Chapter 9
Scenario of Worldwide Preponderance of Contaminants of Emerging Concern in the Hydrosphere

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9.1 Introduction

Humans always tend to deteriorate the provided natural sources. Organic contaminants introduced in the environment are an emerging issue from a long time. They are getting introduced in the hydrosphere which significantly affects both human health and the environment. Hydrosphere consists of total amount of water present in the planet. Hydrosphere includes water that is present on the surface of the earth, underground and in the air. In the early 1800s, a new class of pollutants called emerging contaminants (ECs) also known as contaminants of emerging concern (CECs), and emerging organic contaminants came into light in water and aquatic environment (Miraji et al. 2016; Kumar et al. 2019a, b; Dey et al. 2019). Various definitions have been proposed to define emerging contaminants. ECs or CECs may be defined as the substances which are released in the environment, but no regulations are established for their environmental monitoring (Thomaidis et al. 2012). According to Alexandros, ECs may be defined as the recently discovered group of unregulated contaminants that are present in groundwater and surface water (Stefanakis and Becker 2015). They are known as emerging contaminants because previously they were unrecognized and lacked standard guidelines for their monitoring, but now due

Objectives This book chapter consists of description of various CECs in aquatic environment, their classification and various conventional and advanced techniques available for the removal of these contaminants.

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to their health effects, they are gaining scientific attention (Nosek et al. 2014). They form a newly discovered class of chemicals present in groundwater and surface water. These emerging contaminants include compounds that are being used in our daily life and are involved with various industrial activities. These emerging contaminants are also known as micropollutants, and the reason behind their presence can be anthropogenic as well as natural. They are present in water sources at trace levels ranging from nanograms per liter (ng/L) to micrograms per liter (μg/L) (Luo et al. 2014). All the chemical pollutants like Dechlorane plus (DP), hexabromocyclododecanes (HBCDs), phthalate esters, pyrethroids, etc., were being used as the replacement of toxic chemicals in the following manner: DP was being used as a substitute of mirex which is a persistent organic pollutant (Xian et al. 2011), HBCDs were being used as a halogenated flame retardant and as an alternative of polybrominated diphenyl ethers (PBDEs). Nowadays, short-chain chlorinated paraffin (SCPPs) is gaining a lot of interest among scientists, and they are working on the persistence of SCPPs in the environment and its accumulation in humans (Zeng et al. 2011). Contaminants of emerging concern are not newly developed chemicals, they are dwelling in the environment for decades, but their presence is being investigated recently after noticing their health hazards.

The number of contaminating pollutants is increasing continuously which include industrial compounds, pharmaceuticals, personal care product, antibiotics, hormones, biocides, alkylphenols, plasticizers, plant protection product, perfluorinated compounds, nanomaterials, pesticides, flame retardant (Montagner et al. 2019). Many natural water sources, e.g., river, lakes, reservoir, contain these contaminants worldwide (Lai et al. 2016; Mukherjee et al. 2020; Singh et al. 2020; Wanda et al. 2017; Jaimes et al. 2018). These emerging contaminants get introduced in the water through discharge of wastewater and surface water including urban stormwater runoff (Kolpin et al. 2004; Fairbairn et al. 2018), agricultural runoff, streams, rivers (Kolpin et al. 2002; Lee et al. 2011), lakes (Ferrey et al. 2015), source drinking water and in shallow groundwater (Furlong et al. 2017). Their presence can be a cause of concern if used for drinking purposes (Riva et al. 2018). Sometimes, the transformation products (TPs) are more hazardous in comparison with their parent ECs (Richardson and Ternes 2018).

There are various conventional methods available for the removal of CECs from the water like coagulation, sedimentation, sand filtration, chlorination and advanced treatment processes like ozonation, activated carbon and ultra-membrane filtration (Lv et al. 2016). In addition to this, it is also important to evaluate the concentration of these emerging contaminants in water as they are being a serious issue concerning health and safety. Aquatic life is found to be the most affected due to these contaminants, so there is an urge for immediate research in the field of ECs. The USA, China, Canada, Spain, Germany, Japan, Africa, India, Brazil, Sweden, Norway and Switzerland are some countries that are involved in research on ECs (Bao et al. 2014).

9.2 Occurrence and Fate of CECs

The CECs in our environment can occur as pharmaceutical drugs, herbicides, pesticides, insecticides, etc. Antibiotics, analgesics, anti-epileptic, anti-inflammatory, betablockers, fragrances, barbiturates, diuretics, lipid-lowering agents, etc., are some classes of drugs that comprise emerging contaminants. Also, various insecticides, pesticides, herbicides, etc., which are frequently used in agricultural practices, enter the water bodies and form the CECs. CECs can enter the water bodies through diffuse sources and point sources of pollution. Examples of point sources of pollution that can lead to the occurrence of CECs in water bodies include municipal sewage treatment plants, septic tanks, industrial effluents, etc. Diffuse sources of pollution include urban and stormwater runoff, runoff from agricultural manures, runoff from leakage of urban sewage. It has been found that pharmaceutical products find their presence in various water bodies throughout the world. Like in Germany, effluents from sewage treatment units and rivers have been found to contain carbamazepine, diclofenac, naproxen, etc. Also, CECs like carbamazepine have been found in rivers of Madrid, Spain. In sludge of sewage, synthetic musk has been detected in countries like Germany, United Kingdom, China, Switzerland, Spain, Hong Kong, etc. It is found that the concentration of CECs varies to different extents in different countries. This probably depends upon the extent of use of various CECs and the efficiency of the technology of the particular country in removing CECs from waste material and sewage. The fate of a CECs can depend upon various factors. Factors like physicochemical properties (water solubility) of a particular CEC and also environmental conditions will dictate the dissipation of a particular CEC. The duration for which a particular CEC will persist in the subsurface and groundwater will depend upon various factors. Some of these factors are groundwater residence time, properties of the contaminant, redox conditions, etc. Certain mechanisms that operate to control the levels of CECs in nature are ion exchange in the aquifers and soils, sorption and degradation by microbes (Thomaidis et al. 2012).

9.2.1 Classification of Contaminants of Emerging Concern

There is a wide range of contaminants which are called as emerging. Some of them are represented below in Table 9.1 (with their molecular formula and possible sources of contamination) and Fig. 9.1 (representing structures of some of the CECs).

9.2.1.1 Endocrine-Disrupting Chemicals (EDCs)

EDCs are a group of natural or synthetic compounds that interfere with the functioning of the hormone system resulting in unnatural responses in the receiving organism. It may also be classified as a group of endocrine disruptors that alter the

Table 9.1 Representation of various contaminants of emerging concern (https://pubchem.ncbi.nlm.nih.gov)

S. No.	Contaminants of emerging concern	Examples	Molecular formula	Source
1	Pharmaceuticals and personal care products (PPCs)	Bisphenol A	$C_{15}H_{16}O_2$	Release of antibiotic to the environment, shampoos, soaps, deodorants, cosmetics
		Triclosan	$C_{12}H_7Cl_3O_2$	
		Triclocarban	$C_{13}H_9Cl_3N_2O$	
2	Perfluorochemicals	Perfluoromethanesulfonic acid	$C_8HF_{17}O_3S$	Used for the preparation of heat, oil, grease, water-resistant products
		Perfluorooctanoic acid	$C_8HF_{15}O_2$	
3	Siloxanes	Polydimethylsiloxanes	$C_8H_{24}O_2Si_3$	Used in paints, cosmetics, medical products
4	Quaternary ammonium compound	Benzyldimethyltetradecylammonium chloride	C_{23}H42ClN	Disinfectants, fabric softner, surfactants, antistatics
5	Artificial sweetners	Sucralose	$C_{12}H_{19}Cl_3O_8$	Domestic wastewater, groundwater
		Acesulfame	$C_4H_5NO_4S$	
		Saccharin	$C_7H_5NO_3S$	
6	Anticorrosives	Benzotriazoles	$C_6H_5N_3$	Used as corrosion inhibitors, herbicides, antialgal agent, slimicides in paper and pulp industry
		Benzothiazoles	C_7H_5NS	
7	Polybrominated-diphenyl ethers	2,3,4,5,6 penta bromo diphenyl ethers	$C_{12}H_5Br_5O$	Used in dielectric fluids, engine oil additives, electroplating masking compounds, wood preservatives, lubricants and for dye production

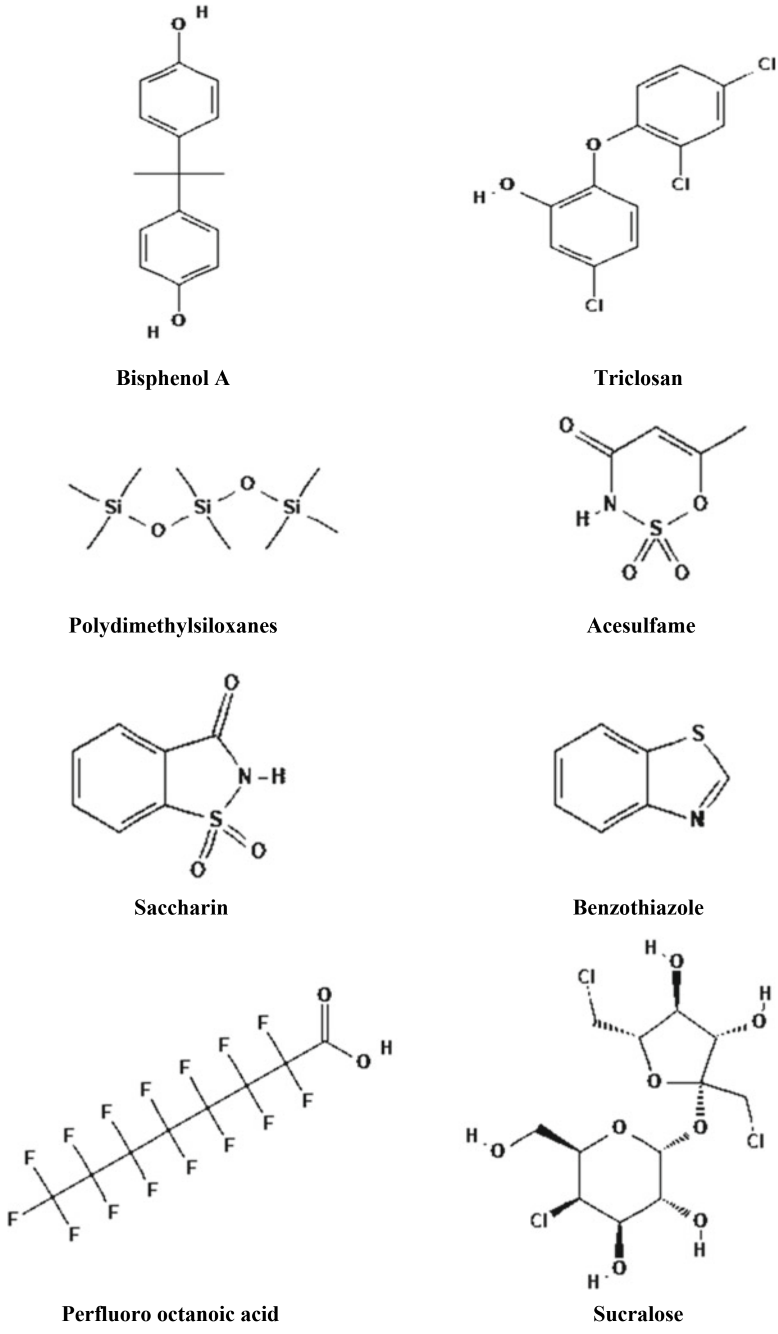
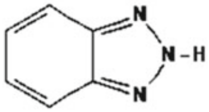
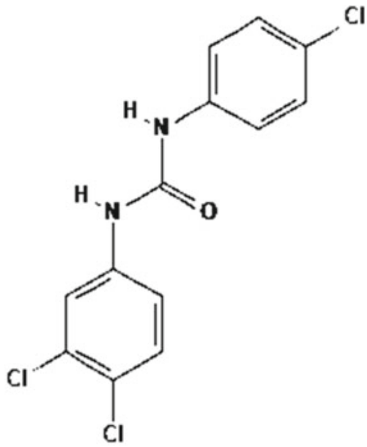


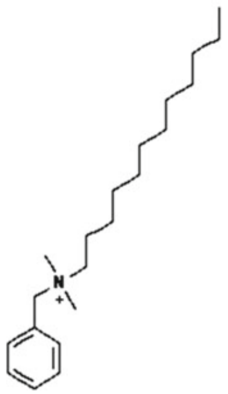
Fig. 9.1 Structures of various emerging contaminants. *Source* https://www.pubchem.ncbi.nlm.nih.gov



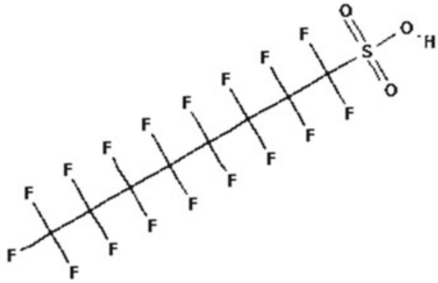
Benzotriazoles



Triclocarbon



Benzyldodecyldimethylammonium



Perfluorooctanesulfonic acid

Fig. 9.1 (continued)

functions of the endocrine system resulting in adverse health effects (Damstra et al. 2002). EDCs can be introduced through sewage effluents and industrial wastewater in the mainstream and affect aquatic life as well as humans and animals. Initially, EDCs were studied for their influence on estrogenic hormones (Gómez et al. 2013), but later research showed that they disrupt thyroid hormones (TH) and androgenic hormones (AH) as well (Gong et al. 2014). Some irreversible changes like mental retardation, neurological deficits and testicular cancers are observed as a result of TH or AH disruption. Some chemicals that interact with the endogenous system cause serious health risks and classified as emerging contaminants are polycyclic aromatic hydrocarbons (PAHs), pesticides, alkylphenol, phthalate esters, 17 β estradiol (E2, natural estrogenic steroid), 17 α-ethynylestradiol (EE2, synthetic steroid), 4-tert-octylphenol (4-t-OP), 4-n-nonylphenol (4-n-NP), bisphenol A (BPA, an industrial chemical), nonylphenol and octylphenol (Shi et al. 2016; Ying and Kookana 2003). Infertility, impairments in pregnancy, birth defects, ovarian failure and growth retardation can also be caused due to EDCs. At present, EDCs are being considered as a possible reason for the degradation of aquatic life (Wang and Zhou 2013). A lot of literature is available which indicates that endocrine disruption in aquatic life occurs at a higher rate in comparison with the telluric lives since water body forms the most common sink for the disposal of almost all domestic wastes, industrial effluents, etc. (Jafari et al. 2009). Seven hundred and eighty-five species including mammals, seabirds, fish, crustaceans and gastropods have become extinct or are at the edge of extinction (Stork 2010) over the last 100 years and the reasons suggested for this extinction are overexploitation, climate change, loss of habitat, pollution, etc. Studies suggest that EDCs are one of the reasons for the decrease in wildlife in recent years (Millsa and Chichester 2005).

9.2.1.2 Pharmaceuticals and Personal Care Products (PPCPs)

The aquatic occurrence of PPCPs is getting more attention nowadays. Chemicals used in these products cause a harmful effect on the public. Pharmaceuticals have gained attention as EC due to their pharmacological activities. Many countries are being aware of these ECs and adopting a precautionary approach by dealing with ECs at their point sources like hospitals and WWTP. ECs enter the aquatic environment through the discharge of effluents released from the wastewater treatment plant (WWTP). PPCPs are such products that are resistant to degradation, persist in the aqueous system, environment and cause harmful effects (Kümmerer 2009). Personal care products (PCPs) consist of a wide range of products like soaps, shampoos, lipsticks, lotions, creams, cologne, toiletries, etc. (Sang and Leung 2016). PCPs may get introduced in the aquatic environment through showers, cleaning, washing machines, use of sunscreen/lotions, etc. (Rodil and Moeder 2008; Tsui et al. 2014). PCPs are prevalent and are considered as ‘pseudo-persistent’ because of their constant presence and inefficient removal from water (Blüthgen et al. 2014). Octocrylene (OC) which acts as a UV-filter is a main component of sunscreen to protect the skin from harmful UV-radiation. OC is used in other skincare products also and acts as a stabilizer for other UV-filters in different formulations or in plastics. OC is non-degradable, photostable and a lipophilic neutral compound (Zhu et al. 2016). Other factors like population, climate, dilution potential of water, availability of manufacturing sites, anthropogenic activities in that particular region are also responsible for the accumulation of chemicals in the environment and aquatic life. Most of the antibiotics are not metabolized completely and get excreted in urine and feces. They then enter sewage treatment plant (STP)/WWTP from where after degradation, they finally get introduced in surface/groundwater (Behera et al. 2011). Due to all these reasons, STP/WWTP effluents require efficient monitoring regarding antibiotics as they are being used excessively for treating the infection as well as for promoting fruit growth (Samaraweera et al. 2019).

9.2.1.3 Artificial Sweetner

Artificial sweeteners are used as a substitute for sugar all over the world in food, beverages, drugs, etc. Artificial sweeteners are regarded as water contaminants. Two artificial sweeteners acesulfame (ACE) and sucralose (SUC) are found to be present in the aquatic environment in higher concentrations in comparison with other waste specific anthropogenic organic chemicals (Lange et al. 2012). Due to their use as food additives, artificial sweeteners are extensively tested for adverse health effects in humans. Few studies are available regarding the ecotoxicological impact of SUC, which was the first artificial sweetener detected in the environment (Lange et al. 2012).

9.2.1.4 Perfluorooctane Sulfonate/Perfluorooctanoic Acid (PFOS/PFOA)

Perfluorooctane sulfonate and perfluorooctanoic acid are globally present compounds (Squadrone et al. 2015). Due to their chemical stability, surface tension lowering properties, they find use in coating, fire-fighting, foams; as water repellent agents in leather; paper and textiles (Van Asselt et al. 2013). Various health problems like hepatotoxicity, developmental toxicity, neurobehavioral toxicity, immunotoxicity, reproductive toxicity, lung toxicity, etc., were encountered due to the continuous use of PFOS and PFOA (EFSA 2011).

9.2.1.5 Benzotriazoles and Naphthenic Acid

Benzotriazoles are used as anti-corrosives and widely used in engine coolants, aircraft deicers and antifreeze liquid. It can cause harmful effect on endocrine system. Neurotoxicity in fish was also found due to benzotriazoles (Casado et al. 2014).

9.2.1.6 Algal Toxins

Blue–green algal (cyanobacterial) blooms can cause the production of toxins that pollute the drinking water. Some of the most common species of algae involved in this process are *Anabaena bergii*, *Aphanizomenon ovalisporum*, *Microcystis aeruginosa*, *Aphanizomenon flosaquae*, *Umezakia natans*, and *Raphidiopsis curvata* (Falconer and Humpage 2006). In America, Europe and Australia, algal toxins have shown hazardous effects on humans (Falconer and Humpage 2005). *Microcystis aeruginosa* acts as a hepatotoxin that can cause liver damage, and *Anabaena flos aquae* produces a neurotoxin that can attack the central nervous system (Hal et al. 2007).

9.2.1.7 Perchlorate

Perchlorate is a highly stable anion that resides in nature due to anthropogenic activities as well as natural reasons. It is a strong oxidizing agent used for various purposes like missile fuel, fireworks, vehicle airbags and fertilizers (Steinmaus 2016). Perchlorate can be found in water, soil and plants. Perchlorate is soluble in water and shows high mobility in soil (Steinmaus 2016). The higher concentration of perchlorate may result in thyroid disorder (Cal Baier-Anderson and Anderson 2006).

9.2.1.8 Herbicides

Herbicides are used widely for the protection of crops by killing weeds. Herbicides can be classified as organic and inorganic herbicides. Chloroacetanilide and chloroacetamide are widely used herbicides. The primary degradation of these herbicides includes metabolism in the soil, and the prime metabolites obtained are ethane sulfonic acid (ESA) and oxalic acid (OXA), which are water-soluble (Vargo 2013). Although many of the available herbicides are not toxic, yet they can be converted to toxic products, which can produce various carcinogens, teratogens, phytotoxins and insecticidal or fungicidal products. There are many herbicides that pass through farms and agricultural lands to water bodies in the nearby area. Some of these herbicides like oryzalin, ronstar, roundup and trifluralin can be harmful to the aquatic life found in these water bodies (Rashid et al. 2010).

9.3 Methods of Removal of CECs

The presence of the contaminants of emerging concern has been a barrier in the field of water pollution control, so the proper disposal and treatment of these contaminants become very necessary. There are various methods proposed for the removal of these contaminants viz. biological method, physical and chemical separation, coagulation and sorption, chemical oxidation, etc.

9.3.1 Biological Treatment for the Removal of CECs

Out of the total available techniques present for the removal of CECs, biological treatment method is one of the effective, sustainable and economical technique. It is one of the methods, which is widely used for the removal of CECs from wastewater (Ahmed et al. 2016). Biological treatment involves the removal of CECs through biodegradation method in which high molecular weight CECs are degraded into small molecules and biomineralized to small inorganic molecules like water and carbon dioxide with the help of bacteria, algae and fungi (Rodríguez et al. 2014). This process can be divided into conventional and non-conventional methods. Conventional methods for the removal of CECs consist of biological activated carbon, biological nitrification and denitrification, microalgae/fungi-based treatment and activated sludge process. Non-conventional methods consist of biosorption, membrane bioreactor (MBR) and constructed wetlands which are discussed below.

9.3.2 Conventional Biological Treatment Methods for the Removal of CECs

9.3.2.1 Activated Sludge

Activated sludge is one of the most used treatments for the removal of CECs, in which bacteria and protozoa are used for treating sewage and wastewater. It is a process in which biomass produced in wastewater by the growth of microorganisms in aeration tanks takes place in the presence of dissolved oxygen (Buttiglieri and Knepper 2008). This method is generally designed to remove the pathogens, organic and inorganic contaminants. This process has lower capital cost in comparison with advanced oxidation processes (AOPs) and is more ecological than chlorination process (Luo et al. 2014). This process is helpful in the removal of almost 102 target contaminants which include EDCs, pesticides, beta blockers, personal care products (78–90%, except for celestolide which is degraded up to 60% only), surfactants and pharmaceuticals (65–100%). Some beta blockers viz. atenolol, metoprolol were not removed efficiently through this method. For the better removal of contaminants, activated sludge method can be coupled with ozonation or MBR also.

9.3.2.2 Biological Activated Carbon (BAC)

Biological activated carbon is developed on the basis of activated carbon process. Mostly, BAC process is coupled with some other oxidation processes like ozonation in order to obtain better removal of the contaminants (Jin et al. 2013). At present, BAC has become a widely used treatment for the removal of contaminants from industrial wastewater as well as for wastewater reclamation. It is generally applied after ozonation process for further removal of contaminants (Kalkan et al. 2011), and it was found to be more effective in the removal of some pesticides, betablockers and pharmaceuticals when used after the ozonation process, but some other EDCs (E3, bisphenol A, octylphenol) were not removed efficiently (Gerrity et al. 2011).

9.3.3 Non-conventional Biological Treatment Methods for the Removal of CECs

9.3.3.1 Biosorption

This method is used for the removal of contaminants from water through the united action of adsorption and biological destruction. For adsorption, activated carbon is used, but sometimes, other solids like gravel, sand, clay, porous organic adsorbants are also used (Pidlisnyuk et al. 2003). This method is effective in 100% removal of some pharmaceuticals like ibuprofen, naprox and gemifibrozil. Along with this, some other contaminants like 17 β-estradiol- 17 α-acetate, pentachlorophenol, 4-tert-octylphenol and triclosan were also removed very efficiently (Banihashemi and Droste 2014). Estrogens can be removed effectively by the combination of biosorption and biodegradation interaction due to low Henry's law coefficient, low biodegradation and high octanol-water partition coefficients (K_{ow}) (Kumar et al. 2009).

9.3.3.2 Membrane Bioreactor (MBR)

MBR is a widely used technology for removal of contaminants from municipal and industrial wastewater treatment plant. It can effectively remove a large number of pollutants which are resistant to activated sludge process and constructed wetland (Radjenović et al. 2009). Even, when higher removal of effluents is required, some amount of activated carbon can also be added which can remove the contaminants more efficiently (Li et al. 2015). Various pesticides, beta blockers, PCPs and EDCs can be removed through this technology. MBR is a better technology than conventional sludge process as it can remove high amount of EDCs from water (Nguyen et al. 2013).

9.3.3.3 Constructed Wetlands (CWs)

Constructed wetland is an engineered land-based treatment method which is an integrated combination of biological, physicochemical and chemical interactions (Töre et al. 2012). CWs can be classified as subsurface/surface flow (SFWC), horizontal flow (HFWC) and vertical flow (VFWC) on the basis of the wastewater flow management, and hybrid CWs can also be formed by mixing of these different systems (Rodríguez et al. 2014). CWs are highly effective in the removal of pharmaceuticals and personal care products. It can easily remove pesticides, herbicides, beta blockers, NSAIDs, diuretics, etc. Some EDCs like E1, E2, EE2, bisphenol A, phthalates can also be removed successfully (75–100%) through this method (Matamoros et al. 2008). Although out of total available treatment methods, this method for the removal of contaminants is only partially explored. It is a very environmental friendly, low operating cost and green method available for the removal of contaminants (Töre et al. 2012).

9.3.4 Chemical Treatment for the Removal of CECs

All the biological treatments are not effective for the removal of CECs from water, so a wide range of chemical treatments is used for that purpose. Chemical treatment for the removal of CECs can be broadly classified into conventional chemical treatment methods and advanced oxidation processes (AOP). Conventional methods consist of photolysis, chlorination, Fenton process, and AOPs consist of ozonation, heterogeneous photocatalysis (UV/TiO_2), photo-Fenton process (UV/H_2O_2), electro-Fenton process, etc.

9.3.5 Conventional Chemical Treatment Methods for the Removal of CECs

9.3.5.1 Photolysis

Photolysis is one of the conventional methods, used for the decomposition of CECs in water. In this process, removal of CECs using UV remains a commonly used technique. Basically, there are two types of photolysis viz. direct photolysis in which there occur the direct absorption of photons, resulting in the degradation of CECs and another one is indirect photolysis in which photosensitizers are used for processing the reaction. This process is helpful in the complete removal of some pharmaceuticals like diclofenac, iopamidol, ketoprofen, mefenamic acid, oxytetracycline and tetracycline. Although UV photolysis was found to be less effective in the removal of beta blockers (Rodríguez et al. 2008), some pesticides were removed efficiently (80–100%) through this method (Liu et al. 2009; Nguyen et al. 2013).

9.3.5.2 Chlorination

Chlorination is one of the conventional treatment method used to reduce the pathogenic content of biologically treated wastewater. Endocrine-disrupting chemicals (EDCs) and non-steroidal inflammatory drugs (NSAIDs) are characterized as CECs, and they cannot be removed completely through biological wastewater treatment methods (Noutsopoulos et al. 2014). So, this method is used for their removal. It was also found that 17 β Estradiol was 100% removed within 10 min using chlorination method (Belgiorno et al. 2007). But on comparing chlorination process with ozonation, it was found that rate constant value for ozonation was around three orders of magnitude higher than that of chlorination during the removal of some ECs viz. amitriptyline hydrochloride, methyl salicylate, etc. (Real et al. 2014). Along with this, it is also found that during wastewater treatment through this process, some sub-products are formed (Utrilla et al. 2013).

9.3.5.3 Fenton Process

It is an oxidation process in which hydrogen peroxide reacts in the presence of iron to produce hydroxyl radicals. pH plays a very important role in Fenton process as it has been observed that maximum degradation occurs at pH range 2–4 (Petrovic and Barcelo 2007).

Fenton process is represented below:

$$Fe^{+2} + H_2O_2 = Fe^{+3}OH^{\cdot} + OH^{-} \quad (1)$$

$$Fe^{+3} + H_2O_2 = Fe^{+2} + HO_2^{\cdot} + H^{+} \quad (2)$$

Although Fe^{+2} can be regenerated from Fe^{+3}, but reaction (2) is much slower than reaction (1), due to which Fe^{+3} accumulates in solution and forms precipitate of $Fe(OH)_3$. Along with this, this process requires significant amount of reagents due to which it becomes costly, and there occurs the unintended consumption of OH and ferrous ions. The removal of CECs using Fenton process was not found to be satisfactory in comparison with other oxidation processes (Ahmed et al. 2015).

9.3.6 Advanced Oxidation Process for the Removal of CECs

9.3.6.1 Ozonation

Ozonation is one of the AO processes, which can go through two mechanisms direct and indirect for the removal of CECs. In direct mechanism, there occurs the reaction with ozone directly, and in indirect mechanism, hydroxyl radical ($OH^{\cdot}$) obtained from ozone in aqueous solutions participates in the reaction (Rizzo et al. 2019; Utrilla et al. 2013). Ozone selectively reacts with olefins and aromatic ring containing emerging contaminants (Acero et al. 2015). Ozonation is effective in the removal of ECs viz. E1, E3, E2, EE2, bisphenol A and nonylphenol, atrazine, chlorfenvinphos, alachlor, diuron, isobroturum with 90% or higher removal efficiency (Esplugas et al. 2007). The drawback of this process is that it requires high amount of energy, formation of by-products and interference of radical scavengers (Luo et al. 2014).

9.3.6.2 Heterogeneous Photocatalysis (UV/TiO_2)

In photolysis process, the rate of degradation of CECs is quite low, so this advance process is used for the better results. In this process, heterogeneous catalyst is used for the removal of CECs, which is activated in the presence of light (Macwan et al. 2011). TiO_2-based materials are widely used as catalyst for this process which may be due to its photo stability, economic, particle size and inert nature (Gaya and Abdullah 2008). UV/TiO_2 process is effective in degradation of E1, E2, EE2, E3, bisphenol A, progesterone up to 100%. Along with this, this method can also be used for the degradation of pharmaceuticals (mainly analgesics) and pesticides (Gaya and Abdullah 2008).

9.3.6.3 Photo-Fenton Process (UV/H_2O_2)

This method is also widely used for the removal of CECs from wastewater. In this method, UV light is used for the formation of radicals, and the formation occurs by the reaction of hydrogen peroxide in the presence of ferrous ion, but this process can also be possible in the absence of UV light, by using sunlight only. Photo-Fenton process is a pH dependent method, and generally, this reaction takes place in acidic medium (optimum pH = 2.8). Ferrous ion in acidic medium forms $[Fe(OH)_2]^{+2,}$ which by the absorption of $h\nu$, go through photoreduction and form OH and Fe^{+2} (Eq. 3).

$$[Fe(OH)]^{+2} + h\nu = Fe^{+2} + OH \tag{3}$$

Now, this Fe^{+2} ion can further react with H_2O_2 and form OH again (Will et al. 2004). In this process, amount of Fe^{+2} is increased continuously (Tamimi et al. 2008), and during this process, pH reaches to near neutral. The oxidized ligand can further involve in various reactions for the degradation of CECs (Cruz et al. 2012). H_2O_2 and iron concentrations, pH and organic/inorganic content in wastewater are some factors that govern the efficiency of Photo-Fenton process. This process is effective in the removal of various types of pharmaceuticals (except penicillin). In the degradation of some anti-inflammatory pharmaceuticals, viz. antipyrine, 4AA, 4AAA, 4FAA, 4MAA and metronidazole, this process is more effective in comparison with other processes (Tijani et al. 2013). Various pesticides including atrazine, diuron, mecoprop and terbutryn were also oxidized efficiently with the help of photo-Fenton process (Klamerth et al. 2013).

9.3.6.4 Electro-Fenton Process

It is an advanced process of classical Fenton process which has been developed for the better removal of CECs. In this process, H_2O_2 is generated electrochemically in a controlled way (Roth et al. 2016). This method is useful in the removal of iopromide, atenolol, metoprolol, propranolol, triclosan, triclocarban and some antibiotics also (Ganzenko et al. 2014; Estrada et al. 2012). This process of CECs removal is very effective as it avoids the cost of reagent and formation of sludge, etc. (Ganzenko et al. 2014).

9.3.7 Physical Treatment for the Removal of CECs

There are various physical techniques like membrane process, carbon adsorption, mineral surface adsorption and ion exchange, which can be used for the treatment of CECs in water.

9.3.8 Membrane Process

This process is one of the assuring methods among the physical methods of removal of contaminants from surface water and wastewater. Ultrafiltration (UF) and microfiltration (MF) are used for the advanced treatment of urban wastewater to remove the total suspended solids (TSS) and microorganism. Nano-filtration (NF) and RO membranes are used for treating that water which is already filtered and has low TSS concentration. Various studies show that the pharmaceutical compound, carbamazepine can be removed by 60–90%, 32–40% and >97% by using NF membranes, and in the case of RO membranes, the rejection of carbamazepine was reported to be >99%. Other than carbamazepine, other CECs like diclofenac, E2 a natural steroid hormone, NDMA (undesired by-product of oxidation and disinfection processes) can also be removed using NF and RO process (Rizzo et al. 2019).

9.3.9 Activated Carbon Adsorption

In this process, there occurs the transfer of CECs from liquid phase to the solid phase. Activated carbon (AC) can be applied in two forms namely powdered activated carbon (PAC) and granular activated carbon (GAC), which will be decided on the basis of the nature of adsorbate and absorbant both (Luo et al. 2014). Along with this, the effectiveness of the process also depends upon adsorbate solubility, the adsorbate and adsorbent hydrophobicity. This process is very useful for the removal of pharmaceuticals, and the advantage of this method is that it does not form toxic and pharmacologically active products (Utrilla et al. 2013).

9.4 Conclusion

Emerging contaminants are present in our environment due to various activities of humans. ECs or CECs have been defined as those contaminants for which no strict regulations have been imposed. Thus, there is a constant need to monitor ECs or CECs. With increase in globalization and industrialization, their number and concentration are increasing day by day. However, concern regarding emerging contaminants is only being developed lately. Emerging contaminants have been present in industries, wastewater treatment plants, cosmetics, pharmaceuticals, etc., but it is only recently that scientists and common people are realizing their non-degradable and long-lasting nature in the environment. The above-mentioned problem combined with their harmful effects on human and animal health has emerged as a threat for both humans and animals. Many CECs like PPCPs, POPs, disinfectants, insecticides, PFOS, PFOA, algal toxins, etc., are harmful to health. Detection of these CECs from time to time is the need of the hour. Many countries around the world are suffering from problem related to CECs. Anthropogenic activities are the key factors responsible for occurrence of these contaminants in the environment and water bodies. Various conventional and advanced techniques are available for the detection of these emerging contaminants. The ECs can be dealt with by biological, chemical and physical processes. Sedimentation, membrane filtration, chemical treatments are some important methods for the removal of ECs from our environment. The threat of ECs can be fought by avoiding/limiting the use of harmful chemicals in industries. Also, the threat can be tackled by using bio-degradable substances obtained from nature in the manufacturing process and developing newer technologies to remove emerging contaminants from our environment. It is very important for humans to identify the substances, drugs and chemicals having the characteristics of ECs or CECs. After identification of ECs or CECs, governments around the world should take quick actions to set up regulations which will help in the removal of these contaminants so that the environment in which mankind resides remains safe and pure. Extensive and exhaustive research needs to be carried out by various countries around the world for developing newer methods for eradication and removal of ECs and CECs from our environment.

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