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Review

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Treatment Technologies for Emerging Contaminants in water: A review

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Abstract. In recent years, the presence of a group of contaminants, termed as emerging contaminants (ECs) has been recognized as significant water pollutants that have adverse effects on human and wildlife endocrine systems. Natural attenuation and conventional treatment processes are not capable of removing these micropollutants which are reported to bioaccummulate in macro invertebrates, other organisms in the aquatic food web and humans. An in-depth review of the state-of-the-art technologies available to remove emerging contaminants (ECs) in water was undertaken. The results of the review show that the majority of the research in recent years has focused on using phase-changing processes, including adsorption in different solid matrices and membrane processes, followed by biological treatment and advanced oxidation processes. This paper focuses on the type of EC being removed, the conditions of the process and the outcomes achieved. The main trends in the field are also highlighted along with perceptive comments and recommendations for further developments as well as the identification of the current knowledge gaps and future research directions related to the application of these technologies for water treatment and restoration.

Keywords: Emerging contaminants, water treatment technologies, phase-changing technologies, biological treatment, advanced oxidation processes.

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1. Introduction

Investigations into water quality commonly focus on nutrients, microbial pollutants, heavy metals, and priority pollutants. However, recent research reveals the presence of a multitude of organic contaminants that significantly affect water quality. These contaminants originate from diverse sources and typically in concentrations that range from ng L^{-1} to μg L^{-1} [1]. This group of contaminants, termed as emerging contaminants (ECs), are chemical compounds that are commonly present in water, but are only recently being recognized as significant water pollutants. Emerging contaminants are natural or synthetically occurring substances not commonly monitored in the environment and having known or suspected undesirable effects on humans and the ecosystem. This group include compounds such as pharmaceutical and personal care products (PPCPs), pesticides, and hormones that have adverse effects on human and wildlife endocrine systems. Therefore, these are included in the endocrine disrupting compounds (EDCs) group. Natural attenuation and conventional treatment processes are not capable of removing these micropollutants from wastewater and surface and drinking water and are reported to bioaccummulate in macro invertebrates, other organisms in the aquatic food web and humans [2–4].

The significance of this issue needs to be viewed in the context of increasing detrimental impacts of climate change on rainfall patterns and compounded by limited opportunities to further expand conventional water sources to enhance urban water supplies [1,5]. Unfortunately, the variety of ECs in water has increased over the past years, mainly as a result of advances in analytical techniques, resulting in its detection at very low concentrations in water samples [5–9]. Successful water reuse not only depends on availability, but appropriate treatment is also essential. Although in-depth scientific investigations of pollutants such as nutrients, hydrocarbons, and heavy metals in stormwater and wastewater have been undertaken, only a very limited number of systematic studies have reported on the presence of ECs and even fewer related to the identification of appropriate treatment. Consequently, sustainable reuse of water contaminated with ECs is an ongoing challenge.

It is imperative that before the detrimental impacts of climate change compel communities to reuse water without adequate safeguards, good practices underpinned by scientifically robust policies are adopted to mitigate potential human health and environmental risks. Inability to appropriately manage ECs in water, risks squandering the opportunity to gainfully use one of the last available and largely uncommitted water source for many urban areas. Identifying the technological trends and knowledge gaps in relation to the removal of emerging contaminants in water is a priority that must be addressed in order to inform the scientific community towards the adoption of best practices to ensure the use of safe drinking water for the community. Accordingly, the primary focus of this study was to undertake an in-depth review of state-of-the-art processes currently available for removing emerging contaminants so that this alternative water source can be used without creating potential human or ecosystem health risks and the identification of current knowledge gaps and to determine future research directions.

2. ECs in water: causes, effects and analysis

The number of chemical groups constituting ECs is large and continues to grow as new chemicals are identified to be part of this classification. In their biannual review of ECs in water, Richardson and Ternes [10] include a wide variety of compounds to the EC group, including sucralose and other artificial sweeteners, nanomaterials, perfluorinated compounds, drinking water and swimming pool disinfection by-products, sunscreens and UV filters, flame retardants, benzotriazoles and benzothiazoles, siloxanes, naphthenic acids, musks, algal toxins, and ionic liquids and prions. With advancements in the chemical industry, the variety of compounds being released to the environment which are potentially harmful to humans and ecosystem over the long-term is expected to grow significantly over the years [11,12]. In recent years, researchers have shown an increased interest in monitoring ECs, but little agreement exists on the list of substances that should be monitored [13].

2.1 Pharmaceuticals

Pharmaceuticals are an important group of ECs and their presence in drinking water has generated significant concerns regarding the risk of estrogenic and other adverse effects on humans and fauna [14]. Approximately 3,000 different substances are estimated to be used as pharmaceutical ingredients, including painkillers, antibiotics, antidiabetics, beta blockers, contraceptives, lipid regulators, antidepressants, and impotence drugs. Only a small subset of these ECs has been investigated in environmental studies. The large-scale use of pharmaceuticals has also increased their presence in surface water, groundwater, wastewater and stormwater runoff in urban areas [15–18].

2.2 Antibiotics, biocides, and pesticides

The major concerns in relation to antibiotics, biocides, and pesticides, is the development of bacterial resistance after their release into the environment [19–21] and the detrimental effect on the biodegradation of plant materials, which disrupts the primary food chain in aquatic ecosystems [10]. The term “pesticide” refers to chemicals used for agricultural purposes, whereas the term “biocide” refers to chemicals used in urban environments [22]. Biocides are mainly used in bituminous roof sealing membranes and external facades or for grass management and weed control. During rain events, biocides and pesticides are incorporated in surface and groundwater via stormwater runoff [23–29].

2.3 Personal care products

These chemicals are found widely in urban environments and include fragrances, sunscreens, insect repellents, and antifungal agents [1]. Since these compounds are designed for external usage, no metabolic changes occur in their chemical structure and are easily released into aquatic environments. Their presence in urban runoff and groundwater has also increased significantly in recent years [18,22,30–34].

2.4 Current analytical methodologies for ECs quantification

Due to the chemical structure of several compounds included in the ECs group, they can be easily dissolved in water and transported through the water cycle with highly potential as a threat to aquatic organisms and humans [35]. The long list of compounds included as ECs has grown significantly in recent years leading to an unknown amount of parent compounds and transformation products being present in wastewater effluent, surface and groundwater and drinking water [36]. The identification and quantification of these compounds in water or wastewater has become a major scientific task requiring highly sophisticated analytical methodologies which are able to detect in levels of nanograms per liter (ng L^{-1}) [37]. Consequently, there is a clear need for in-depth information on ECs from an analytical chemistry perspective, which can provide knowledge on the application of wide ranging monitoring methods and for developing rapid and efficient screening methods for determining these compounds [36].

Table 1 depicts representative examples of recent advances on analytical tools available for ECs analysis in surface and groundwater and wastewater samples. As shown, the main analytical tools available for these types of compounds are chromatography (either gas or liquid) coupled to mass spectrometry (MS). The use of MS technology in the detection and quantification of ECs is primarily linked to the significant advancements witnessed in recent years, particularly in terms of selectivity, sensitivity and specificity, allowing an accurate identification and quantification of specific pollutants even in very complex matrices such as surface or wastewater [36]. For example, advanced MS technologies such as triple quadrupole (QqQ) and ion trap (IT) allow ECs quantification in the ng L^{-1} level and other more recent developments such as linear ion traps (LITs) quadrupole, triple quadrupole, quadrupole-time of flight (QqTOF) and quadrupole-linear ion trap (QqLIT) have been used for transformation products structure elucidation [35]. Other analytical methodologies such as, capillary electrophoresis (CE), immunoanalytical techniques (IAT) or microbiological assays (MA) have been reported for ECs determination. However CE is generally considered less sensitive than LC methods, whilst IAT is highly dependent on the antibody used for the immunoassay and limited for simultaneous determination of different analytes and MA is highly dependent on the nature of the sample [38].

Despite the development that all these analytical tools have achieved in recent years, further scientific work is still needed primarily for the detection and quantification of non-target and unknown compounds. In the case of unknown ECs, novel approaches are needed to reduce uncertainty and enhance identification. The use of novel software and the development of state-of-the-art techniques at low cost and reduced analytical time that can substitute the use of complementary analysis in providing high certainty in the case of identification of unknown substance is urgently needed.

Sample pretreatment is another significant analytical step that should be considered for accurate measurement of ECs in water. Most studies reported involve liquid-liquid extraction (LLE). However, the trend in the recent years relates to the use of solid phase extraction (SPE). SPE presents several advantages over LLE, such as simplicity, reproducibility and applicability and it is considered good practice to pre-concentrate water samples prior the final quantification in order to lower detection limits (LOD) and quantification limits (LOQ) of the method. Other pre concentrating techniques reported include automated SPE, on-line SPE, use of molecularly imprinted polymers, solid phase microextraction (SPME) and magnetic SPE [39] which have advantages such as reduced cross contamination, minimized solvent consumption, reduced effort and enhanced sample throughput [37]. In the sample pretreatment arena, the main challenges are related to the reduction of effort, minimizing LODs and enhancing selectivity. One interesting possibility for further research in this field is related to the use of nanomaterials (NMs). Some very recent studies have reported on the application of magnetic iron nanoparticles as the substrate for SPE applications [39] with very interesting results. Considering the wide variety of NMs available and the even wider possibility of NMs synthesis and novel materials which can be developed with enhanced capabilities, this is a research area that merits further investigations.

Table 1. Representative examples of recent developments in EC analytical tools for water samples

ECs number/type	Sample pre-treatment	Equipment and analysis conditions	Notes	References.
27 ECs including pharmaceuticals, sunscreens compounds, fragrances, antiseptics, fire retardants,	Methylation of carboxyl groups with trimethylsulfonium hydroxide at 270˚C	Gas chromatography-Mass spectrometry (GC-MS) with electron impact mode (70 eV ionization energy) using a TRB5-MS column (5% diphenyl-95% dimethylpolisoxane).	Sample type: wastewater. LOD and LOQ in the range 1 to 40 and 3 to 80 ng L^{-1}, respectively. Recoveries and repeatability were greater than 80%	[40–43]
105 pharmaceuticals and life style products; 21 drugs of abuse, metabolites	Solid phase extraction (SPE) using polymeric cartridges	Liquid chromatography electrospray time-of-flight mass spectrometry in positive and negative modes	Sample type: surface and wastewater. LOQ raged 0.2 to 777.9 mgL^{-1}	[44]
8 artificial sweeteners	Reverse phase SPE extraction for sample pre-concentration and clean-up	LC-MS and LC-MS/MS with electrospray interface (ESI)	Sample type: Surface and drinking water. LOD in the range of 0.82 and 2.8 µgL^{-1}	[45]
44 pharmaceuticals and 13 EDCs	Pressurized liquid extraction, SPE purification	Ultraperformance liquid chromatograph coupled to a mass spectrometer (UPLC-MS/MS)	Sample type: River water and biofilms. LOD in the range 0.2-2.4 ngg^{-1} for EDCs and 0.07-6.7 ngg^{-1} for pharmaceuticals	[46]
90 ECs including pharmaceuticals and estrogens	Microwave assisted extraction (MAE) protocol followed by SPE	UPLC-MS/MS with ESI and using an Acquity BEH C_{18} column for both positive and negative modes.	Recoveries in the range 40-152%. LOQ from 0.1-24.1 ngL^{-1}	[47]
8 ECs including perfluorinated compounds, pharmaceuticals	Polar organic chemical integrative samplers (POCIS) for in-situ pre-concentration	Fast LC-MS/MS with ESI and using a Zorbax XDB-C_{18} column.	Sample type: Drinking water. Concentration in the range 4.2 to 15.9 ngL^{-1}	[48]

3. Treatment technologies

Non-conventional water treatment technologies have changed over time as a result of new techniques being developed. These treatments can be broadly divided into phase-changing technologies, biological treatment and advanced oxidation processes. This paper evaluates the treatment processes most often reported and their performance characteristics. It is important to note that, despite the fact that there is no agreement about the way that authors report removal efficiencies, the most common way to estimate it is in terms of ECs concentration before and after the treatment process. For this work, removal efficiencies were taken directly from the literature without any further modification. For those cases where calculations were undertaken differently to what was described above, appropriate notes have been provided to avoid confusion.

3.1 Phase-changing technologies

Technologies capable of moving contaminants from one phase (e.g., water) into another (e.g., solid) have been widely reported in the removal of emerging contaminants. Adsorption processes have been extensively studied for the removal of several different pollutants [49,50]. Following sections provide a detailed review of the application of different phase-changing processes for removal of ECs in water.

Adsorption using activated carbon (AC)

Activated carbon (AC) is the most frequently used material because of its high porosity and specific surface area [51,52]. These features make AC highly adsorptive and effective in removing a range of contaminants [53–55]. Table 2 gives a selective list of research studies on the removal of different emerging contaminants using AC. Using AC for removal of ECs show greater than 90% removal for a wide variety of compounds [56,57] and confirm that it will selectively remove some ECs in water. An example of AC selectivity is the case of ciprofloxacin. This contaminant can be immediately removed using AC, bringing the overall concentration rapidly to below the method detection limit [58]. In comparison, several other contaminants tested has removal rates as high as 90%, but only after a significantly longer period of time [59,60]. Figure 1 shows an example of the different removal efficiencies for a group of Emerging Contaminants (Lincomycin, levofloxacin, diclofenac, ibuprofen, trimethoprim, ciprofloxacin, erythromycin, carbamazepine, caffeine, primidone and N,N-diethyl-m-toluamide (DEET)) using granular activated carbon in an advanced wastewater reclamation plant [61].

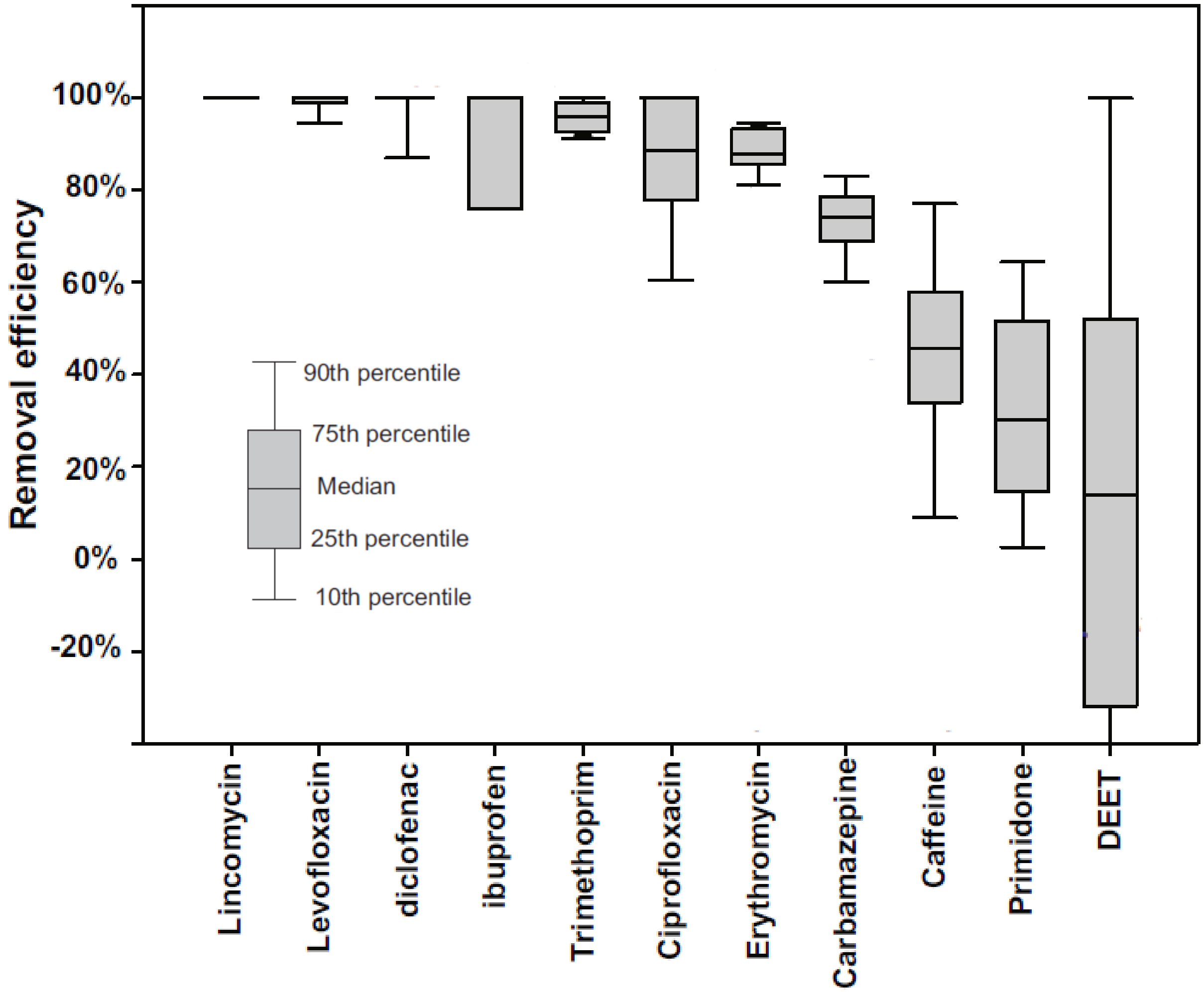

Figure 1. Removal efficiency of different ECs by AC [61].

The source of the raw material for AC is an important factor, with different sources generating significantly different removal rates. As shown in Table 2, an example is the case of acetaminophen where the removal was >90% using AC from wood and removal values are in the range of 60-87% using AC from other sources [62]. Likewise, diclofenac removal was >90% using olive-waste cake and granular AC [56,57], whereas poor removal was observed using Filtrasorb 400 [63]. Tetracycline was removed from water using AC from four different sources, namely, sugar beet pulp, peanut hulls, coconut shell and wood activated with phosphoric acid. High tetracycline removal (>90%) were found for the former two while the AC from activated wood was able to remove 75% and, coconut shell only produced 30% removal [64]. The reason for the differences among the types of sources is attributed to the carbon structure of the raw material, with compacted fibers in coconut shell producing smaller pore sizes and the absence of additional activation prevents the generation of new pores and/or unclogging and widening of existing pores [51,53]. In general, fairly good results have been obtained using AC in the removal of ECs from water. The removal efficiencies range from 30% for tetracycline using coconut shell AC [50] to greater than 99% in the case of ciprofloxacin removal using the Norit Rox AC from Sigma [44]. Particularly, Calgon Filtrasorb 400 was reported performing as low as 5% removal of diclofenac [49], but showing outstanding performance for the removal of caffeine and norfloxacin. Also interestingly, AC originating from waste sources has been reported with noteworthy performance in the removal of some specific ECs such as Paracetamol [48], antibiotics [56], and anti-inflammatory drugs [42].

Adsorption-based systems can be used sequentially coupled with other treatment processes. For example, the combination of three different treatments - AC, ultrafiltration, and coagulation - to remove ECs has been proposed [66]. The removal obtained, based on the chemical oxygen demand (COD), from the coupling of the three treatments was in the range of 84-88%, with high removal of the individual contaminants. However, limited knowledge is available on the effect of other parameters on the performance of adsorption-based systems. Another significant knowledge gap is the lack of understanding on scaling-up parameters. Most research studies discuss laboratory scale tests and do not provide insights for scaling-up or the full-scale feasibility of the processes. This is a significant constraint in the practical application of the research outcomes.

Table 2. Removal efficiency of ECs with activated carbon

AC Source	EC	Removal efficiency, %	Notes	Reference
Lotus Stalk-derivatives	Trimethoprim	79	Activated with phosphorus oxyacids	[67]
Lignin-activated	Tetracycline Ciprofloxacin	76 79.5	$[C]_0$= 420 mgL^{-1}, pH=5.5	[59]
Lotus Stalk-based	Norfloxacin	95	pH= 5.5	[68]
Macadamia nut shell	Tetracycline	100 80 70	pH= 3 pH= 4 pH= 5	[69]
LS by wet oxidation (LSN) Chemical activation of cork (CAC) Cork powder waste (CPAC) Physical activation of coal (Q) Physical activation of wood (LS) Physical activation of PET (P)	Ibuprofen	60 70 62 85 95 70	pH= 4; 10 mg AC, 0.5 h Ultra-pure water	[60]
Sugar beet pulp Peanut hulls Coconut shell H_3PO_4-activated wood	Tetracycline	>90 >90 30 75	Batch, 250 h	[64]
Vine woods	Amoxicillin Cephalexin Penicillin G Tetracycline	88 88 88 88	T= 45℃, pH= 2, 0.4 gL^{-1} AC	[70]
Olive-waste cake	Ibuprofen Ketoprofen Naproxen Diclofenac	70 88 90 91	T= 25℃, pH= 4.12	[56]
Coal Wood Plastic waste Powder waste	Paracetamol	74 97 60 87	T = 30℃	[62]

Peach stones		82		
Norit® Rox 0.8 from Sigma	Ciprofloxacin	>99	T= 25 °C, pH= 5	[58]
Albizia lebbeck seeds pods	Cephalexin	57	Activated with KOH	[71]
		52.5	Activated with K_2CO_3	
Calgon Filtrasorb 400	Diclofenac	5	T= 25 °C	[63]
	Caffeine	98		
	Norfloxacin	100		

Adsorption using biochar

Biochar is a charcoal-based material commonly used as a soil amendment. Like most carbon-based materials, biochar is made from heating biomass at high temperature in the absence of oxygen, which is a process known as pyrolysis [72,73]. In recent years, biochar has been investigated for the adsorption of ECs [74–76]. Table 3 provides a selected list of studies on biochar application in EC removal.

Pyrolysis conditions is one of the essential characteristics of biochar production process affecting its capability for ECs adsorption and treatment efficiency [77,78]. For example, a species of cane classified as *Arundo donax L* has been used as the feedstock for biochar production for the removal of sulfamethoxazole. Using the same experimental conditions, biochar without thermal activation was able to achieve 35% removal, while using thermal activation the maximum removal achieved was <16% [78]. These results are related to the effect of thermal activation on the hydrophilic-hydrophobic, acid-base properties of biochar as it can transform the feedstock biomass in terms of particle size and porosity, influencing its capability to remove ECs.

Same as for AC, the feedstock used for biochar production significantly influences its treatment efficiency and selectivity in relation to EC removal. As illustrated in Table 3, removal of sulfamethoxazole were in the range of 12% for two types of wood feedstock, while using sugarcane as the feedstock produced a biochar able to achieve removal up to 21% [79]. Using rice husk and rice straw as the feedstock, sulfamethoxazole removal was as low as 11.6% except when using alkali treated rice husk feedstock where almost

30% removal was achieved [67]. The carbon, nitrogen and phosphorus content in the feedstock has been found to create significant differences in the treatment performance of biochar [67,79].

As in the case of activated carbon, chemical or thermal treatment exerts a significant influence on the final chemical characteristics which influences EC removal performance. However, the study undertaken by Jeong et al. [80] found that despite using biochar from different feedstock materials and different thermal treatment conditions for the removal of tylosin, the removal rate was in the range of 10% for all the products. This outcome is attributed to the chemical structure of tylosin which includes several hydroxyl groups when compared with other antibiotics such as sulfamethoxazole. Due to the higher oxidation state of the chemical structure, tylosin has higher water solubility than other less oxidized antibiotics and presents relatively high values of water-octanol partition coefficient, producing the low removal results shown in Table 3.

Despite having similar characteristics, biochar has not performed similar to AC for coupled systems. This is attributed to the type of contaminants that can be removed by this technology due to the material used for production. Nonetheless, as biochar has different selectivity, it may be more efficient in the removal of some ECs compared AC [77]. Therefore, the application of biochar in sequentially coupled treatment systems merits further investigation.

Table 3. Removal efficiency of ECs using biochar

BC feedstock	Activation temperature, ˚C	EC	Removal efficiency, %	Notes	Reference
Brazilian pepper wood	NR		4-12	T=22℃	
Hickory wood	450	Sulfamethoxazole	0-12	$[C]_0$= 10 mgL^{-1}	[79]
Sugarcane waste	600		19-21	2 mgL^{-1} of absorbent	
Bamboo	NR		5-12		
Arundo donax L.	NR		25.5	$[C]_0$= 50mgL^{-1}	
Arundo donax L.	300-600	Sulfamethoxazole	5-16	C_e= 50 mgL^{-1}	
Demineralized A. donax L.	300-600		8-17	pH= 5	[78]
Graphite	NR		7	7.14 gL^{-1} of absorbent	
Ash	NR		31		
Raw rice husk	450-500		8.5	5gL^{-1} of absorbent	
Acid rice husk	450-500	Tetracycline	12	$[C]_0$=1 gL^{-1}	[67]
Alkali rice husk	450-500		29		
Forest soil/sweet gum/oak	850		10	0.1gmL^{-1} of absorbent	
Forest soil/yellow pine	900		10	$[C]_0$=250mgL^{-1}	
Cornfield/sweet gum/oak	850	Tylosin	10	Time: 239 h	[80]
Cornfield/yellow pine	900		10	10% amended of biochar	

A key knowledge gap in the use of biochar relates to the sustainability of the production process. The feedstock used for biochar production may originate from agricultural waste. However, life cycle analysis is needed in order to ensure that the use of waste feedstock does not have more worthy application instead of conversion to biochar. The scaling-up of the biochar production process is another significant knowledge gap. In many of the cases, biochar production is undertaken in inefficient small-scale kilns requiring high energy input. Accurate assessment of the carbon footprint related to biochar production process and identification of cleaner production processes is essential to ensure its sustainable use.

Adsorption in carbon nanotubes

Carbon nanotubes (CNTs) are a carbon allotrope with a graphite-like structure and displays different adsorption characteristics depending on the degree of curl, the generation of the original sheet, diameter, internal geometry, physical-chemical properties and the treatment process used for synthesis [71,81–85]. Usually, CNTs are defined as single-walled nanotubes (SWNT), which have an internal diameter of about 1 nm [86,87] and multi-walled nanotubes (MWNT), which consist of several concentric tubes or laminated graphene layers [87–89]. Table 4 gives a selected list of studies where CNTs have been used for the removal of ECs from water.

Table 4. Removal efficiency of ECs using CNTs.

CNT Type	EC	Removal efficiency, %	Notes	Reference
MWNT	Amoxicillin	>90	MWCNT (50 mg) pH=4	[90]
MWNT	Ciprofloxacin	67.5	Temp= 25℃ pH= 5	[91]
SWNT	Ibuprofen/Triclosan	100	100 mgL^{-1} absorbent $[C]_0$=2 mg mg^{-1}	[92]
MWNT		100		
Oxidized MWNT		97-100		
SWNT	Tetracycline	92	$[C]_0$=0.19 $mmolL^{-1}$ pH=5; 0.25 gL^{-1} absorbent	[93]
MWNT		16.5		
Hydroxylized MWNT	Ofloxacin/Norfloxacin	11-99	$[OFL]_0$= 0.7 gL^{-1} $[NOR]_0$= 60 mgL^{-1} pH=7 75 mgL^{-1} absorbent	[94]
Carboxylized MWNT		7-63		
Multi-walled graphite		5-70		
15 nm-ID CNT		11-99		
30 nm-ID CNT		7-63		
50 nm-ID CNT		5-50		
Hydroxylized SWNT		11-99		
Carboxylized SWNT		17-100		
Purified SWNT		17-100		
MWNT	Norfloxacin	35	0.5 gL^{-1} absorbent $[C]_0$= 100 mgL^{-1} T= 27˚C; pH= 5.4	[95]

Note:

SWNT – single-walled nanotubes

MWNT – multi-walled nanotubes

Carbon-based materials vary according to the treatment used for their production, which is evident from the comparison of treatment performance of AC, biochars, and CNTs. Surface area plays an important role in the performance of CNTs for removing ECs. The surface area of CNTs usually depends on the presence of single- or multi-walled structures, which can result in different removal rates even though the same contaminant is involved. For example, Ji et al. [93] were able to achieve 92% removal of tetracycline using SWNT and only 16% removal with MWNT despite the same experimental conditions being adopted. MWNT worked also fairly well in the removal of other ECs such as amoxicillin (>90% [76]), ciprofloxacin (6.7% [77]), and ibuprofen/triclosan (100% [78]). Similarly, 100% removal of norfloxacin was achieved using single-walled CNTs [94], whereas only 35% removal was achieved using of multi-walled CNTs [95]. Multi-walled CNTs can be prepared from single-walled CNTs by using additional chemical processes [92] to increase the contact zone by several times and the amount of active sites for adsorption and enhancing contaminant removal efficiency. However, it has been found that all these features may not necessarily mean improved performance due to molecular sieving effects occurring in MWNTs [58,92,96].

Using CNTs, ECs removal is an important area for further research as only limited studies are currently available and more experimental evidence is needed to support the previously described trends. Only limited studies are available comparing the performance of single- and multi-walled CNTs, most of them showing better performance for the former than the latter and even contradictory results in the use of the same type of CNTs in the removal of the same contaminant [97–99]. Combining the adsorptive nature of CNTs with other reactive nanomaterials is an area of importance which requires further research. For example, the use of zero valent iron nanoparticles immobilized within the surface of the CNTs to promote degradation reactions or coupling CNTs with other adsorption processes may lead to a completely novel research field with interesting application opportunities.

Adsorption by clay minerals

Table 5 provides a selected list of studies on using clay minerals for removal of ECs. From Table 5 it is evident that the characteristics of the adsorbent material dictates the efficiency of the removal process. The same type of clay may produce different removal efficiencies depending on the specific amount of nitrogen, iron or other minerals present [100–102]. This is evident from the studies undertaken by Wu et al. [103] and Wu et al. [104], for the removal of ciprofloxacin using montmorillonite (MMT) which resulted in 100% and 35% removal, respectively. This difference in treatment performance is attributed to the source of the clay material. For the former, the montmorillonite was obtained from the Source of Clays Repository of the Clay Mineral Society in Wyoming which had a cation exchange capacity (CEC) value of 85 meq 100 g^{-1} and specific surface area (SSA) of 23 m^2 g^{-1}, respectively [103]. In the case of the latter, the source was a supplier in China (San Ding Corp., Zhengjiang) and the CEC and SSA values were 1.1 mmol g^{-1} and 35 m^2 g^{-1} [104]. However, the SSA or CEC values can be modified by impregnating with various ions to enhance treatment performance and selectivity [105,106].

Table 5. Removal efficiency of ECs using clay minerals

Clay mineral	EC	Removal efficiency, %	Notes	Reference
Bentonite	Ciprofloxacin	91	T= 22℃	[107]
MMT	Tetracycline	50	[TC]$_0$=0.225 mML^{-1} pH=5.5	[106]
MMT	Sulfadimethoxine	13	pH=7.2 Synthetic effluent	[108]
	Sulfamethoxazole	10		
	Tetracycline	99		
	Oxytetracycline	90		
Kaolinite	Ciprofloxacin	95	q$_e$=19 mmolL^{-1}	[109]
Natural bentonite	Ampicillin	90	Synthetic wastewater	[102]
Organic-bentonite		100		
Na-MMT	Ciprofloxacin	100	25 mgL^{-1} MMT, pH= 3, 11	[109]
Ca-MMT		100		
Al-MMT		100		
Na-MMT	Tetracycline hydrochloride	59	5 gL^{-1} adsorbent [C]$_0$=6.25 mmolL^{-1}	[101]
Ca-MMT		77		
Synthetic mica-MMT		29		
Hectorite		60		
Na-MMT	Tetracycline	35.5	[C]$_0$= 0.76 mM 0.9 g MMT	[105]
Ca-MMT		59		
Ca-MMT in 0.01 M CaCl$_2$		95		

Another interesting application is the creation of coupled processes that uses the adsorptive characteristics of the clay combined with ions able to produce reactions inside the structure of the porous matrix as in the case of metal oxide-pillared clays. This porous matrix can have sizes ranging from 1.49 to 3.2 nm, which provides adequate space inside the clay mineral to undertake catalysis [110]. Pillared clays have received considerable attention in recent years as they provide the opportunity for using semiconductors for the degradation of contaminants and to increase the activity of the metal oxide by enhancing the active surface area [111]. This type of system has been used with advanced oxidation processes, in special Fenton and Fenton-like reaction, in order to prevent catalyst impregnation in the matrix after the reaction (e.g., clay mineral) and later recovering the matrix using conventional (e.g., settling) or non-conventional (e.g., magnetic) procedures [112,113]. These approaches have demonstrated very promising results, but require further investigations as the contaminant fate and the removal mechanisms involved remains largely unknown. For example, studies have not confirmed whether in the treatment process contaminant degradation takes place first and then the adsorption, or whether the contaminant is absorbed first and the degradation occurs inside the clay mineral.

Other adsorbents

Several other adsorbent materials have been reported in research literature for removing ECs. These include zeolites, meso- and micro-porous materials, resins, and metal oxides [50,114]. Table 6 provides a selective list of results reported in recent literature relating to the use of other adsorbents to remove ECs in water. As evident, the material type is one of the most important characteristics to be considered when choosing adsorption as the removal process, mainly because this determines other features such as pore size, metallic or nonmetallic nature and ability to couple with a second treatment. From Table 6 it is worthy to note that the capability of the different materials in the removal of ECs varies greatly.

Table 6. Removal efficiency of ECs using others adsorbents

Adsorbent	EC	Removal efficiency, %	Notes	Reference
Zeolite Pumice	Ciprofloxacin	51 25	T= 22°C	[107]
Fe-Mn binary oxide	Tetracycline	>98 >98 90 88 35 30	Mn oxide Fe/Mn 1:1 Fe/Mn 3:1 Fe/Mn 5:1 Fe/Mn 7:1 FeOOH	[115]
Al_2O_3/Fe	Norfloxacin	90	pH=6.5	[68]
Al_2O_3	Tetracycline Chlorotetracycline Oxytetracycline	43 57 44	pH=5 T= 22°C	[116]
Graphene oxide	Tetracycline	71	q_e= 313 mgg^{-1}	[117]
Nano scale zero valent iron (NZVI) Polyvinyl pyrrolidone (PVP-K30) PVP-NZVI Hydrous Fe oxide	Tetracycline	60 0 95 55	[NZVI]=0.1gL^{-1} [PVP-K30]= 2gL^{-1} PVP-NZVI= 0.1gL^{-1} 1 h	[118]
Molecularly imprinted polymer Non-imprinted polymer	Diclofenac	99 15	pH= 7 $[DFC]_0$= 300 mgL^{-1}	[119]
Molecularly imprinted polymer Molecularly no-imprinted polymer	Carbamazepine	40-100	71 mg of absorbent $[C]_0$= 50 mgL^{-1}	[120]
Graphene oxide/magnetite composites	Ciprofloxacin Norfloxacin	73 89	0.2 gL^{-1} absorbent pH=6.2 T= 25˚C $[C]_0$= 5 mgL^{-1}	[121]
Bi_2WO_6	Tetracycline	97	$[C]_0$= 20 mgL^{-1} 0.5 gL^{-1} Bi_2WO_6 120 min	[122]

The structure of the adsorbent material has a significant influence on the process efficiency. An example is the study by Liu et al. [115] in the use of Fe-Mn binary oxides for the removal of tetracycline. Mn and Fe oxides were tested alone and Mn oxide removed over 98% of the tetracycline, whereas Fe oxide removed only 30%. However, increasing the amount of Mn in the binary oxide formulation led to significant decrease in EC removal. The nature of the pollutant, as in the case of other adsorbents has a significant influence on the efficiency of the process. The combination of aluminum oxide with CNTs improved carbamazepine removal from 0 to 70% when the CNTs/Al_2O_3 ratio was set at 1:1. Other adsorbent materials may also perform relatively well in the removal of ECs. For example, zeolite or pumice for the removal of ciprofloxacin [93] or the use of alum oxide in the adsorption of different antibiotics with variable removal results ranging from 43 to 90% [54,102] and the application of molecularly imprinted polymers and materials of diverse nature for the removal of a variety of pharmaceuticals [104-108].

The sustainability of the production of these adsorbent materials is a significant issue. In many of the cases, the use of soils, clays or other natural materials may prove to be unsustainable in the long-term. Reducing the environmental footprint associated with the use of naturally occurring adsorbent materials by modifying their physical or chemical characteristics to create engineered nanomaterials with enhanced capabilities for ECs removal from water is an area for further research [123]. Recent studies have reported on the generation of metal and non-metallic pillared clays with enhanced properties for use in environmental applications [123,124]. However, there has been only limited application of these materials for the removal of ECs. This is an important area for further research.

Membrane technology

Membrane processes are another type of phase changing processes with a variety of applications in ECs removal. Membranes are produced from different materials, which give rise to specific filtering features (e.g., pore size, surface charge, and hydrophobicity) that determine the contaminant type that can be retained [125,126]. Membrane processes are based on the use of hydrostatic pressure to remove suspended solids and high molecular weight solutes and allow water and low molecular weight solutes to pass through. Membrane filtration can be classified as: ultrafiltration (UF), nanofiltration (NF), microfiltration (MF), forward osmosis (FO), and reverse osmosis (RO). Figure 2 shows a schematic representation of the different membrane types, pore size ranges and typical water contaminants removed by the different pore size ranges.

Microfiltration is widely used because it can be undertaken at atmospheric pressure. Despite several advantages, MF cannot remove contaminants of size <1 µm (i.e., dissolved solids) and it is not useful for the removal of ECs [127,128].

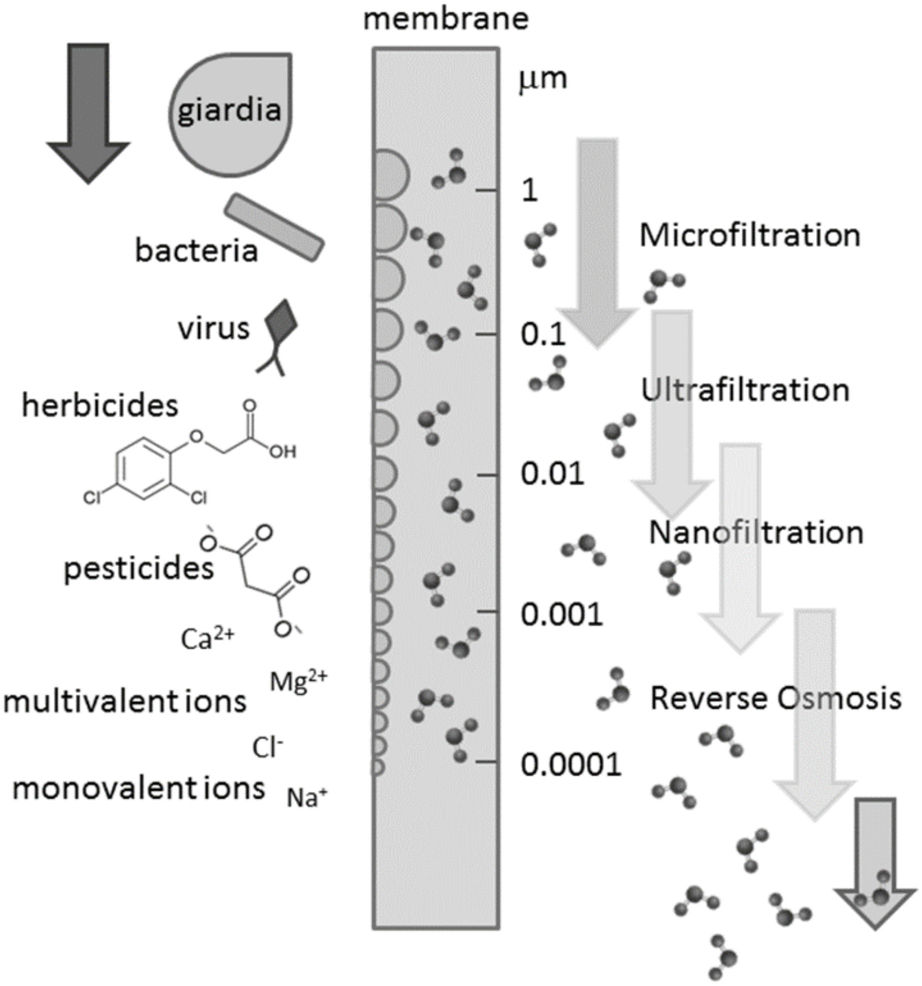

Figure 2. Types of membrane, pore size ranges and representative water contaminants removed for every pore size [129].

Ultrafiltration has been used for the removal of a significant variety of emerging contaminants because these possess a pore size smaller than MF (in the range of 0.001 - 0.1 µm) [130–133]. The removal efficiency can vary widely depending on the membrane type and closely related to the contaminant type [134]. For example, the removal of bisphenol A from water was tested using polysulfone- and polyvinylidene-made UF membranes. The former was able to achieve 75% removal, whereas the latter was able to eliminate up to 98% of the load in the experimental influent [134,135]. Similarly, Melo-Guimaraes et al. [135] used two different phthalate acid derivatives (Bis-2-ethylhexylphthalate and buthylbenzylphthalate) with the same type of UF membrane (Polyninylidene fluoride-made; 100 KDa pore size from ABSCOR-Koch Systems), achieving 15% and 78% removal, respectively. Generally, polar, highly water soluble ECs are efficiently removed by UF compared to non-polar, low water soluble compounds. For example, female hormone derivatives and organic acid-like ECs (e.g., Estrone, EE2, E2, diclofenac, ketoprofen) are reported to have the highest removal efficiencies, whereas less polar phthalate esters report poor removal rates [96,135–137].

Nanofiltration can be used for ECs removal because of its small pore size (in the range of 10-100 Å) [138–140]. Additionally, NF membrane processes operate at a low feed water pressure [133,141,142], which means a significant advantage if the operation cost should be considered. NF has been demonstrated with higher efficiency than UF in the removal of some ECs. For example, caffeine removal efficiency was in the range of 2-21% using UF, whereas the reported efficiency for NF was 46-84% and the same trend was identified for ketorolac tromethamine [130].

Similarly, membrane material also influences the process efficiency. The previously mentioned caffeine removal was achieved using NF membranes (HL, CK and DK series from GE Osmonics Inc.), whereas caffeine removal was in the range of 62-93% using polyamide thin-film composite (NF-90 and NF-200, from Dow Filmtec) membranes

[130,143]. However, this trend, may not be universal because ECs with different characteristics may behave differently. For example, high molar mass compounds such as estrone can have high removal rates using either, UF (e.g., 98% removal) or NF (removal range 79-97%) [116,120,121,129].

Reverse and forward osmosis (RO and FO, respectively) uses a semi-permeable membrane to separate water from dissolved solutes. In both cases, osmotic pressure gradients are related to the separation process. In FO, the gradient works as a draw solution of high concentration to induce a net flow of water through the membrane whereas in RO, the process uses hydraulic pressure as the driving force for separation. RO has a greater efficiency as it can remove particles as small as 10 Å and colloidal particles. Table 7 provides comparison showing the efficiency of different membrane systems for ECs removal [144,145].

As the pore size decreases, the efficiency of the removal process for ECs improves significantly. FO and RO have been reported with high removal efficiency for treating water contaminated with a variety of ECs, as shown in Table 7. Carbamazepine, for example, has been eliminated from water with removal efficiency in the range of 80% to 99%, and the effective removal of caffeine (e.g., in the 80-99% removal range) has been achieved using FO processes. In general, only a few ECs have been reported with removal efficiency values lower than 50%, as the case of acetaminophen, using FO or RO processes [132].

Table 7. Removal of ECs using membranes

Membrane process	EC	Removal efficiency, %	Notes	Reference
UF	Acetaminophen	11-20	(UF): GK, PT, PW; from GE Osmonics, Ultrapure water	[130]
	Metoprolol	8-49		
	Caffeine	2-21		
	Antipyrine	6-23		
	Sulfamethoxazole	10-40		
	Flumequine	23-43		
	Ketorolac	6-49		
	Atrazine	18-39		
	Isoproturon	17-42		
	Hydroxybiphenyl	85-95		
	Diclofenac	26.5-53		
UF	Bisphenol A	75	polysulfone from Koch Membrane Systems	[134]
	17α-ethynilestradiol	85		
UF	Salicylic acid	40	ABCOR from Koch Systems made of polyvinylidene fluoride 100 KDa pore size	[135]
	Naproxen	70		
	Diclofenac	68		
	Gemfibrozil	95		
	Ibuprofen	60		
	Carbamazepine	15		
	Ketoprofen	70		
	Bis-2-ethylhexylphthalate	78		
	4-Nonylphenol	50		
	Buthylbenzylphthalate	98		
	Bisphenol-A	85		
	Triclosan	98		
	Estrone	98		
	EE2	98		
	E2	99		
NF	Acetaminophen	18-81	NF-200 and NF-90	[143]
	Phenacetin	70-78		
	Caffeine	62-93		

	Metronidazole	47-93		
	Phenazone	69-96		
	Sulfamethoxazole	71-98.5		
	Carbamazepine	74-98		
	Ibuprofen	88-98		
	Naproxen	94-99		
	Atrazine	94-99		
	17α-ethynilestradiol	76.5-98		
	Estrone	79-97.5		
	Nonylphenol	90-98		
	Bisphenol A	51-97		
FO	1,4-dioxane	55-68	FO: Hydration Innovations (HTI, Albany)	[146]
	Acetaminophen	45-89		
	Metronidazole	70-99		
	Phenazone	85-99		
	Caffeine	80-99		
	Bisphenol A	40-99		
	Carbamazepine	65-99		
RO	17α-ethynilestradiol	85-99	RO: Aromatic polyamide membrane (Midland, MI)	
	Ibuprofen	90-99		
	Naproxen	95-99		
	Fenoprofen	95-99		
	Gemfibrozil	95-99		
	Ketoprofen	95-99		
Membrane bioreactor	Acetaminophen	100	Two 0.04 µm polyethersulfone: MBR-15, -30 membranes	[147]
	Ketoprofen	98-100		
	Naproxen	86-89		
	Roxithromycin	57-81		
	Sulfamethoxazole	55-64		
	Trimethoprim	86-94		

Despite the fact that only limited knowledge is available about the mechanisms involved, some researchers have suggested that ionic contaminants may possess higher affinity for the membrane surface, generating higher removal efficiency values compared to neutrally charged contaminants. This knowledge gap creates the opportunity for future research in structure-response analysis of different ECs using membranes with a variety of chemical composition and physical properties in order to develop a better understanding of the actual mechanisms occurring and thereby optimize the processes.

Perspectives and further developments required in Phase-changing technologies

Phase changing processes, as reviewed above, can be effective for the removal of some emerging contaminants. However, there is a significant challenge in relation to the final disposal of the contaminants, as the treatments produce two effluents streams, a dilute and a concentrated phase. The contaminants being removed will go to the solid phase in the case of adsorption processes or will flow with the rejected effluent, in the case of membrane processes. A significant concern related with the use of phase changing processes is that the ECs only change places, but may remain as a problem for the environment. Several methods are under investigation to provide a sustainable alternative to the use of conventional treatment processes. For example, the combination of membrane filtration and chemical oxidation has been proposed [148]. In their work, the researchers found that the combination of these two processes in sequential mode achieved global removals higher than 97% for the ECs tested.

The search for novel materials capable of carrying out different processes simultaneously is another research area which merits further investigation. For example, the synthesis of semiconductor nanoparticles (e.g. TiO_2) on the surface of hydrophilic membranes has been reported [149]. In their work, the addition of non-aggregated, strongly bonded semiconductor nanoparticles on the membrane surface was found to improve its anti-fouling properties and demonstrated a highly active capability for photocatalytic oxidation of pharmaceuticals. Interestingly, titanium dioxide is not the only semiconductor available with the capability for creating materials with novel characteristics. Other semiconductors such as zinc-, copper-, silver- or platinum-based materials should also be investigated for this type of approach to enhance the capability of phase changing processes for ECs removal. Table 8 presents a comparative analysis of the different phase change technologies described above, including removal efficiencies achieved by the system.

As previously highlighted, it is difficult to identify which process performs the best without reviewing the material type, origin, treatment, and all the features described before. However, from the removal efficiency data included in Table 8, the process having the best removal performance are Bi_2WO_6 and the binary Fe-Mn adsorbents capable, under specific experimental conditions, to remove up to 97 and 98% of EC (e.g., tetracycline). The improved performance could be due to the fact that these materials were specifically developed for the removal of the compound while the other materials tested (e.g., AC, biochar, MMT) would have been designed for a broader spectrum of compounds to be removed and the variety of efficiencies is a reflection of this condition (ranging from 8.5 for biochar to >90% in the case of AC). Of particular interest, single- and multi-walled nanotubes show a high variation in the overall removal results (ranging from 16.5 to 92% removal of tetracycline), which can be attributed to the specific affinity that the target compound has for the structure of the nanotubes. From the results included in Table 8, it can be concluded that further research is required to be undertaken on the different phase change processes based on a systematic approach and using comparable conditions in order to perform a fair comparison between the different technologies. To our best knowledge, very limited knowledge is currently available. This creates a significant knowledge gap and a productive area for future research.

3.2 Biological processes

Several different biological processes are available, with activated sludge systems being commonly used to treat ECs because of its effectiveness [150]. Either aerobic or anaerobic processes can be applied depending on the type of contaminant, usually sequentially coupled with other tertiary treatment processes [151–153]. Table 9 shows a summary of the main biological processes used for EC removal in water, along with the contaminant type and the removal efficiency achieved.

Table 8. Comparison of phase-change technologies

Phase-change technology	EC	Notes	Removal Efficiency, %	Reference
Active carbon	Tetracycline	Batch reactor; 250 h; AC sources: Sugar beet pulp, peanut and coconut shell	30 - >90	[64]
Biochar	Tetracycline	Biochar from rice husk with different treatments; 5 g L^{-1} of adsorbent; $[C_0]$=1 g L^{-1}	8.5-29	[53]
MWNT SWNT	Tetracycline	$[C_0]$=0.19 mmol L^{-1}; pH=5; 0.25 g L^{-1} adsorbent	16.5-92	[79]
MMT	Tetracycline	Different modified MMT materials; $[C_0]$=6.25 mmol L^{-1}; 5 g L^{-1} adsorbent	35.5-95	[91]
Fe-Mn binary oxide	Tetracycline	Different Fe/Mn proportions	30->98	[101]
Bi_2WO_6		$[C_0]$=20 mg L^{-1}; 0.5 g L^{-1} Bi_2WO_6; 120 min	97	[108]

Table 9. Removal efficiency of ECs using biological processes

pe	System	EC	Removal efficiency, %	Notes	Reference
Anaerobic digestion	Activated Sludge	Estrone	79	WWTP in UK	[154]
		17β-Estradiol	0		
		Estriol	45		
		Estrone-3-Sulfate	36		
		17β-Ethinyl estradiol	34		
		4-Nonylphenol	0		
		mono- and diethoxylated nonylphenol	88		
		polyethoxylated nonylphenols	66		
Aerobic and anaerobic	Activated Sludge	Bezafibrate	19-80	WWTP in Beijing	[155]
		Caffeine	78-100		
		N,N-diethyl-meta-toluamide	23-30		
		Trimethoprim	38-55		
		Naproxen	97-100		
Aerobic	Soil Filtration	Estrogens	26	Land applications in Lubbock, TX	[156]
		17β-Estradiol	99		
		17β-Ethinyl estradiol	27		
		Triclosan	90		
		Ibuprofen	18		
Aerobic	Biological Filtration	Cashmeran	68	Biological filtration pilot plant based on *Daphnia sp.*	[157]
		Ibuprofen	86		
		Benzothiazole, 2-(methylthio)-	66		
		tributyl phosphate	22		
		Methyl dihydrojasmonate	97		
		tri(2-chloroethyl) phosphate	2		
		Diazone	8		
		Caffeine	49		
		Galaxolide	89		

		Tonalide	90		
		Terbutryn	94		
		Carbamazepine	5		
		Naproxen	72		
		Oxybenzone	89		
		Triclosan	87		
		Ketoprofen	99		
		Diclofenac	93		
Aerobic	Activated sludge	Salicylic acid	97	WWTP in Mexico	[135]
		Naproxen	75		
		Diclofenac	75		
		Gemfibrozil	70		
		Ibuprofen	83		
		2,4-D	>60		
		Carbamazepine	9		
		Ketoprofen	71		
		DEHP	46		
		4-Nonylphenol	53		
		buthylbenzylphthalate	72		
		Bisphenol-A	84		
		Triclosan	41		
		Estrone	>95		
		EE2	>93		
		17β-Ethinyl estradiol	>96		
Adsorption	Activated sludge	Tetracycline	30	T= 25˚C, 0.1 g of active sludge, 210 h	[158]
			80		
			75		
			62		
			68		
			68		

As evident, despite activated sludge being the most common, other biological systems (e.g., soil filtration or biological filtration) have been tested for the removal of ECs with interesting results. The success of the application of aerobic or anaerobic conditions is related to the predominant terminal electron-accepting conditions. Liu et al. [159] suggested that depending on these characteristics, benzotriazoles seems to be better removed under aerobic conditions when natural attenuation mechanisms drive the biodegradation process. However, they also identified that different electron-acceptors available in the natural environment may play a key role in the biodegradation process leading to specific biodegradability.

The removal of natural and synthetic estrogen and nonylphenol-derivatives has been reported under mesophilic and thermophilic conditions using anaerobic processes with removals in the range of 60% to 90% of ECs [154]. The researchers note that one of the main difficulties in the application of biological processes for the removal of ECs is the lack of accurate analytical methodologies able to identify and quantify these compounds in such complex matrix. This knowledge gap creates opportunity for further research related to the development of extraction methodologies for the isolation and quantification of ECs in activated sludge and/or other biological process by-products. Additionally, the search for accurate analytical technologies for the detection of ECs in complex matrices is an emerging area of opportunity.

Research investigating different biological treatment processes including conventional activated sludge, biological nutrient removal and membrane bioreactors [155] have reported that only easily biodegradable ECs (e.g., caffeine, diclofenac, trimethoprim) can be removed, whereas low biodegradables (e.g., sulpiride, metoprolol, bezafibrate) may not be eliminated at all by biological processes.

The evaluation of soil microorganisms for the biodegradation of ECs was carried out by Carr et al. [156] and it was found that estradiol derivatives were relatively easy to remove whereas other compounds like ibuprofen or triclosan were just slightly removed. The authors suggested that soil under saturated conditions exhibited, in general, better conditions for running biodegradative processes than those soils that remained non-saturated. Another interesting application of biological processes is the use of biological filtration where the organism carrying out the degradation process is *Daphnia magna* [157]. Compounds such as Ketoprofen, diclofenac or Terbutrin achieved high removal rates, whereas others such as carbamazepine, diazinone or tri-(2-chloroethyl)-phosphate showed the low removal rates. Table 10 shows a comparison of the common biological processes that have already been tested in treatment plants, especially in Europe where the removal efficiencies are very diverse dependent on the contaminant.

From results included in Table 10, the wide diversity of performances in biological processes for the removal of ECs is evident. Depending on the specific compound and the treatment conditions (e.g., aerobic or anaerobic), removal efficiency values range from no removal (e.g., in the case of carbamazepine or diatrizoic acid using aerobic activated sludge in Germany [150]) to nearly complete removal (e.g., 97-100% removal using aerobic/anaerobic activated sludge for the removal of naproxen in Finland [148]).

Evidently, the biological effect caused for some of the ECs included in the biological process can significantly impact the process removal efficiency as well as the environmental conditions in the different locations reported. The lack of comparable results, as in the case of the phase changing process, is an important knowledge gap that requires attention. Additionally, relatively limited information on the microorganisms involved in the degradation process is available representing another fundamental research need. Finally, little has been reported on the influence of other compounds present in the wastewater effluents may have on the overall EC removal efficiencies reported in Table 10. The characteristics of wastewater from the different geographical locations vary, depending on the relevant anthropogenic activities, pre-treatment processes undertaken and the process design applied.

Table 10. Comparison of biological processes

pe of biological process	System	EC	Removal efficiency, %	Notes	Reference
Aerobic and anaerobic	Activated Sludge	Benzotriazole	36-46	WWTP in Australia	[159]
		5-Methylbenzotriazole	61-100		
		5-Chlorobenzotriazole	52-71		
Anaerobic	Activated Sludge	Estrone	0-36	WWTP in Paris and Southern France	[160]
		17β-Estradiol	0-8		
		Estriol	0-1.67		
		17β-Ethinyl estradiol	0-4.2		
Aerobic and anaerobic	Activated sludge	Diclofenac	0-26	WWTP in Finland	[161]
		Bisoprolol	28-46		
		Naproxen	97-100		
Aerobic	Activated sludge	Ibuprofen	90	Wastewater from agricultural industry in Malaysia	[162]
		Ketoprofen	92		
Aerobic	Activated sludge	Bezafibrate	>90	WWTP in Germany	[163]
		Carbamazepine	0		
		Naproxen	>90		
		Ibuprofen	>90		
		Diclofenac	>90		
		Diatrizoic acid	0		

Perspectives and further developments required in Biological processes

Many of the compounds included within the emerging contaminant group possess biological activity. In some cases of antibiotic activity, their toxicity towards microorganisms involved in conventional biological processes may be significantly high. The search for alternative biological treatment continues and some interesting processes have emerged. For example, bioelectrochemical systems (BES) have been proposed (Yuan and He, 2015) as the next generation wastewater treatment technology. BES can generate energy in-situ to reduce energy requirements [164]. In BES, biological oxidation of the organic contaminants occurs at the anode by bacteria forming a biofilm simultaneously with the transfer of electrons from the microorganisms to the electrode surface. The electrons are then transferred through an external electrical circuit to the cathode where reduction reactions may occur. The system has demonstrated high efficiency in the removal of some selected contaminants.

Another recent development is the combination of phase changing, biological and electrochemical processes. For example, Figure 3 shows the removal efficiency of some specific ECs using activated sludge biological treatment sequentially coupled with membrane microfiltration. In this specific case, the membrane process was considered a mere particle removal technology allowing the microorganisms in the activated sludge the complete removal of the ECs in the effluent [61]. Another example is electrochemical membrane bioreactors (EMBR) [165]. EMBR are membrane bioreactors where bioelectrogenesis has been integrated. EMBR have been claimed to possess low bio-fouling generation, high removal capability and the opportunity to reduce energy consumption in wastewater treatment [166].

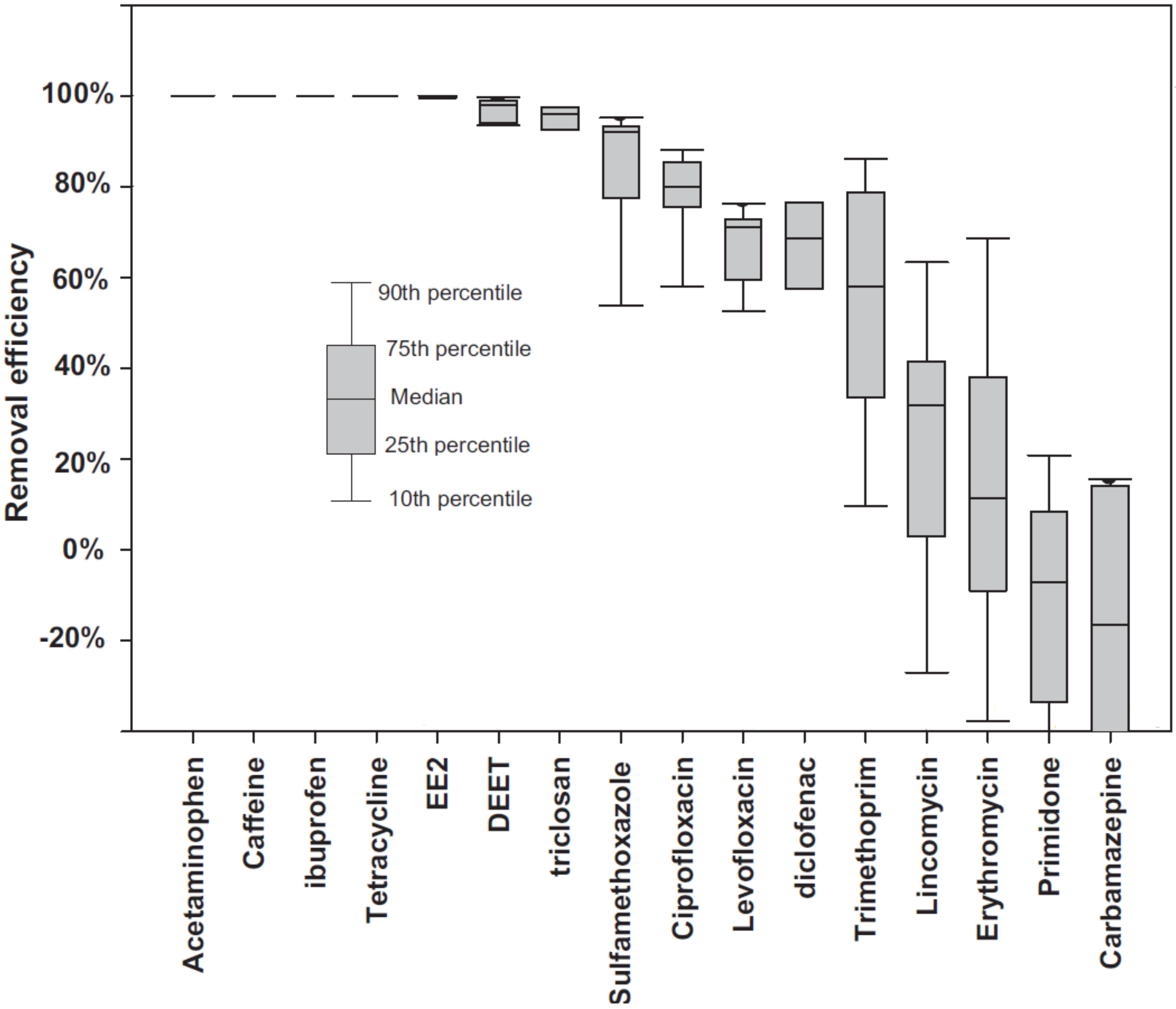

Figure 3. Efficiency of the removal of ECs in wastewater effluents by combination of activated sludge biological treatment and membrane filtration (adapted from [61]).

Managing the biosolids produced during the application of activated sludge technologies is an important issue when dealing with conventional biological degradation processes. The complexity of the biosolids matrix and the lack of analytical methodologies for the extraction, isolation and analysis of ECs in this type of matrix have produced an important knowledge gap in relation to the presence of ECs. Past studies have reported significant concentration of hydrophobic, recalcitrant ECs (e.g., flame retardants, polybrominated diphenyleters, and antibacterial agents) which may remain in the biosolids after biological treatment [167]. Since conventional biosolids treatment is usually related with de-watering and volume compression, these waste materials are usually an important source of ECs to the environment because the compounds accumulated may desorb and contaminate soil and water resources after final disposal.

Another interesting research avenue is related to the identification and quantification of metabolites and transformation products. Transformation processes, such as biological degradation can produce transformation products with remaining biological activity or even higher toxicity than the parent compounds [167]. The release of these by-products to the environment after treatment processes should be a significant concern because some of them may be masked by conjugation processes that can be easily reversed by environmental conditions yielding stable products with higher ecotoxicity. Biological treatment, for example, have shown a higher generation of perfluoroalkyl acid derivatives (e.g., perfluorooctanoic acid and perfluorooctanesulfonic acid) than chemically assisted primary treatment, highly related to temperature and long hydraulic detention times involved [167]. For this reason, following up the toxicity or remaining biological activity of the effluent after treatment can be as important as the analytical quantification of the parent compounds.

3.3 Advanced oxidation processes

Interest in advanced oxidation processes (AOPs) has increased in recent years related to their capability in the removal of pollutants, compared with conventional water treatment processes. The high removal rates have been associated with the production of hydroxyl radicals (oxidation potential, 2.8 V), the main characteristic of the AOPs. The processes included in the AOPs group have different routes of free radical production and specific work conditions, and may involve different materials. Table 11 compares the different types of AOPs used to remove ECs in water.

Table 11. Removal of ECs using AOPs

System	EC	Removal efficiency, %	Notes	Reference
UV	Estrone	90	$[C]_0$= 5 mgL^{-1} pH= 6.5; 13 W low-pressure Hg lamp (254 nm; 18 $mWcm^{-2}$) T= 20℃; 30 min	[168]
UV/H_2O_2	Doxycycline	100	pH= 3; $[Dox]_0$= 10 mgL^{-1}; $[H_2O_2]_0$= 100 µ$molL^{-1}$ UV-C radiation; 5.03x10^{-5} Es^{-1}; 20 min	[169]
UV/Ozone	Caffeine	>95	$[C]_0$=40 mgL^{-1}; pH= 7; UV 32W; 22.5 min	[170]
Ozone	Estradiol (E2)	>99	$[O_3]_{0\ E2}$=2.4 $molL^{-1}$; 1 s	[171]
	Ethynilestradiol (EE2)	80	$[O_3]_{0EE2}$=3.7 $molL^{-1}$; 3 s	
	Naproxen (NPX)	80	$[O_3]_{0\ NPX}$=4.75 $molL^{-1}$; 30 s	
	Ibuprofen (IBP)	90	$[O_3]_{0\ IBP}$=100 µ$molL^{-1}$; 2500 s	
Ozone/H_2O_2	Ketoprofen	90–96	Lab water; T=24℃; $[O_3]$= 2, 4 mgL^{-1}	[172]
	Naproxen	96–98	H_2O_2/O3 ratio= 0.5; 1; 2 min; $[C]_0$= 1 mgL^{-1}	
	Piroxicam	96–98		
Ozone/H_20_2/UV	Estrone	>99	$[C]_0$= 5 mgL^{-1}; pH= 6.5; low-pressure Hg lamp (254 nm; 18 $mWcm^{-2}$); T= 20℃; 30 min	[168]
Fenton process	Doxycycline	100	$[C]_0$= 100 mgL^{-1}; $[Fe^{+2}]_0$= 25 mgL^{-1}; $[H_2O_2]_0$= 611 $mgL^{-1;}$ T=35℃	[173]
Photo-Fenton	Acetamiprid	70–90 90–100 100-100	[Fe]= 1,2,3 mgL^{-1}; H_2O_2/Fe ratio: 2:1; 4:1; pH= 2.8 synthetic secondary effluent; 15 min; low pressure UV lamp (30 Wm^{-2}; 254 nm)	[174]
Sono chemical	Dicloxacillin	>99	pH= 5.5; 600 KHz; $[C]_0$= 0.21 mM; 180 min	[175]

Although the main feature of AOPs is the production of hydroxyl radicals, the type of reaction for hydroxyl radical production and the experimental conditions are highly significant. For example, dicloxacilin degradation has been attempted using UV photolysis [155,163], the decomposition of hydrogen peroxide [156] or ozone [155,157-159] using UV radiation, titanium dioxide photocatalysis [177] and sono-chemical oxidation [175]. A range of studies have reported that dicloxacilin is inert to UV radiation alone, slightly degradable by photocatalysis, but highly sensitive to sono-chemical conditions [175,176]. This is attributed to the fact that long wavelength UV radiation may not be able to generate any change in the chemical structure of the ECs and could explain the persistence in the environment of some of the compounds.

On the other hand, the use of a semiconductor photocatalyst such as titanium oxide may enhance the hydroxyl radical production with the consequent improvement in the degradation process. It is also well known that under- or over-dosing the photocatalyst load may lead to slow degradation [178,179]. In the case of the sono-chemical process, it has been proposed that the direct generation of hydroxyl radicals from water molecules without the use of intermediate species being capable of totally degrading some contaminants [175]. Similar results have been achieved by comparing different AOPs in the degradation of ECs. Oxacillin was tested for its degradation using white light lamps, photo-assisted Fenton processes, titanium oxide photocatalysis and use of ultrasound vibration, that is similar to sono-chemical treatment [180].

As previously reported for dicloxacillin, the UV-visible radiation emitted by white light lamps was unable to degrade oxacillin. The combination of radiation with the Fenton reagents is similar to two independent treatments, in the best case leading to slight oxacillin degradation (e.g., 10-15%). The use of the Fenton reaction produced a significant overall degradation achieving as high as 90% and the photo-assisted Fenton process was able to completely degrade oxacillin in the reaction mixture [181]. In this case, using titanium dioxide and UV radiation was capable of complete photocatalytic degradation of the EC, whereas the sono-chemical process achieved only 80% degradation. As evident from these two examples, there is no unique AOP capable of eliminating all the ECs.

Ozone and its combination with hydrogen peroxide or UV radiation are other interesting AOPs for ECs removal [159]. As evident from Table 11, these processes have been applied for the removal of several different emerging contaminants. Similar to the other AOPs reviewed, the concentration of the oxidant agent, pH of the reaction mixture, chemical structure and initial concentration of the target contaminant and wavelength and intensity of the radiation source (if included) significantly influences the outcomes.

Table 12 shows the comparison of the different AOP technologies that have been scaled to a treatment plant. It can be observed how the Fenton process excels and how some scaling of AOPs are better than conventional treatment. From results presented in Table 12, it is evident that the performance of AOPs in the degradation of ECs is similarly high for all the studies, the main difference being the source of energy provided for the process. Solar radiation is reported [171,172] as an alternate possibility to driving the degradation process instead of using lamps [169,170] with interesting implications from different points of view including the use of renewable energy. Both heterogeneous and homogeneous solar driven processes are reported with high degradation success. However, some gaps can also be identified. For example, limited knowledge is currently available to guide the assessment of scaling up parameters for solar- or even lamp-driven AOPs as well as the use of photocatalysts other than TiO_2 with enhanced capabilities with more efficient use of radiative energy. Furthermore, there is lack of information on the comparison between the experimental conditions used in the different studies on AOPs application for ECs removal in water. The catalyst source, radiative source, water characteristics, type of target EC, radiation exposure time and many other variables are reported with a wide range of magnitudes which makes it difficult to compare between the different studies. A systematic approach is needed in order to appropriately compare the research results reported to-date.

Table 12. Comparison of AOP performance

AOP´s technology	EC	Notes	Removal efficient, %	Reference
TiO_2	Acetaminophen Caffeine Ofloxacin Antipyrine Sulfamethoxazole Carbamazepine Flumequine Ketorolac Atrazine Isoproturon Hydroxybiphenyl Diclofenac Ibuprofen Progesterone Triclosan	Degussa P-25; $[TiO_2]_0$= 5mgL^{-1}; pH= 2.4–2.5; UV (290-400 nm); 68.85 Wm^{-2}; 100 min	90	[182]
TiO_2	Trimethoprim Ofloxacin Enrofloxacin Clarithromycin Acetaminophen Diclofenac Caffeine Thiabendazole Carbamazepine	Wastewater effluent; 3 h; $[TiO_2]$=0.5 gL^{-1}; 30 Wm^{-2}	90	[183]
Solar photocatalysis with TiO_2	Bisphenol-A Ibuprofen Hydrochlorothiazide Diuron	475 min; solar energy= 212 KJL^{-1}; $[TiO_2]$=20 mgL^{-1}	85	[184]

	Atenolol 4-AAA			
	Diclofenac Ofloxacin Trimethoprim Gemfibrozil 4-MAA Naproxen 4-FAA Caffeine Paraxanthine			
Solar photo-Fenton	4-AAA 4-FAA 4-MAA Antipyrine Atenolol Caffeine Ciprofloxacin Cotinine Diclofenac Diuron Furosemide Gemfibrozil Hydrochlorothiazide Ketoprofen Naproxen Nicotine Ofloxacin Paraxanthine Ranitidine Sulfamethoxazole Sulfapyridine	[Fe]= 5 mgL^{-1}; [H_2O_2] = 50 mgL^{-1}; pH= 3,7; 144 min; 30 Wm^{-2}; 10 mgL^{-1} humic acid	95 – 97.5	[185]

	Trimethoprim			
Solar photo-Fenton	Bisphenol-A Ibuprofen Hydrochlorothiazide Diuron Atenolol 4-AAA Diclofenac Ofloxacin Trimethoprim Gemfibrozil 4-MAA Naproxen 4-FAA Caffeine Paraxanthine	20 min; solar energy= 2.3 KJL^{-1}; 54 mgL^{-1} of H_2O_2 consumed; 5 mgL^{-1} Fe(II)	98	[184]
Ozonation	Bisphenol-A Ibuprofen Hydrochlorothiazide Diuron Atenolol 4-AAA Diclofenac Ofloxacin Trimethoprim Gemfibrozil 4-MAA Naproxen 4-FAA Caffeine Paraxanthine	60 min; 9.5 mgL^{-1} of O_3 consumed	98	[184]

Perspectives and further developments required in advanced oxidation processes

Being present in small amounts, ECs have proven to be a challenge for water treatment technologies. Several researchers have suggested coupling different processes that can act together to enhance removal efficiency [148,186–191]. The application of sequentially coupled treatment processes for the removal of ECs in water has been barely attempted and represent an important knowledge gap to be bridged.

Another interesting research avenue in the application of AOPs in the removal of emerging contaminants is the search for novel 'greener' synthetic processes for nanomaterials production. The conventional chemical processes used for the generation of nano-sized materials has significant drawbacks, such as defective surface formation, poor production rate, high cost, and high energy requirements [192]. Chemical synthesis procedures use toxic chemicals, generate hazardous by-products, and potentially release precursor chemicals to the environment [193]. The search for 'greener' procedures to generate environmentally friendly, non-toxic processes for synthesizing nanoparticles is needed to avoid detrimental environmental impacts. Using biologically mediated synthetic protocols to generate nanoparticles (NPs) has increased over the past years. These protocols have important advantages, such as: being eco-friendly and not using toxic chemicals; being lower in cost because they avoid high-pressure and high-energy expenses; and being able to produce relatively small-sized nanoparticles [192]. Several different biological resources have been used to synthesize nanoparticles, including microorganisms (bacteria, fungi, yeasts, algae, and viruses) and plant extracts [194,195]. To our knowledge, there are no studies available on the application of bio-synthesized nanomaterials for the generation of AOPs in the degradation of ECs. This highlights a potential area of research relating to the development of environmentally friendly degradation processes.

4. Conclusions

As highlighted in the review undertaken, in recent years significant research has been undertaken for the development of technologies for the removal of emerging pollutants (ECs) in water. However, significant knowledge gaps still exist, which highlights the ongoing challenge to ensure the safety of reused water for human consumption.

The key findings of this review are:

- Degradation of ECs using a single treatment technology is likely not the best approach for the removal of ECs in water. It is necessary to investigate the use of coupled systems which can bridge the deficiencies in a single technology for the removal of these complex contaminants present in the water environment.
- Phase-change processes, in spite of being effective for wastewater treatment, is not altogether effective in the case of low concentrations of EC's in water. In addition, these processes do not provide a permanent solution to the problem as a concentrated phase is generated after application. As such, these processes can be used for concentration pretreatment and sequentially coupled with further treatment(s) able to degrade ECs in the aqueous phase.

- Scaling-up studies for biological processes do not identify the microorganisms used for ECs degradation, but only report their use as activated sludge capable of removing contaminants. Additionally, though this type of processes has been presented as an efficient treatment, scaling-up studies do not include experimental development or detailed characterization of many of the processes tested. This has resulted in a significant number of questions about the fundamental processes occurring within the system yet to be answered.
- Advanced oxidation processes are presented in research literature as efficient in the degradation of ECs. However, a significant knowledge gap exists related to their industrial development or process scaling-up. There are only limited number of studies that have been undertaken in this regard.

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Highlights

- Despite significant research in ECs removal, significant knowledge gaps remain
- Phase-change, biological, AOP technologies, most common for removal of ECs in water
- Phase-change processes creates a challenge due to the concentrated waste streams
- Most research studies are laboratory scale, limited guidance for process scale-up