the wastewater has been one of the major challenges for researchers in the last few decades since EDPs are present in a minimal concentration which limits their detection and some EDPs possess complex molecular structures, which makes them a persistent contaminant; as a result one of the most challenging wastewater effluent to be treated (Jung et al., 2015).

12.3 Removal processes of endocrine disrupting pollutants in wastewater

12.3.1 Sequestration technologies developed for endocrine disrupting pollutants

Currently, various technologies for instance coagulation, sedimentation, reverse osmosis (RO), filtration, conventional oxidation processes (such as ozonation), transformation, flocculation, activated sludge, degradation, enzymatic treatment, and volatilization are in the application for removal of EDPs from wastewater. To obtain a good result in the removal process, the wastewater treatment plants (WWTPs) adopt specific removal procedures based on the EDPs physiochemical characteristics (Gadupudi et al., 2021). Studies have shown that methods such as flocculation, coagulation and precipitation cannot eliminate EDPs efficiently. Reports reveal that the removal efficiency of BPA by such methods is lower than 10%, while separation of insecticides such as atrazine from water treatment was below 50% (Benotti et al., 2009; Gao et al., 2020). Previous studies have also shown that coagulation eliminates a small percentage of EDPs in aqueous solutions. For example, the elimination rate of diclofenac by chemical coagulation was less than 25% (Ternes et al., 2002; Gao et al., 2020). It has been found that coagulation techniques effectively remove only hydrophobic EDPs with high organic carbon content when associated with particulate or colloidal material (Gao et al., 2020; Gadupudi et al., 2021). Chlorination is a popular method for disinfection and oxidation (removal) of EDPs (particularly phenolic and PAH compounds) in the WWTPs of the USA (Jung et al., 2015). However, the ozonation method is now being replaced by the chlorination method due to the demonstration of the high reactivity of organic compounds with ozonizing agents (molecular ozone or hydroxyl radicals). Photolytic degradation is considered an effective and promising method for degradation technology due to its high degradation rate, better chemical stability, and ultraviolet sensitivity. Titanium oxide, zinc oxide, and composites of silver orthophosphate and perovskite-type transition metal oxide are the most studied photocatalysts for removing pesticides from wastewater (Ayati et al., 2014; Guo et al., 2016; Zatloukalová et al., 2017; Meenakshi and Sivasamy, 2018; Gao et al., 2020). There are also studies (Reis and Sakakibara, 2012; Li et al., 2013; Saiyood et al., 2013; Reis et al., 2014) that have evaluated the EDPs removal by biodegradation mechanism. Reis et al. (2014) have successfully demonstrated the removal of phenolic EDPs by aquatic plants through reactions catalyzed by peroxidases. Among biological treatments, microbes or enzymes for the degradation of EDPs are gaining interest among scientists (Becker et al., 2016; Becker et al., 2017; Gao et al., 2020). Fischer et al. (2010) identified a gram-negative bacterium with the ability to degrade BPA, which was the source of carbon and energy for the microbe. Fungal laccases and manganese peroxidase have been widely studied for the degradation of xenobiotics ranging from phenols, PAHs, hormones to plasticizers (Becker et al., 2017). Microbes such as *Pleurotus ostreatus*, *Trametes versicolor*, *Fusarium falciforme*, *Chlorella vulgaris*, *Chlamydomonas reihardtii* are found to degrade EDPs such as BPA, E2, EE2, triclosan (TCS) and 4-tert-Octylphenol (4-t-OP) effectively.

There are limitations in the removal of EDP by chemical and biological methods. Thus, membrane technology (ultrafiltration, nanofiltration, and reverse osmosis) which constitutes the tertiary stage of the treatment process in WWTPs, is adopted to enhance EDP removal efficiency (Arola et al., 2019). The membrane technology effectively removes BPA compounds by sieving and electrostatic mechanisms (Yoon et al., 2007; Muhamad, 2016). However, these technologies have several limitations, including high set-up cost, incomplete decontamination, and release of toxic byproducts (Becker et al., 2017).

12.3.2 Removal of endocrine disrupting pollutants by adsorption process

EDP's fondness for clinging to solid surfaces has been maneuvered as a strategy to remove the compounds via the sorption method in many studies. Further, the simplicity and cost-effectiveness of adsorption techniques have resulted in its growing popularity for controlling EDPs from aqueous systems.

Although few scientists and chemists already knew some basic idea about adsorption, and its correlated phenomena from ancient times; however, in 1773, C.W. Scheele was one of the firsts to report quantitative studies on the adsorption of gases by charcoal and clays (Dabrowski, 2001). Lowitz's study on the ability of charcoal to uptake organic impurities by observing the decolorization of tartaric acid solutions indicates the modern era of application of the adsorption process. The works done by de Saussure in 1814 mark the start of systematic studies of adsorption (Dabrowski, 2001). He concluded that permeable materials such as cork, charcoal, sea-foam, and asbestos could adsorb all types of gases; moreover, he was observant about the increase in the uptake of the gases to the extreme degree by porous substances when the gases underwent condensation readily. de Saussure was also aware of the evolution of heat accompanying the adsorption process. Thus, he not only revealed the exothermic nature of adsorption processes but also was the first one to observe the commonness of adsorption.

In the 19th century, there were very few papers on adsorption, and some of them are worth mentioning, such as works by Chappuis, Joulian, and Kayser. Chappuis studied the adsorption process at constant temperature by experimenting with ammonia adsorption on charcoal and asbestos. Although the term "adsorption" was coined by du Bois-Reymond; however, the term was first documented by Kayser in the literature (Dabrowski, 2001).

Between the 19th and 20th centuries, more scientists were intrigued by the adsorption process. Moreover, the period saw a considerable surge in the investigation of sorption on solid surfaces. The adsorption occurring at the solid–liquid interface imparts a crucial role not only in numerous areas of sciences but also acts as an essential technique for several high-tech processes. The applications of adsorption process are quite popular and ubiquitous in many fields of practical importance, such as chromatography, catalysis, electrochemistry flotation, microelectronics, ecology, purification of air and water, material science, separation of mixtures, etc. (Toth, 2002). In fact, the past years have witnessed a tsunami of research probes undertaken by various scientists to treat wastewater via the adsorption process. This process is utilized as a medium for the combined physical and chemo-biological process to treat wastewater or simultaneous application of all three processes (Seow et al., 2016). Adsorption is a surface phenomenon which used to remove solutes from liquid or gases from the atmosphere. Thus, this process involves removing a multicomponent fluid (gas or liquid) mixture by adhering it to the adsorbent surface via physical or chemical bonds (Seow et al., 2016). The entity which provides the solid surface for other materials to adhere to is termed an adsorbent, while the term adsorbate is used for the material which adheres itself to an adsorbent or gets eliminated from the solution/atmosphere/fluid mixture. Contaminants are suspended particles in the air as a gas or in the solution as a solute. Thus, it can be separated from gas or liquid phases by exploiting the characteristics of adsorption technique attached to an adsorbent for decontaminating the phases. Adsorption is the alteration in the amount of a known substance at the interface compared to its neighboring phases (Dabrowski, 2001).

The adsorption process can occur in different systems such as solid–liquid, liquid–gas, liquid–liquid, solid–gas depending on the nature of phases in contact (Dabrowski, 2001). The equilibrium state of the adsorbent in contact with the bulk phase and the interfacial layers can be used to define the adsorption system. The adsorption process is the accumulation of molecules in the interfacial layer for removing the solutes from its contaminated media. The term "absorptive" denotes the substance present in the gas or vapor phase before being adsorbed while the same material is defined as the "adsorbate" when in the adsorbed state (Dabrowski, 2001).

Adsorption is of two types—chemical or chemisorption and physical or physisorption. Chemical sorption occurs due to forming a strong bond association among molecules or ions of the adsorbate. This is usually due to the electron exchange property, and the process is nonreversible most of the time (Dabrowski, 2001). Chemisorption involves a monolayer surface, and it generally occurs at temperatures above the critical temperature. The monolayer concept associated with the homogenous surface of a sorbent in chemisorption was introduced by Langmuir.

On the other hand, physical sorption or physisorption is reversible in most cases as it involves the weak van der Waals intraparticle force between adsorbent and adsorbate (Dabrowski, 2001). In contrast to the chemisorption process, the physical absorption takes place below the critical temperature or at a temperature close to that of an adsorbed entity. Thus, physisorption is correlatable to the condensation process of the material before being adsorbed (Dabrowski, 2001). Physical adsorption is exothermic in nature caused by a reduction in the disorder and Gibbs free energy of the adsorption system. Under favorable conditions, the chemisorption and physisorption processes can occur concurrently or alternately.

The generally preferred solid adsorbents have pores with complicated structures and varying magnitude and configuration for industrial applications. The terms such as "width" and "diameter" are frequently used for the pores, which are slit-shaped and cylindrical in shape, respectively. In the adsorption field, total porosity is generally categorized as micropores, mesopores, and macropores. As per the IUPAC recommendation (Dabrowski, 2001), the micropores are pores of a width less than 2 nm, mesopores having width ranging from 2 to 50 nm, and macropores possess a width greater than 50 nm. Currently, in the field of adsorption material science, the term "nanopore" encompasses both micropores and mesopores.

The adsorption process is one of the interesting event connected with the behavior of gas/liquids along with a solid surface. In fact, the interaction of sorbate and sorbent is a demanding scientific area for the development of theories and models. Thus, developing the understanding of the adsorption mechanism is essential from the perspective of science. Therefore, thermodynamic and kinetic functions are also considered necessary for the adsorption study of material because more details about the adsorption process performance and mechanisms can be learned. Thereby, various isotherm and kinetic models are applied for examining and understanding the adsorption mechanistic steps and surface chemistry. Adsorption isotherm, one of the fundamental concepts in adsorption science, involves understanding the equilibrium relation between adsorbate and the different parameters in the bulk fluid phase (Dabrowski, 2001). The parameters such as the pressure or concentration of the adsorbate in the bulk phase at constant temperature are considered during the investigation. Therefore, thermodynamic and kinetic functions are also considered necessary for the adsorption study of material. The experimental adsorption data are interpreted in terms of mathematical adsorption equations, that is, in terms of adsorption isotherms graphs for proper appreciation of the adsorption science. While graphical representing the mathematical expressions, each isotherm equations give specific curves for specific sorbate–sorbent interaction. The obtained precise graphs can be then elucidated to extract particulars regarding the adsorption mechanism involved in the adsorbate–adsorbent interactions. There are different isotherm models which are often used for adsorption study. Some of the popular ones are Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, etc. The adsorption isotherm allows the appraisal of the efficiency of various industrial adsorbents developed for the applications such as separation and purification.

Moreover, the kinetic study of an adsorbent is also necessary for the industrial application at a pilot scale. The solute uptake rate, which determines the residence time required for completion of adsorption reaction, can be used to control the residence time of sorbate uptake at the solid-solution interface (Ho, 2006). Therefore, it is crucial to predict the removal rate of pollutants from aqueous solutions to design appropriate sorption treatment methods/plants. For effective wastewater treatments, the kinetic study of sorption process is of utmost importance for unveiling the mystery of mechanisms and chemical pathways involved in sorption reactions. Thereby, helping to formulate a convenient and well-designed sorption process that has better efficiency in the removal process to result in a recyclable and high-quality effluent after the treatment. Furthermore, the cost of adsorbent can be reduced if research successfully develops low-cost sorbents or feasible regeneration of sorbents after its application (Ho, 2006). Over the decades, several mathematical models have been proposed and developed to describe and analyze the adsorption data. These can generally be classified as adsorption reaction models (pseudo-first-order reaction, pseudo-second-order reaction, Elovich model, etc.) and adsorption diffusion models (liquid film diffusion, intraparticle diffusion, double exponential model, etc.).

Many factors affect the adsorption process, such as pH of the solution, adsorbent dosage, initial adsorbate concentration, and temperature. Detail study and optimization of such parameters are required during the adsorption study because this will significantly help develop the industrial-scale wastewater treatment process. In fact, since the last few decades, there has been an intensive study on adsorption and simultaneous surge in number of scientific publications. This progress in the field of adsorption has been possible due to the advancement in detection systems and numerous experimental techniques, such as scanning electron microscope-electronic dispersive X-rays (SEM-EDX), temperature-programmed desorption (TPD), X-ray diffraction (XRD), Raman spectroscopy, nuclear magnetic resonance (NMR), zeta potential analysis, scanning tunneling microscopy, and many others. The application of these techniques provides in-depth and explicit information about the morphological, topographical, and physicochemical properties of the adsorbent and adsorbates.

The adsorption process transfers the EDPs from the liquid effluent to a solid adsorbent, keeping the effluent volume to a minimum. Some common adsorbents are silica gel, activated alumina, zeolites, clay minerals, chitosan beads, metal organic frameworks, and carbon nanotubes (CNTs) (Jun et al., 2019; Gao et al., 2020).

In comparison to other adsorbents, the high adsorption capacity of CNTs makes it a suitable material to separate pollutants such as heavy metals, dyes, phenols and organic chemicals from wastewater (Chen et al., 2008; Ren et al., 2011; Salam et al., 2014; Baghapour et al., 2014). Recent studies (Cho et al., 2011; Fang and Chen, 2012; Bohdziewicz and Kamińska, 2013; Jung et al., 2015) have evaluated the efficacy of CNTs for elimination of organic and inorganic EDPs. The studies have revealed the ability of CNTs for the elimination of a broad range of EDPs from wastewater. However, its high cost operation and toxicological effect still calls for more research into this field.

Another popular adsorbent is activated carbon (AC). AC is developed from a carbonaceous source using either physical or chemical activation processes. The commonly AC forms are powdered activated carbon (PAC) and granular activated carbon (GAC). In fact, AC is considered an effective adsorbent for removing low-level occurring organic contaminants such as EDPs due to their high surface area, micropore volume, and adsorption capacity (Redding et al., 2009). Many studies (Lee et al., 2009; Li et al., 2011) have used commercialized AC or its modified version by certain acid and thermal treatments to remove EDPs. The capability of GAC (oxidized with nitric acid) to remove cadmium was attempted, and the experimental results suggested that the adsorption process is exothermic (Huang et al., 2007). The equilibrium data fitted well to pseudo-second-order kinetics and Langmuir isotherm with a maximum sorption capacity of 51.02 μmol/g. Ifelebuegu (2012) investigated the removal of E2 and EE2 using commercial AC. Liu et al. (2009) explored the adsorption capacity of two commercial AC (W20 and F20) and their treated modified versions for removal of BPA. W20 and its modified version showed better adsorption ability than F20.

Adsorption of EDPs onto commercial activated carbon is quite a valuable technique to get pure water. However, the involvement of initial high cost and the need for a costly regeneration system limits the application of commercial carbon as a less economically feasible adsorbent on a larger scale (Crini, 2006).

In the last few years, natural sources, agricultural by-products, and wastes have emerged as a viable option for adsorbents due to their characteristics such as biodegradability, high volume yet low-cost value. However, the low adsorption capacity of raw/crude agricultural by-products limits its applicability. Scientists are trying to modify these biomaterials into biochar, hydrochar, and activated carbon via thermal/chemical treatments to improve their adsorption and cation exchange capacity.

Many biomaterials are being explored as the feedstock for the development of activated carbon. Thereby, much interest has emanated among the scientific communities for finding and developing alternative cheaper and effective biomaterials or search for inexpensive and readily available sources for the production of activated carbon for EDPs removal from aqueous solutions.

12.3.2.1 Development of different bioadsorbents

Generally, a material that is profuse in its natural form or is a waste or by-product of industries or needs minimum processing prior its use is considered a low-cost sorbent. “Biosorbents” surfaced up as the new low-cost material for different applications, among which treatment of wastewater is one of the applications. Biosorption is a physicochemical process employed to remove substances from solution by biological material. Biomaterials can be both living and dead, organic and inorganic, which may be again present in a soluble or insoluble form, has emerged as viable biotechnology for removing contaminants from solution (Asgher and Bhatti, 2012). Most biosorption research is related to the removal of dyes, metals, and organic substances, and most recently, EDPs. The significant advantages of biosorption technology are less investment in terms of initial development cost, simple design, easy operation, free from or less generation of toxic substances and its ability in reducing the amount of pollutants to minimal levels and the utilization of cheap biosorbent substances (Akar et al., 2013).

Some of the reported biomaterials that have been used to develop AC are eucalyptus sawdust, fir saw dust, sugarcane bagasse, orange peel, rice husk, rice straw, coconut shell, date

Table 12.1 A glimpse of various bioadsorbents used either in natural or modified forms for removal of EDPs.

EDPs compounds	Material	References
Diclofenac sodium, Salicylic acid, Flurbiprofen	Hydrochar (Orange peels)	Fernanadez et al., 2015
Bisphenol A	Natural form-peat, rice husk, bagasse, saw dust. Modified peat	Zhou et al., 2012
Bisphenol A and Diuron	Hydrochar (Argan nut shell)	Zbair et al., 2020
Triclosan	Activated carbon derived from rice straw	Liu et al., 2014
17beta-estradiol	Hydrocharnanocomposites (rice husk+ Fe–Mn binary oxide	Ning et al., 2017
17β-estradiol (E2) and 17α-ethynylestradiol (EE2).	Montmorillonite/hydrochar	Tian et al., 2018
Herbicide (Isoproturon)	Pyrochar and hydrochar (corn digestate, miscanthus, woodchips of willow, and poplar)	Eibisch et al., 2015

seeds, tea leaves, Rattan, *Salix psammophila*, flax shive, cotton gin waste, bamboo, sun flower oil cake (Chang et al., 2012; Delgado et al., 2012; Ifelebuegu et al., 2015; Qureshi et al., 2020). Table 12.1 shows few more biomaterials which have been either used in its natural form or modified to remove different types of EDPs.

In applying AC (derived from biomaterials) as adsorbents for the treatment of EDPs containing wastewater, the search and preference have been more inclined toward developed and modified versions of bioadsorbents. The main research has been focused on deriving the modified versions of adsorbents from locally available waste materials whether agricultural, industrial or domestic wastes. Till now, many adsorption studies have been undertaken and a plethora of publication is available on the development and use of low-cost adsorbents.

The adsorption of naproxen, carbamazepine and nonylphenol onto coal-based and coconut shell-based GAC particles was used to study the effect of background natural organic matter (NOM) on the bed service of the material (Yu et al., 2009). The study revealed that preloading of NOM reduces the adsorption capacity for naproxen by both biomaterials, which implies the impact of NOM on adsorption capacity and kinetics of the sorption process (Yu et al., 2009). AC derived from rice straw was investigated to remove EDPs from aqueous solutions. The maximum adsorption capacity of the material for BPA was 181.19 mg/g (Chang et al., 2012). The maximum adsorption capacities of black tea leaves for E2, EE2 and BPA were 3.46, 2.44, and 18.35 mg/g, respectively (Ifelebuegu et al., 2015). The adsorption performance of chemically activated biochars was compared against commercialized PAC. Jung et al. (2013) produced biochars from pine chips under oxygenated (O-biochar) and oxygen-free conditions (N-biochar) as an adsorbent to remove a variety of chemicals such as BPA, atrazine, EE2, sulfamethoxazole (SMX), carbamazepine (CBM), diclofenac (DCF), ibuprofen

(IBP). N-biochar showed the highest adsorption capacity for the chemicals as compared to O-biochar and PAC. This study implies the possible application of N-biochar for the removal of pollutants in environmental and agricultural practices. The poor performance of AC for the removal of diclofenac was also demonstrated by Sotelo et al. (2012). In another experiment, the TCS of 50–60 mg/L concentration was removed using charcoal-based GAC (Behera et al., 2010; Delgado et al., 2012). The investigated equilibrium studies of cork-based AC in removing clorifibric acid and ibuprofen from aqueous solution revealed that it outperformed commercial carbons (Mestre et al., 2009, 2010). The investigation of AC derived via chemical activation from *Sterculiaalata* nutshells, as a possible low-cost adsorbent for removing phenols, revealed that the adsorption process is pH-dependent, and the equilibrium data fits Langmuir and Freundlich models (Mohanty et al., 2006). Removal of phenol was also investigated by using highly porous corn grain-based AC (Park et al., 2010), where well-fitted Langmuir and pseudo-second-order models explained the adsorption process. Flax shive and cotton gin are agricultural residues, which also acted as a successful adsorbent for the adsorption of trichloroethylene (Klasson et al., 2009). The investigation showed that the AC derived from flax shive had better adsorption capacity than some commercial ACs. A recent study investigated the adsorption capacity of a biomaterial that is four species of marine microalgae for the removal of NP. The removal efficiency of the microalgae ranged from 43.43% to 90.94% (Wang et al., 2019). There are also reports regarding the usefulness of carbonized material for the removal of EDPs. The investigated potential of carbonized wood chips for the treatment of BPA polluted wastewater revealed that carbonized wood chips had better adsorption capacity than coconut shell derived AC (Nakanishi et al., 2002).

Another investigation regarding the removal capabilities of coir pith 4.308 mg/g, durian peel 4.178 mg/g, and coconut shell 4.159 mg/g for BPA was carried out (Lazim et al., 2015). Their results showed that the modified phyto-waste were promising materials as an alternative material to eliminate BPA from an aqueous solution.

The removal of metals that acts as EDPs is also a prevalent study among scientists. The performance of chitosan and commercialized PAC to remove hexavalent chromium from an aqueous solution has been found to be 35.6 and 46.9 mg/g, respectively (Jung et al., 2013). In the biosorption study of mercury (II) by lignocellulosic material derived from the Spanish Broom plant, the reaction was found to be fitted well to pseudo-second-order kinetics with an maximum removal efficiency of 86% (Arias et al., 2017). Removal of lead from aqueous solution has been investigated for different bioadsorbents in their natural forms such as sugarcane bagasse, rice straw, tree bark, hulls of peanut, soybean and walnut, waste tea leaves, leaves of *Aegle marmelos*, mango leaves, and peels of *Punicagranatum* (Sud et al., 2008; Yoshita et al., 2009; Chakravarty et al., 2010; Ay et al., 2012). Even modified bioadsorbents by acid/base treatment such as *Manilkarazapota* leaves, apple and orange residues, pine cone powder, and rose petals were also used for lead removal (Sud et al., 2008; Suresh et al., 2015). Bamboo charcoal, wheat bran, and mango leaves have been used as an adsorbent to remove cadmium (II) from an aqueous solution (Singh et al., 2006; Wang et al., 2010). The maximum adsorption capacity for bamboo charcoal was found to be 12.08 mg/g and fitted the Langmuir model precisely.

12.4 Conclusions and perspectives

This chapter focused on the EDPs' impact on the environment and health and recent studies on sequestration of EDPs. Today we are in an era where chemicals are intricately involved in our lifestyle through food, clothe, personal care products and medicines. Unfortunately, many of the products are constituted of EDPs and the concentrations of EDPs are not well documented. The removal of EDPs from water is the crying need of the hour.

Further, developing a cost-effective, efficient, and environmentally safe method is a challenging and herculean task for researchers, technologists and engineers. Though a wide range of nonconventional low-cost adsorbents serves as a promising option against the commercial AC. Still, much work is yet to be done to understand better the adsorption mechanisms resulting in an appropriate prediction of the performance of the adsorption processes for EDPs removal from effluents in an actual industrial-scale application under a range of operating conditions. Few measures which can be taken for control of EDPs are:

1. Initiatives that insist on extensive identification of EDPs, accurate measurement of EDPs, proper knowledge, and in-depth understanding of EDPs' behavior, transportation mechanism in the environment, and fundamental fate.
2. Stimulate studies of EDPs in the local context since the behavior of EDPs may vary depending on the environmental conditions and the presence of other chemicals in different areas.
3. More attention should be given to reducing the production and use of EDPs and their replacement with environment-friendly and less hazardous chemicals.
4. The life cycle assessment of chemicals must be encouraged to understand better and trace out the exact economic profits and ecological risks of EDPs.
5. Future research can be focused more on bioremediation technology.

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13

Biochar-mediated removal of hazardous dyes

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13.1 Introduction

Water pollution is a major global concern that is increasing gradually with the continuous rise in industrialization. The enormous consumption of fuel and energy by the industrial sector significantly contributes to the decrease in the amount of drinking water which in turn, results in the production of toxic wastewater (Lellis et al., 2019). The discharge of several kinds of organic and inorganic pollutants further facilitates water pollution because of the toxic, mutagenic, and carcinogenic properties of the majority of these pollutants (Praveen et al., 2022). One of the primary contributors to water pollution is the excessive discharge of toxic dye effluents from industries which are reported to cause serious health issues in humans such as cancer, skin diseases, and allergies along with other complications after ingestion of these dyes present in the contaminated waters (Srivastav et al., 2020). Moreover, majority of the toxic dyes are ingested by fish and other aquatic organisms which results in the disruption of the normal architecture of vital organs such as the liver, kidney as well as gills (Al-Tohamy et al., 2022). Therefore, several methods are devised for the treatment of wastewater for the removal of dyes some of which include ion exchange, filtration, irradiation, coagulation, oxidation, Fenton process, ozonation, electrochemical destruction, and adsorption (Praveen et al., 2022). The general process of wastewater treatment involves a physical or mechanical pretreatment followed by the primary physicochemical or chemical treatment. Later, secondary and tertiary purification steps are carried out which are either chemical or biological processes wherein the sludge formed during the purification process is recycled or incinerated (Crini and Lichtfouse, 2019). The biological treatment process is an environmentally benign process. A number of studies have investigated the potential of several bacterial, fungal, and algal species for the removal of color from azo dyes which majorly involved the production of catalytic enzymes such as azoreductases that facilitated cleavage and reduction of azo bonds (Sarayu and Sandhya, 2012; Ghosh et al., 2022a,2022b, 2022c, 2022d, 2022e, 2022f, 2022bg; Bhattacharya et al., 2021; Nitnavare et al., 2022a, 2022b; Kulkarni et al., 2018). However, the majority of these techniques have certain

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drawbacks pertaining to efficiency, cost-effectiveness, and production of toxic by-products (Kanaujiya et al., 2019). Hence, novel and effective strategies for dye removal from wastewaters are extensively being explored and developed.

Biochar is one such material that has the potential to effectively remove harmful dye contaminants during wastewater treatment. Biochar is the charred organic matter that can be produced from an extensive range of organic feedstocks such as wood and agricultural wastes, manure, rice husks and straw, leaves, food waste, paper sludge as well as animal and algal biomass and exhibits enhanced sequestration ability and hence, can be used as an effective adsorbent (Moreira et al., 2017; Mohan et al., 2014). The application of biochars has shown great agricultural benefits with a positive influence on the texture, porosity, structure, particle size distribution, and density of the soil (Atkinson et al., 2010). The ability of the biochar to act as an adsorbent was investigated for the successful adsorption and removal of organic soil pollutants (Dai et al., 2019). Likewise, biochars can effectively remove pollutants from water with a high sorption capacity (Sizmur et al., 2017). Hence, this chapter elaborates upon the application and feasibility of biochars for the removal of dye from wastewater samples. Various materials such as rice husk, food waste, corncob waste, goat manure, and crab shells along with plants such as *Terminalia arjuna* and *Opuntia ficus-indica* as well as algae such as *Caulerpa scalpelliformis*, *Spirulina,* and *Spirogyra* are been used for the preparation of biochars which is summarized in Table 13.1. These biochars effectively adsorb different kinds of dyes such as Congo red, methylene blue, malachite green, methyl orange, rhodamine B, and many more. Further optimization of the parameters of biochar-mediated dye adsorption would provide an

Table 13.1 Types of biochar with dye removal application.

Biochar precursor	Method of biochar preparation	Dye degraded	Dye removal capacity or efficiency	References
Plant-based biochar				
Acacia auriculiformis, *Mimosa pigra*, and *Coffea Arabica*	Pyrolysis	Methyl orange	12.3 mg/g	Nguyen et al., 2021
Mentha plant		Methylene blue	86.96 and 588.24 mg/g	Rawat et al., 2020
Opuntia ficus-indica	Carbonization	Malachite green	1341 mg/g	Choudhary et al., 2020
Phoenix dactylifera	Pyrolysis	Congo red	117.647 mg/g	Iqbal et al., 2021
Phragmites karka	Pyrolysis	Methylene blue	438.2 mg/g	Viswanthan et al., 2020
Rice husk	Hydrothermal liquefaction	Congo red	66.82–96.92%	Khan et al., 2020
Rice husk	Pyrolysis	Malachite green	99.98%	Ganguly et al., 2020
Rice straw	Pyrolysis	Brilliant green	111.11 mg/g	Saif Ur Rehman et al., 2016

Biochar precursor	Method of biochar preparation	Dye degraded	Dye removal capacity or efficiency	References
Terminalia arjuna seeds immobilized with *Providencia stuartii*		Congo red	92.0 ± 5.0%	Goswami et al., 2020
Algae-based biochar				
Caulerpa scalpelliformis	Pyrolysis	Remazol dyes	130.11 mg/g	Gokulan et al., 2019
Chlorella sp.	Pyrolysis	Reactive yellow dye-145	99%	Amin et al., 2020
Chlorella sp.	Wet torrefaction	Congo red and methylene blue	164.35 mg/g and 113.0 mg/g	Yu et al., 2021
Chlorella sp., *Scenedesmus* sp., *Synechocystis* sp., and *Spirulina* sp.	Pyrolysis	Malachite green	166 and 500 mg/g	Pathy et al., 2022
Gracilaria Rhodophyta	Carbonization	Brilliant green	17.8 mg/g	Naga Babu et al., 2021
Spirogyra	Mild pyrolysis	Congo red	95.92%	Shaikh et al., 2022
Spirulina	Pyrolysis	Rhodamine B, methylene blue, Congo red, and methyl orange	421.93, 370.24, 287.89, and 177.32 mg/g	Tan et al., 2020
Spirulina platensis	Pyrolysis	Congo red	82.6%	Nautiyal et al., 2016
Undaria Pinnatifida	Pyrolysis	Methylene blue, rhodamine B, and malachite green	841.64, 533.77, and 4066.96 mg/g	Yao et al., 2020
Magnetic biochar				
Alkali-activated rice straw	Carbonization	Rhodamine B	53.66 mg/g	Ren et al., 2020
Corncob waste	Pyrolysis	Acridine orange	116.3 mg/g	Wang et al., 2020
Empty fruit bunch	Pyrolysis	Orange-g and methylene blue	32.36 mg/g and 31.25 mg/g	Mubarak et al., 2015
Food waste	Pyrolysis	Methylene blue and methyl orange	100% and 95%	Chu et al., 2020
nZVI and corn straw	Carbonization	Malachite green	515.77 mg/g	Eltaweil et al., 2020
Sewage sludge	Pyrolysis	Methylene blue	296.52 mg/g	Zeng et al., 2021
Sewage sludge and woodchips	Pyrolysis	Acridine orange 7	110.27 mg/g	Santhosh et al., 2020
Animal-based biochar				
Bovine bones and fish scales	Pyrolysis	Basic red 9	49.5 and 52.3 mg/	Côrtes et al., 2019
Cattle manure	Torrefaction	Methylene blue	241.99 mg/g	Zhu et al., 2018
Crab shells	Pyrolysis	Malachite green and Congo red	12,502 and 20,317 mg/g	Dai et al., 2018
Goat manure	Pyrolysis	Rhodamine b	77.059 mg/g	Lu et al., 2020
Sheep, rabbit, and pig manures	Pyrolysis	Methylene blue	238.31, 104.02, and 53.68 mg/g	Huang et al., 2018

excellent method for effective wastewater treatment whereas additional studies exploring the in situ biochar-mediated dye adsorption from wastewater samples can give useful insights into the feasibility of this technique at an industrial level (Gautam et al., 2021).

13.2 Types of biochar for dyes removal

13.2.1 Plant-based biochar

Agro waste and plants are used for the preparation of biochar which is considered as a cheap and green approach. Nguyen et al. (2021) highlighted the ability of plant-based biochar to act as sustainable adsorbents for the removal of methyl orange dye from wastewater. The carbonaceous biochars in this study were prepared using three plants namely, *Acacia auriculiformis*, *Mimosa pigra*, and *Coffea arabica*. A slow pyrolysis process was carried out at 500°C with a heating rate of 10°C/min. The specific surface area of biochar prepared using *A. auriculiformis* were highest (393.15 m^2/g) whereas *C. arabica* biochar showed a specific surface area of 2.62 m^2/g. A maximum methyl orange dye adsorption capacity of 12.3 mg/g was achieved using the prepared biochars wherein maximum adsorption efficiency of 95–96% was maintained at a pH value of 2.0–3.0 which was then reduced with a subsequent increase in the pH value. Electrostatic adsorption and pore diffusion were the primary proposed mechanisms of adsorption. An optimal biochar concentration of 5.0 g/L demonstrated maximum adsorption efficiency wherein biochar prepared from *A. auriculiformis* displayed the highest adsorption efficiency which was attributed to its abundant active adsorption sites.

Rawat et al. (2020) demonstrated the dye adsorption potential of biochar prepared from Mentha plant waste. The stems of the plant obtained from an oil distillation unit were cleaned and oven-dried followed by heating in a muffled furnace for 120 min at 450°C and 700°C with a 5°C/min rise in the temperature. The obtained biochar was then homogenized to obtain a fine powder. Scanning electron microscope (SEM) images of the biochar samples heated at 450°C (BC_{450}) and demonstrated a flat and smooth surface with minute pores whereas biochar prepared through pyrolysis at 700°C (BC_{700}) had deposits present on its surface. In addition, energy dispersive X-ray (EDX) spectral analysis revealed the presence of higher amounts of C, O, and Al in BC_{450} and while BC_{700} had higher mineral depositions with a significant presence of Mg, Cl, Si, K, Fe, and Ca. The Brunauer–Emmett–Teller (BET)-specific surface areas of BC_{450} and BC_{700} were 1.058 and 7.169 m^2/g, respectively. The lower surface area of BC_{450} was attributed to the filling of pores with resins and minerals which were suggested to interfere with nitrogen diffusion. In addition, the average pore diameter of BC_{450} and BC_{700} was 11.612 and 12.915 nm, respectively, which highlighted its mesoporous nature. X-ray diffraction (XRD) pattern confirmed the presence of calcite, quartz, crystalline cellulose, and dolomite in both biochars. Fourier-transform infrared (FTIR) spectroscopy results demonstrated the involvement of surface functional groups such as carboxylic, methyl, aliphatic hydrocarbons, as well as carbonyl groups in the adsorption of methylene blue dye. The increase in pH value from 4 to 10 increased the amount of dye adsorbed from 14.21 and 15.51 to 22.34 and 23.13 mg/g in the case of BC_{450} and BC_{700}, respectively. This highlighted the importance of alkaline pH for the favorable adsorption of the cationic dye molecule. The adsorption kinetic studies provided a maximum dye adsorption capacity of 86.96 and 588.24 mg/g using BC_{450} and BC_{700} biosorbents under ideal conditions, respectively.

Activated biochar was also prepared from *Opuntia ficus-indica* by Choudhary et al. (2020) which was utilized for dye adsorption as well. The dried biomass obtained from cladodes of the *Opuntia ficus-indica* plant was used for the preparation of activated biochar through carbonization at 400°C followed by activation through NaOH impregnation at 1:1 (ABC1) and 1:2 (ABC2) ratios, respectively. SEM images of the plant cladodes were highly packed with an absence of any pores or cavities wherein carbonization resulted in the removal of organic matter from the biomass which in turn, increased the porosity of the biochar as evident from Fig. 13.1. Activation of the biochar further improved its porosity with irregular pores and broken surfaces observed with a higher NaOH ratio. In addition, activated biochars displayed a

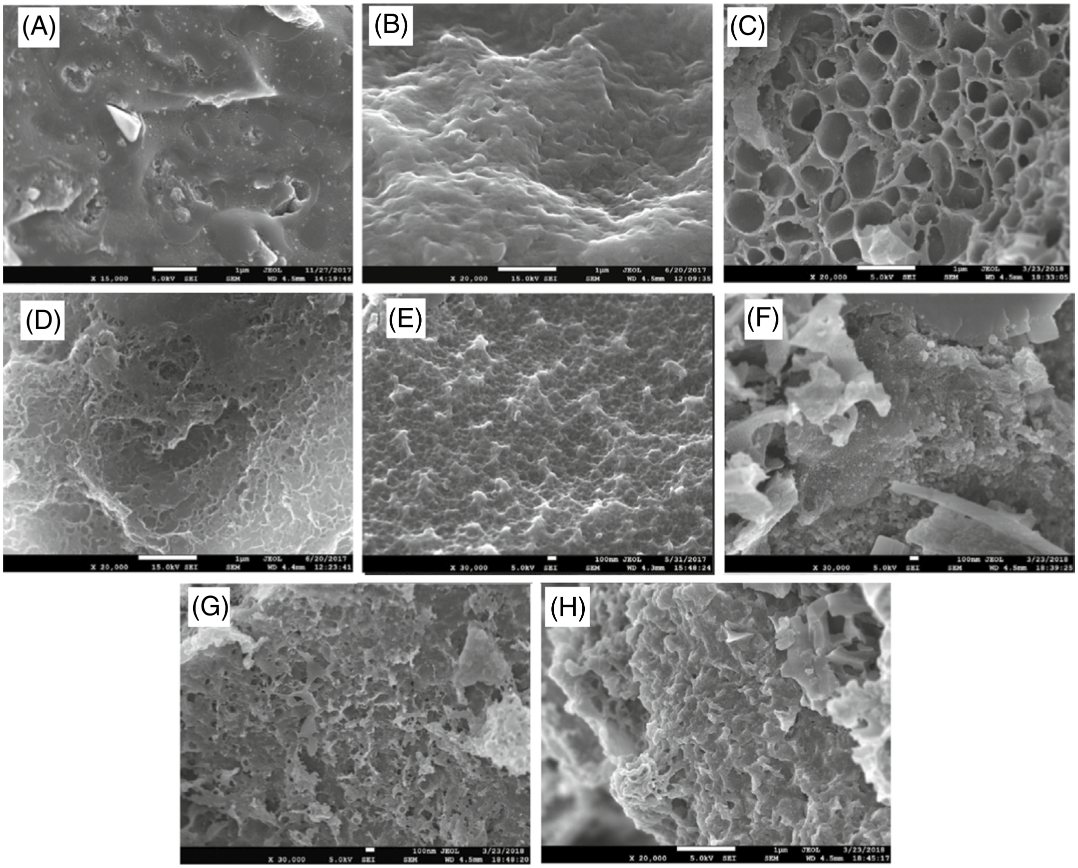

FIG. 13.1 SEM images of (A) OFI cladodes powder; (B) biochar; (C) ABC1; (D) ABC2; (E) ABC1 loaded with MG dye; (F) ABC1 loaded with Cu^{+2}; (G) ABC1 loaded with Ni^{+2}; (H) ABC1 loaded with MG dye and heavy metals. ABC, activated biochar; MG, malachite green dye, OFI, *Opuntia ficus-indica*. Reprinted with permission from Choudhary, M., Kumar, R., Neogi, S., 2020. Activated biochar derived from Opuntia ficus-indica for the efficient adsorption of malachite green dye, Cu^{+2} and Ni^{+2} from water. J. Hazard. Mater. 392, 122441. Copyright © 2020 Elsevier B.V.

type-IV adsorption–desorption isotherm along with a broad hysteresis loop which highlighted its mesoporous nature. The average pore diameters and surface area of the activated biochars were 11.51, 11.32 nm, and 32.07, 33.62 m^2/g, respectively. The activated biochars were then investigated for their adsorption capacity wherein 1341 mg/g of malachite green dye was successfully removed according to the Langmuir isotherm model. The ability of dye adsorption by the biochar was primarily attributed to film diffusion and chemisorption which was best fitted by pseudo-second-order and Elovich models as well.

Iqbal et al. (2021) recently demonstrated the Congo red adsorptive capacity of biochar composite from aqueous solutions. Leaves of *Phoenix dactylifera* were pyrolyzed at 400°C for 60 min for the preparation of biochar which was then successfully conjugated with nanozerovalent manganese (nZVMn) through chemical reduction. SEM micrographs then revealed well dispersion of nZVMn on the surface of the biochar. Adsorptive studies of the biochar composite demonstrated 117.647 mg/g of Congo red dye adsorption from water whereas the biochar alone was able to adsorb 25.316 mg/g of the dye present in the solution. Kinetic studies revealed the best fit of the pseudo-first-order kinetic model for explaining the Congo red adsorption process. The biochar composite showed enhanced reusability with good adsorption capacity even after seven cycles of the dye removal process. Liquid chromatography–mass spectrometry (LC–MS) results then revealed the formation of hydroxyl radicals in the presence of H_2O_2 which mediated the dye degradation and resulted in the formation of six organic and one inorganic degraded product.

Invasive wetland weed plants such as *Phragmites karka* were also used for the preparation of biochar that showed methylene blue adsorptive property (Viswanthan et al., 2020). The plant biomass was pyrolyzed at 450°C for 1 h which resulted in the formation of biochar with a bulk density of 0.146 ± 0.02 g/cm^3 along with a negative zeta potential of −37.6 mV. SEM micrographs then revealed fibrous like structures of the biochar. Moreover, the specific surface area of the biochar was 659.2 m^2/g with an average pore size of 0.5 nm. Kinetic studies highlighted a best fit of Langmuir model wherein the maximum methylene blue dye adsorption capacity was 438.2 mg/g.

In another study, Khan et al. (2020) carried out the hydrothermal liquefaction of rice (*Oryza sativa* L.), husk (RH), and cow dung (CD) for the production of biochar which was then used for dye removal. A mixed bed rotating pyrolyzer (MBRP) was used for the preparation of RH and CD biochar that was characterized using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) which showed the presence of C, O, Al, Mg, Si, Ca, P, K, and Cl. In addition, elemental sulfur was also present on the surface of the biochar. Thereafter, RH and CD biochar was applied to remove 100 ppm of Congo red using a PBBR which resulted in 66.82–96.92% and 68.98–98.84% of decolorization, respectively.

Similarly, Ganguly et al. (2020) also synthesized RH biochar through pyrolysis and evaluated its dye removal capacity. The RH was pyrolyzed at 400–600°C for 1 h under anaerobic conditions. Thereafter, the malachite green dye removal ability of the biochar was investigated at a constant pH and dye concentration of 6.5 and 20 mg/L, respectively within a dose range of 0.5–2.0 g/L. The efficiency of dye removal was then increased with a subsequent increase in the concentration of biochar. Moreover, a maximum dye removal capacity of around 99.98% was achieved after 2 h of incubation in the presence of 0.2 mg/L of adsorbent at pH 6.2 along with 20 mg/L of initial dye concentration. Kinetic studies further revealed the best fit of the pseudo-second-order model for explaining the dye adsorption kinetics of the malachite green dye.

Similarly, Saif Ur Rehman et al. (2016) reported brilliant green dye adsorption using plant-based biochar. In this study, hydrolyzed rice straw was used as the raw material for the biochar production carried out through pyrolysis at 723 K in a muffle furnace for 1 h. The surface area of the obtained biochar was 232.31 m^2/g along with a total pore volume and average pore width of 0.30 cm^3/g and 5.22 nm, respectively. The optimal pH, temperature, initial dye concentration, and biochar dose were 6.0 ± 0.15, 40°C, 100 mg/L, and 0.75 g/L, respectively. Kinetic studies of the adsorption process further indicated a best fit for the Langmuir isotherm which suggested monolayered adsorption of brilliant green dye on the surface of the biochar. Moreover, a pseudo-second-order kinetic model was considered for the adsorption which was a spontaneous and physical process. Hence, 111.11 mg/g of dye adsorption capacity was attained under optimized conditions.

Goswami et al. (2020) demonstrated the bioremediation of Congo red dye using biochar prepared from the seeds of *Terminalia arjuna* (Arjuna plant) which was immobilized with bacteria, *Providencia stuartii*. The bacterial strain was isolated from a wastewater sample which showed efficient Congo red dye degradation. FTIR spectra analysis of the biochar showed multiple peaks after dye adsorption corresponding to the primary components of Congo red dye. The BET surface area of 170 m^2/g was associated with a pore size of 2.873 nm. Scanning electron microscope (SEM) images also displayed a considerable amount of pores on the surface of the Arjuna plant seeds biochar which was suggested to act as adsorption sites for the dye molecule. An inoculum concentration of 3.0×10^5 colony forming units (CFU)/mL was optimal for dye degradation. Likewise, 65.2% degradation efficiency was attained at a temperature of 30 °C while 95% degradation was achieved after 6 days of incubation. In addition, 85.39% of 100 ppm of Congo red dye was efficiently removed by immobilized *P. stuartii* cells as compared to 65.95% degradation by free cells. Therefore, under optimal conditions, a maximum of 92.0 ± 5.0% Congo red dye degradation was achieved. Attachment of the bacterial cells to the biochar was suggested to increase the contact time between the dye molecule and microbes which in turn, enhanced the dye degradation ability. Thereafter, a continuous borosilicate packed bed bioreactor (PBBR) was used for a continuous dye degradation study wherein 82.38% of 100 ppm of Congo red dye was effectively removed using immobilized microbial cells on the plant-based biochar. Kinetic studies further demonstrated a maximum specific growth rate (μ_{max}) and half-velocity constant (K_s) of 0.461/day and 39.44 mg/L, respectively. Ozone treatment was carried out after the biological treatment which resulted in the complete removal of Congo red dye within 30 min with an ozone flow rate of 10 mg/min.

13.2.2 Algae-based biochar

Algal biomass has also been extensively utilized as naturally available adsorbent material for the synthesis of biochar. In one such study, Gokulan et al. (2019) derived biochar from *Caulerpa scalpelliformis* which is a green marine alga, and then evaluated its dye removal capabilities against remazol dyes namely Remazol brilliant blue R (RBBR), Remazol brilliant orange 3R

(RBO3R), Remazol brilliant violet 5R (RBV5R), and Remazol Black B (RBB). Thermal pyrolysis of the dried algal biomass was carried out at various temperatures with a heating rate of 5°C/min. However, the maximum biochar yield of 52 ± 0.22% was achieved at a pyrolysis temperature of 300°C. SEM images as seen in Fig. 13.2 then demonstrated the rough surface of the biochar after pyrolysis which was attributed to the thermal breakdown of biomass that in turn facilitated an increase in the surface area of the biochar for improved dye adsorption. Moreover, an optimal biochar dosage of 2 g/L resulted in efficient removal of Remazol dye at pH 2 and a temperature of 30°C. Kinetic studies further revealed the best fit of the Toth model for explaining dye adsorption. NaOH exhibited 99.8% overall elution efficiency. Remazol brilliant orange 3 R (RBO3R) dye adsorbed on the biochar with higher affinity compared to other dyes with a maximum adsorption capacity of 130.11 mg/g.

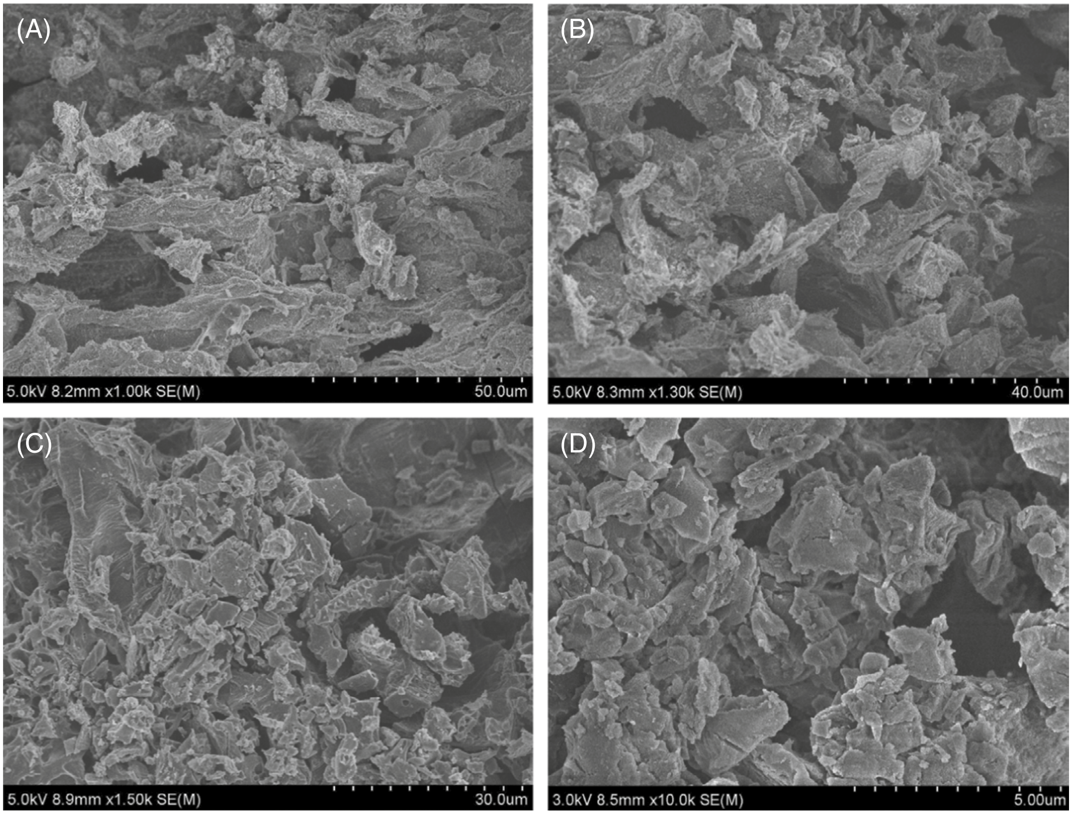

FIG. 13.2 Scanning electron micrographs of (A) RBB-loaded biochar; (B) RBV5R-loaded biochar; (C) RBO3R-loaded biochar; and (D) RBBR-loaded biochar. RBB, Remazol Black B; RBV5R, Remazol brilliant violet 5R; RBO3R, Remazol brilliant orange 3R; RBBR, Remazol brilliant blue R. Reprinted with permission from Gokulan, R., Avinash, A., Prabhu, G.G., Jegan, J., 2019. Remediation of remazol dyes by biochar derived from *Caulerpa scalpelliformis*—an eco-friendly approach. J. Environ. Chem. Eng. 7, 103297. Copyright © 2019 Elsevier Ltd.

Amin et al. (2020) also reported algal biochar-mediated dye adsorption. In this study, the biomass of marine *Chlorella* sp. was slowly pyrolyzed at a temperature of 550°C for 60 min which resulted in the formation of porous biochar with a high surface area of 351 m^2/g and a negative surface charge. Thereafter, reactive yellow dye-145 was adsorbed using the biochar wherein 99% of the dye was effectively removed under optimal conditions. The initial dye concentration, initial pH value, adsorbent dose, adsorption time, and ultrasonic frequency of 50 mg/L, 2.0, 0.3 g/L, 1 min, and 35 kHz, respectively, were optimal for the maximum dye adsorption. The kinetic studies highlighted the best fit of the Freundlich isotherm and pseudo-second-order model for the adsorption process. Chemisorption was proposed as the primary mechanism of adsorption wherein the adsorbent was suggested to be heterogeneous in nature.

Wet-torrefied *Chlorella* sp. microalgal biochar effectively removed both cationic and anionic dyes such as methylene blue and Congo red (Yu et al., 2021). The wet torrefaction process was carried out in a nitrogen-purged inert condition for the preparation of the microalgal biochar which exhibited an irregular porous and coarse morphology in field emission scanning electron microscopy (FESEM) images. The BET surface area was 2.66 m^2/g with an average pore diameter of 0.65 nm. Hence the material was considered as microporous in nature. The point of zero charge (pH_{pzc}) of wet-torrefied biochar was 3.7 wherein cationic dye such as methylene blue was adsorbed when the pH was greater than pH_{pzc} whereas anionic dye such as Congo red was adsorbed under opposite conditions. A biochar concentration of 1 g/L was optimal for the removal of 85.47% of methylene blue dye whereas 2 g/L of biochar showed maximum adsorption of 95.61% of Congo red dye. A pH range of 6.0–8.0 was ideal for the adsorption of both the dyes. The contact time required for attaining the equilibrium adsorption was higher for methylene blue as compared to Congo red. The maximum adsorption capacities for methylene blue and Congo red were 113.0 mg/g and 164.35 mg/g along with removal percentages of 26.32–89.78% and 54.72–97.10%, respectively. The Langmuir isotherm model was the best fit which highlighted the monolayer coverage adsorption of the dyes on the biochar which made the availability of adsorption sites the rate-limiting factor.

Pathy et al. (2022) recently reported the removal of malachite green using algal biochar. A mixed consortium of algal strains with the dominance of *Chlorella* sp., *Scenedesmus* sp., *Synechocystis* sp., and *Spirulina* sp. were cultured in a photobioreactor followed by the harvesting of its microalgal biomass. In addition, composite biochar was also prepared using a symbiotic culture of bacteria and yeast (SCOBY) along with kombucha and microalgae. Three different biochars namely, algal biochar (AB), kombucha SCOBY biochar (KB), and algal-kombucha biochar (AKB) were prepared through pyrolysis of the respective organic matter at 500°C for 45 min with a heating rate of 5°C/min. The contact time of the prepared biochars affected the efficiency of the malachite green removal wherein AB and AKB showed an equilibrium within 180 min while KB reached equilibrium within 1 h however, the removal efficiency of KB was around 20% due to the absence of adsorption sites on the KB surface. Likewise, the pH also affected the adsorption process with effective dye removal observed within pH 4–7 while increasing the initial biochar concentration resulted in a subsequent increase in the dye removal efficiency as well. Moreover, the maximum adsorption capacity of AB and AKB was 166 and 500 mg/g, respectively. Kinetic studies demonstrated that the pseudo-second-order model was the best fit for both AB and AKB biochar-mediated dye adsorption. Chemisorption and diffusion were the primary mechanisms that facilitated the adsorption process. The dye removal ability of the biochar was then integrated with phycoremediation which resulted in the removal of more than 98% dye from the wastewater sample along with a 1.33- and 1.55-fold increase in the microalgal growth after AB and AKB biochar treatment, respectively.

Gracilaria Rhodophyta red weed biomass was also utilized for biochar preparation which displayed efficient removal of brilliant green dye from wastewater (Naga Babu et al., 2021). The dried algal biomass was carbonized at 450°C for 1 h after which the biochar obtained was used in sequential batch adsorption studies. The optimal conditions for maximal dye adsorption efficiency of 17.8 mg/g were observed at a pH range, biochar dosage, initial dye concentration, and operating time of 6.0, 0.5 g/100 mL, 100 mg/L, and 60 min, respectively. Kinetic investigations further confirmed monolayered homogeneous physisorption of the dye wherein the adsorption process carried out at the surface of the biochar was described by Langmuir pseudo-second-order models.

In another recent study, Shaikh et al. (2022) fabricated a biochar-based hybrid Ag nanocomposite using *Spirogyra* sp. biomass which was evaluated for its potential application in toxic dye removal from wastewater. Mild thermal pyrolysis was carried out using *Spirogyra* sp. biomass while silver nanoparticles (AgNPs) were synthesized by reduction of Ag^{1+} using *Shorea robusta* leaf extract as the reducing agent after which the biochar-based nanocomposite was prepared by following a modified chemical coprecipitation method. FESEM images of the obtained nanocomposite then revealed its irregular and heterogeneous surface with a significant number of pores and cavities. The specific surface area of the nanocomposite was 8.77 m^2/g with an average pore size of 25 nm while the XRD pattern highlighted the semicrystalline nature of the adsorbent with an amorphous phase of the biochar matrix and crystalline phase of *n*Ag. The Congo red dye adsorption property of the nanocomposite was optimized wherein a maximum adsorption efficiency of 77.63% was achieved with an initial dye concentration of 18 mg/L. The mean energy of 1290.99 kJ/mol for the dye adsorption suggested that chemisorption is the primary mechanism of dye removal by the nanocomposite. Optimization of the dye adsorption parameters resulted in a maximum adsorption efficiency of 95.92% for 18 mg/L of Congo red with a contact time, pH value, and initial nanocomposite concentration of 60 min, 6.0, and 0.5 g/L, respectively. The nanocomposite also exhibited its reusability with more than 80% removal efficiency retained after two continuous adsorption–desorption cycles.

Tan et al. (2020) also derived biochar from high salinity microalgal residues (HSBC) which were used for the sorption of ionized dyes. *Spirulina* residue composed primarily of minerals was annealed for the preparation of HSBC using pyrolysis at different temperatures with a heating rate of 15°C/min. XRD pattern analysis of the prepared HSBC displayed its crystalline nature because of the abundance of calcium phosphate, hydroxy calcium phosphate, and sodium chloride along with other salts. Moreover, acid washing of the HSBCs resulted in a significant increase in the carbon content from 20.98–28.09% to 71.23–75.67% which highlighted that carbon phases were the main component in the washed HSBCs (WHSBCs) which had a low thermal resistance. The hydrophilicity of the HSBCs was also higher as compared to WHSBCs which was attributed to the higher mineral content in HSBCs in the form of metal oxides. The specific surface area and organic content along with the porosity of the biochars were maximum at a pyrolysis temperature of 700°C while it was minimum at 300°C. SEM images further confirmed the crystallinity of the HSBCs with stick-like crystals on the surface of the biochar. The maximum adsorption capacities of rhodamine B, methylene blue, Congo red, and methyl orange were 421.93, 370.24, 287.89, and 177.32 mg/g by HSBC pyrolyzed at 700°C. The kinetic studies highlighted the importance of Ca^{2+} and Na^{+} in dye adsorption.

Spirulina platensis was also used by Nautiyal et al. (2016) for the derivation of biochar after in situ transesterification which was then exploited for the adsorption of Congo red dye. The dried biomass of *S. platensis* was pyrolyzed at 450°C for 2 h with a heating rate of 20°C/min. SEM images of the biochar revealed its porous surface. The obtained biochar then demonstrated 82.6% adsorption efficiency as compared to 78.1% dye adsorption by the dried algal biomass. Additionally, 0.2 g/100 mL of biochar concentration and 90 mg/L of initial dye concentration were optimal for maximum dye adsorption under acidic conditions.

In a similar study, *Undaria pinnatifida* was used for the preparation of porous biochar that had dye removal ability from aqueous solutions (Yao et al., 2020). The algal biomass was activated by KOH prior to its pyrolysis at 800°C for 2 h. The synthesized biochar was mesoporous in nature with a high specific surface area of 1156.25 m^2/g. The dye adsorption studies then showed maximum adsorption of 841.64, 533.77, and 4066.96 mg/g of methylene blue, rhodamine B, and malachite green dyes, respectively. In addition, kinetic studies showed the best fit of pseudo-second-order and Langmuir models for explaining the adsorption process.

13.2.3 Magnetic biochar

Biochar having magnetic behavior also exhibits dye adsorption capability. Alkali-activated rice straw was used as the precursor for the successful synthesis of magnetic biochar which then exhibited effective removal of rhodamine B dye from aqueous solutions (Ren et al., 2020). Rice straws were loaded with Fe^{3+} ions prior to pyrolysis at 650°C for 60 min which resulted in the formation of the magnetic biochar. SEM images then revealed the porous surface of the biochar with an abundance of cracks. The specific surface area of the magnetic biochar was 396.9 m^2/g along with iron content and magnetization saturation of 37.49 mg/g and 3.12 emu/g, respectively. The rhodamine B dye adsorption kinetics was evaluated which showed a rapid rate of adsorption within the first 5 min of incubation with maximum absorption of 53.66 mg/g. A contact time of 60 min was considered ideal for further adsorption studies. The pseudo-second-order model was considered the best fit to describe the adsorption process which highlighted the chemisorption of the dye as the rate-limiting mechanism.

Wang et al. (2020) also prepared magnetic biochar from waste corncob which was modified with a double oxide layer composed of nickel and aluminum. The biomass of corncob was mixed with $FeCl_3$ followed by pyrolysis of the mixture at 700°C for 3 h. The obtained magnetic biochar was reacted with $Ni(NO_3)_2•6H_2O$, $Al(NO_3)_2•9H_2O$, and CON_2H_4 for preparing the magnetic biochar/NiAl-layered double oxide (NiAl-LDO) composite. SEM images revealed a smaller size of the composite particles as compared to the unmodified magnetic biochar. The clusters of slender nanoparticles were observed on the surface of the magnetic biochar/NiAl-LDO composite. The surface area of the composite was 552.62 m^2/g while pristine magnetic biochar had a smaller surface area of 26.83 m^2/g. Kinetic studies revealed the best fit of the Langmuir isotherm model with a maximum adsorption capacity of 116.3 mg/g of acridine orange dye at a temperature of 323 K which was higher when compared with the unmodified magnetic biochar. The recyclability of the modified biochar was also enhanced wherein the adsorption efficiency remained intact after nine successful adsorption–desorption cycles.

Similarly, magnetic biochar was synthesized by Mubarak et al. (2015) using an empty fruit bunch (EFB) which was used for the treatment of wastewater contaminated with toxic dyes. The biomass was pyrolyzed for 30 min after its chemical treatment with ferric chloride to obtain the biochar. Optimization of process parameters for effective dye removal using the magnetic biochar was carried out in which maximum adsorption of 90.76% of orange-G dye was achieved at pH 2 while 96.86% of methylene blue dye was removed under similar pH conditions. The contact time of the biochar with the wastewater was also an important factor for the dye removal efficiency wherein the percentage of dye removal increased with a concomitant increase in the contact time. The initial biochar dosage of 1 g facilitated the highest removal of both the dyes from wastewater samples. Kinetic studies then described the Langmuir isotherm model as the best fit for explaining the adsorption mechanism with a maximum methylene blue and orange-G dye adsorption capacity of 31.25 mg/g and 32.36 mg/g, respectively.

In another study, food waste from disposal facility with the highest abundance of glucan and protein was used for the preparation of magnetic biochar with considerable organic dye removal properties (Chu et al., 2020). The magnetic biochar was prepared by pyrolysis of the food waste and iron (II) chloride tetrahydrate mixture at 300°C for 7 h with a heating rate of 5°/min. FESEM images demonstrated the aggregations of iron precipitate on the surface of the biochar composites which was further confirmed by the high-intensity Fe peaks observed in EDS spectral analysis. The crystalline nature of the biochar matrix was also confirmed by XRD analysis along with the cubic structure of the maghemite. The biochar composite was mesoporous with a specific surface area and magnetic saturation of 65.555 m^2/g and 43.8 emu/g, respectively. The resulting magnetic biochar was used as a catalyst for Fenton-like processes wherein a triple system combining the synergistic action of ultrasound and hydrogen peroxide was utilized for obtaining efficient methylene blue and methyl orange dye reduction ability. The enhanced system exhibited an enhanced dye removal capacity with a maximum of 100% and 95% for methylene blue and methyl orange removed after 60 and 180 min of incubation, respectively. The synergy factors for methylene blue and methyl orange were 5.73 and 10.95, respectively. The reusability of the biochar-based catalyst was also highlighted with retention of more than 84% methylene blue degradation efficiency after five successive cycles.

Eltaweil et al. (2020) prepared a mesoporous magnetic biochar composite for improved malachite green dye removal. The biochar was derived from corn straw through carbonization at 500°C which was supported with nanozero-valent iron (nZVI) for enhanced dye remediation potential. XRD pattern of the biochar revealed its amorphous nature whereas nZVI showed diffraction peaks which highlighted its cubic phase structure as well as its successful loading on the surface of the biochar. High-resolution transmission electron microscope (HRTEM) images revealed the chain-like structure of nZVI nanoparticles with a particle size ranging from 40 to 50 nm along with its core–shell structure while the nanocomposite had less aggregation of nZVI as evident from Fig. 13.3. The magnetic behavior of the nanocomposite was studied using a vibrating sample magnetometer (VSM) which exhibited a saturation magnetization of 70.5 and

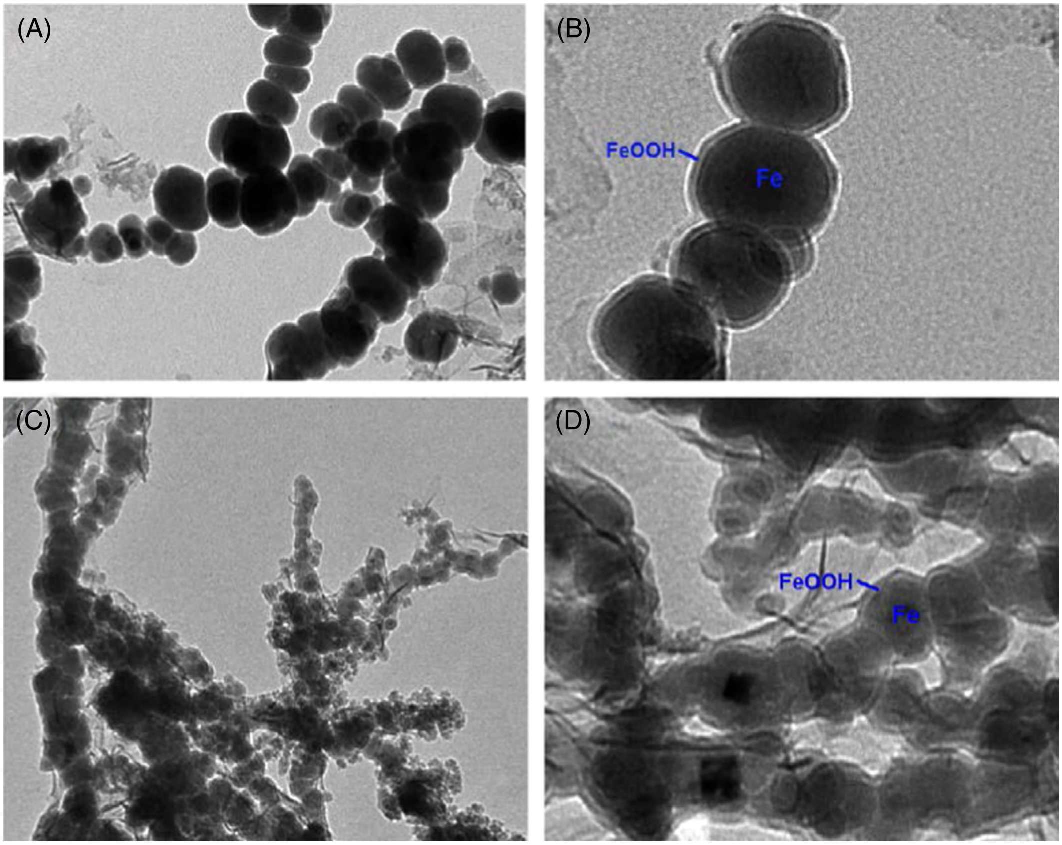

FIG. 13.3 HR-TEM images of nZVI (A and B), nZVI/BC composite (C and D). Reprinted with permission from Eltaweil, A.S., Mohamed, H.A., Abd El-Monaem, E.M., El-Subruiti, G.M., 2020. Mesoporous magnetic biochar composite for enhanced adsorption of malachite green dye: characterization, adsorption kinetics, thermodynamics and isotherms. Adv. Powder Technol. 31, 1253-1263. Copyright © 2020 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan.

38.7 emu/g for the nZVI nanoparticles and the nZVI/biochar composite, respectively. The soft ferromagnetic behavior of the nZVI/biochar composite was also evident with a coercivity of 26.36 G. The N_2 isotherm of the nZVI/biochar composite showed a type II isotherm with a specific surface area, pore diameter, and total pore volume of 36.2 m^2/g, 1.49 nm, and 0.179 cm^3/g, respectively. The dye removal ability of the nanocomposite was investigated which showed 99.9% removal of 100 mg/L of malachite green within 20 min at 25°C as compared to 17.8% and 34% dye adsorption by biochar and nZVI alone, respectively under similar conditions. The adsorption capacity of the nanocomposite further increased from 199.2 to 515.77 mg/g with a concomitant increase in the initial dye concentration from 50 to 150 mg/L, respectively.

Zeng et al. (2021) recently prepared sludge-based magnetic biochar for the removal of methylene blue from wastewater. The sewage sludge was pyrolyzed at 600°C for 1 h followed by backwashing iron mud without any chemical agents. The saturation magnetization of the resulting biochar was 25.60 emu/g while the dye adsorption ability of 47.44 mg/g was achieved at a temperature of 289 K. The maximum adsorption capacity of 296.52 mg/g was obtained after modification with hydrochloric acid. Hence, pH was considered an important factor in this study for obtaining the maximum dye adsorption capacity. Kinetic studies further revealed Langmuir isotherm and pseudo-second-order models exhibit the best fit for explaining the process of dye removal. The renewability of the biochar adsorption capacity was also confirmed wherein 61.73% of adsorption capacity was retained even after five regenerations.

In another study, Santhosh et al. (2020) synthesized magnetic biochar using sewage sludge and woodchips which were then modified with magnetic (Fe_3O_4) nanoparticles. The sewage sludge and woodchip samples were pyrolyzed at 450°C and 700°C, respectively, and then modified with magnetic nanoparticles using the coprecipitation method. SEM images displayed the flake-like shape of the unmodified biochars which were then decorated with magnetic nanoparticles after modification. In addition, the size of the nanoparticles ranged from 50 to 100 nm. The maximum magnetization of the modified biochar was 41.87 emu/g for those prepared using woodchips. The specific surface area of the modified sewage sludge and woodchips biochars were 127.98 and 99.83 m^2/g, respectively. Later, the dye adsorption capacity of the modified biochars was investigated wherein 110.27 mg/g of acridine orange 7 dye was maximally adsorbed.

13.2.4 Animal-based biochar

Several animal wastes are used as cheap precursors for the successful production of biochar. Côrtes et al. (2019) in one such study demonstrated the application of bovine bones (BB) and fish scales (FS) for the preparation of biochar which was eventually used for the removal of dyes from aqueous solutions. Both BB and FS were pyrolyzed for the preparation of biochar with a yield of 62.82% and 43.14%, respectively. XRD pattern analysis then displayed the primary presence of hydroxyapatite in obtained biochar samples. FTIR spectra further confirmed the presence of similar hydroxyapatite functional groups in biochars prepared from BB and FS. An uneven structure with surface cracks was observed in SEM images of the biochars as observed in Fig. 13.4. The mesoporous nature of the biochars was also reflected in the N_2 adsorption/desorption isotherms. The pore diameter of BB- and FS-biochar ranged from 25 to 100 Å along with a specific surface area of 90 and 94 m^2/g, respectively. The pyrolytic oil composition was also analyzed using gas chromatography coupled with mass spectrometry (GC–MS) which showed hexadecenoic acid and imidazolidinedione as the primary component in the pyrolyzed product of BB and FS, respectively. The dye adsorption efficiency of BB- and FS-biochar was investigated wherein 49.5 and 52.3 mg/g of basic red 9 dye was effectively adsorbed, respectively.

Zhu et al. (2018) also prepared animal-derived biochar using cattle manure that efficiently removed methylene blue from aqueous solutions. The cattle manure sample was torrefied at 200°C for 30 min which created biochar with a specific surface area, pore volume, and average pore diameter of 0.3276 m^2/g, 0.00613 cm^3/g, and 75.02 nm, respectively. The dye saturation adsorption capacity of the biochar was 241.99 mg/g which followed pseudo-second-order

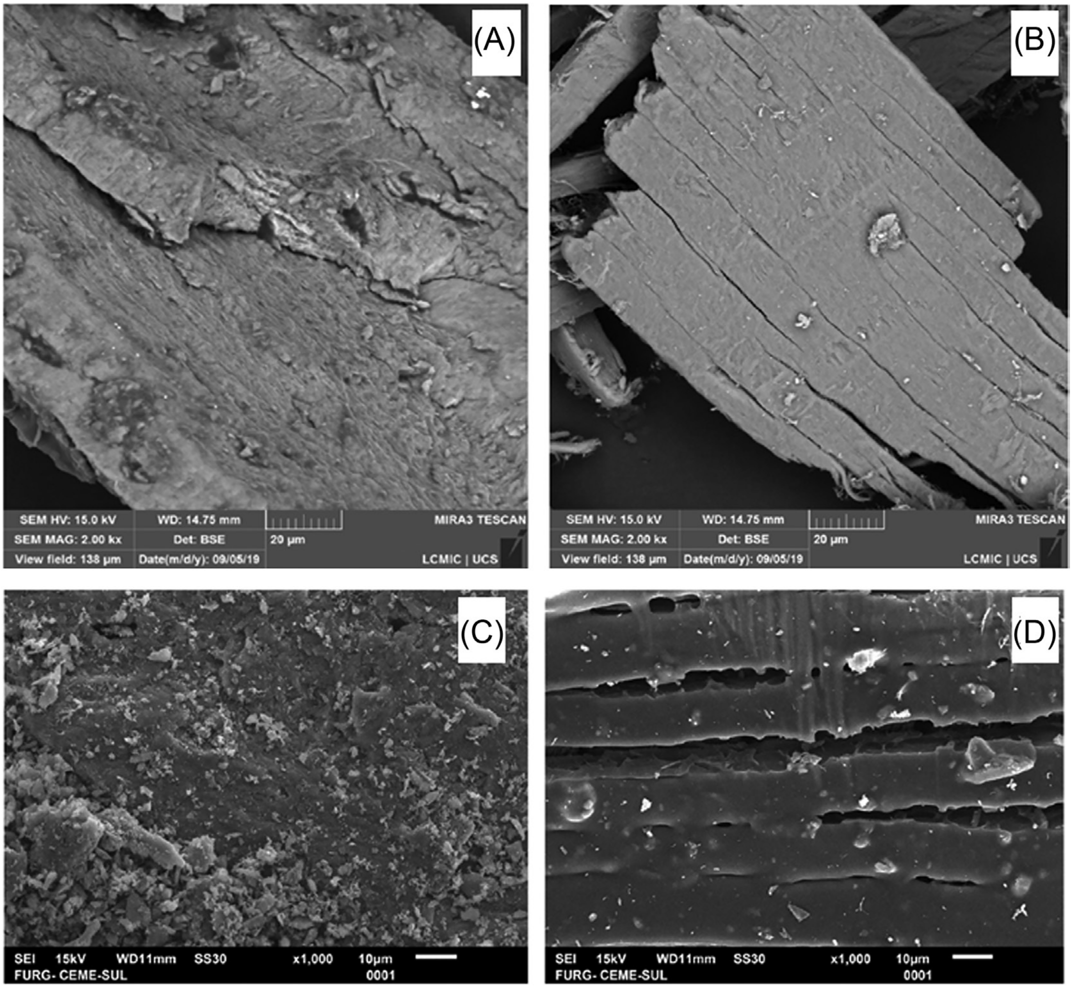

FIG. 13.4 SEM micrographs of (A) bovine bone; (B) fish scale; (C) bovine bone biochar; and (D) fish scale biochar. Reprinted with permission from Côrtes, L.N., Druzian, S.P., Streit, A.F.M., Godinho, M., Perondi, D., Collazzo, G.C., Oliveira, M.L.S., Cadaval Jr., T.R.S., Dotto, G.L., 2019. Biochars from animal wastes as alternative materials to treat colored effluents containing basic red 9. J. Environ. Chem. Eng. 7, 103446. Copyright © 2019 Elsevier Ltd.

kinetics. The optimal dye concentration of 200 mg/L and the biochar dose of 0.05 g resulted in 95.36% adsorption efficiency. The kinetic studies suggested single-layer adsorption of dye on the surface of the biochar which was thermodynamically spontaneous and exothermic in nature.

Crustaceous waste such as crab shells was also reported to be an efficient precursor for the preparation of calcium-rich biochar (Dai et al., 2018). Crab shells were pyrolyzed in a nitrogenous atmosphere for 2 h followed by the pulverization of the obtained material through a 0.18 mm sieve. Transmission electron microscopy (TEM) images of the prepared biochar displayed a novel multilayered structure made up of calcite. The zeta potential of the calcium-rich biochar was 20 mV at pH 4.0 which was reduced to −4 mV under alkaline pH conditions. A high adsorption capacity of 12,502 and 20,317 mg/g of malachite green and Congo red dyes were achieved using the prepared biochar, respectively. In addition, the Congo red dye adsorption equilibrium by the calcium-rich biochar was achieved within 2 min.

In another similar study, Lu et al. (2020) reported biochar-mediated rhodamine B dye adsorption. The biochar was prepared using goat manure using pyrolysis at 600°C which had a rough and uneven surface along with a large specific surface area of 181.76 m^2/g as well as a high number of pores. The total pore volume of the biochar was 0.245 cm^3/g. The dye removal rate of the animal-based biochar was pH dependent wherein over 97% of rhodamine B dye removal was achieved at pH 5 beyond which the dye removal decreased. The initial biochar dosage of 0.2 g/L was optimal for the maximum adsorption capacity of 77.059 mg/g. The adsorption process was divided into three phases in which the first phase was the rapid adsorption phase followed by a slow diffusion phase, and then an equilibrium phase which lasted for 500 min. Optimization studies concluded that the initial biochar concentration of 0.4 g/L along with a contact time of 150 min and initial rhodamine B dye concentration of 20 mg/L displayed the highest adsorption capacity when the temperature of the system was 25°C. Kinetic studies confirmed that the adsorption process was spontaneous, and endothermic associated with an increase in entropy.

Huang et al. (2018) also adsorbed methylene blue using animal manure-derived biochar. In this study, sheep, rabbit, and pig manures were thermally decomposed at 500°C for 20 min. The biochar obtained from sheep manure exhibited higher specific surface area and average pore diameter as compared to the biochar derived from the other two manure samples. Hence, it was assumed that sheep manure-derived biochar had a larger surface area and porous nature as compared to other biochars which were evident in SEM images. Thereafter, batch studies showed adsorption equilibrium attained within 210 min at an initial dye concentration and pH value of 50 mg/L and 11.0, respectively. Kinetic evaluations confirmed pseudo-second-order process wherein liquid film diffusion, surface adsorption, and intraparticle diffusion contributed to the rate of adsorption. Moreover, Langmuir models showed best consistency of the adsorption process with maximum adsorption capacity of 238.31, 104.02, and 53.68 mg/g by sheep, rabbit, and pig manure biochars, respectively.

13.3 Conclusions and perspectives

Plant, animal, and microbe derived biochar-mediated dye removal can be a potential complementary and alternative effluent treatment process. Wastes from industries associated with agriculture, dairy, food, and pharmaceuticals where residual biomass is considered as by-product, can be efficiently utilized to produce biochar. This provides a cheap and economical strategy to convert waste to wealth. These biochars can be explored for removal of refractory pollutants such as agrochemicals containing pesticides, herbicides, and insecticides from the environment. Nanoparticles can be further impregnated within the biochar to fabricate novel nanocomposites that can potentially remove hazardous dyes from the effluents of textile, pharmaceutical and paper industries that release large volumes of dye contaminated water in the environment every year. Tunable porosity of the biochar that can be controlled by careful incorporation of the suitable nanomaterial can play a vital role in determining its overall efficiency in removal of dye and other contaminants from the industrial effluents. However, various process parameters like the source and concentration of biochar, volume of the effluent, contact time, initial dye concentration, and pH should be optimized to get maximum dye removal efficiency. Fabrication of functionalized biochars with maximum activity at neutral pH is of utmost importance. Likewise, single biochar with broad spectrum applications in removal of dye, heavy metals, pesticides, and oil can have more acceptability. Also in-depth studies should be carried out to understand the reaction kinetics using Langmuir and Freundlich isotherm models. Detailed study regarding the thermodynamics involved in biochar-mediated removal of pollutants will help to explore the mechanism behind the activity and promote rational improvization of the adsorption capacity. Regeneration of the used biochar will ensure recycle and reuse of the same which will make biochar-mediated water treatment a sustainable, economical, and affordable. In view of the background biochar with attractive physical properties such as large surface area, high porosity, defined composition, and convenient fabrication can be a powerful material for removal of refractory pollutants to ensure clean and safe water.

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14

Bioremediation approaches for the removal of emerging contaminants from industrial wastewater

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14.1 Introduction

Water is the most vital component of life, and industrialization and access to clean, pure water for people are crucial for economic growth. Only 1% of the planet's surface is suitable for human consumption and economic use, despite water making up 71% of it. Additionally, the untreated or only partially treated effluent that is released into water bodies, whether legally or illegally, further depletes water supplies, creating a water deficit. The World Water Council is one of the organizations attempting to document and improve new water-scarcity strategies. Inaccessibility to clean, safe drinking water affects nearly 2.2 billion people, according to the United Nations' 2020 Water Development Report (Hasan et al., 2019). Cholera, dysentery, hepatitis A, typhoid, polio, and other illnesses are brought on by a severe lack of potable water and a high level of water pollution, both of which affect the healthcare system (Siddiqui et al., 2021; Haq et al., 2016a, 2016b). It has become crucial to clean and reuse wastewater in areas with a shortage of water in order to address issues related to water pollution and scarcity.

However, due to emerging contaminants like micropollutants, traditional water filtration methods face a significant challenge (Liu et al., 2020; Haq et al., 2020). Emerging pollutants can be created naturally or artificially by human endeavors like mining, agriculture, and industry. Pharmaceutical chemicals, detergents, surfactants like triclosan and alkylphenols, fertilizers, insecticides, plasticizers like phthalates, and flame retardants like polybrominated diphenyl ether are examples of emerging contaminants. Cadmium, iron, lead, mercury, and other trace metals are among the other significant contaminants (Gavrilescu et al., 2015; Haq and Raj, 2020). Ozone, chlorination, and membrane filtering are current technologies for removing developing contaminants. However, they are ineffective due to their high energy requirements, water loss that causes secondary contamination, and high cost (Rathi et al., 2020; Haq et al., 2022). Therefore, developing new technologies or improving existing ones is necessary to deal with emerging pollutants effectively.

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Using living organisms to remove dangerous toxic compounds, known as bioremediation, has grown in popularity in recent years (Dangi et al., 2019; Haq and Raj, 2019). Utilizing helpful microorganisms and plants, bioremediation transforms highly complex, dangerous chemicals into relatively simple harmless gases like methane and carbon dioxide by using the toxins as a food source for the organisms (Azubuike et al., 2016). The main factor affecting pollution reduction is the type of pollutants, which may include heavy metals, sewage, hydrocarbons, plastics, agrochemicals, and dyes. Bioremediation procedures consider the application site, the level of pollution, the location, the cost, and the surrounding environment, in addition to the type of pollutant. The two bioremediation techniques that are most frequently used are microremediation and phytoremediation. The process of using microorganisms to change hazardous contaminants into nonhazardous ones is known as microremediation. Under harsh environmental conditions, extremophilic microbes, for example, detoxify harmful substances through their cellular metabolism (Singh et al., 2008; Haq and Kalamdhad, 2021). Similar to bioremediation, phytoremediation uses plants' ability to absorb contaminants to lessen their mobility in contaminated soil and water. Water phosphorus and nitrogen are removed by macrophytic plants (Yu et al., 2019).

Even though microremediation and phytoremediation are safe for the environment, the mechanisms involved are very unstable because of the small number of nutrients that microorganisms and plants can absorb, which varies greatly depending on many physiological and environmental factors (Ojuederie and Babalola, 2017). These microbes and plants can now be used in bioremediation to advances in nanotechnology, which improve absorption and lower costs. Nanomaterials like carbon nanotubes are used to absorb heavy metal compounds like cadmium, chromium, lead, zinc, and arsenic because of their superior adsorption abilities. In its simplest form, nanobioremediation is the fusion of bioremediation and nanotechnology to provide remediation with twice the advantages of the individual processes. It has been shown that exposing the created nanoparticle to the necessary microorganism increases its degrading ability (Galdames et al., 2017). Nanostimulated phytoremediation and microbial remediation break down refractory organic molecules into simpler shapes by combining the functions of microbes, plants, and nanoencapsulated enzymes. Integrating remediation strategies may solve remediation issues because each strategy has benefits and drawbacks. Nanobioremediation is one such method that has attracted much attention recently. The benefits of nanotechnology are combined with bioremediation in nanobioremediation. The method, application cycles, and strategies for nanobioremediation are covered in the following section.

14.2 Bioremediation techniques

Two bioremediation methods used to purge contaminated environments are microbial remediation and phytoremediation.

14.2.1 Microbial remediation

Microbial remediation was developed due to physical and chemical repair limitations, including their ineffectiveness, cost, length of time, and numerous environmental considerations (Dangi et al., 2019). Microorganisms and their metabolic pathways are used in the remediation process to either reduce the concentration of contaminants or change harmful substances into benign ones. Microbial remediation is frequently carried out by either introducing a sizable population of the bred bacteria to the polluted site or by creating ideal conditions for the microbes to grow in the polluted site, such as the right temperature, pH, and food source and oxygen. Typically, oxidation–reduction reactions are used in microbial remediation processes (Sharma, 2019). Typically, oxygen is used as an electron acceptor in these reactions to speed the breakdown of reduced contaminants like hydrocarbons (Canak et al., 2019). In order to neutralize oxidized pollutants like nitrates, oxidized metals, perchlorates, chlorinated solvents, and propellants, an organic material may also be added as an electron donor (Gu et al., 2018). Depending on the type of microorganism used in microbial remediation, there are two main classifications: aerobic and anaerobic. Microorganisms like bacteria and fungi perform aerobic microbial remediation in the presence of oxygen, breaking down hazardous chemicals into carbon dioxide, water, and a few specific inorganic ions (Mikkonen et al., 2018; Haq et al., 2017, 2018). Without oxygen, anaerobic microbial remediation produces by-products like methane, hydrogen gas, sulfides, and nitrogen gases (Logeshwaran et al., 2018). Depending on where the degradants are applied, there are two types of bioremediation: ex situ and in situ.

14.2.2 Phytoremediation

Heavy metal resistance in plants served as the first demonstration of phytoremediation. Treatment of contaminated air, water, and soil by plants and microbes is known as phytoremediation. Metals are taken up by plants' roots and then transferred to the shoots. After that, these plants are harvested to produce bioore phytomining (Pirzadah et al., 2014). The plants displayed metal accumulators, metal indicators, and metal excluders. Metal excluders limit metal penetration by altering the permeability of the membrane. Monitoring the buildup of metal in estuaries is aided by bioindicators or metal indicators (Phillips et al., 2015). Large amounts of metal have been stored in its aerial components using metal accumulators and hyperaccumulators (Pirzadah et al., 2014). The hyperaccumulation-related metal buildup also significantly increases herbivore resistance. Hazardous metals like Zn, Co, Cu, Cd, Ni, and Se, as well as organic and inorganic chemicals, have been removed using certain plants (Pirzadah et al., 2014). There are six different types of phytoremediation: phytosequestration, rhizodegradation, phytohydraulics, phytoextraction, and phytovolatilization (Bolan et al., 2011; Nwadinigwe and Ugwu, 2019).

The process of stabilizing or immobilizing pollutants taken up by roots, adsorbing to the surface of roots, or producing biochemicals that can sequester, precipitate, or immobilize the pollutants is known as phytosequestration or phytostabilization. Both aquatic and terrestrial plants contained sizeable amounts of metals such as Fe, Zn, Cu, Cr, Pb, Hg, and As. Using genetic engineering techniques, phytosequestration has been improved.

Rhizodegradation is the breakdown of soil pollutants by plant roots, stimulating soil microorganisms by releasing organic materials like root exudates and secretions (Li et al., 2020). The combination of biochar and the rhizosphere environment effectively removes soil that has been contaminated with polycyclic aromatic hydrocarbons (PAH). Numerous rhizosphere microorganisms, such as *Bacteroidetes* sp., *Verrucomicrobia* sp., *Actinobacteria* sp., and *Ascomycota* sp., are involved in PAH degradation. However, because of its fibrous root structure, *Lolium multiflorum* Lam. is frequently used for PAH elimination (Li et al., 2020; Kotoky and Pandey, 2020).

The process of controlling the passage of toxins in groundwater through reverse osmosis or biological pumps used by plants or trees to remove impurities from groundwater is known as phytohydraulics. Cottonwood, Willow, and hybrid poplar trees separated water-soluble organic and inorganic components (Liu et al., 2017).

Phytoextraction is the process by which plant roots absorb contaminants from wastewater or soil and accumulate them in the plant's leaves. Arbuscular mycorrhizal (AM) fungus helps plants absorb enormous quantities of toxins. Genetic engineering is also employed to generate transgenic plants with increased tolerance to heavy metals, enhancing phytoextraction.

Through the capture of organic pollutants and other metals by plants, their synthesis into a volatile state, and their release into the atmosphere, phytovolatilization is the process by which toxins are eliminated. It deals with organic and inorganic substances, including Se, As, and Hg. Pteris vittata's vapors were successful in removing arsenic-containing substances. The hazardous substance Se is eliminated through this process by utilizing a variety of plant species and microorganisms.

Photodegradation is known as the breakdown of pollutants by root-driven microorganisms in the water and soil. Scirpusgrossus has been used in conjunction with rhizobacterial bacteria to clean up diesel-contaminated water (Nash et al., 2020). Photodegradation is known as the breakdown of pollutants by root-driven microorganisms in the water and soil. Scirpusgrossus has been used in conjunction with rhizobacterial bacteria to clean up diesel-contaminated water (Nash et al., 2020).

14.2.3 Bioremediation's benefits and drawbacks

The right microorganisms must be present in the right place, and the right environmental conditions must be present for degradation to occur for bioremediation solutions to be effective. Beneficial microorganisms are microscopic creatures or parasites with the physiology and metabolism needed to eliminate pollutants. There are several advantages in comparing bioremediation to more traditional remediation methods like land rolling and cremation. On-site bioremediation is practical, frequently less expensive, and causes little site disruption. It also eliminates long-term liability and obligation, has greater administrative support and public recognition, and is frequently combined with other physical or chemical treatment methods. The limitations of bioremediation are numerous (Roychowdhury et al., 2019). Treatment accumulations typically contain harmless substances like carbon dioxide, water, and cell biomass. Hazardous substances are transformed from toxic ones.

14.3 Nanobioaugmentation

Nanotechnology has been used in many industries over the past few decades, including electronics, medicine, sports, pharmaceutics, cosmetics, textiles, and optics. One of these industries is environmental remediation. The vast amount of published articles and ongoing research in this nanotechnology field indicate that it can successfully overcome challenges and tasks requiring remediation (Singh et al., 2020). Lowering pollutant concentrations while simultaneously enhancing other environmental impacts is the goal of sustainable remediation.

For various reasons, including the increased surface area per unit mass of a material achieved at the nanoscale, which results in higher interaction between the substance and surrounding material, different nanomaterials are used in bioaugmentation (Nanjwade et al., 2018). Chemical processes that are viable require less activation energy, which is another significant factor. This explains the quantum effect observed in NMs. The NPs also exhibit surface plasmon resonance, which can be used to detect dangerous substances. Environmental NMs of different shapes and sizes, both metallic and nonmetallic, can be used (Rizwan et al., 2014). Different types of carbon bases, single metal nanoparticles, bimetallic nanoparticles, and nanomaterials are examples of nanoparticles and used because they are more reactive to redox-sensitive pollutants and can easily pass through polluted areas or areas where microparticles cannot. For instance, carbon tetrachloride (CT) and oxide-coated Fe0 can combine to form weak compounds. Benzoquinone, bytrichloroethene, and other chlorinated aliphatic hydrocarbons are broken down into less dangerous compounds, whereas CT can be converted through electron transfer into CH_4, CO, or formate (Rizwan et al., 2014). TiO_2 nanotubes are used for field applications as well as for photo-electrocatalytic pentachlorophenol (PCP) destruction.

A single metal NP can act as a biocatalyst for reductive dichlorination. When *Shewanella oneidensis* is subjected to a bioreductive assay with palladium (II), different electron donors such as formate, acetate, and hydrogen are added. Pd (0) NPs are then deposited inside the cytoplasm and on the cell wall of the microorganisms and charged with H radicals. The chlorine molecule is eliminated when a chlorinated substance comes into contact with this charged Pd (0) that has been deposited on *S. oneidensis* cells because the H radical on the Pd (0) may catalyze a reaction with PCP. Additionally, microbial cells can be immobilized using nanoparticles in order to break down specific compounds. *Pseudomonas delafieldii* was coated with magnetic nanoparticles that had been ammonium oleate functionalized using a novel immobilization technique. These magnetic NP-coated microbial cells, which have been isolated from the bulk solution and reused to treat the same substrate, are concentrated at a specific location on the reactor wall by applying an external magnetic field to them (Sriplai and Pinitsoontorn, 2021). These microbial cells were shown to desulfurize organic sulfur from dibenzothiophene, or fossil fuels, as effectively as non–nanoparticle-coated cells when fed at high biomass concentrations to a bioreactor (Rizwan et al., 2014). This location's specific NMs will focus on waste remediation, including applications for groundwater and wastewater, solid waste, petroleum and petroleum products (hydrocarbon), soil, heavy metal contamination, and uranium remediation. NMs' potential to reduce pollution is currently being researched and has the potential to be one of the most revolutionary developments in the field of the environment over the coming decades.

A large surface area, adsorption, and reactivity are just a few of the distinctive properties of nanoparticles with sizes ranging from 1 to 100 nm. Wastewater, contaminated soil, and air pollution have all been cleaned up using nanotechnology. Quantum dots, carbon nanotubes, magnetic nanoparticles, and metal nanoparticles are examples of nanomaterials. Numerous shapes, such as nanospheres, nanorods, nanocubes, and nanotriangles, are possible for nanoparticles. Nanoparticle production can occur top-down or bottom-up using physical, chemical, or biological methods (Singh et al., 2020). Organic and inorganic nanoparticles are the two types (Nwadinigwe and Ugwu, 2019). According to their production locations, natural nanoparticles, unintentional nanoparticles produced by human activity, such as burning fossil fuels, and synthetic nanoparticles, such as nanosilver and nanogold, are divided into three categories (Rai et al., 2018). Metal pollutants like Ni, Fe, Pb, and Cr as well as industrial dye effluents, arsenite, tetracycline, sulfate, copper, phenol, and atrazine may be eliminated by nanoparticles. Among the nanoparticles used are Fe/Ni bimetallic nanoparticles, MnO_2, Pd, ZnO, TiO_2, CuO, CeO_2, and nZVI. Bioremediation uses nanoparticles because of their rapid processing, low cost, and high removal efficiency (Singh et al., 2020). Total petroleum hydrocarbons, heavy metals like As, Cr, Cu, Pb, and Hg, trichloroethylene, brominated methanes, and many other organic compounds have all been removed using Fe nanoparticles, whereas organic dyes like methylene blue, fuchsin, resorcinol, and malachite green have all been removed using Zn nanoparticles. Methylene blue, methyl orange, and dichloromethane have been removed using Cu nanoparticles; organic dyes and textile effluents have been removed using Ag NPs; and tertiary dye effluents have been treated using Au NPs.

As opposed to the individual procedure, nanobioaugmentation combines bioaugmentation with nanotechnology to produce both time- and money-effective and ecologically safe remediation. The combined strategy's benefits outweigh the drawbacks of the individual technologies, producing superior degradation. For instance, the effectiveness of nZVI particles in cleaning up pollution increased when they were combined with specific microbial strains. It was found that using nZVI and organochlorine respiring bacteria (ORB) separately cannot effectively remove resistant chemicals, such as chlorinated aliphatic hydrocarbons (CAH). An optimally formulated mixture of nanoparticles and microbes efficiently removed CAH (Li et al., 2020). The bacterial environment for the regeneration of used nZVI contains cysteine and vitamins. The nZVI nanoparticle was found to be more effective for the remediation of polybrominated diphenyl ethers when combined with anaerobic bacteria like *Sphingomonas* sp. in a reductive–oxidative method (PBDEs). When nZVI particles were reductively brominated with PBDEs, aerobic bacteria significantly reduced the amount of BDEs produced. The most significant disadvantage of abiotic nitrate reduction is that temperature fluctuations are unaffected by the biostimulation of nFEO nanoparticles with the nitrate-reducing microbial culture (Singh et al., 2020). Another study found that combining *Sphingomonas* sp. and bimetallic nanoparticles, such as Pb/nFeo, effectively decomposed contaminants made of carboxymethyl cellulose (CMC) (Singh et al., 2013).

Polychlorinated biphenyls (PCBs) can be effectively treated with Pd/Fe nanoparticles followed by *B. xenovorans* bioremediation, according to Le et al.'s (2015) investigation into the treatment of PCBs using a nanobioaugmentation strategy. The toxic levels of PCBs in *E. coli* DH5 before and after treatment were further analyzed using toxic equivalent values, and reports indicate that the cytotoxicity of residual PCBs toward *E. coli* was decreased after treatment. Nmeek et al. (2016) discovered that the Cr (VI) removal in an integrated system consisting of nZVI and whey produced up to 97–99% microorganisms when Cr (VI)-contaminated groundwater was injected with both nZVI and whey. Microorganisms were involved in renewing the oxidized Fe0 nanoparticles in addition to removing pollutants, which reduced the dose of nanoparticles by accelerating the rate of remediation.

There are two possible applications for the treatment system's nanobioaugmentation technique. In order to complete the process, a bioagent is added after the pollutant has been exposed to nanoparticles. The first method is described above, and then comes the second. A concurrent or mixed approach is used. This method simultaneously introduces a nanoparticle and a bioagent into the body. A summary of various findings on the use of bioagents and nanoparticles alone or in combination for bioremediation of different contaminants is provided in Table 14.1.

14.3.1 Microbial bioaugmentation induced by nanotechnology

Nanostimulated microbial bioaugmentation is the degradation of contaminants by nanoparticles generated with the aid of microbes (Yadav et al., 2017). Due to their tiny size and high surface area to volume ratio, nanotechnology-based clean-up is more systematic (Baruah et al., 2019). The most effective and environmentally safe methods of pollution removal combine the aforementioned advantages of nanotechnology with those of microbial restoration (Singh et al., 2020). Green nanoparticle production depends heavily on microorganisms like bacteria, fungi, and algae (Bolade et al., 2020). Microorganisms produce nanoparticles through intracellular and extracellular processes. In the extracellular method, metal ions are reduced enzymatically to create nanoparticles with a broader distribution of sizes. Proteins, peptides, and DNA are natural capping factors that give nanoparticles solidity and prevent them from aggregating (McClements, 2018). Metal ions interact with internal cell enzymes via diffusion in the intracellular mode of action to create nanoparticles (Ovais et al., 2018). Iron oxide nanoparticle-based *Aspergillus tubingensis* (STSP 25) was found to be more than 90% effective at removing heavy metals from wastewater (Mahanty et al., 2020). In a different study, exopolysaccharides from *Chlorella vulgaris* sp. were used to decompose 91% of PO_4^3 effectively and 85% of NH_4^+ in wastewater by coprecipitating iron oxide nanoparticles (Govarthanan et al., 2020). *Escherichia* sp. SINT7, a native copper-resistant bacterial strain, produces biogenic copper nanoparticles that reduce the color of azo dyes like Congo red, malachite green, direct blue-1, and reactive black-5 by 97.07%, 90.55%, 88.42%, and 83.61%, respectively (Noman et al., 2020). The study shows that the marine bacteria *Pseudoalteromonas* sp. CF10-13 converts the metal complex dye Naphthol Green B (NGB) into benzamide by producing stable black iron–sulfur nanoparticles on their own, which minimizes H_2S release, exogenous sulfur addition, and the formation of metal sludge (Cheng et al., 2019). It is a very sophisticated technology to create biogenic nanoparticles exogenously or endogenously for clean-up purposes. Table 14.2 lists the various nanoparticles that are used in conjunction with microbes to treat pollution.

14.3.2 Nanophytoremediation

Iron nanoparticles play a significant role in lowering pollution. *Panicum maximum* was used to remove 2,4,6-trinitrotoluene when nZVI nanoparticles were added to the soil (Jiamjitrpanich et al., 2013). Impatiens balsamina removed polychlorinated biphenyls (PCBs) from e-waste-contaminated soil (Gao and Zhou, 2013). Heavy metals like Pb, Cd, Ni, Zn, and Cu were

Table 14.1 For the nanobioaugmentation process of pollutant detoxification, various nanoparticles are used in conjunction with bioagents (microbes, enzymes).

S. No.	Bioagents	Nanoparticle	Contaminant	Mechanism	References
1.	*Pseudomonas delafieldii*	Magnetic Fe_3O_4 nanoparticles	Dibenzothiophene	Magnetic Fe_3O_4 nanoparticles-coated *Pseudomonas delafieldii* desulfurized dibenzothiophene more efficiently than free cells. It also has the advantage of being reusable.	(Shan et al., 2005)
2.	*Shewanellaoneidensis* MR-1	Pd(0) nanoparticles	PCBs	The reduction of 90% of PCBs by the action of Pd(0) nanoparticles formed from *Shewanellaoneidensis* MR-1 species results in less harmful by-products.	(Windt et al., 2005)
3.	*Sphingomonas*sp. strain XLDN2–5 cells	Fe_3O_4 nanoparticles/ gellan gum gel beads	Carbazole	The reusability of *Sphingomonas* sp. strain XLDN2-5 cells coated with Fe_3O_4 nanoparticles/gellan gum gel beads was higher than increased degradation, and nanoparticles can be easily separated from microbes using an external magnet.	(Wang et al., 2007)
4.	*Dehalococcoides* spp.	nZVI	TCE	nZVI activates the metabolic activity of *Dehalococcoides* spp. to reduce the presence of chlorinating compounds. TCE was also removed by dechlorinating bacterial species and generating by-products.	(Xiu et al., 2010)
5.	*Sphingomonaswittichii*	Pd/nFe	2,3,7,8-Tetrachlorodibenzop-dioxin (2,3,7,8-TeCDD	The combination of *Sphingomonaswittichii* and Pd/nFe nanoparticles successfully degraded a highly toxic dioxin compound.	(Bokare et al., 2010)
6.	Laccase derived from *Trametes versicolor*	Pd/nFe	Triclosan	To remediate the triclosan, iron nanoparticles were used in conjunction with the laccase produced by *Trametes versicolor*, which converts toxic by-products into nontoxic compounds.	(Bokare et al., 2012)
7.	*Acinetobacter junii, Bacillus subtilis, E. coli*	nZVI-C-A beads	Cr(VI)	More than 90% of the Cr(VI) was removed by nZVI-C-A beads covered by a thin biofilm. The combined effects of nanoparticles and biofilm resulted in enhanced chromium removal.	(Ravikumar et al., 2016)

Table 14.2 The remediation of pollutants by nanobioaugmentation uses nanoparticles and related microorganisms.

S. No.	Microorganism associated	Nanoparticles	Advantages	The system where it was used	References
1.	*Sphingomonas* sp. PH-07	nanoscale zero-valent iron (nZVI)	Polybrominated diphenyl ether biodegradation	Soil	(Kim et al., 2012)
2.	*Rhodococcus strain*	Fe_3O_4 nanoparticles	Chlorophenol biodegradation	Aqueous phase	(Hou et al., 2016)
3.	*P. aeruginosa*	Electrospun nanofibrous webs	Methylene blue dye bioremediation	Water	(Sarioglu et al., 2017)
4.	*P. ostreatus*	Enzyme immobilized TiO_2 nanoparticles	Bisphenol-A and carbamazepine biodegradation	Sewage	(Ji et al., 2017)
5.	*Lysinibacillus* sp. NOSK	Electrospun cyclodextrin fibers	Heavy metal and dye bioremediation	Wastewater	(San et al., 2018)
6.	*P. aeruginosa*	Zirconia nanoparticles	Tetracycline bioremediation	Wastewater	(Debnath et al., 2020)

eliminated by phytoremediation using *Noaea mucronate* and *Euphorbia macroclada* nanoparticles (Nwadinigwe and Ugwu, 2019). Additionally, it aids in the removal of organic pollutants like atrazine and molinate, as well as heavy metal pollution in soil (Verma et al., 2021). The removal of significant organic pollutants through phytoremediation has been improved by using nanoencapsulated enzymes (Chauhan et al., 2020).

14.4 Current technological barriers to using nanoparticles

When nanoparticles are used, they accumulate in the environment and dissolve into water sources, endangering human and animal health. It also increases the environment's toxicity. If other animals eat the plants, heavy metal bioaccumulation in the plants might impact the food chain (Cecchin et al., 2017). Less than 1% of nanotechnology strategies have been made into products. Physical and biochemical traits control plants' ability to absorb pollutants (Kvesitadze et al., 2015). Nanoparticles often persist in the environment (Guedes et al., 2020).

14.5 Conclusions and perspectives

Because of the expanding population, the scarcity of freshwater, the effects of climate change, industrial activity, and other factors, the sustainability of water resources has become a critical challenge. New pollutants, such as micropollutants released with untreated municipal and industrial wastewaters and other effluents discharged from wastewater treatment plants, negatively impact environmental matrices and living things throughout their life cycles. Concern for environmental protection and its health risks have become widespread due to the toxicological effects of emerging pollutants released with different industrial wastewaters and their human-caused effects. In addition, the chemical makeup and intensity of emerging pollutants change over time due to the addition and removal of various industrial and municipal effluents, making it extremely difficult for researchers to develop a standard method for treating effluent. According to studies, bioremediation techniques are increasingly being used to treat emerging pollutants because they are compatible, effective, and affordable. Due to its cost-effectiveness and high emerging pollutants removal efficiency at higher concentrations, bioremediation, which includes microbial remediation and phytoremediation, can be a potential wastewater treatment process over other treatment techniques. The effectiveness of various bioremediation techniques in removing emerging pollutants was impressive. Therefore, to optimize a well-organized and economically viable wastewater treatment approach, in-depth knowledge of the discharging source of emerging pollutants, along with their physicochemical characteristics, fate and life cycle, and their environmental effects, is required. Heavy toxic metals that are harmful to humans and the environment were considered to be amenable to treatment with nanobioremediation. Nanotechnology, with help from plants and microorganisms, has been found to be effective and environmentally friendly for effluent remediation. Nanotechnology with enzyme encapsulation will be stable and highly effective at treating pollutants in a cost-effective way. To mitigate the effects and advance nanotechnology in pollutant treatment, it is necessary to address the risks that nanoparticles pose to the environment.

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