Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review

Mohammad Boshir Ahmed[a], John L. Zhou[a,*], Huu Hao Ngo[a], Wenshan Guo[a], Nikolaos S Thomaidis[b], Jiang Xu[c]

[a]School of Civil and Environmental Engineering, University of Technology Sydney, Broadway, NSW 2007, Australia

[b]Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

[c]State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China

Corresponding author:

Prof John L. Zhou

School of Civil and Environmental Engineering

University of Technology Sydney

Broadway, NSW 2007

Australia

Tel: +61 2 95142023

Fax: +61 2 95147803

Email: junliang.zhou@uts.edu.au

Abstract

This review focuses on the removal of emerging contaminants (ECs) by biological, chemical and hybrid technologies in effluents from wastewater treatment plants (WWTPs). Results showed that endocrine disruption chemicals (EDCs) were better removed by membrane bioreactor (MBR), activated sludge and aeration processes among different biological processes. Surfactants, EDCs and personal care products (PCPs) can be well removed by activated sludge process. Pesticides and pharmaceuticals showed good removal efficiencies by biological activated carbon. Microalgae treatment processes can remove almost all types of ECs to some extent. Other biological processes were found less effective in ECs removal from wastewater. Chemical oxidation processes such as ozonation/H_2O_2, UV photolysis/H_2O_2 and photo-Fenton processes can successfully remove up to 100% of pesticides, beta blockers and pharmaceuticals, while EDCs can be better removed by ozonation and UV photocatalysis. Fenton process was found less effective in the removal of any types of ECs. A hybrid system based on ozonation followed by biological activated carbon was found highly efficient in the removal of pesticides, beta blockers and pharmaceuticals. A hybrid ozonation-ultrasound system can remove up to 100% of many pharmaceuticals. Future research directions to enhance the removal of ECs have been elaborated.

Keywords: Emerging contaminants; Activated sludge; Photocatalysis; Ozonation; Hybrid systems

Contents

1. Introduction

Emerging contaminants (ECs) are primarily synthetic organic chemicals that have been recently detected in natural environments [1-3]. ECs are a large and relatively new group of unregulated compounds [4] and can potentially cause deleterious effects in aquatic and human life at environmentally relevant concentrations which are becoming a growing concern [1, 5, 6]. They are the ingredients mostly detected in municipal sewage, daily household products, pharmaceutical production plants, wastewater, hospitals, landfills, and natural aquatic environment [7-9]. ECs concentration may range from a few ng L^{-1} to a few hundred μg L^{-1} [8, 10]. Such concentrations in the aquatic environment may cause ecological risk such as interference with endocrine system of high organisms, microbiological resistance, and accumulation in soil, plants and animals [11], as these ECs are not completely removed by conventional wastewater treatments processes [6, 12, 13]. ECs include mostly pharmaceutical organic contaminants, personal care products (PCPs), endocrine disrupting compounds (EDCs), surfactants, pesticides, flame retardants, and industrial additives among others.

Pharmaceutical organic contaminants and PCPs include analgesics, lipid regulators, antibiotics, diuretics, non-steroid anti-inflammatory drugs (NSAIDs), stimulant drug, antiseptics, analgesic, beta blockers, antimicrobials, cosmetics, sun screen agents, food supplements, fragrances and their metabolites and transformation products. They can affect

water quality and potentially affect drinking water supplies, ecosystem and human health [13-15]. Their environmental bioaccumulation exacerbates the abnormal hormonal control causing reproductive impairments, decreased fecundity, increased incidence of breast and testosterone cancers, and persistent antibiotic resistance [16]. Of particular concern are antibiotic residues which can induce the development of antibiotic resistant genes potentially favouring superbugs [6].

EDCs are exogenous substances or mixtures that alter the functions of the endocrine systems and consequently cause adverse health effect in an intact organism, or its progeny or populations [17]. The effects associated with EDCs are breakage of eggs of birds, fishes and turtles, problems in reproductive systems, change in immunologic system of marine mammals, reduction of sperm of human organ, increase in the incidence of breast, testicle and prostate cancers, and endometriosis [14]. Pesticides have immune-depressive effects in fishes, mammals and can modify haemopoietic tissue of anterior kidney [18]. Surfactant can affect physical stability of human growth hormone formulations and are responsible for the endocrine activity [19].

The potential long-term effects of ECs in water are still uncertain and need further investigation. At present, different government and non-government organizations including the European Union (EU), the North American Environmental Protection Agency (EPA), the World Health Organization (WHO), or the International Program of Chemical Safety (IPCS) are considering these problems and setting up directives and legal frameworks to protect and improve the quality of freshwater resources [14].

A variety of different physical, chemical and biological technologies have already been used to remove or degrade the residues of ECs over the last few decades [20, 21]. Biological treatment technologies are by far the most widely used for ECs removal, including activated sludge, constructed wetland, membrane bioreactor (MBR), aerobic bioreactor,

anaerobic bioreactor, microalgae bioreactor, fungal bioreactor, trickling filter, rotating biological reactor, nitrification, enzyme treatment and biosorption. It has been reported that some non-biodegradable organic micropollutants cannot be sufficiently removed using biological treatment processes. Chemical treatment technologies are also widely used for the degradation of these micropollutants, including conventional oxidation methods such as Fenton, ozonation, photolysis and advanced oxidation processes (AOPs) such as ferrate, photo-Fenton, photocatalysis, solar driven processes, ultra sound process, and electro-Fenton process. Moreover, some hybrid systems have recently been applied to enhance the removal of a wide range of ECs. The advantages and challenges of different processes for the removal of ECs are outlined in the **Table 1**.

The majority of polar and semi polar pesticides and pharmaceuticals will remain partitioned in the aqueous phase due to their relatively high water solubility, hence their removal by physical processes such as sedimentation and flocculation is not effective [22], and has been reported to be less than 10% [23, 24]. Thus further discussions of those processes are not reviewed here. The discussion of other physical treatment processes such as membrane, reverse osmosis, ultrafiltration, microfiltration, nanofiltration and adsorption processes is also excluded from this review, although these physical processes can be part of hybrid or integrated treatment technologies for ECs removal.

Thus, the aim of this review is to critically evaluate the viability of biological, chemical, and hybrid treatment processes as a means to remove ECs from wastewater. Specifically the article provided a summary of effectiveness of different wastewater treatment processes for ECs removal, discussed conventional wastewater treatment processes along with advance and hybrid treatment processes for ECs removal, and discussed the challenges and the current knowledge gaps limiting the effectiveness of biological and chemical treatment processes. Some of the future research directions have also been suggested.

2. Biological treatment technologies

Biological treatment technologies have been widely applied for the removal of ECs predominantly by the mechanism of biodegradation. Biodegradation is the process by which large molecular weight ECs are degraded by microorganisms such as bacteria, algal and fungi into small molecules [4], and even biomineralised to simple inorganic molecules such as water and carbon dioxide. In conventional biodegradation process, microorganisms use organic compounds as primary substrates for their cell growth and induce enzymes for their assimilation [10]. Some ECs are toxic and resistant to microbial growth hence inhibiting biodegradation, in which case a growth substrate is needed to maintain microbial growth for biodegradation, a process known as cometabolism [10]. Biodegradation methods have traditionally been used in wastewater treatment systems for the removal of ECs. They can be divided into aerobic and anaerobic processes. Aerobic applications include activated sludge, membrane bioreactor, and sequence batch reactor. Anaerobic methods include anaerobic sludge reactors, and anaerobic film reactors. The wastewater characteristics play a key role in the selection of biological treatments [7, 28]. The wastewater treatment processes can be broadly classified as conventional processes and non-conventional processes, which are described in subsequent sections.

2.1. Progress and challenges in conventional treatment processes

Removal or degradation capacity of ECs depends on the chemical and biological persistence of ECs, their physicochemical properties, the technology used, and operation conditions. For the highly polar substances e.g. most pharmaceuticals and their corresponding metabolites, the most important removal process is through the biological transformation or mineralization by microorganisms. The removal rates strongly depend upon the treatment technology, the operation conditions, and target contaminants [36]. The identification of degradation products in environmental samples is a challenging task because not only are they present at very low

concentrations but also they are present in complex matrices that may interfere with detection [36, 37].

2.1.1. Biological trickling filter and biofilm reactor

A biological trickling filter is a three-phase system with fixed biofilm carriers. Wastewater enters the bioreactor through a distribution zone, trickles downward over the biofilm surface, and air moves upward or downward in the third phase [38]. Bio-trickling filters have been used in wastewater treatment plants (WWTPs) for decades in the removal of biochemical oxygen demand (BOD), chemical oxygen demand (COD), pathogen decontamination, odor and air pollution control, but their application to ECs removal has not become wide practice [39-41]. Trickling filters or biobeds were used either alone or in combination with other treatment processes such as activated sludge. Some bio-processes such as activated sludge, aerated lagoon and trickling filters have reported very different removal efficiencies from almost complete removal to no removal of some pharmaceuticals from different wastewater sources [42]. Kasprzyk-Hordern et al. [43] monitored 55 pharmaceuticals, PCPs, EDCs and illicit drugs during wastewater treatment by trickling filter and activated sludge processes from South Wales, UK over a period of five months. They concluded that the activated sludge treatment was a much more efficient process than trickling filter beds for the removal of organic micropollutants. Overall, out of 55 pharmaceuticals and PCPs studied only a few were characterised by low removal efficiency (< 50%) during activated sludge treatment. In comparison, the WWTP utilising trickling filter beds resulted in, on average, less than 70% removal of all 55 PPCPs studied with half of them not being removed, while the WWTP utilising activated sludge treatment gave a much higher removal efficiency of over 85% [43, 44]. Hence there is a need to develop or modify the present bio-trickling process to attain higher and steadier removal efficiency for a wide range of ECs.

In addition, moving bed biofilm reactors were investigated for the removal of analgesic pharmaceuticals, with high removal efficiencies being found for ibuprofen (94%), naproxen (70-80%) and diclofenac (74-85%) but poor and inconsistent removal being observed for clofibric acid (5-28%), ketoprofen (63-73%) and carbamazepine (0-1%) [45]. The recalcitrant nature of carbamazepine was the main reason for its almost no observed removal. A comparison of removal efficiencies between suspended activated sludge and moving bed biofilm reactors, with the use of the Student's t-test, showed significantly different removals in the case of ibuprofen, ketoprofen, carbamazepine and diclofenac [45]. As a relatively new technology, the moving bed biofilm reactor has not yet been widely explored for EC removal.

2.1.2. Biological nitrification and denitrification

Nitrification is the biological oxidation of ammonium to nitrite and nitrate, and denitrification is the biological process which is used to reduce nitrate/nitrite to nitrogen gas [10, 46]. Denitrification process is carried out at anoxic (i.e. absence of oxygen) conditions [47, 48]. Differences in results from recent studies may originate from the variation in operating conditions such as hydraulic retention time, sludge retention time, mixed liquor pH and temperature. This kind of process is mostly applied together with MBR for wastewater treatment. For example, Phan et al. [47] studied ECs removal from wastewater using nitrifying and denitrifying condition in MBR (**Table S1**). The sludge retention time was 25 d and nitrification was carried out by autotrophic bacteria under aerobic conditions and denitrification process carried out under anoxic conditions. The treatment duration was adequate to support proliferation of both heterotrophic and slow growing nitrifying microorganisms that supported high organics removal.

The removal of EDCs such as estrone (E1), 17α-ethinylestradiol (EE2), 17β-estradiol (E3), bisphenol A, 4-*tert*-butylphenol and 4-*tert*-octylphenol and PCPs (such as

benzophenone, galaxolide, oxybenze, salicyclic acid and tonalide) by denitrification has been found to be 82-100% at μg L^{-1} level influent concentration. Pesticides such as atrazine and fenoprop showed lower removal efficiencies (8-32%) while triclosan and pentachlorophenol were found to be better removed (88-98%) by denitrification process [47]. Pharmaceuticals such as ibuprofen, metronidazole and ketofenac were well removed (82-97%) but carbamazepine, diclofenac, clofibric acid, gembrozil, erythromycin and roxythromycin were less well removed by denitrification process (**Table S1**). The fate of some EDCs and pharmaceuticals by denitrification process was also studied but result was not satisfactory [49]. On the other hand, nitrification process was found suitable to remove some ECs such as E1, E2 and EE2, galaxolide, tonalide, ibuprofen, naproxen, erythromycin and roxythromycin. The removal efficiency during nitrification process followed the order: EDCs > PCPs > pharmaceuticals. In case of denitrification process, removal of ECs followed the order of EDCs > PCPs > pesticides > pharmaceuticals. In comparison, denitrification process seems to be more suitable than nitrification process (denitrification > nitrification) for the removal of ECs (**Table S1**). A challenge in the denitrification and nitrification process is the relatively low removal efficiencies for a wide range of ECs, but this process can be merged with MBR and other processes to improve its removal efficiencies.

2.1.3. Biological activated carbon

The accumulation or artificial immobilization of microorganisms under proper temperature and nutrition condition on the surface of activated carbon produces the biological activated carbon. In that case activated carbon (mostly granular form) acts as a carrier which can exert the adsorption and biodegradation roles simultaneously [50-52]. The mechanism involves the interaction of granular activated carbon particles, microorganisms, contaminants and the dissolved oxygen in solution [53]. In most cases biological activated carbon process is used after ozonation for the removal of contaminants, and biological activated carbon can be part

of a tertiary treatment process for reclamation purpose as it can efficiently remove both nitrogen and organic carbon [52]. Such comparative removal efficiencies by filtration, ozonation followed by biological activated carbon are listed in **Supplementary Table S2**, where it can be observed that biological activated carbon process can be more effective in the removal of ECs (ng L^{-1} level) especially pesticides (e.g. atrazine and triclosan), beta blockers (e.g. atendol) and pharmaceuticals (analgesics, antibiotics, lipid regulator and anti-depressant) when ozonation process has been carried out first. Biological activated carbon process showed lower efficiency in the removal of some EDCs such as E3, bisphenol A, and octylphenol but did remove 99% of E1 [50]. Thus biological activated carbon process can be very attractive if this process is combined with some oxidation process such as ozonation. Therefore for the removal of ECs, it can be concluded that biological activated carbon process followed the order of pesticides > beta blockers > pharmaceuticals > EDCs > PCPs. As biological activated carbon process was found to be less effective in the removal of EDCs and PCPs including some pharmaceuticals, thus this process should mostly be applied in hybrid system. Hybrid system was found very impressive in the removal of ECs and discussion of such system is covered in section 4.

2.1.4. Microalgae/Fungi based treatment

Biologically based wastewater treatment by microorganisms (bacteria, algae and fungi) can simulate the ability of natural ecosystems to attenuate pollution from water in a cost effective and sustainable way. Microorganism based treatment systems have been proved to effectively remove some ECs with the mechanism of degradation and phytoremediation [4, 54, 55]. Microorganisms produce some enzymes which are responsible for the biodegradation of the ECs. For example, some fungi produce extracellular enzymes with low substrate specificity and are very suitable for the degradation of some ECs even at low water solubility [56]. On the other hand, microalgae (phytoplankton) based wastewater treatment technologies such as

high rate algal ponds has high attention due to the resource recovery of algal biomass, use of fertilizer, protein-rich feed or biofuel and high quality effluent. High rate algal pond is shallow raceway reactors in which microalgae and bacteria grow in symbiosis. Such system is responsible for the degradation of organic matter by heterotrophic bacteria, which consume oxygen by micro-algal photosynthesis. Such system does not require aeration [27, 57]. Comparative removal of different ECs has been shown in **Table 2**. Some of the ECs such as pharmaceutical beta blockers (atendol, propranolol and sotalol), gastroesophageals and anticancer drugs (crimetidine, famotidine ranitidine, acridone and citalopram), anti-inflamatory drugs (acetaminophen including stimulant butalbital), and antibiotics (azithromycin, erythromycin, sulfathazole, sulfapyridine and sulfamethazine) can be removed up to 100% by fungal reactors. EDCs such as E1, E2 and EE2 can be removed by more than 95% at a concentration level of 1 μg L^{-1} in algae based polishing pond treatment based system. Microalgae based treatment system can efficiently remove many types of ECs including EDCs, PCPs and pharmaceuticals (analgesic and anti-inflammatory including stimulant caffeine) at concentrations of 9-24 μg L^{-1}. But this kind of system has lower affinity towards pesticides removal (**Table 2**). It can be stated that microalgae based treatment system has better removal efficiencies of ECs even at high concentration than algae based polishing pond. Microalgae based removal of ECs followed the general trend of pharmaceuticals > PCPs > EDCs > pesticides. On the other hand, fungi based treatment system followed the order of beta blockers > gastroesophageal > anti-inflammatory and stimulants > antibiotics > analgesics > lipid regulators > NSAIDs. The comparative data in **Table 2** show that microalgae based treatment system has better removal efficiencies with high influent concentration of ECs. Thus microorganism based treatment processes require further in-depth study on the culture and growth of the microorganisms for the efficient removal of ECs.

Moreover, in order to improve pesticides removal efficiencies this type of process can be integrated with biological activated carbon process.

2.1.5. Activated sludge process

Activated sludge is a process where biomass produced in wastewater by the growth of microorganisms in aeration tanks takes place in presence of dissolved oxygen [63]. Among all conventional wastewater treatment processes, the activated sludge process is the most widely used and applied in so many ECs removal around the world, and as the proportion of removal by primary setting, chemical precipitation, aerating volatilization and sludge absorption is small, the majority of ECs in wastewater is removed by biodegradation [64-66]. This process utilizes bacteria and protozoa for treating sewage and industrial wastewaters by the utilization of air and a biological floc. These kinds of microorganisms can break down the organic matter into carbon dioxide, water and other inorganic compounds. It has lower capital cost than advance oxidation processes and generally more environmentally friendly than chlorination process [13, 29]. **Figure 1** shows the removal of 102 target ECs including 23 EDCs, 3 pesticides, 4 beta blockers, 11 PCPs, 10 surfactants, and pharmaceuticals by activated sludge processes [13, 63, 64, 67-73]. All the data for activated sludge based treatment systems are listed in **Appendix Table S3.** Ten types of surfactants have been successfully removed (95-98%) by the activated sludge processes at a concentration of several mg L^{-1}. Higher removal efficiencies of surfactants by activated sludge may be due to their sorption susceptibility toward microorganisms and also degradation nature of the contaminants (**Figure 1b**) [63]. Activated sludge process is also very effective in the removal of EDCs in the range of 75-100% (**Figure 1a**). Some EDCs such as androstenedione, androsterone, EE2, coumestrol, E3, E1, 2 hydroxy estrone (2-OH E1), alpha hydroxyl estrone (α-OH E1), progesterone, testosterone, bisphenol A and octylphenol have highest estrogenic removal up to 100% at 15-700 ng L^{-1} concentration level. This is due to their structure,

relative binding, biotransformation and affinity. Thus microorganisms can easily accumulate and degrade such compounds into simpler substances [64, 74]. Environmental condition such as dissolved oxygen is a vital factor for the removal of EDCs and their removal efficiency is higher in aerobic conditions than in anaerobic conditions [75]. Activated sludge is also suitable for the removal of many PCPs at 78-90% although cashmeran, celestolide and 2,4-D are less well degraded (around 60%) due to both sorption and biodegradation [63]. The removal of polar herbicides (atrazine, diuron, and triclosan) and beta blockers (metrolol, atenolol, metoprolol) was found to be poor during activated sludge treatment (**Figure 1a**), which was due to adsorption onto suspended solids rather than biodegradation [63]. Activated sludge process based treatment plant with lower retention time has a limited capacity to remove highly polar pharmaceuticals, since most of such compounds cannot be metabolized by microorganisms as a source of carbon and may even inhibit the activity of the microorganisms [15, 63, 76]. But some pharmaceuticals such as stimulant drugs (caffeine, nicotine and paraxanthine) and some metabolites (carbamazepine 10-OH, carbamazepine 2-OH, carbamazepine 3-OH, and carbamazepine–DiOH) were found to be well removed (95-99.9%) from wastewater due to their sorption onto the suspended solids (**Figure 1b**). Pharmaceuticals such analgesic ECs can be removed up to 65 to 100%. The removal of pharmaceutical ECs by activated sludge system followed the general order of stimulant drugs > metabolites > analgesics > antibiotics > anti-inflammatory > lipid regulator > NSAIDs > other pharmaceuticals (fluoxetine, iopromide, omeprazole, ranitidine and tamoxifen). Overall trend for ECs removal by activated sludge process can be written as surfactants > EDCs > PCPs > pesticides > pharmaceuticals > beta blockers. Finally, current knowledge about the degradation mechanism in activated sludge is not complete and activated sludge can generate some human and natural metabolites that can be more toxic than the parental compounds [63]

which should be carefully addressed. The activated sludge process can also be integrated with ozonation or MBR in order to improve the removal efficiencies of ECs.

2.1.6. Aerobic, anaerobic and facultative microbiological treatment

During wastewater treatment many ECs are sorbed (if not degraded) to some extent on suspended solids and as a result they are found in sludge through sedimentation occurring in primary and secondary clarifiers [77]. Aerobic, anaerobic and facultative bioreactor based biological treatment process is used for the stabilization of excess sludge derived from activated sludge [78-80]. The main mechanism involves bacteria present in the activated sludge consuming ECs and converting them into carbon dioxide. Anaerobic digestion is one of the most widely used processes for sludge stabilization where treated sludge is often discharged on the soil or reused for agricultural purposes, and the fate of ECs is mainly governed by ECs molecular properties such as the presence of electron accepting or donating functional groups [81]. If the sludge containing ECs is directly used in agricultural then it may be a threat for the environment and human health [82, 83]. Degradation of ECs may be influenced by the sludge retention time and temperature. Some other factors such as microbial population, target compounds bioavailability and co-metabolic phenomena can affect the biodegradation of some ECs [84]. Degradation by aerobic, anaerobic and facultative digesters, ponds, lagoons or bioreactors of different categories of ECs is represented in **Table S4** [84-86], which shows that anaerobic process for ECs degradation has been mostly studied in EDCs removal from activated sludge. The removal efficiencies ranged from 60 to 100% with high concentrations of ECs [87]. Some of EDCs such as E2, EE2, bisphenol A and nonylphenol have been found to show high removal efficiencies by aerobic biodegradation process. Pharmaceuticals have been well been removed (65-100%) by the treatment in aerobic lagoons due to the increase in hydraulic retention time [63, 85]. PCPs and some beta blockers have also been treated with aerobic and anaerobic process but the

removal efficiencies were not satisfactory due to slow degradation nature of these ECs. However, it can be observed from **Table S4** that pharmaceuticals can be more effectively removed by aerobic than anaerobic biodegradation process, while EDCs can be slightly more effectively removed by anaerobic than by aerobic processes. In summary, ECs removal followed the trend of aerobic > anaerobic > facultative process. These kinds of processes need long hydraulic and sludge retention time to ensure a satisfactory removal of ECs.

To summarise, conventional treatment systems such as activated sludge, biological activated carbon and microalgae systems can successfully be applied to some extent for specific class of ECs removal. More effective and specific treatment is required to reduce the environmental and potential impact of the effluents. Thus these processes can be coupled with other chemical and physical treatment processes such as ozonation, ultrasound, ultrafiltration, and photo-Fenton processes. In addition, there is a need to increase our knowledge about the fate of ECs during wastewater treatment for the implementation of better removal technologies. Future work on WWTP should demonstrate to what extent ECs can be removed from wastewater and to what extent the implementation of an improved technology is feasible, taking into account other micropollutants as well as the broad variety of complex matrices.

2.2. Progress and challenges in non-conventional treatment processes

2.2.1. Biosorption

Biosorption is a biologically based treatment process functioning with a different mechanism than biodegrading process. In biosorption, microorganisms are immobilized onto an adsorbent and thus sorption and bio-oxidation occur [88]. After that pollutants can passively concentrate and bind onto certain biomass cellular structure. Nguyen et al. [89] compared the role between biosorption and biodegradation in ECs removal from wastewater, by using live

cultured and harvested white rot fungus (*T. versicolour*) and that inactivated by sodium azide. Biosorption based removal of some ECs is shown in **Table 3**. The removal of ECs such as 17β-estradiol-17α-acetate, pentachlorophenol, 4-*tert*-octylphenol and triclosan was achieved by more than 80% as their octanol water partitioning coefficient (K_{ow}) is high. Some pharmaceuticals such as ibuprofen, naprox, and gemifibrozil were found to achieve 100% removal efficiency by using live white rot fungi. It is clearly seen that often live white rot fungi based treatment of ECs had higher efficiency than inactivated white rot fungus based treatment (biosorption). Biosorption of ECs such as EE2, bisphenol A and benzophenone has also been studied by Banihashemi and Droste [92] who indicated that the soluble concentration decreased rapidly for selected micro-constituents (triclosan > EE2 > bisphenol A) and the soluble and solid phase concentrations continued to decrease slowly during the length of the experiment which indicates the possible biodegradation of these compound in both phases. The removal of estrogens can occur by a combination of biosorption and biodegradation interactions due to their high K_{ow} values and low biodegradable nature with low Henry's Law constant [98].

2.2.2. Membrane bioreactor

Recently, MBR is widely viewed as being a state-of-the-art technology for municipal and industrial wastewater treatment due to its high effluent quality achieved with respect to many ECs [99-102]. MBR is able to effectively remove a wide range of ECs including compounds that are resistant to activate sludge process and constructed wetland [13, 24, 103]. This can be achieved due to sludge retention on the membrane surface which can promote microbial degradation and physical retention of all molecules larger than the molecular weight of the membrane. The removal of ECs in MBR system can be affected by sludge age, concentration, and existence of anoxic and anaerobic compartments, composition of wastewater, operating temperature, pH and conductivity [13]. Ozonation process is most widely used together with

MBR process. Adsorption and biodegradation were found to be responsible for the removal of ECs by MBR treatment. Adsorption mechanism will be dominating when the log K_{ow} is greater than 3.2. Highly hydrophobic compounds (log K_{ow} > 3.2) did not accumulate in the membrane and some compounds with a moderate hydrophobicity accumulate significantly in the solid phase. The results provide a framework to predict the removal and fate of some ECs by MBR treatment [104]. **Table 3** shows the removal efficiency of EDCs, pesticides, beta blockers, PCPs and antiplatelet agents by MBR technology, which is high for 15 target EDCs varying from 92 to 99% at relatively high concentrations (1-5 μg L^{-1}). In comparison to conventional activated sludge process, MBR can remove higher amount of EDCs from wastewater [89-93, 105]. PCPs such as salicylic acid and propyl parabene were removed by around 100% in MBR system. The removal of pesticides such as atrazine, dicamba, fenoprop, 2,4-D and pentachlorophenol from wastewater by MBR was not satisfactory except for triclosan removal which can be up to 99%. Some ECs such as beta blockers can be removed by this process at 70-80% and atendol can be removed by up to 97%. In the case of pharmaceuticals removal, MBR showed a mixed performance. Some pharmaceuticals can be well removed whilst other pharmaceuticals were found to be poorly degraded in MBR [5, 91-93, 105]. For example, antibiotics (azithromycin, clarithromycin, erythromycin, ofloxacin and sulfamethaxazole), analgesics (carbamazepine, citalopram, ibuprofen, lorazepan, metronidazole, preimidone and trazodone), anti-inflammatory drug (acetaminophen) and stimulant (caffeine) were found to be removed by MBR at 75-95%. The removal of other pharmaceuticals was not satisfactory, although the removal rate of some of them was higher than biosorption and algal based polishing ponds treatment processes (**Table 3**). In general, the removal of some slowly degradable pharmaceuticals such as antibiotics and analgesics in MBRs is better due to the relatively long sludge ages, which leads to the development of distinct microbial communities in MBRs compared to activated sludge plants. But the

removal of pharmaceuticals such as anti-inflammatory and stimulant drugs by MBR and activated sludge is comparable. In summary, from the literature results it could not be concluded that pharmaceutical removal in MBR reactors is better as many other factors have been indicated that may affect biodegradation rates, which are not directly related to the reactor configuration [106]. For the removal of pharmaceuticals in MBR (as listed in **Table 3**), their efficiency followed the order of analgesics > antibiotics > anti-inflammatory and stimulants > others pharmaceuticals. The overall trend of ECs removal by MBR can be written as EDCs > PCPs > beta blockers > pharmaceuticals > pesticides. The efficiencies of diverse microbial populations in the elimination of selected ECs (especially pesticides and pharmaceuticals) and the optimization of design and operating parameters are needed to provide focus for further research in this area. Other factors such as membrane fouling, clogging, operational failures are still costly compared to constructed wetland and other established technologies [31, 63]. Moreover, scale-up from pilot plant to industry-scale MBR should also be investigated to assess if the processes and ECs elimination can be extrapolated to commercial scale operations.

2.2.3. Constructed wetland

Constructed wetland is a biologically based wastewater treatment engineered system that is designed and constructed to reproduce the processes occurring in natural wetland within a more controlled environment. Constructed wetland based wastewater treatment is achieved through an integrated combination of biological (biodegradation), physicochemical (sorption) and chemical (oxidation) interactions among plants, substrate and soil [30]. Soil acts as the main supporting material for plant growth and microbial films. Moreover, the soil matrix has a decisive influence on the hydraulic processes. Both chemical soil composition and physical parameters such as grain-size distributions, interstitial pore spaces, effective grain sizes, degrees of irregularity and the coefficient of permeability are all important factors influencing

the biological treatment systems [9]. Constructed wetland is classified as subsurface/surface flow (SFCW), horizontal flow (HFCW) and vertical flow (VFCW) systems according to their wastewater flow regime [107]. Moreover, constructed wetland can be combined to form hybrid systems to take advantage of the characteristics of each different system [4]. ECs removal efficiencies by different constructed wetland are shown in **Table 4**. EDCs such as E1, E2, EE2, steroid estrogens, bisphenol A and phthalates can be successfully removed by 75-100% [30, 108].

SFCW has been found effective for the removal of pesticides, beta blockers such as mecoprop, MCPA, terbuthylazine and triclosan at 80-100%. In the removal of PCPs all the constructed wetland processes showed good performance, and PCPs removal followed the general order of HFCW > VFCW > SFCW (**Table 4**). Constructed wetland also showed a good removal capacity for pharmaceuticals. For example, pharmaceutical analgesics and antibiotics can be effectively removed by different constructed wetland with high removal efficiencies. Some analgesics such as diclofenac, ibuprofen, and naproxen can be removed by up to 100%. Full scale surface flow constructed wetland has pronounced effect in the removal of analgesics from wastewater [109]. The general trend for analgesics followed the order of SFCW > HFCW > VFCW. On the other hand, HFCW was found to be better than SFCW for the removal of antibiotics from wastewater. Overall removal efficiencies based on the effluent quality by constructed wetland can be written as EDCs (constructed wetland) > pesticides (SFCW) > PCPs (HFCW > VFCW > SFCW) > pharmaceuticals (HFCW > SFCW > VFCW). Constructed wetland technology can be successfully applied for small communities for the remediation of a wide range of ECs but it will be difficult to use it in large cities due to the lack of space to perform such wastewater treatment processes [110]. Moreover, the future applications of constructed wetland can be extended as a result of high

costs of other technologies such as MBR, ultrafiltration and oxidation processes, or the removal efficiency was not satisfactory for a wide range of ECs using existing technologies.

Biological treatment processes can be applied to remove a wide range of ECs from wastewater. The comparison of different conventional and non-conventional biological treatment processes is carried out in terms of their average removal efficiencies, and this relationship is represented in **Figure 2**. EDCs can be well removed by MBR and activated sludge processes, and treatment efficiency follows the order: MBR > activated sludge > aerobic > constructed wetland > microalgae > biological activated carbon > anaerobic process. A wide range of EDCs can be removed by activated sludge process. Pesticides can be efficiently removed by biological activated carbon technology, with the average removal efficiencies by different biological processes decreasing as biological activated carbon > microalgae > constructed wetland > MBR > activated sludge. Beta blockers can be best removed by MBR process, followed by aerobic process and finally activated sludge process (**Figure 2**). The application of other biological processes in the removal of beta blockers was not studied sufficiently. Average removal efficiencies of different PCPs were found to be better removed by MBR processes. Based on the average removal efficiencies by biological treatment processes, PCPs followed the trend of MBR > microalgae > constructed wetland > activated sludge > biological activated carbon > anaerobic process. Surfactant based ECs can be well removed by activated sludge process. Surfactants removal by other biological processes has not been studied extensively. On the removal of analgesic pharmaceuticals, biological activated carbon and aerobic processes were found to be more efficient than activated sludge process. The average removal efficiencies of analgesic ECs by different biological processes can be written as aerobic > biological activated carbon > microalgae > constructed wetland > MBR > anaerobic > activated sludge. Some of the pharmaceutical lipid regulators and anti-inflammatories were found to be removed by activated sludge only.

Average removal efficiency of antibiotics was found to be higher than by biological activated carbon process. The general trend of different antibiotics removal followed the order of biological activated carbon > aerobic > MBR > anaerobic > constructed wetland > activated sludge. Finally, some of miscellaneous pharmaceuticals can be better removed by microalgae process, as represented in **Figure 2**.

3. Chemical treatment technologies

Biological wastewater treatment technologies can be effective in removing many class of ECs depending on the target compounds, type of wastewater, and operation conditions. For example, polar pharmaceuticals and beta blockers showed variable removal efficiencies in different biological processes. Therefore, chemical treatment technologies should be explored as alternatives with the intention of finding suitable polishing techniques to further remove ECs. These technologies are broadly defined as aqueous phase oxidation methods based on the intermediary of highly reactive chemical species [124]. Oxidation reactions have primarily been used to supplement rather than replace conventional systems and to enhance the treatment of ECs [125]. Chemical agents such as chlorine, hydrogen peroxide, ozone as well as the combination of these oxidants including transition metals and metal oxides based catalysts in the so-called advanced oxidation processes (AOPs) are required for chemical oxidation of ECs from wastewater. In addition, an energy source such as ultraviolet-visible radiation, electric current, solar, gamma-radiation and ultrasound are also used [126]. In AOPs, the oxidations of ECs are based on the production of free radicals, in particular the hydroxyl radicals that facilitate the conversion of pollutants to less harmful and more biodegradable compounds [126, 127]. The ultimate aim of chemical oxidation is the mineralisation of pollutants, with their conversion to carbon dioxide, water, nitrogen and other minerals. The rate constants for most reactions involving hydroxyl radicals in aqueous

solution are usually in the order of 106-109 M^{-1} s^{-1} [33]. Chemical oxidation processes may change pharmaceuticals' polarity and the number of functional groups which in turn affect their functionality in the organisms. All the data for chemical based treatment systems have been listed in **Supplementary Table S5**. Some of the oxidation based chemical treatments of ECs have been described in the subsections 3.1 and 3.2.

3.1. Progress and challenges in conventional oxidation processes

3.1.1. Chlorination

Most of chemical oxidation processes have demonstrated high effectiveness in the degradation of ECs present in wastewater system which are oxidized to readily biodegradable and less toxic compounds. Sometime less reactive species such as chlorine (gaseous chlorine and hypochlorite) and bromine have also been used in wastewater treatment. The effect of chlorine on the removal of some ECs has been carried out by Noutsopoulos et al. [128] using 1000 ng L^{-1} of each ECs pollutant after exposing initial chlorine dose of 11 mg L^{-1} for 60 min. The maximum removal efficiencies were 95% and 100%, respectively for naproxen and diclofenac. The removal of EE2 by chlorination was found to be up to 100% within 10 min [129]. The removal efficiencies of other ECs such as nonylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate, bisphenol A, triclosan, ibuprofen and ketoprofen ranged from 34% to 83%. The removal of some ECs may be enhanced using increased chlorine dose, extended contact time or changing pH [130]. Moreover, it was observed that the reaction rate of chlorination process was three orders of magnitude lower than that of ozonation process during the removal of ECs such as amitriptyline hydrochloride, methyl salicylate and 2–phenoxyethanol [131]. In addition, chlorine and chlorine dioxide are potent oxidants which may produce some sub-products during wastewater treatment and the degree of mineralization achieved is not acceptable [15].

3.1.2. Ozonation

Ozone is a very powerful oxidant that reacts selectively with double bonds and aromatic rings of ECs with a high electron density [132]. Ozonation is also an AOP which involves direct reaction of ECs with ozone molecules through the action of secondary oxidants such as hydroxyl radicals produced from ozone in aqueous solution [15, 133], which increase the oxidation capacity. Ozonation has been implemented as the principal treatment method or to enhance the biodegradability and efficiency of subsequent treatment. Ozone production is an energy intensive process, therefore making it costly to implement. An ozone treatment system may increase the energy demand over a conventional WWTP by 40-50%. The use of ozone as a means of breaking down pharmaceuticals in wastewater has been the subject of numerous studies over the last decade [7]. Ozonation has shown a broad range of effective removal of ECs and in general, this process can remove all types of ECs by 90-100% (**Figure 3**). From **Figure 3a,** it can be seen that ozonation process has pronounced effect in the degradation of EDCs such as E1, E3, E2, EE2, bisphenol A and nonylphenol at a high concentration level (up to 50 μg L^{-1}) with 100% removal efficiencies except for E1 (90%). This may be due to the high K_{ow} and high susceptibility of EDCs toward degradation by ozonation [14, 133]. A degradation of 95-100% of pesticides including alachlor, atrazine, chlorfenyvinphos, diuron and isobroturum rapidly occurred at even higher concentration level (up to 18 mg L^{-1}). But 2,4-D and diazinon have shown less tendency toward ozonation oxidation process [134]. Many pharmaceuticals were found to be effectively removed by ozonation except perindopril, phenytoin, sertraline and ketoprofen (**Figure 3b**) [14, 135, 136].

Figure 4a shows the removal efficiencies of ECs by ozonation in the presence of hydrogen peroxide. Pesticides, pharmaceuticals and beta blockers were very successfully removed by up to 97-100% during ozonation in the presence of H_2O_2 at environmental

relevant concentrations [14, 133]. The problem with ozonation is the high energy consumption, formation of some oxidative by-products and interference of radical scavenger [13, 25]. Thus these are the areas which need to be considered for future ozonation research.

3.1.3. Fenton process

Fenton is an oxidation process that involves reactions of hydrogen peroxide in the presence of iron to produce hydroxyl radicals [137]. Since iron is abundant and non-toxic, Fenton reactions are a viable option for wastewater treatment. Oxidation power of H_2O_2 is enhanced by its oxidation to $OH^{\cdot}$ and the chain reactions of Fenton chemistry can be represented as:

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

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

Ferrous ion can be regenerated from Fe(III) through above reaction [138]. But reaction 2 is much slower than reaction 1. As a result, Fe(III) accumulates in the solution and then precipitates as $Fe(OH)_3$ sludge [138]. Thus the removal of Fe from solution can decrease the process efficiency. Moreover, it requires a significant amount of reagents that increases the operational costs. Another drawback of classical Fenton process is the unintended consumption of formed $OH^{\cdot}$ by hydrogen peroxide and ferrous ions through the following reactions:

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \quad (5)$$

At high reagent concentrations, these reactions can strongly hinder the efficiency of the process since $HO_2^{\cdot}$ formed is a weak oxidant compared to $OH^{\cdot}$. For the remediation of ECs in wastewater the iron concentrations used, normally added as ferrous sulphate, are commonly in the range of 10–50 mg L^{-1}. As hydrogen peroxide is consumed in the reaction, the added amount of this reagent is strongly dependent on the amount of organic matter and on the intensity of treatment that is required. **Figure S1** shows the removal of some ECs

using only Fenton process. By applying only Fenton process the removal of ECs was not satisfactory compared to other oxidation processes such as photo-Fenton and ozonation (**Figure S1a**). Thus it requires the addition of other compounds such as hydrogen peroxide, or using a catalyst, solar or any other light source to promote the ECs removal from wastewater.

3.1.4. Photolysis

Photolysis is a process in which molecules of ECs undergo decomposition as a result of the absorption of light or radiations [139]. Though different sources of light are utilised, disinfection of water using UV remains as a commonly used technique. There are two types of photolysis, namely direct photolysis where the direct absorption of photons lead to degradation of pollutants and indirect photolysis which occurs in the presence of photosensitisers such as using of hydrogen peroxide or other photosensitisers. **Figures 4** and **S1** show the UV photolytic removal of some ECs in the absence (**Figure S1b**) and presence of hydrogen peroxide (**Figure 4b**), respectively. **Figure S1b** shows that photolytic process has high efficiency in the removal of EDCs (5-10 μg L^{-1}) and pesticides from 80% to 100% [64, 91]. Some pharmaceuticals such as diclofenac, iopamidol, ketoprofen, mefanamic acid, oxytetracycline and tetracycline can be completely removed. On the other hand, UV photolysis process was found to be less effective in the removal of beta blockers. In general, UV photolysis process followed the order of beta blockers < other pharmaceuticals < analgesics pharmaceuticals < antibiotics < pesticides < EDCs.

In addition, UV photolysis in the presence of hydrogen peroxide has much more pronounced effect on the removal of ECs as represented in **Figure 4b**. In terms of removal efficiencies, UV photolysis in the presence of hydrogen peroxide has been found better than only UV photolysis. UV photolysis/H_2O_2 process can remove most of ECs successfully by up to 100% with the exception of some ECs such as lincomycin and diclofenac (around 80%), when ECs concentrations were mg L^{-1}. Thus it can be stated that UV photolysis is less

effective than UV photolysis/H_2O_2 for the removal of all ECs except EDCs where they followed the order of UV photolysis > UV photolysis/H_2O_2.

Moreover, gamma radiations have also successfully been applied in the removal of ECs from wastewater. Data for the removal of some pharmaceuticals are represented in **Table 5**, which show that gamma radiation based oxidation process can successfully remove 100% of ECs such as metoprolol, carbazepine, diclofenac, ketoprofen, mefenamic acid, clofibric acid, cefaclor, and chloramphenicol at mg L^{-1} concentration level [140-144]. Other ECs showed removal efficiencies in a range of 80-95% except sulfamethoxazole (53%). The maintenance and production cost of gamma radiation can be a burden in order to obtain a cost effective removal of ECs. Therefore this kind of process is still at early stage and requires more research.

3.2. Progress and challenges in advanced oxidation processes

3.2.1. Ferrate

Ferrate (FeO_4^{2-}) is an excellent oxidizing agent which has a powerful disinfection action. It can generate a $Fe(OH)_3$ type gel which precipitates and removes other ions. Over the last decade, the high oxidation state of ferrate was of interest due to its environmental, industrial and biological importance. Ferrate can be used for the removal of arsenic and ECs such as estrogens, pharmaceuticals and PCPs [145]. The main mechanism involved in ECs treatment is oxidation/disinfection by Fe^{6+} and coagulation/flocculation by Fe^{3+}. Several ECs such as E1, E2, EE2, bisphenol A, 4-*tert*-octylphenol and sulfamethoxazole were degraded at a rate of 6400 to 7700 M^{-1} s^{-1} at pH 7 [146]. Ferrate can oxidize some organic micropollutants by up to 90% at ng L^{-1} level concentrations. Ferrate has been observed to be superior in disinfecting coliforms in WWTPs and sewage sludge. However the main problems with ferrate process are high preparation costs and poor stability of ferrate ions in solution.

Moreover, there have been limited applications in using ferrate for ECs removal. Overall, there has been no adverse effects from ferrate which should thus be further explored for ECs removal with good potential [147].

3.2.2. Electro-Fenton processes

Electro-Fenton process has recently been developed to overcome the drawbacks of the classical Fenton process and to increase the efficiency of pollutant removal [138]. In this process, H_2O_2 is electrochemically generated in situ in a controlled way [148]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (6)$$

Another electrochemical process named photoelectron–Fenton process is also used, in which the conditions remain the same as electro–Fenton process but it is simultaneously irradiated with UVA light. Thus UVA light accelerates the degradation rate of contaminants in the reaction phase and increases the regeneration rate of Fe^{2+}. Moreover, $OH^{\cdot}$ can also be produced from the following reactions [138]:

$$[Fe(OH)]^{2+} + hv \rightarrow Fe^{2+} + OH^{\cdot} \qquad (7)$$

$$Fe(OOCR)^{2+} + hv \rightarrow Fe^{2+} + CO_2 + R^{\cdot} \qquad (8)$$

Electro-Fenton processes appear to be environmentally friendly and efficient with in situ generation of the Fenton's thereby avoiding (i) the cost of reagents and risks related to their transport and storage, (ii) the formation of sludge, and (iii) side reactions due to maintenance of small reagent concentrations in the medium [149]. Electrochemical Fenton processes can be enhanced by the additional application of UV radiation or ultrasound. Solar radiation can also be used (solar photoelectro-Fenton process). But problem is that additional energy is required for photo or sound assistance and their installation and operational costs are involved in comparison to classical electrochemical AOPs except solar photoelectron-Fenton process [146]. Some of the ECs removal by electro-Fenton, electro photo-Fenton and bi-electro-Fenton processes has been presented in **Table 5**. These kinds of AOPs based

treatment can oxidize ECs at higher concentration (mg L^{-1} or g L^{-1}) than relevant to the environmental levels. Some pesticides such as atendol, metoprolol, propranolol, triclosan and triclocarban and some antibiotics such as cephalexin, sulfamthazine, sulfamethaxazole, tetracycline and acetaminophen were found to show enhanced removal capacity by electro-Fenton process [149, 150]. Solar photoelectro-Fenton process has also been applied for the removal of beta blockers such as atendol, metoprolol tartrate, propranolol hydrochloride, with 88-93% efficiency [151]. Thus electro-Fenton process seems to be better than solar photoelectro-Fenton process.

The most important advantage of these processes is that they can degrade pharmaceuticals of higher concentrations very effectively than by some conventional processes. The problem with such kinds of AOPs based treatment is that the maintenance and operation cost is high. Conventional treatment processes such as activated sludge, constructed wetland, microorganism based algal treatment and biosorption based treatment are more cost effective but cannot maintain their performance when influent contaminant concentration is high.

3.2.3. Photo-Fenton process

Photo-Fenton reactions are widely used AOPs for the removal of ECs in wastewater. These processes involve the use of UV light to produce radicals by reactions of hydrogen peroxide in the presence of iron. Photo-Fenton reactions are also possible in sunlight avoiding the use of UV light. Photo-Fenton studies are usually developed in acidic or near neutral conditions which are optimum for aquatic solutions not containing organic matter. In acidic solutions, Fe^{3+} forms the hydroxyl complexes such as $Fe(OH)^{2+}$ and $Fe(OH)_2^{4+}$, which absorb light in the UV/visible region, undergoing photoreduction to generate $OH^{\cdot}$ and Fe^{2+} (reaction 7). Thus the whole mechanism is enhanced as more $OH^{\cdot}$ are being produced and Fe^{2+} can be recycled at higher rate for the reaction with H_2O_2. In the case that the pH increases to near

neutral, the ferric ions precipitate to form amorphous ferric oxyhydroxides, in the absence of other ion complex substances. Thus Fe^{2+} can react with hydrogen peroxide to produce $OH^{\cdot}$, and the oxidized ligand can be involved in new reactions for the micropollutants degradation [2]. Therefore, the effluent should be acidified to reach this value and then neutralization is required before discharge. However, important efforts are being devoted to develop photo-Fenton processes under milder conditions. Oxidation of different ECs by photo-Fenton process is represented in **Figure 5a**. In general, many types of pharmaceuticals have been found to show higher removal efficiencies (95-100%) by photo–Fenton process except penicillin G [2, 12, 16, 137]. Six anti-inflammatory pharmaceuticals such as antipyrine, 4AA, 4AAA, 4FAA, 4MAA and metronidazole have been successful degraded by this process with higher removal efficiencies than by other processes. However photo-Fenton was found to be less effective in the removal of EDCs with relatively high K_{ow} values. Pesticides including atrazine, diuron, mecoprop and terbutrynwere were found to be better oxidized by photo-Fenton process with the exception of triclosan and abamectin (**Figure 5a**).

Alternatively, solar photo-Fenton process was also applied in the removal of ECs by up to 90% at a contaminant concentration of 5 μg L^{-1} (**Table 5**) [9]. Thus it can be concluded that UV based photo–Fenton process can remove higher amount of pharmaceuticals and beta blockers than solar photo–Fenton based process: UV photo-Fenton > solar photo-Fenton.

3.2.4. Photocatalysis

Photocatalysis is the transformation of chemicals by a catalyst that is activated in the presence of light that provides adequate energy [152, 153]. Most photocatalysts are semiconductor metal oxides which characteristically possess a narrow energy band gap. Photocatalysis is used to overcome the disadvantages of photolysis, especially the slow rate of degradation. The catalyst takes part in the reaction, increases the rate of reaction but remains unchanged in the end [154]. Titania is the most widely investigated of the

heterogeneous photocatalysts due to its cost effectiveness, inert nature and photo stability [155]. In addition, ZnO has been reported to catalyse the photo-oxidation of pharmaceuticals such as carbamazepine and antibiotic tetracycline. In fact, fast removal of tetracycline was observed with ZnO under optimized conditions (basic pH), although the major drawback of this material is that it suffers from corrosion at low pH values. The removal efficiencies of ECs by photocatalysis are presented in **Figure 5**. EDCs such as E1, E2, EE2, E3, bisphenol A and progesterone can be highly degraded by up to 100% and the removal efficiencies are higher than by photo-Fenton based AOPs (**Figure 5b**). High degradation rate of pharmaceuticals such as analgesics can be easily achieved using photocatalysis process. The removal of ECs by photocatalytic process generally followed the order of EDCs > analgesics pharmaceuticals > pesticides > other pharmaceuticals. For the removal of pesticides such as aldrin, diazinon, malathion and some antibiotics such as amoxicillin, ampicillin and chloxacclin, an alternative process such as photocatalysis in the presence of hydrogen peroxide can also be applied with excellent removal efficiencies (99-100%) [156, 157].

3.2.5. Solar photocatalysis

Solar photocatalytic process is an emerging and promising technology both as an alternative treatment to conventional wastewater treatment methods and enhancement of biodegradability of highly toxic and recalcitrant pollutants [167]. A promising alternative to semiconductor-based solar photocatalysis of some pharmaceuticals can also be applied. Data in **Table 5** show that many ECs can be removed by up to 85% by solar photocatalysis process [129, 155]. The removal of analgesic pharmaceuticals is better achieved by UV photo-Fenton process.

3.2.6. Miscellaneous processes

Besides AOP based processes some other technologies have also been applied for the removal of ECs from WWTPs, which include anodic oxidation [168, 169], ultrasound

irradiation (also called sonochemical irradiation) and titanium based ultrasound irradiation. EDCs such as E1, E2, E3 and equilin were found to be removed by up to 80-90% from aqueous solution by ultrasound processes at a concentration of 10 μg L^{-1} [65, 172]. Naddeo et al. [173] investigated sonochemical degradation of 23 ECs (such as acetaminophen, atenolol, atrazine, carbamazepine, diclofenac, progesterone, metoprolol, dilantin, DEET, pentoxifylline, oxybenzone, caffeine, iopromide, erythromycin, fluoxetine, trimethoprim, propranolol, sulfamethoxazole, ibuprofen, naproxen, bisphenol-A, gemfibrozil, and triclosan) from WWTP at 1 μg L^{-1}concentration. A strong degradation for all ECs at an average value of 70% occurred due to the breakdown of conjugated double bonds. Triclosan showed faster degradation rate (95%) while erythromycin the lowest degradation rate (50%). The degradation of all ECs followed the pseudo first order kinetic model. Therefore a significant reduction of the discharge of ECs into the environment could be expected through the use of catalysis, ultrasound irradiation and solar energy. Recent investigations increasingly focus on these systems; however, commercial applications are still scarce.

The comparative removal of ECs by different chemical based oxidation processes is shown in **Figure 6**, where the average removal of different categories of ECs by Fenton and UV photolysis processes was found less effective than other chemical oxidation processes. It is also clearly seen that ozonation, ozonation in presence of hydrogen peroxide and photo-Fenton processes showed greater efficiency in the removal of a wide range of ECs. Other processes were found to have a mixed effect in the removal of ECs. The average removal efficiencies of EDCs followed the order: ozonation ≥ UV photocatalysis > photo-Fenton > UV photolysis/H_2O_2 > solar photo-Fenton > UV photolysis. On the removal of pesticides, UV photolysis/H_2O_2 and electro-Fenton processes showed very similar high average removal efficiencies. The order of the removal of pesticides can be written as electro-Fenton ≈ UV photolysis/H_2O_2 > ozonation/H_2O_2 > photo-Fenton > Fenton ≈ ozonation > UV photolysis >

solar photo-Fenton. On the other hand, the average removal efficiencies of beta blockers can be written as ozonation/ H_2O_2 ≈ UV photolysis/ H_2O_2 ≈ photo-Fenton > electro-Fenton> ozonation > UV photocatalysis > UV photolysis > Fenton process. The average removal efficiencies of analgesic pharmaceuticals by different chemical oxidation methods can be written as UV photolysis/H_2O_2 ≈ ozonation/H_2O_2 = photo-Fenton > ozonation > photocatalysis ≈ solar photo–Fenton > UV photolysis > Fenton process. For antibiotics, their average removal efficiencies can be ranked as ozonation/H_2O_2 > UV photolysis/H_2O_2 > ozonation > Photo-Fenton ≈ electro-Fenton > solar photo-Fenton > UV photocatalysis > UV photolysis. This kind of relationships for pharmaceutical lipid regulators, anti-inflammatory and miscellaneous pharmaceuticals can be developed (**Figure 6**). Thus it can be concluded that chemical based oxidation processes possess excellent oxidation characteristics in the removal of a wide range of ECs, although they involve comparatively high costs associated with the maintenance and operation, power consumption and different by-products in solution. The by-products can create problems due to their potential toxicity which can further increase the cost of the processes.

4. Progress and challenges in hybrid systems

The conventional wastewater treatment processes are not adequate for the effective removal of many ECs. A variety of hybrid treatment technologies are reported in the literature and during the last few years significant improvements have been achieved in their application in wastewater treatment, to prevent the release of ECs into the aquatic environment via effluent discharge. Most of the hybrid systems consist of biological based treatment system followed by some physical or chemical treatment systems. Chemical oxidation based treatment such as ozonation is the most widely used process to combine with biological process. Some examples of these combinations include ozonation followed by biological activated carbon**,**

MBR-reverse osmosis/ultrafiltration/microfiltration/ozonation, filtration and activated sludge followed by ultrafiltration. Microfiltration and ultrafiltration are increasingly being considered as alternatives to granular media filtration [174].

The remediation of 31 target ECs such as EDCs, pesticides and beta blockers by hybrid systems is represented in **Table 6**. Some EDCs such as E1, E2, EE2, E3, 17β-estradiol 17-acetate, bisphenol A, 4-n-nonylphenol and 4-*tert*-butylphenol can be better removed by up to 99% through the combined use of MBR and some physical treatment technologies such as reverse osmosis, ultrafiltration or nanofiltration at concentrations up to 5 μg L^{-1}. Combination of flocculation, activated sludge and ultrafiltration can also be employed but removal efficiencies of EDCs were low in some cases. This kind of combination can be more cost effective than MBR based hybrid systems. In term of removal of high influent concentrations of EDCs, MBR based hybrid system can become more effective and should be employed. The general trend for EDCs removal can be written as hybrid MBR with reverse osmosis or nanofiltration or ultrafiltration > flocculation–activated sludge–ultrafiltration > constructed wetland.

A combination of flocculation, activated sludge and ultrafiltration was found less effective in the removal of pesticides such as 2,4-D and triclosan. Ozonation followed by biological activated carbon hybrid process is better than other processes such as MBR based hybrid systems (MBR-reverse osmosis/nanofiltration/ultrafiltration) for the removal of pesticides from WWTP or synthetic wastewater. For example, atrazine, 2,4-D, diazinon, diuron, metolochlor, praziquantel and triclopyr can be effectively removed using ozonation followed by biological activated carbon hybrid system. On the other hand, MBR based hybrid systems were found to be less effective for the removal of fenoprop and pentachlorophenol from synthetic wastewater. Triclosan was found to be well removed by MBR based hybrid treatment systems (**Table 6**). The general trend for the removal of pesticides can be written as

ozonation-biological activated carbon > flocculation–activated sludge–ultrafiltration > constructed wetland > MBR plus reverse osmosis or nanofiltration or ultrafiltration.

Hybrid treatment technologies such as MBR-reverse osmosis and ozonation–biological activated carbon were applied for the removal of atenolol, metoprolol and propranolol beta blockers, and both hybrid systems were found to achieve high removal efficiencies of over 99%. Ozonation followed by biological activated carbon system was slightly better than MBR-reverse osmosis for the removal of those beta blockers. On the other hand, sotalol, salbutamol, and salicylic acid beta blockers were found highly degraded in MBR-reverse osmosis hybrid system. Some of beta blockers such as butylated hydroxyanisole, butylated hydroxytoluene, DEHP, galaxolide, methyl dihydrojasmonate and tonalide showed low removal efficiencies during treatment using SFCW and HFCW (**Table 6**). In some cases such as on the removal of salicylic acid and DEHP, activated sludge based hybrid system was found more effective than constructed wetland based hybrid systems. The general trend for the removal of beta blockers is ozonation–biological activated carbon > MBR with reverse osmosis or nanofiltration or ultrafiltration > flocculation–activated sludge–ultrafiltration > constructed wetland.

Overall, on the removal of pharmaceuticals, the most widely employed hybrid systems are MBR-reverse osmosis, ozonation–MBR, activated sludge–gamma radiation, and ozonation–ultrasound. Ozonation followed by biological activated carbon hybrid system can successfully remove 94% to more than 99% of analgesics pharmaceuticals such as carbamazepine, codeine, diclofenac, ibuprofen, naproxen, paracetamol and tramadol (**Figure 7a, Table S6**). Activated sludge followed by gamma radiation was found to be highly efficient for the removal of carbamazepine, diclosan and ibuprofen. Combined application of ultrafiltration, activated carbon and ultrasound hybrid system showed excellent performance in the removal of carbamazepine and ibuprofen even at high concentrations, due to the joint

effect of adsorption onto activated carbon and ultrasonic irradiation [177]. Other hybrid systems such as ozonation-ultrasound and MBR-reverse osmosis presented mixed removal efficiencies. Although some analgesics such as carbamazepine, diclofenac, metronidazole and primidone were degraded less efficiently in both types of hybrid systems, other analgesics such as codeine and ibuprofen can be completed removed. Flocculation followed by activated sludge and ultrafiltration can remove some analgesic pharmaceuticals and removal efficiencies were not so high like other hybrid systems such as ozonation-biological activated carbon or ozonation-gamma radiation, but this system is sometimes better than MBR based nanofiltration or ultrafiltration. As shown in **Figure 7b,** ozonation followed by gamma radiation hybrid system was found to be the best process for the removal of pain relievers, lipid regulators and diuretics. Ozonation–biological activated carbon hybrid system was found good for the removal of indomethacin, ketoprofen, gemfibrazil and furosemide but not for the removal of atorvastatin. Activated sludge followed by gamma radiation can remove 100% of ketoprofen, mefanamic acid and clofibric acid. The same recommendation can be made for the hybrid flocculation–activated sludge-ultrafiltration process as made earlier. Thus on the removal of pharmaceutical analgesics, pain relievers, lipid regulators and diretics, ozonation-ultrasound and ozonation-biological activated carbon hybrid systems can be better employed than MBR based reverse osmosis/nanofiltration/ultrafiltration hybrid systems except for gemfibrozil removal (**Figure 7**). The general tread for the removal of analgesics, lipid regulators and pain relievers by hybrid systems can be written as ozonation-ultrasound ≥ ozonation-biological activated carbon > activated-gamma radiation > flocculation-activated sludge > MBR with reverse osmosis or ultrafiltration.

The removal of antibiotics and other pharmaceuticals is represented in **Table 7**, which shows that MBR–reverse osmosis can successfully remove more than 99% of azithromycin, clarithromycin, erythromycin, ofloxacin, sulfamethaxazole, diazepam, lorazepam,

famotidine, ranitidine and clopidogrel. Ozonation followed by biological activated carbon hybrid system can be well applied in the removal of a wide range of ECs such as erythromycin, licomycin, roxithromycin, trimethoprim, caffeine, citalopram, doxylamine, phenytoin, risperidone, sertraline, hydrochlorothiazole and perindopril. But this hybrid system was found less effective in the removal of chloramphenicol, sulfamethaxazole, tylosin, dapsone and perindopril. The combined application of ultrafiltration, activated carbon and ultrasound was found highly effective in the removal of antibiotic amoxicillin even at 10 mg L^{-1} level [177]. Ozonation followed by ultrafiltration hybrid system could remove up to 100% of pharmaceuticals such as clarithromycin, clindamycin, sulfamethazine, 4-aminoantipyrine, enalapril and norbenzoylecgonine, but was found less effective in the removal of licomycin, ofloxacin, venlafaxine and irbesartan (**Table 7**). Thus on the removal of antibiotics and miscellaneous pharmaceuticals hybrid systems followed the order of MBR-reverse osmosis ≥ ozonation-biological activated carbon > ozonation-ultrafiltration.

In summary, MBR based reverse osmosis/nanofiltration/ultrafiltration has been found highly efficient in the removal of a wide range of ECs such as EDCs, antibiotics and other pharmaceuticals. Other issues such as process cost, membrane fouling and energy demand need to be considered in designing such hybrid systems. Ozonation followed by biological activated carbon was found to more effective in the removal of pesticides, beta blockers, pain relievers, lipid regulators, analgesics, antibiotics and miscellaneous pharmaceuticals. But this process still suffers from lower efficiencies for some ECs. Ozonation followed by ultrasound hybrid system is a recent development in the removal of ECs, but this process may involve high costs and lower efficiencies in the removal of some ECs. In terms of cost, activated sludge based hybrid systems (activated sludge-ultrafiltration, activated sludge-gamma radiation) can also be a good alternative but need to consider the high retention time and sludge processing costs. Constructed wetland based hybrid system was found less effective in

the removal of many ECs. Data on the removal of PCPs and surfactants by hybrid systems are scarce. In future, some AOPs based treatment processes such as photolysis in the presence of hydrogen peroxide and photo-Fenton processes can be carefully integrated with the conventional processes.

5. Future perspectives

Different ECs can be effectively removed through different biological and chemical based methods but there are still deficiencies in the complete removal of ECs from wastewater. Some further research areas are suggested as follows:

- There is a lack of detailed information on the degradation mechanisms involved, influence of operational variables on ECs removal, reaction kinetics and reactor design for optimum performance.
- Integration of existing treatment systems with nanoscale science and engineering.
- Challenges associated with wastewater sample preparations, analytical techniques and validation protocols for the reliable analysis of ECs in complex environmental samples.
- Removal performance of different WWTP processes at various operational conditions should be re-evaluated with suitable sampling protocols.
- Use of solar irradiation should be explored as an alternative AOP approach for reducing the costs of large scale commercial applications.
- Hybrid technologies based on combined chemical and biological treatment processes, e.g. UV photolysis in the presence of H_2O_2 followed by MBR or biological activated carbon, ozonation in presence of H_2O_2 followed by MBR or biological activated carbon, photo-Fenton followed by MBR or biological activated carbon should be further developed.

- Combination of physical processes such as gamma radiation and ultrasound with adsorption on activated carbon or similar adsorbents (e.g. biochar) can also be integrated with the current wastewater treatment systems.
- Ferrate process is a relatively green process and should be more extensively researched for industrial-scale applications.
- New knowledge in genetic engineering should be introduced to select and amplify the most effective microbes for ECs degradation, which will reduce hydraulic retention time and save capital cost in reactor design.
- The robustness and feasibility of full-scale chemical oxidation processes need to be extensively investigated to ensure ECs removal efficiencies and minimise toxic by-products.

6. Conclusions

Different biological processes were found to enhance the removal efficiency of different classes of ECs. For example, conventional activated sludge process has shown better removal efficiencies for surfactants, EDCs and PCPs than trickling filter and biofilm reactors, nitrification and denitrification processes. Biological activated carbon process has been reported with enhanced efficiencies in the removal of pesticides, analgesics and antibiotics. MBR process has been found to be highly effective in the removal of EDCs, PCPs and beta blockers than constructed wetland. Novel microalgae based technology has the highest efficiency in the removal of many categories of ECs especially pharmaceuticals and PCPs, although no data were reported on their removal of beta blockers, antibiotics and surfactants.

On the other hand, chemical oxidation methods such as ozonation/H_2O_2, UV photolysis/H_2O_2 and photo-Fenton processes have been found to be the best processes for the removal of pesticides, beta blockers and pharmaceuticals. Ozonation and UV photocatalysis processes are highly effective in the removal of EDCs. The Fenton process has been observed

to be the least effective among all types of conventional and AOPs treatment technologies. The removal of surfactants and PCPs has not yet been well studied by chemical processes.

Finally, hybrid systems such as MBR followed by reverse osmosis, nanofiltration or ultrafiltration are better for the removal of EDCs and pharmaceuticals, but less effective in the removal of pesticides. Ozonation followed by biological activated carbon hybrid system has been observed to be effective in the removal of pesticides, beta blockers and pharmaceuticals. Ozonation followed by ultrasound hybrid system can remove up to 100% of certain pharmaceuticals such as salicylic acid, ibuprofen, naproxen, acetaminophen, cocaethylene, benzoylecgonine, enalapril, norbenzoylecgonine, ketoprofen, atorvastatin, bezafibrate, clindamycin, sulfamethazine and 4-aminoantipyrine. Other hybrid systems based on activated sludge followed by ultrafiltration or activated sludge followed by gamma radiation are cost effective for the removal of certain EDCs, pesticides and analgesic pharmaceuticals. Hybrid systems using ultrafiltration, activated carbon followed by ultrasound process can be a better process to remove a wide range of ECs but may not be cost effective.

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Appendix A. Supplementary data

7. References

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Figure legends

Fig. 1. ECs removal achieved by activated sludge process with corresponding reference after compound name. a = antidepressant, b = contrast agent, c = gastroesophageal, d = vasodilator, e = antineoplastic, f = diuretic. The concentrations are in mg L^{-1} for empty columns.

Fig. 2. Comparative average removal efficiency of ECs with standard deviation (error bar) for wastewater treatment (activated sludge, biological activated carbon, microalgae, MBR and constructed wetlands) and for sludge treatment (aerobic and anaerobic).

Fig. 3. ECs removal efficiencies achieved by ozonation process with corresponding reference after compound name. Concentrations are in mg L^{-1} for empty columns and in g L^{-1} for dark columns.

Fig. 4. ECs removal efficiencies achieved by ozonation in the presence of H_2O_2 (Figure 4a) and UV in the presence of H_2O_2 (Fig. 4b), with corresponding reference after compound name. Concentrations are in mg L^{-1} for empty columns and in g L^{-1} for dark columns. 1 = corrosion inhibitor, 2 = pain reliever, 3 = contrast agent, 4 = anti-inflammatory.

Fig. 5. ECs removal efficiencies achieved by photo-Fenton (Fig. 5a) and UV photocatalysis (UV/TiO_2) (Fig. 5b), with corresponding reference after compound name. Concentrations are in mg L^{-1} for empty columns and in g L^{-1} for chloramphenicol. 1 = pesticide, 2 = corrosion inhibitor, 3 = contrast agent, 4 = antidepressant, 5 = anti-diabetic, 6 = gastroesophageal, 7 = lipid regulator, 8 = diuretic, 9 = beta blocker, 10 = pain reliever, 11 = NSAID, 12 = stimulant.

Fig. 6. Comparative average removal efficiency of ECs with standard deviation (error bar) by different chemical treatment technologies.

Fig. 7. Pharmaceuticals removal efficiencies achieved by hybrid systems with corresponding reference after compound name. Concentrations are in mg L^{-1} for dark columns. 1 = codeine, 2 = paracetamol, 3 = tramadol, 4 = benzoylecgonine, 5 = cocaethylene, 6 = hydrocodone, 7 =

indomethacin, 8 = mefanamic acid, 9 = atorvastatin, 10 = bezafibrate, 11 = clofibric acid, 12 = furosemide.