

Review



# Emerging Contaminants and Their Removal from Aqueous Media Using Conventional/Non-Conventional Adsorbents: A Glance at the Relationship between Materials, Processes, and Technologies

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**Abstract:** Emerging contaminants (ECs) are causing negative effects on the environment and even on people, so their removal has become a priority worldwide. Adsorption and the associated technologies where this process occurs (filtration/biofiltration) have gained great interest, due to its low cost, easy operation, and effectiveness mainly in the removal (up to 100%) of lipophilic ECs (log K<sub>ow</sub> > 4). Activated carbon continues to be the most efficient material in the removal of ECs (>850 mg/g). However, other conventional materials (activated carbon, clays, zeolites) and nonconventional materials (agro-industrial/forestry/industrial residues, nanomaterials, among others) have shown efficiencies greater than 90%. Adsorption depends on the physicochemical properties of the materials and ECs. Thus, physical/chemical/thermal modifications and nanomaterial synthesis are the most used procedures to improve adsorption capacity. A material with good adsorptive properties could be used efficiently in filtration/biofiltration technologies. Agro-industrial residues are promising alternatives to be used in these technologies, due to their high availability, low toxicity, and adsorption capacities (up to 350 mg/g). In filtration/biofiltration technologies, the material, in addition to acting as adsorbent, plays a fundamental role in operation and hydraulics. Therefore, selecting the appropriate material improves the efficiency/useful life of the filter/biofilter.

**Keywords:** conventional/non-conventional adsorbents; nanocomposites; lipophilic contaminants; filtration

# 1. Introduction

ECs are organic, pseudo-persistent, and unregulated "new" contaminants detected in water/wastewater in trace concentrations  $(ng/L-\mu g/L)$  [1]. Pharmaceutical and personal care products, hormones, pesticides, and microplastics, among other chemical substances, are some examples of ECs. They reach the environment through effluents from municipal wastewater treatment plants (WWTPs), septic tanks, hospital effluents, livestock activities, and subsurface storage of household and industrial wastes [1,2]. In fact, several antibiotics, such as azithromycin, amoxicillin, and ciprofloxacin, have been found in influents wastewater from Asian, European, and North American countries at concentrations (ng/L) between 3 and 303,500, 0.4 and 13,625, and 6.1 and 246,100, respectively [3,4].



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After reaching the environment, or even inside the WWTPs, some ECs should be degraded/biodegraded to metabolites or gases. An environmental degradation route of ECs is photochemical transformation, which can occur directly by solar UV radiation absorption [5] and indirectly by photosensitized species reaction [6]. For example, diclofenac has demonstrated being photochemically degraded to 1-(8-chlorocarbazolyl) acetic acid and carbazole. ECs' biodegradability depends on their bioavailability, being a more viable process for ECs with octanol-water partitioning coefficients (log  $K_{ow}$ ) between < 1 and > 4 and high polarity (pKa > 0.5) [5,6]. Ibuprofen, natural estrogens, bisphenol A (BPA), and triclosan are some examples of biodegradable ECs, which generate transformation products or metabolites (e.g., triclosan to 2,8-dichlorodibenzo-p-dioxin under UV light), achieving degradation percentages greater than 50% [6]. However, since ECs with Henry's constant values from  $10^{-2}$  to  $10^{-3}$  mol/m<sup>3</sup>Pa do not degrade but rather volatilize, ECs such as dibutyl phthalate, di(2-ethylhexyl) phthalate, and nonylphenol have been found in air samples (0.031–0.055 ng/L) [5–7]. Another important factor controlling the fate/behavior of ECs (removal/bioavailability/degradation/volatilization/transport) is their ease of being sorbed-desorbed. Sorption-desorption processes are related to the partitioning soils/sediments coefficient measured by  $K_d$  [8]. Some antibiotics, hormones, biocides, and artificial sweeteners with low K<sub>d</sub> (300–500 L/kg MLSS) have showed insignificant sorption into sludge [1].

Differences between properties/characteristics/behavior/mobility of different ECs have turned them into substances with potential environmental and human risk, despite their low concentrations. Figure 1 shows the main routes of entry of ECs into the environment, their behavior in it, and the possible effects they could cause in different living beings. Conventional WWTPs do not perform effectively for the removal of ECs. Moreover, conventional wastewater treatment processes/systems/technologies are generally not available or efficient for developing countries, and thus it is necessary to search for options that fit each place [9].



Figure 1. Routes of entry of ECs into the environment, its behavior, and effects.

Adsorption has proven to be the most effective, sustainable, renewable, and selective method with low cost and energy consumption [10]. It allows the removal of contaminants such as heavy metals (metal/adsorbent: nickel, lead/nano polypyrrolepolyethyleneimine [11,12]; zinc/modified fruit peels, graphene oxide + magnetite [13,14]) and dyes (dye/adsorbent: methylene blue, acid orange 10/activated carbon from oil palm waste; methylene blue and crystal violet/Bauhinia forficata residual fruit) [10,15]. Activated carbon is the most used adsorbent, but the high costs of this adsorbent, added to the loss of efficiency in the regeneration process, have made it necessary to search for other alternatives [16].

Although some reviews/research studies have dealt with the removal of ECs through adsorption processes, no bibliographic reviews exist that address the relationship between adsorbent materials and the technologies in which they could be used. This is a limitation because it is necessary to propose real-scale alternatives to remove contaminants from wastewater. Therefore, the objectives of this review are (i) to identify the different adsorbents used in the removal of ECs, (ii) to find the mechanisms involved in the removal of ECs, and (iii) to analyze the relationship between the adsorbent material and the different technologies in which it can be used. To achieve these objectives, the issues presented in Figure 2 are addressed. The different types of ECs, their characteristics, concentration in water resources, and toxicity to some species are first presented. Subsequently, different conventional/non-conventional adsorbents used in the removal of ECs from aqueous media in batch adsorption processes are described. The adsorbent characteristics (e.g., surface area, porosity, functional groups) and their efficiencies/adsorption capacities in the removal of different ECs are shown. The limitation of batch adsorption processes is the volume of treated wastewater/water. Therefore, a relationship between the material and filtration/biofiltration technologies (where adsorption processes occur) used in the removal of ECs is presented. Finally, the conclusions of the work and the outlooks are discussed. To this end, reviews/research papers investigating conventional and non-conventional materials published in the last 10 years were analyzed. However, very little information was found in some materials reviewed, and therefore the search criteria were extended to articles published in the last 20 years.



Figure 2. Topics featured in this review.

# 2. Characteristics, Concentration, and Toxicity of Some ECs in Water Bodies

# 2.1. Pharmaceuticals and Personal Care Products (PPCPs)

There are more than 3000 substances (50-150 g/inhab) used as analgesics/antiinflammatories, antibiotics, contraceptives, antidepressants, and pressure regulators, among others [17]. Meanwhile, around 2000 chemical compounds are used as personal care products, which include fragrances, preservatives, disinfectants, and sun protection agents, among others [18]. Indeed, the PPCPs production has reached about 20 million tons/year [19]. PPCPs have been found in surface water (up to 10,000 mg/L), groundwater (up to 100 mg/L), influents (75–73,730 ng/L), and effluents (24–4800 ng/L) of WWTP, sludge, sediments, and even in living beings (e.g., triclosan in fish at 2100 ng/g) [20,21]. In general, PPCPs can be made of several complex molecules with different structures and shapes, which vary widely according to their molecular weight (88.5 - 900.0 g/mol) [4,14]. Moreover, they are polar molecules with ionizable groups, i.e., in the solid phase, they have different adsorption mechanisms (e.g., ion exchange). Most of them are lipophilic [4]. However, PPCPs have log  $K_{ow}$  values in a wide range (-2.4-13.1), from acid to basic substances under environmental conditions (pKa = 0.6-13.9) [4,22]. PPCPs reach K<sub>d</sub> values between 1.9 and 39,000, are partially/completely soluble in water (0.02–3.12  $\times$  10<sup>5</sup> mg/L, T = 20 °C) [4,19], and have dissipation times between <3 and up to 300 days [18].

Recurrent discharges of PPCPs could cause endocrine problems, genotoxicity, aquatic toxicity, and resistance in pathogenic microorganisms [23]. For instance, diclofenac at concentrations between 5 and 50 mg/L can increase the plasma vitellogenin in fish. It has even caused effects on steppe eagles and vultures [1,18]. Meanwhile, ciprofloxacin, tetracycline, ampicillin, trimethoprim, erythromycin, and sulfamethoxazole can increase the antibiotic resistance of *E. coli* and *Xanthomonas maltophilia* [18,19]. Personal care products, such as benzophenone-3 threaten coral reefs and 4-methylbenzylidene camphor, have been demonstrated to generate embryonic malformations in frogs. Additionally, triclosan produces adverse effects on the first stages of the frog's life [21,24,25]. However, PPCPs also affect humans, as their presence has been detected in breast milk, blood, and urine of children [21]. Furthermore, benzyl paraben and benzophenone-4 were found in the placenta, which could indicate a transfer from mother to fetus [26].

#### 2.2. Pesticides

Until 2020, a use of around 3.5 million tons/year of pesticides was estimated, but only less than 0.1% was used for plants [27]. Some pesticides, such as glyphosate or its main metabolite (amino methyl-phosphonic acid), have been found in surface waters (0.02–6.0 g/L), soil (15.9–1025.5 kg/kg), deep waters ( $0.1 \mu g/L$ ), and sediments (0.1–100 mg/L). Moreover, pesticides with high vapor pressure ( $1.51 \times 10^{-7}$ – $1.29 \times 10^{-1}$  Pa)/high volatility (e.g., pentachlorophenol) are released to the air during their application (between 5 and 90% of them), moving long distances and even reaching pristine areas [28–30]. They have been found in rainfall, e.g., methyl parathion, and also near agricultural sites where they were not applied (~23 µg/L) [28]. According to their molecular structure, pesticides have different chemical properties, reaching weak to strong acid character (pKa = 0.7–9.1), medium to high solubility in water (2.0– $1.2 \times 10^6$  mg/L, T = 20–25 °C), very low to very high bioaccumulation (log K<sub>ow</sub> = -4.6–8.0), and high persistence (7 days–>5 years) [28,30].

Pesticides mainly affect non-target organisms, e.g., atrazine (concentrations in water >200 ng/L) [29] causes sex change in male frogs and affected/altered the reproductive system and fertility of mice, fish, and humans [28,29,31]. Another widely used herbicide is glyphosate, which affects the entire food chain, delaying periphytic colonization and reducing the abundance of aquatic organisms such as *Pseudokirchneriella subcapitata* and *Lemma minor* (EC<sub>50-7d</sub> = 11.2–46.9 and EC<sub>50-4d</sub> = 64.7–270.0 mg a.i./L, respectively) [30,31]. Paraquat produced neurotoxicity and systemic and pulmonary inflammation (inhalation for 16 days) in rats [32]. Furthermore, its use in edible crops is related to antibiotic resistance in humans, even it was classified as a carcinogenic by the World Health Organization [33]. The byproducts/metabolites of pesticides also cause negative effects [28]. For example, aminomethylphosphonic acid produced acute toxicity in *Vibrio fischeri* at concentrations between 50 and 167 mg/L [30].

#### 2.3. Steroid Hormones

The human population generates about 30,000 and 700 kg/year of natural and synthetic estrogens, respectively. Natural estrogens are excreted by the adrenal cortex, testes, ovaries, and placenta of humans and animals (e.g., estrone/E1, 17 $\beta$ -estradiol/E2, estroil/E3) [34]. Meanwhile, synthetic hormones are synthesized from cholesterol (e.g., 17 $\alpha$ -ethinylestradiol/EE2) [34,35]. In specific, synthetic estrogens come from oral contraceptives. However, the estrogen generated by cattle is much higher, amounting to 83,000 kg/year in the US and the European Union alone [36].

WWTPs or feedlot effluents are the main pathways for hormones entering soil, surface water, sediment, and groundwater. They have been found within WWTP influents (>802 ng/L), WWTP effluents (>275 ng/L), surface waters (0.04–667 ng/L), groundwater (5-> 1000 ng/L), drinking water (up to 3500 ng/L), and livestock waste (14-533 ng/g) [3,4]. Steroid hormones are characterized by having a molecular weight between 242 and >296 g/mol, being poorly soluble in water (8.8–441.0 mg/L, at 20  $^{\circ}$ C), with low to moderate hydrophobicity (log  $K_{ow} = 1.6-4.7$ ), weak acid character (pKa = 10.3-18.9), and non-volatile (vapor pressure=  $9 \times 10^{-13}$ - $3 \times 10^{-8}$  Pa) [34,36]. Despite their low persistence ( $t_{half-life} = 0.2-9.0$  days in water/sediments) compared with other ECs, they cause negative effects on ecosystems and humans (cancer and infertility) by their endocrinedisrupting character [4,36]. Chronic exposure of fathead minnow to EE2 (5–6 ng/L) led to feminization of male fish by the development of the ovary cavity, and impaired oogenesis in females [4,34]. E2 at 1 ng/L induced changes in vitellogenin production in males, and produced the feminization of some species of male fish (1–10 ng/L) [34,35]. Levonorgestrel at 6.5 ng/L inhibited spermatogenesis, reduced fish egg production and reproduction, increased female weight and length, and promoted female masculinization [34]. Likewise, EE2 at 10 ng/L affected cardiac function in bullfrog tadpoles [34], reducing the fish biomass and interrupting the aquatic food chain [36].

#### 2.4. Micellaneous ECs

The use/consumption of different products such as fire retardants, food additives, plasticizers, solvent stabilizers, surfactants/detergents, industrial additives (fluorinated organic compounds), and corrosion inhibitors is considerable worldwide [3,37]. In fact, the worldwide production of surfactants was projected to 24.2 million tons for 2022 [38], and plasticizers such as BPA had a production of 2.0 million metric tons/year [5]. Moreover, around 159,000 metric tons/year of synthetic non-nutritional sweeteners are consumed [39,40].

The physicochemical characteristics of these substances are very varied due to the differences between them, which also makes their behavior in the environment different. For instance, artificial sweeteners present between medium and very high solubility (4–1000 g/L, 20 °C), from low to high acid character (pKa = 1.9–11.8), and very low bioaccumulation (log K<sub>ow</sub> = -1.61-0.91) [6,39]. However, other substances such as BPA (plasticizer), nonylphenol (detergent). and Tris(2-chloroethyl) phosphate (TCEP, fire retardant) have from low to high bioaccumulation with log K<sub>ow</sub> values of 3.2, 4.4, and 1.8, respectively [5,41]. Moreover, BPA and phthalates are semi-volatiles, so they easily move into the environment. They have a short half-life (5–18 days) in air because they could be photodegraded [5]. Likewise, fluorinated organic compounds have longer chains exhibiting persistence, from moderately solubility (e.g., perfluoro octane sulfonate = 1.08 g/L) to high solubility (e.g., perfluoro octane sulfonate = 4.5-6.9), and toxic effects [42,43].

In turn, plasticizers are commonly found in surface water (<1–12,000 ng/L), runoff (50–2410 ng/L), and other water sources [5,7]. They include bisphenol type -A/-S/-F and phthalates [5,7,41]. Fluorinated organic compounds have been detected in surface water

(0.09–578,970 ng/L), groundwater (0.17–8.54 ng/L), WWTP influents (65–112  $\mu$ g/L) and WWTPs effluents (43–78  $\mu$ g/L), runoff (~2 ng/L), and drinking water (~54 ng/L) [5,41]. Furthermore, traces of fluorides (0.023–>1600 ng/g) have been found in some species of fish, amphibians, crustaceans, seals, whales, and polar bears [41]. Artificial sweeteners were found in drinking water (36–2400 ng/L), surface water (0.03–9600 ng/L), groundwater (non-detected–33,600  $\mu$ g/L), seawater (200–393 ng/L), and lakes (non-detected–780 ng/L) [6,39].

Ethoxylated alcohol (surfactant) has been reported to affect fish and invertebrates. In fathead minnows, it affects egg production/larval survival, with a non-observed effect concentration (NOEC) ~0.73 mg/L. In species such as bluegills, it affects survival and growth at concentrations ~5.7 mg/L [44]. Non-ionic surfactants and nonylphenol ethoxylates have exhibited acute toxic effects ( $EC_{50} = 1.1-25.4$  mg/L) on tadpoles of four Australian and two exotic frogs [39,44]. In turn, artificial sweeteners such as aspartame (2000–50,000 mg/L) have been reported to cause cancer in rats and headaches, nausea, and vomiting in humans. Meanwhile, 5% sucralose produced thymus shrinkage and migraine in rats and humans, respectively [39].

## 2.5. Microplastics

Microplastics (size = 1-5000 nm) are classified as primary (microbeads from personal care products and cosmetics) and secondary (degradation/fragmentation/leaching of plastics) [45]. Approximately 4130 tons/year of microbeads are used in different personal care products in EU countries plus Norway and Switzerland [45]. In total, plastic waste has reached values around 6300 million tons (oceans = 1.6-4.1%) between 1950 and 2015 [45,46]. More than 400,000 tons microplastics/year (95% from WWTPs) could enter the environment [45]. They were found in lakes and rivers (0.05-320 particles/L)and sediments from shore, water, and benthic at concentrations of 75-1300 particles/m<sup>2</sup>, 2.5–25,800.0 particles/m<sup>3</sup>, and 6.2–980 particles/kg, respectively [45]. A problem associated with microplastics is that those with low density (910–2200 kg/m<sup>3</sup>) could move hydrophobic contaminants long distances [47]. Dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons, chlorinated benzenes, polychlorinated biphenyls (PCBs), organohalogenated pesticides, and endocrine disruptors have been found in microplastics such as polyethylene, polypropylene, PVC, and polystyrene [47]. BPA, polybrominated diphenyl ethers and phthalates, and microplastic additives also have been found in plastic debris at concentrations from 0.1 to 700 ng/g, up to 990 ng/g, and up to 3940 ng/g, respectively [48].

Microplastics produce digestive and locomotion problems, and changes in metabolic profiles in organisms, such as planktonic, crustaceans (e.g., Daphnia magna), fish (e.g., zebrafish), turtles, and whales [47,49]. These ECs could even compromise human health since they have been found in consumer species such as brown shrimp [47,48]. The surface area/shape/size/texture of microplastics is also related to toxicity. Particularly, the smallest microplastics in the form of fibers and a greater surface area have been reported to generate greater toxicity [48]. High-density polyethylene ( $0-80 \mu m$ ) accumulated in the lysosomal system of blue mussels after 1.0 h of exposure. In addition, earthworms of the species Lumbricus terrestris exposed to 450 and 600 g/kg of polyethylene increased their mortality rate between 8 and 25%, respectively. There was also a decrease in their growth and negative effects on the construction of burrows [42]. Polypropylene fibers were more toxic than polyethylene spheres for Hyalella Azteca [45]. Among the most used methods to eliminate microplastics from aqueous medium are physical (sedimentation, membrane filtration), chemical (photocatalytic oxidation, coagulation, ozonation), and biological (conventional activated sludge systems, activated sludge systems + membrane bioreactor, microorganism biodegradation) [44,47-50]. The use of materials is also essential in the elimination of this type of EC, mainly through magnetic separation. Nanomaterials such as magnetic carbon nanotubes and magnetite have been used efficiently [51]. Shia et al. (2022) removed polyethylene, polypropylene, polystyrene, and polyethylene terephthalate (size: 200–900 μm), reaching efficiencies between 62.8 and 86.9% [52].

Table 1 shows the features of some ECs and their concentrations for different water sources. It is observed that there is a wide range of ECs found in different water bodies in their common concentrations (0.01 ng/L–>6010 mg/L). The EC characteristics are also very varied (log  $K_{ow} = -3.4$ –13.9, water solubility = 0.49–21,600 mg/L), which could be a complication when it comes to removing them from water. Lipophilic substances (high log  $K_{ow}$ ) and low water solubility such as carbamazepine (anticonvulsant), triclosan (disinfectant), EE2 (hormones), and musk xylene (fragrance) suggest higher removal efficiency through adsorption processes. Meanwhile, hydrophilic substances (low log  $K_{ow}$ ) and high-water solubility, such as caffeine (stimulant), clofibric acid (lipid regulator), atenolol (beta blocker), and glyphosate (herbicide), are more difficult to remove through adsorption processes. This was verified in the research carried out by León et al. [53], in which triclosan (48.6–76.4%) was more easily removed than caffeine (40.1–67.4%) using agro-industrial residues, under the same operating conditions. Therefore, lipophilic ECs can be removed more easily than hydrophilic by adsorption processes.

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Table 1. Physical and chemical characteristics of some ECs and their concentrations in water bodies.

Notes: Units for data with  $* = million pieces/m^3$ .

#### 3. Adsorbents Used to Remove ECs from Water

The most used adsorbent in the EC removal is activated carbon, due to its high efficiency (up to 100%), large specific surface area ( $300-2500 \text{ m}^2/\text{g}$ ), and hydrophobic interactions [71,72]. The use of alumina, soil, zeolites, clays, composites, metal-organic frameworks, and nanoparticles (carbon nanotubes, magnetic nanoparticles, graphene, etc.) has also been reported [1,35]. However, the widespread use of activated carbon and other adsorbents is limited by their high costs (2000–4000 to 20,000–22,000 USD/ton) [71,72]. This has promoted the search for alternative materials that are inexpensive, widely available, require little processing, and are environmentally friendly [17]. This section describes the most common conventional/non-conventional materials used for EC removal.

#### 3.1. Conventional Materials

## 3.1.1. Activated Carbon

Activated carbon is the most used adsorbent material within WWTPs, with between 5.5 and 8.1% per year between 2008 and 2018, and 3311 thousand metric tons in 2021 [73]. Activated carbon has been recognized as the best adsorbent (adsorption capacity = 12–up to 7800 mg/g, efficiencies = 20–100%) for EC removal [22,71,72]. It has been used for the removal of diazinon, carbamazepine, diclofenac, ibuprofen, naproxen, ketoprofen, triclosan, p-Chloro-m-xylenol [71,72], acetaminophen, androstenedione, E1, E2, E3, EE2, progesterone, testosterone [71], metronidazole [74], paracetamol [75], and nimesulide [76]. Nevertheless, activated carbon is a costly adsorbent whose recovery is difficult and costly, and its efficiency decreases after regeneration (<40%) [72].

#### 3.1.2. Zeolites

Zeolites are natural (Si/Al ratio = 1–5) and low-cost adsorbents (30–120 USD/ton) that are available worldwide [77]. Furthermore, they are synthesized at the laboratory scale, even from residues such as fly ash to obtain higher Si/Al ratios [77]. Zeolites with Si/Al >5 are more efficient in EC removal because they show a high level of hydrophobicity [58]. High hydrophobicity (lower water absorption) allows more zeolite pores to be available for the diffusion/adsorption of ECs. However, zeolites with high silica content are used only at the laboratory scale [78]. Zeolites such as Faujasite, Mordenite, Beta, and ZSM-5 were efficient in the removal of phenol, dichlorophenol [77], tetracycline, oxytetracycline [79], nitrobenzene, carbamazepine, nicotine, erythromycin, nitrosamines [78], and 2,4,6-trichlorophenol [58]. They reached adsorption capacities between 2.4 and 833 mg/g [58,78,80,81] and removal efficiencies from 45% to 90% [77–79,82,83].

# 3.1.3. Clays

Clays are widely used in contaminant removal due to their worldwide abundance and low cost (40–460 USD/ton), being at least 20 times cheaper than activated carbon. Clays were used efficiently (0.1–1900 mg/g) in the removal of ECs [71,84–87], such as amitriptyline, atenolol, metformin, atenolol, buspirone, cliprofloxacin, ranitidine, timolol [87,88], amoxicillin [71,87], diazepam, carbamazepine, clofibric acid, naproxen, salicylic acid, carbamazepine, diclofenac, ibuprofen, naproxen, phenol, atrazine, trimethoprim [86], methomyl [89], atenolol, sulfamethoxazole, and diclofenac [64]. Furthermore, clays have efficiencies like those of activated carbon (>98%) but achieved in longer times. This is because clays have smaller areas (~11 times) than activated carbon [72,86,87,90].

Some results of previous research about EC adsorption using conventional materials previously described are shown in Table 2. Conventional materials are characterized by a high surface area (10–2500 m<sup>2</sup>/g), porosity (0.1–16.9 cm<sup>3</sup>/g) [72,91,92], and the presence of several functional groups (OH, COOH, CO, NH<sub>2</sub>, SiO<sub>2</sub>, cations, etc.) [86,88], which gives them high efficiency (up to 100%). In some studies, efficiencies of conventional materials used in EC removal have been established to range from 20 to 100% [71,77–79]. However, the most efficient conventional adsorbent is still activated carbon [59]. Therefore, the adsorption parameters experience high variation, such as in EC type, concentration, material

dose, pH, and contact time, with the exception of temperature, which is maintained between 20 and 30 °C [64,71,80,87,93]. The diversity in the parameters used in the adsorption processes can be associated with the researcher's aim, which is generally to optimize the process. The differences that exist between the adsorbents and the ECs used in the different studies influence optimization. Temperature is similar in most studies, except those that analyze the thermodynamics of the adsorption process. Because of increasing, it would not be efficient on a larger scale, due to the high costs that it could imply [52,59,67,81]. In turn, some authors have made physical/chemical modifications (e.g., thermal/acid-basic treatments) to the material in order to increase the EC removal efficiency or decrease the adsorbent dose/contact time [84,92].

Ad	sorbent Characteris	tics			Adsorption	n Behavior																			
Adsorbent	Composition/ Functional Groups/Ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference																
			AC from argan waste	Paracetamol Amoxicillin	CT = 0.8–12, T = 25, Ph = 3–11, AD = 0.1, [EC] = 100		~95	512 319	[96]																
				Caffeine		- –	44.1	71.7																	
			Commercial AC	Ibuprofen	$CT = 4, T = 30 \pm 2, pH = 3-8,$ AD = 0.1 [FC] = 1.125-1.252	_	52.7	72.3	[22]																
				Triclosan		_	60.8	70.0																	
			Commercial	Tetracycline	CT = 180, T = 30	van der Waals forces,	-	845.9	[01]																
	C, H, N, S and O [78] COOH, C=O, OH <sup>-</sup> , -NH <sub>2</sub> , CHO, etc. [91]	SA = 300-2500 [78] P = 0.1-16.9 [91,93-95]	GAC	Ibuprofen	AD = 2.4, [EC] = 100		-	239.8	[91]																
Activated carbon (AC):			SA = 300-2500 [78] - P = 0.1-16.9 [91,93-95] -	SA = 300-2500 [78] - P = 0.1-16.9 [91,93-95] - - -	SA = 300–2500 [78] P = 0.1–16.9 [91,93–95]	AC from olive pomace	Niesulide	AD = 0.1–0.5, CT = 6, [EC] = 10–30, pH = 8–11	H-bonding, – dipole–dipole	-	353.3	[76]													
Carbonized carbonaceous materials (S.O.)						[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	[78] P = 0.1–16.9 [91,93–95]	Commercial GAC	Metronidazole	$CT = 2, T = 20 \pm 1$ pH = 3.9-10.2, AD = 5 [EC] = 99.27	exchange, covalent bonding, cation	69.0-80.0	-	[74]						
[, ~]																	-	-	Modified commercial AC	Triclosan	CT = 4, T = 30 ± 2 pH = 6, AD = 0.07, [EC] = 1.0	<ul> <li>bridging and –</li> <li>water bridging</li> <li>[16.63.79.93]</li> </ul>	98.3	395.2	[24]
																			-	-	-	-	-	-	-
					AC from fruit of Butiacapitate	Paracetamol Ketoprofenon	T = 25–55, AD = 0.9, [EC] = 50–300 pH = 7		73.0–98.2	101.2–134.5	[97]														
														-		GAC from coconut shells	Mix: Caffeine, hydro- chlorothiazide, saccharin, sucralose, sul- famethoxazole	T = 25, AD = 0.07, [EC] = 0.5, pH = 2–12, CT = up to 5.5		-	1.21-4.33	[37]			

**Table 2.** Conventional materials used for ECs removal from synthetic water in batch processes.

Adsorbent Characteristics **Adsorption Behavior** Composition/ Adsorption  $SA[m^2/g]$ Adsorption Adsorption Removal Adsorbent Functional Adsorbent EC Removed Capacity Reference  $P[cm^3/g]$ Conditions Mechanism [%] Groups/Ions [mg/g] Zeolite + Hex-CT = 24, Ta = 32, adecyltrimethy-Tb = 42, Tc = 52, Diclofenac lammonium pH = 2-11, Up to 47.4 [81] bromide or AD = 25,chloride [EC] = 636.28 CT = 2, pH = 6,Tetracycline 90 Natural zeolite AD = 6.0. [79] -Oxytetracycli-ne 75 [EC] = 44.4 - 46.0Zeolites: CT = 72, T = 25,van der Waals Si, Al, O Crystalline SA = 300-2300pH = 6,forces and Modified zeolite Mesosulfuron-methyl 2.4 - 3.4[80] microporous and cations [72] AD = 2.0,[72] acid-base forces, aluminosilicate K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, P = 0.10 - 0.35[EC] = 8 donor-acceptor and Mg<sup>2+</sup> [92] (S.O. and N.O.) [92] interaction CT = 2, [60,66] [72] T = roomCu<sup>2+</sup> zeolite 4A Glyphosate pH = 6-8, 112.7 [33] AD = 2.0,[EC] = 100 CT = 24,2,4-dichlorphe-82.6-175.4  $T=28\pm2$ [82] Zeolite Y (ZY) noxyacetic acid, pH = 3, AD = 1.0paraquat 71.4-92.6 [EC] = 20–250 Powdered 7.0-8.5 CT = 6, pH = 6.5,Azithromycin, ofloxacin, 25.3-31.2 zeolites:  $\geq 80$ [83] sulfamethoxazole [EC] = 0.1FAU 1/FAU 2 -

Table 2. Cont.

Ad	sorbent Characteris	tics		Adsorption Behavior								
Adsorbent	Composition/ Functional Groups/Ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference			
			Natural clay	Methomyl	$CT = 3, T = 25 \pm 1 pH = 6.6, AD = 10 [EC] = 19.99-43.71$		27.6–32.9	0.3–0.5	[85]			
Clays: Hydrous aluminosilicates (N.O.) [86,87,98]	$SiO_2, CO_3^{2-}, MO_x [86,98]/$ $Ca^{2+}, Mg^{2+}, H^+, K^+, NH^{4+}, Na^+, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-, and OH^-$ [73,84]	CO <sub>3</sub> <sup>2-</sup> , 86,98]/ [g <sup>2+</sup> , H <sup>+</sup> , SA: 10–426 [ <sup>4+</sup> , Na <sup>+</sup> , [73,84] -, Cl <sup>-</sup> , P: 0.1–0.5 [99] OH <sup>-</sup> ,84]	Bentonite	Atenolol, sulfamethoxazole, diclofenac	CT = 24, T = 20 pH = 6.5–8.0, AD = 1.6 [EC] = 1–50	Ion exchange, coordination, dipole–dipole interactions, van der Waals forces, H-bonding, acid-base forces, donor–acceptor interaction, acid-base forces [87]	Ion exchange, coordination, dipole-dipole	Ion exchange, coordination, dipole-dipole	Ion exchange, coordination, dipole–dipole	-	5.3–24.5 1.1–3.5 1.1–4.0	[64]
			Sodium smectite	Tramadol, doxepin	CT = 16, T = 20 pH = 6–7, AD = - [EC] = 10		-	210.7 279.4	[88]			
			Bentonite + Surfactant	Diuron and their byproducts	$\begin{array}{c} CT = 24, \\ T = 18 - 20 \\ pH = 3, AD = 0.5 \\ [EC] = 0.25 \end{array}$		-	0.1–0.6	[84]			
			Organo- montmorillonites, organo-pillared- montmorillon, organo-acid- activated montmorillonite	2,4,5-trichlorophenol	CT = 2, T = 20 ± 1 pH = 4, AD = - [EC] = 10-200		-	374.9	[90]			
			Natural/modified bentonite	Methomyl	CT = 2, T = 20, 30, 40 pH = 4, AD = 10 [EC] = 0.1		66–76	5	[89]			

Table 2. Cont.

Notes: S.O. = synthetic origin, N.O. = natural origin, CT = contact time [h], T = temperature [°C], AD = adsorbent dose [g/L], [EC] = Emerging contaminant concentration [mg/L], SA = surface area, P = porosity.

#### 3.2. Inorganic Non-Conventional Materials

The use of inorganic non-conventional materials is most common in the removal of dyes and heavy metals. For EC removal, it is preferred to use inorganic materials with acid/basic modifications or impregnated (metal oxides or other functional groups) since this increases their ability to remove them. The modifications can also reduce the contact time/dosage of the adsorbent, just like conventional materials [63,100]. The most widely used non-conventional inorganic materials are alumina, manganese oxides, and silica.

Alumina is an amphoteric oxide (pH < 7 = charge (+) and pH > 7 = charge (-)) [101] not commonly used in EC removal. However, there are some studies in which tetracycline [102], atrazine, norfloxacin, ciprofloxacin [103], propazine, prometryne, propachlor, propanil, molinate and phenols/chlorinated phenols [104,105], acrylic acid [106] and surfactants (sodium octyl sulfate, sodium decyl sulfate, sodium dodecyl sulfate, sodium tetradecyl sulfate) [107] were removed. The efficiency/adsorption capacities have reached values from 15% to 95% and 0.07 to 312.02 mg/g, respectively [104–109]. Meanwhile, manganese oxides  $(MnO_x)$  are considered efficient adsorbents due to their polymorphism, natural availability, easy synthesis at the industrial scale, low cost (50 USD/ton), and non-toxicity [100]. Some ECs, such as mercaptobenzothiazole, EE2, triclosan, tetracycline, endocrine disruptors, steroid estrogens, BPA, glyphosate, chlorophene, oxytetracycline [100], carbamazepine, niclosamide [110], clarithromycin and roxithromycin [111,112], diclofenac [111,113], and resorcinol [114], have been removed using MnO<sub>x</sub>, reaching removal efficiencies between 40% and >90% [100,111,115]. Likewise, silica-based adsorbents are inexpensive and highly available material [102] used in the removal of ECs such as carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, cloprop, norfloxacin, ciprofloxacin, delta-9tetrahydrocannabinol [63,108], naproxen, phenols, cloprop(2-(3-chlorophenoxy) propionic acid, and dihydrocarbamazepine [108]. Silica achieves removal efficiencies from 0% to >90% with adsorption capacities from 2.1 to 429.0 mg/g [63,108,116].

Table 3 summarizes previous studies using inorganic materials for the removal of ECs. Inorganic materials are less used in EC removal, where fewer previous studies were found probably due to their lower adsorption capacity (0.16-52.00 mg/g). This could be associated with the lower surface area (even  $12 \text{ m}^2/\text{g}$ ), porosity (0.53-1.03), and low variety of functional groups. Like adsorption with conventional materials, there are also very varied parameters, but the temperature has been kept in a range between 19 °C and 30 °C.

A	lsorbent Characterist	ics				Adsorption Behavior			
Adsorbent	Composition/ Functional Groups/Ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference
Manganasa ovida:			Manganese oxide	Diclofenac	CT = 33, T = 30, pH = 7.0, AD = 0.61 [EC] = 49,946.41	Up to 90 $\pm$ 0.7	-	[113]	
	Mn(II), Mn(III),		Manganese oxide	Phenol $CT = 1, T = 19,$ $pH = 6.7 \pm 0.5,$ AD = 10.0 [EC] = 0.5	Electrostatic,	~40	-	[114]	
N.O. and S.O. [111]	Mn(IV) or Mn(VII) [100,111]/ Mn-O, OH <sup></sup> [115]	/) or Mn(VII) SA: 12–236 [111] 00,111]/ Mangan 0, OH <sup>-</sup> [115] Mangan +	Manganese oxide	Clarithromycin Roxithromycin	CT = 24, T= 20, pH = 5.0, AD = 1.0 [EC] = 4.94–83.70	interactions, and van der Waals forces [113]	85–90	-	[112]
			Manganese oxide + Fe	Resorcinol	CT = 0.33-2.0, pH = 5.0, AD = 0.0157 [EC] = 35.0		~100	-	[114]
			Manganese oxide birnessite	Niclosamide	$CT = 24, T = 22 \pm 2, pH = 5.0, AD = 0.015 [EC] = 0.042$		-	-	[110]

Table 3. Inorganic non-conventional materials in ECs removal using synthetic water in batch processes.

Α	dsorbent Characterist	ics				Adsorption Behavior						
Adsorbent	Composition/ Functional Groups/Ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference			
			Alumina and surfactant modified alumina	Ortho-Nitro- Phenol	CT = 1, pH = 6.0, AD = 5.0 [EC] = 55.64		-	4.4–7.3	[104]			
<b>Alumina:</b> N.O. and S.O. [105,117]	$MO_x$ , FeO, $SO_4^{2-}$ ,		$\alpha$ -AluminaCnanoparticles andT =ModifiedCiprofloxacin $\alpha$ -AluminapH =nanoparticles[E	CT = 1.5, $T = 25 \pm 2,$ pH = 6, AD = 5, [EC] = 10	Electrostatic	33.6–97.8	34.5	[103]				
	Al <sub>2</sub> O <sub>3</sub> (α, β, γ) [101]/ O-Al-O, OH <sup>-</sup> [115]	AS: 50–300 [101,118]	MCM-41	Norfloxacin	CT = 1, T = 15,interactions and $PH = 3.0-7.0,$ hydrogen bonding $AD = 0.5$ [103,119] $[EC] = 60.0$	>80	52	[106]				
			Raw alumina and Raw alumina modified with HCl	Acrylic acid	CT = 0.5-120, T = 20-50, pH = 4.5, AD = 66.7, [EC] = 0.08		32.1–36.2	0.29–0.31	[109]			
						Alumina and HDTMA modified alumina	Metha- nitrophenol	CT = 1, T = 25–45, pH = 6.0, AD = 5.0 [EC] = 0.4		-	3.0-8.1	[104]
<b>Silica:</b> N.O. and S.O. [63,108]	SiO <sub>2</sub> <sup>-</sup> [63]/ Si-O-H, OH <sup>-</sup> [108]		Silica	Tetracycline	T = 23, pH = 6.0, AD = - [EC] = -		-	-	[102]			
		SiO <sub>2</sub> <sup>-</sup> [63]/ Si-O-H, OH <sup>-</sup> [108]	SiO <sub>2</sub> <sup>-</sup> [63]/ S. Si-O-H, OH <sup>-</sup> [108] I	SiO <sub>2</sub> <sup>-</sup> [63]/ Si-O-H, OH <sup>-</sup> [108]	SiO <sub>2</sub> <sup>-</sup> [63]/ Si-O-H, OH <sup>-</sup> [108]	SA: 7.5–up to 1000 [108,116] P: 0.53–1.03 [109]	Mesoporous silica SBA-15 Carbamaze Diclofen Ibuprofe Ketopro Clofibric	Carbamazepine Diclofenac Ibuprofen Ketoprofen Clofibric acid	CT = 2, T = 25, pHa-d = 5, pHe = 3, AD = 2.0 [EC] = 0.1	H bonds or cationic exchange [108,109] 2.0	35.6–94.3	0.16 0.34 0.41 0.28 0.07

Table 3. Cont.

Notes: S.O. = synthetic origin, N.O. = natural origin, CT = contact time [h], T = temperature [°C], AD = adsorbent dose [g/L], [EC] = emerging contaminant concentration [mg/L], SA = surface area, P = porosity.

## 3.3. Organic Non-Conventional Materials

## 3.3.1. Chitosan

Chitosan is a highly available (1818 tons/year) and non-porous material from a deacetylated derivative of chitin ( $1362 \times 10^6$  tons/year), which is the second most abundant natural organic resource [119]. Chitosan is a relatively low-cost (2200–4400 USD/ton) adsorbent that is non-toxic, biocompatible, biodegradable, and reactive, and that can be easily modified through physical/chemical methods [120–122]. Due to its low adsorption capacity, which is associated with its crystalline and swellable nature, low porosity, hydrophilicity, surface area, and stability in acid media, chitosan is used in composites within wastewater treatment [119]. Chitosan has been used in the removal of phenols [122,123], pramipexole [124,125], alkylbenzene sulfonate, caffeine, sulpiride, bezafibrate [122], sulfamethoxazole, BPA [126], 2,4-dichlorophenol and 2,4,6-trichlorophenol, clofibric acid, tannic acid, and alkylbenzene sulfonate [127]. This material has reached adsorption capacities from 27 to >1500 mg/g and adsorption efficiencies between 11% and 96% [126–128].

#### 3.3.2. Peat

Peat is a complex product of soil and organic matter decomposition, being available throughout the world from a few meters to tens of meters. Thus, it is a low-cost material (40 USD/ton) [120]. Moreover, peat could compete industrially with adsorbents, such as activated carbon and zeolite, due to their high cation exchange capacity. Peat has been used efficiently (>70%, and 1.71–31.40 mg/g) [8,120,128,129] in the removal of sulfamethoxazole, sulfapyridine [130], metolachlor, phenol, p-chlorophenol [120], BPA [129], p-nitrophenol, tri (n-butyl) phosphate, tris (2-butoxyethyl) phosphate, and tris (2-chloroethyl) phosphate [8].

#### 3.3.3. Agricultural/Agro-Industrial Residues

Agricultural/agro-industrial residues, such as fruit peels and seeds, and husk and shells of legume and cereal, are favorable for EC removal. These materials show a high availability, and chemical stability with the presence of lignin (20–30%), cellulose (35–50%), and hemicellulose (15–30%) [55,131]. They have a renewable nature, and low or no cost (e.g., rice husk between 1.6 and 2.7 USD/ton) [131,132]. Moreover, they are environmentally friendly, require little processing (washing, drying, grinding, and sieving), and add value to material that is generally not used to remove contaminants [16]. Agro-industrial residues have been reported to remove acetaminophen, atenolol, caffeine, carbamazepine, diclofenac, ibuprofen, sulfamethoxazole, tetracycline, levofloxacin, ciprofloxacin, atrazine, clofibric acid [17], oxytetracycline, florfenicol [133], norfloxacin [16], and phenolic compounds [95,134–136]. Their removal efficiencies and adsorption capacities have achieved values between 60% and >90% and from 0.37 to 689 mg/g, respectively [16,17,134,137].

#### 3.3.4. Biochar

Biochar exhibits some advantages over common activated carbon, such as high availability, low cost of renewable raw material (350–1200 USD/ton), high surface density of polar functional groups, and condensed structure [138]. Additionally, raw/modified biochar has more environmental applications than activated carbon, e.g., it behaves as a soil amendment and carbon sequestration agent in fuel cells and supercapacitors [138,139]. Biochar is widely used in EC removal at the lab level, achieving similar efficiencies (~95%) and adsorption capacities (>640 mg/g) to those of activated carbon [139–141]. Sulfamethoxazole, sulfathiazole, sulfamethazine, ibuprofen, triclosan, diclofenac, imidacloprid, atrazine, dibutyl phthalate, dimethyl phthalate [141], tetracyclinbe [142,143], benzophene, benzotriazole [144], BPA, E2 [141,144], carbamazepine, metolachlor, EE2, propranolol, phenols, and somepesticides are among the ECs removed [140].

#### 3.3.5. Industrial Waste

Fly ash (combustion residues), red mud (aluminum industry residues), slag (steel industry residues), slurry, and sewage are industrial waste [77]. The management of these

residues can be costly. For instance, sludge treatment represents between 25% and 65% of the water treatment costs [77], making it a problem for municipalities/industries due to the contaminant loading and huge production of them (e.g., municipal sewage sludge from 27 countries of the European Union ~13 million tons/year for 2020) [145]. A possible use for these residues is EC removal, since they are considered good adsorbents due to their characteristics (Table 4) and low cost (20–100 USD/ton) [77,146]. Industrial waste has been used to remove tetracycline [147], sulfamethoxazole, trimethoprim [148,149], dichlorophenoxyacetic acid, phenols [77], carbamazepine [149], BPA, 17-beta-estradiole, 17-alpha-ethinylestradiol, sulfamethyldiazine, sulfamethazine, sulfathiazole, fluoxetine, ibuprofen, carbofuran [145,150], and nimesulide [151]. Removal efficiencies have oscillated from 2% to >90%, while adsorption capacities are between 0.6 and 212 mg/g [77,145,149,152].

#### 3.3.6. Polymeric Adsorbents

Polymeric adsorbents are easily regenerated (soft washing) and their surface could be modified (polar/non-polar) to remove specific contaminants [63]. Furthermore, polymeric adsorbents have lower costs than activated carbon (up to four times). They are produced in a sustainable way and have higher adsorption (15–200 times faster) than activated carbon [63,153]. ECs, such as cephalosporin C, penicillin V, delta-9-tetrahydrocannabinol, nalidixic acid [63], ibuprofen, cephalexin, caffeine, phenols, cefadroxil, erythromycin, BPA, alachlor, trifluralin, prometryn, amitrole [154], diclofenac, and BPA [153,155], have been removed using polymeric adsorbents. In their removal, polymers, such as  $\beta$ -cyclodextrin polymer [153], post-cross-linked polystyrene/poly (methyl acryloyl diethylenetriamine) [156], polystyrene, polyacrylic ester, polyacrylamide, resins (Amberlite XAD-16, XAD-4, XAD-2, XAD-7), and polymer-based inorganic hybrids (polymeric matrix + inorganic nanoparticles), have been used. They have achieved adsorption capacities between 22.2 and 1401 mg/g and removals higher than 90% [63,153,154].

Table 4 summarizes the performance of non-conventional organic materials used as adsorbents for EC removal. Non-conventional organic materials have been widely used in the ECs removal because some of them have a comparable efficiency with conventional materials (up to 100%). This is because they have comparable physical and chemical characteristics, except for their smaller surface area compared to conventional materials. Moreover, non-conventional organic materials exhibit other advantages, such as high availability and low/null cost, and even their use can avoid final disposal problems since some of these materials are residues [55]. Therefore, the use of materials such as these can be an alternative for the treatment of wastewater in developing countries [157].

Adsorbent

Adsorbent Characteristics Composition/

Functional Groups/Ions

SA[m<sup>2</sup>/g] P [cm<sup>3</sup>/g]

Adsorbent

from synthetic wa	ater in batch process	es.		
	Adsorption Behavior			
Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference

Table 4. Organic non-conventional materials used for EC removal

EC Removed

Biochar:	C, H, O, N [139]/ COOH, C=O, OH <sup><math>-</math></sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C $_{6}H_{5}OH$ ,	C, H, O, N [139]/ COOH, C=O, OH <sup>−</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH,	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH,	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, ( $(BCO)^2O$ at [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>−</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH,	C, H, O, N [139]/ COOH, C=O, OH <sup><math>-</math></sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (BCO) <sup>2</sup> O otc. [159]	C, H, O, N [139]/ COOH, C=O, OH <sup><math>-</math></sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (BCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH $^-$ , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	C, H, O, N [139]/ COOH, C=O, OH <sup>-</sup> , RCOOR, C <sub>6</sub> H <sub>5</sub> OH, (RCO) <sup>2</sup> O etc. [158]	AS: 2.46–1500 [139]	Methanol-modified biochar from rice husk	Tetracycline	CT = 0.33, T = 30, pH = 2.0, AD = 1.0 [EC] = 100	Ion exchange, electrostatic, hydrophobic,	-	~80	[143]
5.0. [139]	(RCO) <sup>2</sup> O etc. [158]	P: 0.21–0.95 [144,158]	Modified biochar + Spiruline sp.	Tetracycline	CT = 120, T = 20–40, pH = 3–9, AD = 0.1 [EC] = 100	pore-filling, and bridging interactions [144]	-	132	[142]													
	α-D-glucosamine [159,160]/ OH <sup>-</sup> , -NH <sub>2</sub> [131]		Chitosan and Modified chitosan with 2-hydroxy-1- naphthaldehyde	Phenol 2-chlorophenol 4-chlorophenol 2,4-dichlorophenol 2,4,6-trichlorophenol	CT = 3, T = 20, pH = 7.0, AD = 1.0 [EC] = 150		-	59.7 70.5 96.4 315.5 375.9	[122]													
<b>Chitosan:</b> S.O. [131]		ne AS: 1.1–23.4 [122,127] 1] P: 0.002–0.7 [122,127]	Chitosan grafted with sulfonic acid and cross-linked with glutaraldehyde	Pramipexole	CT = 24, T = 25, pH = 10, [EC] = 0–500	Electrostatic and hydrophobic interactions and hydrogen bonding	-	181	[125]													
				Sulfonate–grafted chitosan	Pramipexole	CT = 0-24, T = 25, 45, 65, pH = 2-12, AD = 1.0 [EC] = 0-500	[101]	11–82	181–367	[124]												
			Magnetic modified chitosan	Phenol BPA	CT = 0.67, T = 45, pH = 4.5, AD = 0.6 [EC] = 376–913		96 85.5	-	[123]													
	Cellulose, lignin, humic acid, fulvic	AS: 0.9->200	Fibric peat modified.	BPA	CT = 4, T = 25, pH = 6.9, AD = 0.05, [EC] = 45.0	Hydrophobic	-	31.4	[128]													
<b>Peat:</b> N.O. [71]	acid [127,131]/ alcohols, aldehydes, ketones, carboxylic acids, and phenolic hydroxides [71,131]	31]/         AS: 0.9->200           hydes,         [71]           oxylic         P: 70-95%           enolic         [71]	Raw/modified peat	BPA	CT = 4, T = 25, pH = 7.0, AD = 1.0 [EC] = 2.0	<ul> <li>Hydrophobic _ interactions, hydrogen bonding [128,129]</li> </ul>	80	1.7	[129]													
		acids, and phenolic hydroxides [71,131]	acids, and phenolic hydroxides [71,131]	acids, and phenolic hydroxides [71,131]	acids, and phenolic hydroxides [71,131]	acids, and phenolic hydroxides [71,131]	acids, and phenolic hydroxides [71,131]	hydroxides [71,131]	les [71,131]	Commercial peat soil	Sulfamethoxazole, sulfapyridine	$CT = 168, T = 25 \pm 3, \\ AD = 20.0, \\ pH = 4.4-9.5 \\ [EC] = 0.15-13.46$	,	-	Up to 4.05 Up to 0.40	[130]						

Table 4. Cont.

	Adsorbent Characteristics	6				Adsorption Behavior			
Adsorbent	Composition/ Functional Groups/Ions	SA[m²/g] P [cm³/g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference
			Rice husk	Norfloverin	CT = 1, T = 25,	_	96.95	20.1	[16]
			Coffee husk	Nornoxacin	PH = 6.2, AD = 3.0 [EC] = 5	_	99.66	33.6	[10]
	Cellulose (35–50%), lignin (20–30%), hemicellulose al (15–30%), and pectin, S. among others [131]/ OH <sup>-</sup> , COH, COOH, P: 0. ROR, RCO-H, RCOR, C <sub>6</sub> H <sub>5</sub> OH, etc. [16]		Rice husk	E1 + E2 + E3	CT = 4, T = 25, AD = 12, [EC] = 3.5–7	45–90	1.0-2.7	[69]	
			Pinecone + Pig manure (BCP)	Sulfamethazine, ciprofloxacin, oxytetracycline, florfenicol	CT = 48, T = 20, pH = 7.6–8.5, AD = 1.0 w/w %, [EC] = 1.2	CT = 48, T = 20, pH = 7.6–8.5, AD = 1.0 w/w %, [EC] = 1.2	-	-	[133]
Agro-industrial		SA: 0.034–120	Mansonia wood 4-nitrophenol	$CT = 2.5, T = 26 \pm 4, pH = 4.0, AD = 1.5 [EC] = 120$	$\Pi-\pi$ interactions, the formation of H-, -COOH, and C = O	22.5–55.5	7.4–18.0	[136]	
residues: N.O. [131]		[131,134] P: 0.03–4.8 [17,134]	Granulated cork	Phenols Phenol, 2-chlorophenol, 2-nitrophenol, 2,4-dichlorophenol, Pentachlorophenol PPCPs Carbamazepine, naproxen, ketoprofen, diclofenac, triclosan, methyl paraben	CT = 0.5, T = 20 ± 2, pH = 6.0, AD = 5-20 [EC](phenols) = 30.0, [EC](PPCPs) = 1.0	bonds, and electrostatic interactions [29,160,161]	Phenols 20-100 PPCPs 50-100	Phenols 0.6-1.6 PPCPs 1.8-3.6	[135]
				Charred sawdust of sheesham	Phenol	$\begin{array}{l} \text{CT} = 1.5, \ \text{T} = 25 \pm 2, \\ \text{pH} = 2\text{-}6, \\ \text{AD} = 0.1\text{-}10 \\ [\text{EC}] = 10\text{-}1000 \end{array}$		>95.0	300.6–337.5
			Sawdust from Finland wood	Phenol	CT = 3, T = 22, pH = 5.79, AD = 10 [EC] = 20		Up to 70.4	Up to 5.5	[137]

Table 4. Cont.

	Adsorbent Characteristic	2S			Ads	orption Behavior						
Adsorbent	Composition/ Functional Groups/Ions	SA[m²/g] P [cm³/g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference			
			Fertilizer and steel industry wastes	2,4- dichlorophenoxyacetic acid, carbofuran	CT = 1.67, T = 25, pH = 6.5–7.5, AD = 1.0 [EC] = 88.01–132.76		-	212 208	[150]			
			Sewage Sludge and fish waste	Carbamazepine+ sulfamethoxazole+ trimethoprim	cpine+ $CT = 5, T = 30,$ (azole+ $pH = 9.39-11.82, AD = 5.0$ prim         [EC] = 100 (Of each one)	-	Up to 41.3 Up to 3.8 Up to 13.6	[149]				
		Deres 2, 24	Sewage Sludge and fish waste	Trimethoprim, sulfamethoxazole	CT = 180, T = 30, pH = 4.53–7.64, AD = 5.0, [EC] = 100		-	90.0 5.3	[148]			
Industrial residuese	SiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , CaO, MgO, organic	Treated or activated: up to 1800.	Paper pulp-based adsorbents + H <sub>3</sub> PO <sub>4</sub>	Carbamazepine, sulfamethoxazole	T = 25, pH = 7.5, [EC] = 5	Polar interaction, hydrogen bonding,	-	$\begin{array}{c}92\pm19\\13\pm0.6\end{array}$	[163]			
Industrial residues: N.O. [145,148]	OH <sup>-</sup> , C=O, COOH, lactone, quinone, etc. [148,162]	[145,149,161] Treated or activated: 0.098-0.145 [149 161]	Phosphoric acid activated corn porous straw carbon	Tetracycline	CT = 12, T = 30, pH = 4, AD = 0.2–1.0 [EC] = 50	<ul> <li>π-π electron-adolor — acceptor, acid-base interactions [133,136,137]</li> </ul>	8.03–97.0	227.3	[147]			
			Activated carbon. from gas mask	Triclosan	$\begin{array}{c} CT = 10, \ T = 24 \pm 1, \\ pH = \text{-}, \ AD = 1 \times 10^{-3} \\ [EC] = 10\text{-}400 \end{array}$		2–100	85	[152]			
			Carbon slurry waste	2-bromophenol, 4-bromophenol, 2,4-dibromophenol	CT = 11, T = 25 ± 2, pH = 5.8–6.8, AD = 1.0 [EC] = 69.2–100.76		-	40.7 170.4 190.2	[162]			
			Activated carbon from sewage sludge	Nimesulide	CT = 2, pH = 8, AD = 1.0		98.6	275.0	[151]			
	Depends on the	Depends on the	Depends on the	Depends on the	,	Post-cross-linked polystyrene/poly (methyl acryloyl diethylenetriamine)	Phenol, benzoic acid, P-hydroxybenzoic acid	CT = 2.0, T = 25, 35, 45, AD = 2.0 [EC] = 507.3		>90	50 190 242.1	[155]
Polymeric	Tertiary amino, Carboxyl, sulfonic		Hyper-crosslinked β-cyclodextrin	BPA	CT = 0.5–12, T = 25, AD = 0.25, [EC] = 40	Hydrophobic interaction, $\pi$ - $\pi$	94.45	278				
Polymeric adsorbents: S.O. [63,152]	acid, dicyandiamide, amidocyanogen, polyethylene glycol, and 2-Carboxy-3/4-	, dicyandiamide, nidocyanogen, yethylene glycol, 12-Carboxy-3/4	Hyper-crosslinked β-cyclodextrin porous polymer	BPA	CT = 0.17, T = room, AD = 1 [EC] = 22.8	<ul> <li>interaction, ionic</li> <li>attraction, hydrogen</li> <li>bonding; complex</li> <li>formation [63,154]</li> </ul>	80–95	22.2	[156]			
	and 2-Carboxy-3/4- nitrobenzoyl, among others [63]	and 2-Carboxy-3/4- nitrobenzoyl, among others [63]		Molecularly Imprinted Polymer	Diclofenac	CT = 1, T = roomtemperature, pH = 7, AD = 5 [EC] = 1-25		100	160	[164]		

Notes: S.O. = synthetic origin, N.O. = natural origin, CT = contact time [h], T = temperature [°C], AD = adsorbent dose [g/L], [EC] = emerging contaminant concentration [mg/L], SA = surface area, P = porosity.

#### 3.4. Nanomaterials

Nanomaterials have at least one size dimension between 1 and 100 nm. In recent years, nanomaterials (nanoparticles, nanotubes, nanofilms, and nanowires) have attracted a lot of interest as wastewater treatment applications, mainly in adsorption and photocatalysis at the lab scale [165,166]. They are called new-generation adsorbents due to their high performance, large surface area (up to 3200 m<sup>2</sup>/g), appropriate dispersibility, catalytic potential, large surface energy, abundant reactive sites, rapid dissolution, high reactivity, and free surface energy (>surface reactivity) [166]. Nevertheless, the recovery of non-magnetic nanoparticles after the EC adsorption is still complicated and some of them have been found to be toxic [167]. Therefore, adequate techniques must be used to separate the nanoparticles from the aqueous solution to take advantage of the benefits that these materials offer.

EC removal efficiencies close to 100% have been achieved using adsorbent doses smaller than micro-adsorbents [168]. Chemical modifications in nanoparticles have been conducted to improve their adsorption capacities [169]. Nevertheless, no study has used modified materials to explain whether or not modifications are sustainable processes to improve EC removal. Thus, there is not enough information about the residues produced after the modification or to verify if the higher efficiency obtained is comparable with the raw material and is costly representative [55,168]. Furthermore, all studies have been carried out at the lab scale, and none of them has analyzed the feasibility of full-scale synthesis of nanomaterials [168]. Carbon-based nanoparticles, metal oxides, metal nanoparticles, and nanocomposites are among the most used nanomaterials in the EC removal. Some of these nanomaterials are described below.

#### 3.4.1. Carbon-Based Nanomaterials

Carbon-based nanomaterials are the most used to remove contaminants from wastewater, due to their good adsorptive characteristics for the removal of organic/inorganic contaminants and microorganisms [62].

# a. Carbon Nanotubes (CNTs)

CNTs are the most anisotropic materials available. They are formed by hollow and layered structures with a length from nanometers to millimeters [170], and can be single wall (SWCNT, cylindrical) or multiple wall (MWCNT, concentric cylinders), with diameters from 0.4–2.0 to 2.0–25.0 nm, respectively [170,171]. CNTs have chemically inert surfaces that promote physical adsorption. However, their surface could be modified by incorporating heteroatoms, thereby increasing their affinity with different ECs, the selectivity of adsorption through families of compounds, and improving its performance in the desorption process [62]. CNTs have been used to remove ECs such as pharmaceuticals (tetracycline, oxytetracycline, sulfamethoxazole, sulfapyridine, sulfamethazine, ciprofloxacin, norfloxacin, ofloxacin, lincomycin, caffeine, etc.) [62,93,166], and personal care products (triclosan) [166], hormones (EE2), phenols, pesticides (atrazine, diuron, dichlobenil, isoproturon) [72,172], and roxarsone [173]. These materials have achieved removals between 67.5% and 99.8% and adsorption capacities between 8.6 and 554.0 mg/g [72,93,166,173,174].

b. Graphene

Graphene is a new material which is considered the thinnest that exists (~0.03 nm). As a nano adsorbent, it includes three forms: pristine graphene, graphene oxide (GO), and reduced graphene oxide (rGO) [175]. Moreover, graphene has faster diffusion or surface reactions of antibiotics, which allows rapid and effective adsorption, and is cheaper at full-scale production than other adsorbents such as CNTs [176,177]. Nevertheless, the hydrophobicity and limited dispersibility of graphene decrease its potential for adsorbent purposes [178]. Graphene is considered a good adsorbent (large delocalized  $\pi$ electron system and tunable chemical properties) [93,176] for the ECs removal (100% and 19–3710 mg/g) [166,176,179,180]. Graphene has been reported for its use for removal of tetrabromobisphenol A, bisphenol A, phenol [9], EE2, E2 [181], diclofenac, levofloxacin, metformin, nimesulide, sulfamethoxazole, efalexin, ofloxacin, amoxilin, tetracycline, ciprofloxacin [176], atenolol, clofibric acid, aminoglycoside,  $\beta$ -lactams, glycopeptide, macrolide, quinolone, sulphonamide [177], acetaminophen [181], metformin [182], and nicotine [183].

#### 3.4.2. Metal-Based Nano Adsorbents

Metal-based nano adsorbents are characterized by their high efficiency for contaminant removal, relatively low cost, and short distance of intraparticle diffusion. Moreover, they can be compressed without changes in their surface area, and are resistant to abrasion, magnetic, and photocatalytic [167]. Additionally, metal oxide nanomaterials are environmentally friendly. Thus, these nanomaterials (iron oxides, aluminum, manganese, titanium, magnesium, and cerium oxides) could be used combined with living beings in filter media, slurry reactors, powders, and pellets [167,184].

Iron oxide nanoparticles are characterized by their relatively easy synthesis, magnetism, recycling capability, relative low cost (e.g., zero-valent iron: 1.66 USD/m<sup>3</sup> of treated water), fast kinetics, and biocompatibility [185–187]. The iron nanoparticles most used in the adsorption processes for EC removal is zero-valent iron. However, magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), and goethite ( $\alpha$ -FeOOH) are also used, but mainly as composites and in degradation processes [167,186].

Zero-valent iron (ZVI) is characterized by having an iron oxide envelope and a Fe<sup>0</sup> core, which exhibits a core shell structure. ZVI shows a high reactivity, higher than conventional granular iron, dual properties of adsorption and reduction (-0.44 V), and easy dispersion [187]. The removal of amoxicillin, norfloxacin, ampicillin, ciprofloxacin, chloramphenicol, dichloroacetamide, metronidazole, diazepam, tetracycline, oxytetracycline, and cytostatic drugs using ZVI has reported values between 50% and 100% [50]. To improve the capacity of zero-valent iron to remove ECs such as florfenicol, tetracycline, metronidazole, and enrofloxacin, chemical modifications were made, achieving removal efficiencies between more than 90% and 100% [50]. ZVI has also been used in continuous adsorption processes for the removal of pharmaceuticals (carbamazepine, caffeine, sulfamethoxazole, 3,4-methylenedioxyamphetamine, 3,4-methylenedioxymethamphetamine, ibuprofen, gemfibrozil, and naproxen) and sweeteners (acesulfame-K and sucralose), reaching efficiencies greater than 97% and 76%, respectively [188]. However, ZVI presents some disadvantages associated with its very short lifetime since it needs stabilization/surface modification and forms clumps due to the van der Waals and magnetic forces [50].

Magnetite is commonly used in the adsorption of contaminants (mainly heavy metals) due to its low cost, environmentally friendly nature, and the possibility of treating large volumes of wastewater [167]. Magnetite was used in the removal of ECs such as lev-ofloxacin [189], caffeine [167], nalidixic acid, salicylic acid, flumequine, benzotriazole [190], paracetamol, ciprofloxacin, diclofenac, and oxytetracycline [191], reporting removal rates between 36.7% and 100.0%, and adsorption capacities from 6.1 to 100.0 mg/g [189–191]. Maghemite is a low-cost material that is highly available. It has been used in the removal of diclofenac, achieving adsorption capacities between 120 and 261 mg/g [192]. Magnetite and maghemite are characterized by their magnetism, which facilitates their separation after the adsorption process [184]. However, these nanoparticles are very unstable because they can change to other phases, and therefore they need to be stabilized before their use. To avoid this problem, these nanoparticles are employed mainly in composites form [191,192].

The other iron oxides used in EC removal are goethite and hematite. Goethite is not magnetic, so its separation from treated wastewater is more complicated than that of magnetite and maghemite [193]. Goethite is an abundant hydrated iron oxide from soils that is used as a model adsorbent due to its thermodynamic stability at room temperature; PPCPs adsorption has also been studied in iron-rich soils [193,194]. Thus, ECs such as levofloxacin [194], diclofenac, ibuprofen [166,195], tetracycline, and flumequine [166] were removed using goethite, showing removal efficiencies between 25% and 90% and adsorption capacities from 0.025 to 0.72 mg/g [166,194,195]. Hematite is the most stable

phase of magnetic iron oxide [185], being used in the removal of cephalexin [196] and carbamazepine [197], and achieving removal efficiencies higher than 90% with adsorption capacities between 2.8 and 70.0 mg/g [196,197].

There are other metal oxides, such as aluminum oxides, zinc oxides, magnesium oxides, and cerium oxides, that are used in contaminant removal. These oxides are characterized by their low cost, thermal stability, easy synthesis and regeneration, surface reactivity, and versatility, among others [118,198,199]. Nano-alumina (dichlorodiphenyltrichloroethane, polychlorinated biphenyls, ciprofloxacin) [103,199], nano-silica (ciprofloxacin) [168], zinc oxide (naphthalene) [31], and magnesium oxide (linezolid) [199] are some nano-oxides used in EC removal that have reached removal efficiencies between 55% and 100% [31,168,198,199].

#### 3.4.3. Nanocomposites

A nanocomposite is a multiphase material where one or more materials are deposited on a support material. The most used support materials are polymers, graphene, zeolites, biochar, clay, CNT, activated carbon, silica, biopolymers (chitosan/cellulose/alginate), membranes, and magnetic substrates [200–202]. Nanocomposites are used in some environmental applications, including the removal of contaminants from wastewater (e.g., heavy metals, ECs, dyes) [202], since they exhibit better characteristics than many adsorbents, including activated carbon. Some properties that are improved when forming nanocomposites and make them better adsorbents are selectivity, stability (mechanical/chemical), porosity, separation of the aqueous medium (magnetism), reduction of adsorption time/adsorbent dose, and cost, among others [200,201].

Another advantage of nanocomposites is their photocatalytic properties. In the EC adsorption processes, these contaminants are only transferred from the aqueous medium to the adsorbent, but they are not degraded [167]. Removing the ECs from the adsorbent to reuse it could be a difficult and expensive process. Therefore, combining adsorption with photocatalysis could be efficient because the ECs will be degraded into less toxic substances [8]. However, nanocomposites/nanoparticles can also have disadvantages, such as a complex synthesis, probably using toxic substances [203]. Non-magnetic nanomaterials are difficult to separate from the aqueous medium. Even previous studies include nanomaterials within ECs [204]. Furthermore, the use of nanomaterials on a large scale is not possible yet.

Table 5 summarizes some studies about the use of nanomaterials for EC removal. Iron oxide nanoparticles, their composites (magnetic character), graphene, and their composites are the nanomaterials commonly used in EC removal. The former is useful for separating the adsorbent from the aqueous medium (magnetic separation), while the latter and its composites can be associated with the high efficiency of the materials; in fact, they have even been used in the adsorption of microplastics. ECs such as tetracycline, sulfachloropyradazine [205], ametryn, prometryn, simazine, simeton and atrazine [203], metolachlor, BPA, tonalide, triclosan, ketoprofen, estriol [206], linezolid [198], carbamazepine, ibuprofen, clofibric acid [57,207], ciprofloxacin, erythromycin, amoxicillin [200,208], diclofenac [209], and sulfamethoxazole [210] and microplastics such as polystyrene [211,212] have been removed using different nanomaterials. They have achieved removal efficiencies between 25% and 100% with adsorption capacities between 0.9 and 3070.0 mg/g [61,121,177,207,213–217]. The application of nanomaterials in adsorption processes has been suggested as a promising alternative, due to adsorption capacities comparable, and even higher, than conventional materials. Indeed, in some studies, the adsorbent doses are lower than other doses. However, the costs and commercial production of nanomaterials are not discussed in these studies [218].

	Adsorbent Characteristic	cs			Ac	Isorption Behavior			
Adsorbent	Composition/ Functional Groups/ions	SA[m²/g] P [cm³/g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference
			*SWCNT	17a-ethinyl estradiol BPA	CT = 4, pH = 3.5–11, T = room, AD = 0.05 [EC] = 2.28–2.96		95–98 75–80	35.5–35.7 13.4–16.1	[171]
	Graphene or graphite sheet with $\pi$ conjugative	SWCNT SA: 400–1020 [62.93]	SWCNT MWCNT	SWCNTLincomycine, Sulfamethoxazole, iopromide $CT = 72, T = 20 \pm 1,$ $pH = 6.0 \pm 0.2, AD = -$ $[EC] = 12,000$ Hydrophobic effect, $\pi - \pi$ interactions,	-	-	[62]		
<b>CNT:</b> S.O. [170,171]	structure and highly hydrophobic surface [170]/	MWCNTs SA: 38.7->500 [93] B = 0.50 [02]	MWCNT	Roxarsone	CT = -, T = 10, pH = 2–11.7, AD = 2 [EC] = 10	<ul> <li>hydrogen bonding,</li> <li>covalent bonding,</li> <li>and electrostatic</li> <li>interactions</li> </ul>	-	Up to 13.5	[172]
	-0n, -C=0, -C00n [72]	r = 0.39 [93]	MWCNT MWCNT-COOH MWCNT-NH <sup>2</sup> N-CNT	1,8dichlorooctane, nalidixic acid, 2-(4-ethylphenoxy) ethanol	$\begin{array}{l} \text{CT} = 72, \text{T} = 25, \\ \text{pH} = 7.0 \pm 0.5, \\ \text{AD} = 0.020.2 \\ [\text{EC}] = 2080 \end{array}$	[165,166]	-	248–380 79–111-	[173]
			MWCNT modified with HNO <sup>3</sup>	Diclofenac	CT = 1, T = 25, pH = 7.0, AD = 5.4, [EC] = 50		Up to 95	Up to 8.6	[174]
			Graphene oxide	β-estradiol 17α-ethynyl estradiol	CT = 0.83, T = 25, pH = 3.0, AD = 0.40 [EC] = 8.0	_	97.2 98.5	- -	[180]
			Graphene oxide	de Diclofenac $CT = 0.25, T = 60,$ pH = 6.0, AD = 0.16 [EC] = 400	96.2	653.9	[175]		
			Graphene oxide	TetrabromoBPA BPA	CT = 24, T = 15–35, pH = 6.0, AD = 1.25 [EC] = 20	<ul> <li>Hydrophobic effect,</li> <li>π-π interactions,</li> <li>hydrogen bonding,</li> <li>covalent bonding,</li> <li>and electrostatic</li> <li>interactions</li> </ul>		19.1 17.5	[9]
<b>Graphene:</b> S.O. [180]	sp <sup>2</sup> hybridized carbon atom [180]/ Epoxide, carbonyl, carboxyl, and	SA: 46.4–2630 (theoretical) [179,180]	Graphene oxide	Metformin	CT = 1-3, T = 1545, pH = 4.5–8.5, AD = 0.05–0.15 [EC] = 300–700		59–97.6	122.6	[182]
	hydroxyl groups [180]	1.0.003 [219,220]	Graphene oxide	Nicotine	CT = 0.5, T = 25–55 pH = 3–10.5 AD = 0.1 [EC] = 5–150	[153,180]	-	96.5	[183]
			Double-oxidized graphene oxide	Acetaminophen	CT = 0.17, T = 25, pH = 8.0, AD = 0.02 [EC] = 10		83.7	704	[181]
			Graphene oxide nanoflakes	BPA, 4-nonylphenol, tetrabromineBPA	CT = 0.08–24, T = 25, pH = 4–9, AD = 1.25, [EC] = 20		-	19–30	[220]
			3D Graphene oxide	Polystyrene microplastics	CT = 2, T = 26, pH = ~7, AD = 1.25, [EC] = 600		-	617.3	[212]

# **Table 5.** Nanomaterials used in ECs removal using synthetic water in batch processes.

Table 5. Cont.

	Adsorbent Characteristic	s			Ad	lsorption Behavior			
Adsorbent	Composition/ Functional Groups/ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference
			Magnetite	Levofloxacin	CT = 0-4, T = 15-45, pH = 6.5, AD = 1.0, [EC] = 2.5-20		36.7-80.1	6.1–6.8	[189]
			Maghemite	Diclofenac	$\begin{array}{l} \text{CT} = 6.25, \text{T} = 25 \pm 1, \\ \text{pH} = 7, \text{AD} = 1.0, \\ \text{[EC]} = 100500 \end{array}$		~90	261	[192]
Iron oxides:	FeO <sub>x</sub> [193,221]/ FeO, OH-, COOH-, C=O [193]	SA: ZVI > 10 Hematite ~30 Goethite 18–83.5	Goethite	Ibuprofen	CT = 2, T = 25, pH = 7, AD = 0.25, [EC] = 1.65–2.06	-	89–91	0.72–3.47	[195]
N.O. and S.O. [192,193]		Magnetite 40–300 Maghemite 31–178 [40,167,192,193] B: Magnetite = 0.22	Goethite	Diclofenac	CT = 0.08–48, T = 25, pH = 5.3–10, AD = 10, [EC] = 1	hydroxyethyl cleavage and chelation [40,167,192,193,196] –	hydroxyethyl cleavage and chelation	75	-
		[216]	Hematite	Cephalexin	CT = 0.08–6.67, T = 25, pH = 2–10, AD = 2, [EC] = 25–250		~99.7	70	[196]
			Hematite and goethite	4-n-nonylphenol	CT = 24, T = Room T, pH = 7.0–9.0, AD = 100, [EC] = 1.5		-	-	[222]
			Magnetite	Oxytetracycline	T = 5–35, pH = 5.6, AD = 2.5–20, [EC] = 868.86		60–100	-	[191]
Nano-alumina: S.O. [101]	$\begin{array}{c} MO_x, FeO, SO_4^{2-}, \\ Al_2O_3 (\alpha, \beta, \gamma) \\ [101] / O-Al-O, OH-, \\ C=O [101] \end{array}$	SA: 143.7 [223] P: 3 [223]	Nano-alumina	Dichlorodiphenyltri- chloroethane, Polychlorinated biphenyls	CT = 0.33, T = 28–34, [EC] = 10–60	Hydrophobic.	54–68	Up to 0.18 Up to 0.16	[224]
Nano-silica: S.O. [63,102]	SiO <sub>2</sub> [102]/ Si-O-H, OH <sup>-</sup> [63]	Information not available	Nano- silica/modified nano-silica	Ciprofloxacin	$CT = 3.33, T = 25 \pm 2, pH = 3-7, AD = 1-50, [EC] = 20$	hydrogen bonding, and van der Waals, Electrostatic interactions	56.8–89.9	85	[168]
ZnO: S.O.	Zn, O/ Zn-O, O-H, C-H	SA: ~14.8	ZnO	Naphthalene	$\begin{array}{c} {\rm CT}=1,{\rm T}=25\pm2,\\ {\rm pH}=212,{\rm AD}=600\\ [{\rm EC}]=25 \end{array}$	$\begin{array}{c} -  [63,101,102,223] \\ \Pi -\pi \text{ interaction,} \\ \text{electron donor} \\ \text{acceptors} \end{array}$	100	148.3	[26]
<b>MgO:</b> S.O. [200]	MgO [202] Mg-O, OH- [200]	SA: 48–108 [200] P: 0.3–24.8 [200]	MgO	Linezolid	CT = 1, T = 35, pH = 3-8, AD = 0.2-0.8 [EC] = 10-100	[200]	~62	123.4	[198]

Table 5. Cont.

	Adsorbent Characteristics	1			Ad	sorption Behavior															
Adsorbent	Composition/ Functional Groups/ions	SA[m²/g] P [cm³/g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference												
		$\begin{array}{c} \text{MOFs} \\ \text{UIO-66} \end{array} \qquad \begin{array}{c} \text{Sulfachloropyra-} \\ \text{dazine} \end{array} \qquad \begin{array}{c} \text{CT} = 2, \text{ T} = 25, \text{ pH} = 5.5, \\ \text{AD} = 0.1, \\ [\text{EC}] = 10100 \end{array}$		80	417	[205]															
<b>Nano-composites:</b> S.O. [177,179,202,203]	Depends on the components of the composite, e.g., carbon atom, FeOx, graphene, and graphite sheet, among others/ Depends on the composite, e.g., OH-, COOH-, C=O, epoxy, and amino, among others [178,179,223,225]	Denon de en the	Triclosan         Bisphenol-A         Magnetic activated       Tonalide       CT = 1, T = 25-45, pH = 7,         carbon       Metolachlor       AD = -, [EC] = 0.025-0.25         Ketoprofen       E2       Depends on the	96–98	21.32 31.05 29.41 22.37 28.49 20.20	[206]															
		pends on the ponents of the nposite, e.g., n atom, FeO <sub>x</sub> ,	Magnetic activated carbon	Carbamazepine	CT = 0.5, T = 25, pH = 6.65, AD = 0.05, [EC] = 20.0	<ul> <li>components of the composite, are an example hydrogen</li> <li>bonding, π-π interaction, cation-π bonding, and amidation reaction, electrostatic interaction, hydrophobic</li> <li>interaction, ligand exchange, cation-π bonding, chemisorption, etc.</li> </ul>	components of the composite, are an example hydrogen bonding, $\pi$ – $\pi$	components of the composite, are an example hydrogen bonding, $\pi$ – $\pi$	93	189.5	[214]										
		SA: 3.18- around 1260 [201] P: 0.15-0.72 [178,223,225]	Triethoxyphenylsilane (TECs)- functionalized magnetic palm-based powdered AC	BPA, carbamazepine, ibuprofen, clofibric acid	CT = 6, T = Room T, pH = 7, AD = 0.1, [EC] = 10		-	58.1–166.7	[207]												
			Magnetic activated carbon/chitosan	Ciprofloxacin, erythromycin, amoxicillin	CT = 2, T = 25, pH = -, AD = 1.5, [EC] = -		54-82	90.1 178.6 526.3	[200]												
		[1/0,1/7,220,220]	[110,179,223,223]	[1,0,1/7,220,220]	[ <i>1</i> ,0,17,9,223,223]	[1/0,1/9,229,229]	[1/8,1/9,223,225]	[178,179,223,225]	[1/8,1/9,223,225]	[~, 0, 1, 2, 120, 120]	[,,]	[1,0,1,7,220,220]	[110,119,220,220]		Magnetic cellulose ionomer/layered double hydroxide	Diclofenac	CT = 0.5, T = -, pH = 9, AD = 1.0, [EC] = 0.5	[178,225,226]	~100	268	[209]
			Magnetic chitosan grafted graphene oxide	Ciprofloxa-cin	CT= 8, T= -, pH = 5, AD = 0.33, [EC] = 20	-				-	-	282.9	[208]								
		Fe	Fe <sub>3</sub> O <sub>4</sub> /graphene oxide reduced	Ametryn, atrazine prometryn, simazine, simeton	CT = 1.17, T= 25, pH = 5.0, AD = 0.5, [EC] = 10	_	93.6	54.8-63.7	[203]												
			Magnetically modified graphene nanoplatelets	Amoxicillin	CT = 1.5, T = 20, pH = 5, AD = 2.0, [EC] = 10.0	_	84	14.1	[225]												

Table 5. Cont.

Adsorbent Characteristics				Adsorption Behavior					
Adsorbent	Composition/ Functional Groups/ions	SA[m <sup>2</sup> /g] P [cm <sup>3</sup> /g]	Adsorbent	EC Removed	Adsorption Conditions	Adsorption Mechanism	Removal [%]	Adsorption Capacity [mg/g]	Reference
			Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> - Chitosan/GO	Tetracycline	CT = 8, T = 25, pH = 6, AD = 0.4, [EC] = 44.44		>90	-	
			Fe/Cu-GO	Tetracycline	CT = 0.25, T = 22, pH = 6.5, AD = 0.25, [EC] = 20-100		~100%	-	[176]
			GO-BC	Sulfamethazine	CT = 12, T = 25, pH = 6, AD = 1, [EC] = 2031.8–20,332		-	-	_
			Sawdust+ FeCl <sub>3</sub>	Tetracycline	CT = 2.0, T = 22 ± 2, pH = 7.8, AD = 4.0, [EC] = 20		-	~5.4	[213]
			Biochar + Chitosan	Ciprofloxacin	CT = 48, T = 20, pH = 3.0, AD = 5.0, [EC] = 160			>76	[217]
			Magnetic bamboo-based activated carbon	Ciprofloxacin, norfloxacin	CT = 24, T = 25, pH = 6, AD = 2.0, [EC] = 300		-	245.6 293.2	[215]
			Magnetic pine sawdust biochar	Sulfamethoxazole	$CT = 24, pH = 7 \pm 0.10,$ [EC] = 0.17–78		-	51.8-87.9	[216]
			Maize straw + manganese/iron oxides	Tylosin	CT = 0.25–24, T = 25, pH = 3–11, AD = 2, [EC] = 20		-	3070	[226]
			Palm-shell waste AC + magnesium silicate	BPA	$CT = 24, T = 24 \pm 1, \\ pH = 4.5, AD = 0.1, \\ [EC] = 10-100$		_	168.4	[227]
			Chitin + GO+ O-C <sub>3</sub> N <sub>4</sub>	Carboxylate- modified PE, amine-modified PE, PE (~1 µm)	CT = 48, T = 25, pH = 7, [EC] = 1.0		71.6–92.1	5.4–9.7	[213]

Notes: S.O. = synthetic origin, N.O. = natural origin, CT = contact time [h], T = temperature [°C], AD = adsorbent dose [g/L], [EC] = emerging contaminant concentration [mg/L], SA = surface area, P = porosity, PE = polystyrene.

After reviewing a series of adsorbents used in the removal of ECs, it is observed that some parameters that influence the adsorption process are the nature of the adsorbent (morphology, SA, P, functional groups), the adsorbent dose (a higher dose favors adsorption), the contact time (longer contact times do not necessarily favor adsorption), particle size (smaller size favor the adsorption), and pH [52,54,98,168]. pH depends on the isoelectric point of the adsorbent; however, there is no mention of whether the pH modification would be profitable and friendly at real scale [222]. Furthermore, characteristics such as the solubility and lipophilicity of EC influence its removal through adsorption processes [4]. Likewise, it is observed that the removal mechanisms are related to the characteristics/properties/structure of the adsorbent and contaminant [32]. The dominant mechanisms in the removal of ECs are physical interactions such as electrostatic interactions, hydrogen bonds, etc. [32,35,99,222–224]. However, graphene oxide, silica, and some nanocomposites also show chemical interactions such as ion exchange and covalent bonding. Iron oxides also appeared to chelation forces by removing some ECs [167,179,180,182,183].

On the other hand, the regeneration of the adsorbents occurs only in some studies. Among the commonly regenerated materials are activated carbon, zeolite, modified adsorbents, and some nanomaterials [71,158,168,213]. Adsorbent regeneration is associated with the adsorbent cost. In fact, there are materials such as agro-industrial residues that are not regenerated. Probably, it is related to their high availability and low cost [55,161]. In addition, although the efficiency obtained by the adsorbent after regeneration is analyzed, the environmental impact that this process can generate is not indicated. Likewise, the reuse of the saturated material (after the adsorption process) is not shown in the bibliography used in this study [158,169,213].

The results in batch adsorption processes allow orientations to work that involve continuous adsorption processes [55]. However, the optimal conditions of the batch adsorption process cannot be transferred to fixed-bed columns. In fact, other evaluations are carried out, such as the saturation time of the filter material, determination of the rupture curve, etc. [75]. Furthermore, few studies present an adsorption study in batch process and fixed-bed columns [75,98,152].

#### 4. Technologies Using Adsorbent Materials to Remove ECs from Wastewater

Adsorption processes alone or in combination with other mechanisms are used and studied in different filtration and biofiltration technologies at different levels (lab/pilot/full). In biofiltration technologies, the materials used, in addition to adsorbing the contaminants, fulfill other fundamental functions. They act as a support medium for microorganisms (bacteria) and plants and retain nutrients, organic matter, and solids, among others [55,157]. Therefore, the adsorbent materials must meet several requirements to achieve high efficiencies in the contaminant removal and for the proper operation of the technologies. Material characteristics, cost, availability, hydraulic performance (clogging), feasibility, adsorption capacity, toxicity with living beings, chemical/mechanical stability, recoverability, and disposal ease are factors considered [43]. Adequate adsorbent materials improve the operation and the efficiency of filtration/biofiltration technologies. Some of the alternative materials and mechanisms for EC removal are shown in Figure 3. However, very little research has been conducted on the adsorbent material–technology relationship. Therefore, in this section, a review of the subject is carried out.

#### 4.1. Filtration Technologies

Fixed-bed columns or filtration technologies are low-cost and easy to operate technologies (lab/full-scale) that have low energy consumption and are easily scaled. Filtration technologies are used to treat secondary/tertiary effluents, achieving good efficiencies (up to 100%) for organic matter and specific contaminants [157]. The mechanisms for the contaminant removal are produced on the materials used as filter beds. These mechanisms



depend on the contaminant nature, bed depth, quantity, packaging, size, and the feature of the material.

# Alternatives and mechanisms to remove ECs

Figure 3. Alternatives and mechanisms to remove ECs in batch and filtration technologies.

To improve contaminant removal in fixed-bed columns, they are conditioned with microorganisms, giving origin to biofilters. Biofilters are more used than filters in EC removal. Moreover, depending on the retention time (RT) or hydraulic load rate (HLR) used in filters/biofilters, there could be rapid or slow filtration [228]. Considering the feeding type, filters/biofilters could be continuous or intermittent. In the next paragraphs, the main characteristics of these processes are summarized.

#### 4.1.1. Rapid Filtration

Rapid filtration is widely used worldwide in water purification processes (low consumption of energy and chemical products) [228]; they operate with a TOC loading ~3.1 mg/L and organic loading = 3.7-36.7 g/m<sup>3</sup>d [229]. Rapid filters are already used in existing drinking water treatment plants; despite not being designed to eliminate Ecs, rapid filters have partially degraded (even >50%) several of them [230]. Materials such as activated carbon, anthracite, garnet, and pumice have been used. However, sand (0.4–1.5 mm) is the most used material in them [228]. The mechanisms observed in EC removal are adsorption on sand, oxidation, and adsorption by metal oxides (FeO<sub>x</sub>/MnO<sub>x</sub>/bio-MnO<sub>x</sub>), and biodegradation by autotrophic and heterotrophic bacteria. However, biodegradation has been determined to be more significant than adsorption (only 10–15%) [228].

The hydraulic retention time (3.3–33.3 h) in rapid filters is essential in EC removal. Reducing the time by half decreases the removal efficiency (>10%) of triclosan, galaxolide, tonalide, and celestolide [231]. Other ECs such as bentazone [231,232], carbofuran, triclosan, gemfibrozil, ketoprofen, caffeine, erythromycin, naproxen, carbamil, benzenesulfonamide, microsistin-LR [228], dichlorprop [232], atrazine, bentazon, and carbamazepine [231], present in surface and groundwater, were removed. The removal efficiencies in fast filters (microcosm, columns, field) have reported to be variable (0–99%) [228,231–234].

# 4.1.2. Slow Filtration

Slow filtration has a lower filtration rate (1/20 or less) than rapid filtration and does not require prior chemical coagulation [235]. Moreover, slow filtration is a technology with low operational costs (low energy consumption) and simplicity in operation and maintenance. The most common filter material is also sand (0.1–0.4 mm); however, coarse sand and other materials (e.g., GAC, quartz/silica) have been used [236]. Slow filtration is combined with microbiological action, so biosorption/biodegradation occurs, phenomena that predominate over adsorption. Adsorption, mechanical filtration, and degradation processes could occur after biodegradation. In this case, the material not only absorbs ECs, but also fulfills other functions such as being a support for microorganisms and retaining their food until they consume it [237]. Slow filtration has been used in the removal of ECs such as paracetamol, diclofenac, naproxen, ibuprofen, methylparaben, benzophenone-3, E1, E3, EE2 [235], propranolol, iopromide, diclofenac, tebuconazole, and propiconazole [238], among others, achieving removal rates between <15 and >98% [235].

#### 4.2. Biofiltration

Biofiltration is a biological filtration. Initially, the adsorption in the filter bed material is an exclusive process. However, over time, the active sites of the material become saturated, and this mechanism diminishes, so that other mechanisms begin to predominate. In the second stage, biological adsorption–degradation occurs due to the presence of aerobic, anaerobic, facultative microorganisms, bacteria, fungi, algae, and protozoa [55]. At this stage, the function of the adsorbent is also to offer a specific area for the growth of bacteria/plants/earthworm. Adsorption decreases until only biological degradation occurs, in the third stage. Therefore, the parameters that determine the biofilter efficiency are the surface characteristics of the material (pore size, specific surface area, functional groups), the degree of compaction, the hydrophobicity of the bacteria, and the adsorbent [157]. Biofiltration technologies for EC removal are generally used as secondary treatment when there is a high load of organic matter or tertiary treatment. Constructed wetlands (CWs), vermifiltres, and biofilters are the types of biofiltration technology [239–241].

# 4.2.1. Biofilters

In biofilters such as water percolates through filter bed material, microorganisms attach to the material surface (diffusion, convection, sedimentation, and active mobility of microbial cells), colonize it, and form stable biofilms (able to resist/degrade even toxic contaminants) [241]. Materials such as clay, anthracite, activated carbon, and sand are used conventionally as adsorbents to remove ECs in biofilters. Activated carbon has been shown to be efficient in removing pesticides, but not for personal care products and endocrine disruptors. Other materials such as biochar, rice husk (raw/biochar), peanut shells, fruit peels, sawdust, wood chips, or mixtures thereof are used [157,158,240]. These materials have proven to be efficient for removing some ECs (0–100%) [242–245] such as  $17\beta$ -estradiol- $17\alpha$ -acetate, pentachlorophenol, 4-tert-octylphenol, caffeine, gemfibrozil, BPA, benzophenone, atrazine, dicamba, triclosan [246], acetaminophen, erythromycin, sulfamethoxazole, cotinine, aminotrizaole, ibuprofen, atrazine, and naproxen, among others [244]. The removal mechanisms of ECs in biofilters are adsorption and biodegradation, produced by the filter bed material/biofilm and microorganisms, respectively [241]. Nevertheless, oxidation (in the material) could occur if other filter materials are used (e.g., manganese oxide) [244].

#### 4.2.2. Constructed Wetlands

Constructed wetlands (generally used as secondary treatment) are systems formed by plants (macrophytes/ornamental), substrates (support materials), native microorganisms, and water interacting with each other [246]. The substrate is fundamental in the efficiency of CWs since it fulfills physical, chemical, and biological functions to remove contaminants. Furthermore, the materials are the support medium (allow growth) of plants and microorganisms [2]. Other support material functions include physical sedimentation, filtration,

and gas diffusion between the material particle gap [247]. The conventional materials used are soil, sand, and gravel (8–16 mm), even in the removal of ECs [245,248]. Moreover, red soil, volcanic rock, stone, vesuvianite, zeolite, and brick were used. At the lab scale, materials such as rice husk, pine bark, and granulated cork were used for EC removal [247].

Different types of CWs (surface free water, horizontal groundwater flow, vertical groundwater flow, and hybrid CWs) at full/mesocosm/microcosm/pilot/lab scale were used for the removal of several ECs [245,247,248]. The removal mechanisms of the ECs are produced by their sorption in the material support (hydrophobic partitioning, van der Waals interaction, electrostatic interaction, ion exchange, and surface complexation), plant uptake (phytostabilization, phytoaccumulation, phytodegradation), and/or biodegradation aerobic/anaerobic process. However, the main mechanisms in the EC removal are biodegradation and sorption [53,246]. Among the ECs removed (0 and >99%) were phenols, diclofenac, naproxen, atrazine, endosulfan, erythromycin, clarithromycin, azithromycin, E1, E2, carbamazepine, gemfibrozil, sulfamethoxazole, sulfapyridine, ibuprofen, acetaminophen, triclosan, and BPA, among others [245,247,248].

## 4.2.3. Vermifilters

Vermifilters are engineering systems made up of earthworms, microorganisms (biotic component), and a filter material (abiotic component) that maintain symbiotic relationships. The main function of earthworms is to regulate microbial activity and biomass while microorganisms biodegrade waste materials/contaminants [249]. Earthworm species (Eisenia foetida, Lumbricus rubellus, Eudrilus eugeniae, and Eisenia Andrei) are suspended on a filtration bed (active zone of earthworms) that can be soil, compost, and cow manure, where the degradation of contaminants occurs [250]. However, alternative materials (in toxicity tests and mesocosm scale) such as coconut fiber, corn cob, peanut shells, and rice husks are also used [55,157]. In turn, sand, gravel, cobblestone, and quartz sand are used as filter beds [250]. Vermifilters were used in the removal of ECs such as ciprofloxacin, ofloxacin, sulfamethoxazole, trimethoprim, tetracycline, metronidazole [251], amoxicillin, ampicillin, ticarcillin, ceftazidime, cefotaxime, ceftriaxone, streptomycin, gentamicin, erythromycin, tetracycline, chloramphenicol, and ciprofloxacin [249]. Removal efficiencies between 40% and 98% were reached [251]. The mechanisms involved in the removal of ECs were absorption/degradation by earthworms, adsorption/degradation in the biofilm, biodegradation under the load of the microorganisms, and sorption in the bed filter material [249,251].

Table 6 shows the operating conditions of different types of filters/biofilters that were used in the removal of some ECs. In addition, the material(s) used in the technologies and the mechanism by which the ECs were removed are indicated. It is observed that biofilters are more used than filters for the removal of ECs. Biofilters (fast and slow) that use sand as a filter bed are used to remove ECs present mainly in surface and groundwater. Additionally, the presence of living organisms (microorganisms, plants, and earthworms) improves the efficiency of EC removal. However, vermifilters are the least used biofilters (there is little previous research) in the removal of ECs compared to CWs and biofilters.

Type of Filtration (Scale)	Bed Filter Material (Size, mm)	Influent Type	EC Removed	<b>Operational Conditions</b>	Removal Mechanism	Removal [%]	Reference
Aerated rapid filtration.	Sand (3–5)	Anaerobic groundwater	Mecoprop, bentazone, glyphosate, p-nitrophenol	$[EC] = 3 \times 10^{-5} - 2.4 \times 10^{-3},$ RT = 0.17	Biodegradation	1–85	[232]
(interocount scale)			Dichlorprop	$[EC] = 2 \times 10^{-4}$ , RT = 0.93	- –	>50	[232]
Rapid filtration (microcosms scale)	Sand (3–5)	Anaerobic groundwater	Bentazone	[EC] = 5, RT = 312	Biodegradation	92	[231]
Rapid filtration (microcosms scale)	Filtralite clay (0.8–1.6)	Groundwater enriched with Ecs	2,6-dichlorobenzamide, bromoxynil, chlorotoluron, diuron, ioxynil, isoproturon, linuron, 4-chloro-2-methylphenoxy acetic acid	$[EC] = 2.1 \times 10^{-3} - 6.6 \times 10^{-3},$ RT = 0.023, FR = 21	Biodegradation	13–98	[234]
Rapid filtration (lab scale)	Sand	Influent water from the RSF filters (WRK, Nieuwegein, The Netherlands) enriched with Ecs	Atrazine, bentazon, metolachlor and clofibric acid, carbamazepine	[EC] = 0.01, RT = 8 and 96, FR = 80	Biodegradation/Sorption	-	[233]
Rapid filtration: downflow, upflow, dual media down flow (field scale)	Sand (0.7–2.5) Sand + hydroanthracite (1.4–2.5) Sand + anthracite (1.6–2.5)	Surface water from The Netherlands and Belgium	Caffeine, acesulfame-K, sucralose, metformin, phenazone, chloridazon, valsartan, sulfadiazine, sotalol, etc	$\begin{split} [EC] &\leq 1 \times 10^{-5} 5.7 \times 10^{-4} \\ &RT = 15240 \end{split}$	Biodegradation/Sorption (probably)	0–93	[230]
Slow filtration with rapid pulses of a carbon source (lab scale)	Quartz sand (0.210–0.297)	WWTP effluent	Atenolol, metoprolol, iopromide, iomeprol, carbamazepine, diclofenac, sulfadiazine, sulfamethoxazole, etc.	RT = 150, FR = 0.15	Biodegradation	-	[229]
GAC sandwich slow filtration (lab scale)	Coarse sand (0.6) GAC (0.4–1.7) Coarse sand+ GAC	Synthetic wastewater	Mix of DEET, paracetamol, caffeine and triclosan	[EC] = 0.025, HLR = 5, 10, 20	Adsorption (GAC) + Biodegradation	18.8–100	[236]
Slow filtration (pilot scale)	Silica sand (0.15–0.30) Support: pea gravel	Stream water/Stream water+ 1% of primary effluent added, both enriched with Ecs	Caffeine, carbamazepine, 17-β estradiol, E1, gemfibrozil, phenazone	[EC] = 0.05, HLR = 5	Sorption and/or biodegradation	<10–100	[252]
Household slow filtration with intermittent and continuous flows (pilot scale)	Sand (0.09–0.5) Support: coarse sand (1–3)+ fine gravel (3–6) + coarse gravel (10–12) Top: non-woven polyester	Synthetic wastewater	BPA	[EC] = 2.35Continuous flow HLR = 1.58 Intermittent flow HLR = 0-875	Biodegradation	Continuous flow $14 \pm 6$ Intermittent flow $3 \pm 8$	[253]

**Table 6.** Technologies using materials to remove ECs from wastewater.

Table 6. Cont.

Type of Filtration (Scale)	Bed Filter Material (Size, mm)	Influent Type	EC Removed	Operational Conditions	Removal Mechanism	Removal [%]	Reference
Biofilters (bench scale)	GAC (1.0-1.2) and anthracite (0.8–2.0)/sand (0.55–0.65) dual media	Municipal waste streams	Acetaminophen, ibuprofen, erythromycin, sulfamethoxazole, trimethoprim, carbamazepine, atenolol, gemfibrozil, tri(2-chloroethyl) phosphate, DEET, cotinine, aminotrizaole, atrazine, caffeine, E2, iopromide	[EC] = $2.27 \times 10^{-4}$ - $6.44 \times 10^{-3}$ RT = 0.17 and 0.30	Biodegradation	>75	[242]
Biofilters (pilot scale)	Anthracite/sand (1.07/0.52)	Superficial water of Grand River enriched with Ecs	DEET, atrazine, naproxen, ibuprofen, nonylphenol, carbamazepine	$[EC] = 5 \times 10^{-4} - 5 \times 10^{-3}$ , RT = 0.08 and 0.23, HLR = 500	Adsorption (non-biodegradable Ecs) and biodegradation (biodegradable Ecs)	<20-100	[243]
Biofilters (pilot scale)	GAC/sand and anthracite/sand	Water from the full-scale recarbonation chambers enriched with Ecs	Atenolol, atrazine, carbamazepine, fluoxetine, gemfibrozil, metolachlor, sulfamethoxazole, tris(2-chloroethyl) phosphate	$[EC] = 1 \times 10^{-4} - 2 \times 10^{-4},$ $1 \times 10^{-3} - 3 \times 10^{-3},$ RT = 8.4  and  4.2, HLR = 488  and  976	Adsorption and biodegradation	GAC/sand: 49.1–94.4 anthracite/sand: 0–66.1	[254]
Biofilters (pilot scale)	Anthracite-sand and previously used biological activated carbon (BAC)-sand dual media, BAC = (0.9)	Raw surface water (Colorado River) enriched with Ecs	Sulfamethoxazole, caffeine, gemfibrozil, naproxen, DEET, trimethoprim, acetaminophen, ibuprofen, sucralose, meprobamate	$[EC] = 1 \times 10^{-4} - \times 10^{-3},$ RT = 0.17, HLR = 904.56	Biodegradation and BAC sorption	<50->99	[242]
Biofilters (pilot scale)	Natural manganese oxides (3–5)	Secondary effluent of WWTP	1-hydroxybenzotriazol, 4'-hydroxydiclofenac, 10.11-dihydro-10.11- dihydroxycarbamazepine, acyclovir, benzotriazole, diclofenac, carbamazepine, carboxy-acyclovir, diatrizoic acid, erythromycin, gabapentin, iomeprol, tolyltriazole, sulfamethoxazole, tramadol,	RT = 5 and 10, FR = 8000, HLR = 400,	Adsorption, biodegradation, oxidation	70–98	[244]
Horizontal/vertical subsurface flow and hybrid CWs, aerated/unaerated (mesocosm scale)	Zeolite (20–30)	Domestic sewage enriched with Ecs	Sulfamonomethoxine, sulfamethazine, sulfameter, trimethoprim, norfloxacin, ofloxacin, enrofloxacin, erythromycin-H <sub>2</sub> O, roxithromycin, oxytetracycline, lincomycin	$[EC] = 5 \times 10^{-3}$ , HLR = 1.67, PT = Iris tectorum	Sorption and biological processes	87.4–99.1	[255]

Table 6. Cont.

Type of Filtration (Scale)	Bed Filter Material (Size, mm)	Influent Type	EC Removed	Operational Conditions	Removal Mechanism	Removal [%]	Reference
Four CWs of subsurface horizontal flow (pilot scale)	Gravel (12.7–19.05)	Synthetic wastewater	Carbamazepine, sildenafil, methylparaben	[EC] = 0.2, FR = 15, RT = 72, PT = Heliconea Zingiberales and Cyperus Haspan	Biodegradation, adsorption, plant absorption	<10–97	[2]
Combination of partially saturated and unsaturated vertical subsurface flow CWs (experimental scale)	Top: sand layer (1–2) Underneath: gravel (3–8)	Urban wastewater (surrounding residential area) from primary treatment	Ciprofloxacin, ofloxacin, pipemidic acid, azithromycin	$[EC] = 5 \times 10^{-4}, HLR = 0.55, PT = Phragmites australis$	Sorption and biodegradation	<-200->90	[246]
Line 1: Partially vertical flow Line 2: unsaturated vertical flow+ horizontal subsurface flow + free water surface CWs (experimental scale)	-	Urban wastewater from primary treatment	Caffeine, trimethoprim; sulfamethoxazole, DEET, sucralose	HLR = 0.55, FR = 138.89	Biodegradation	<10-~100	[256]
Vertical flow CW	Top: gravel (4.8–9.5) Filter media: sand (0.27) Bottom: medium gravel (4.8–9.5) + coarse gravel (25–32)	Wastewater	Ibuprofen and caffeine	$[EC] \le 0.1$ , HLR = 16, RT = 168, PT = Heliconia rostrata	Biodegradation, adsorption, plant absorption	90–97	[257]
Vermifiltration (pilot scale)	Soil Sand (0.1–0.8) Detritus (3–10) Support: cobblestone (10–50)	Hospital effluent from sedimentation basin	Ciprofloxacin, ofloxacin, sulfamethoxazole, trimethoprim, tetracycline, metronidazole	HLR = 4.17, ET = Eisenia foetida, ED = 10,000	Adsorption, earthworm absorption (mineraliza- tion/transformation), biodegradation	4098	[251]
Integrated CW	Chaff and soil	Domestic + livestock wastewater	Androsta-1,4-diene-3,17- dione, 17α-trenbolone, 17α-boldenone, 17β-boldenone, testosterone, stanozolol, progesterone, ethynyl testosterone, 19-norethindrone, norgestrel, medroxyprogesterone, cortisol, cortisone, prednisone, miconazole, fluconazole, itraconazole, etc.	[EC] = 6.3 × 10 <sup>-7</sup> -1.05 × 10 <sup>-4</sup> , RT = 36, PT = Myriophyllum verticillatum L. and Pontederia cordata	Biodegradation, adsorption, plant absorption	<10-97.6	[249]
Vermifiltration (pilot scale)	Top: vermigratings (0.118) and cow-dung (0.05–5), Small gravel (2–4), Medium gravel (6–8) Support: coarse gravel (12–14)	Clinical laboratory wastewater	Amoxicillin, ampicillin, ticarcillin, ceftazidime, cefotaxime, ceftriaxone, streptomycin, gentamicin, erythromycin, tetracycline, chloramphenicol, ciprofloxacin	HLR = 4.17, RT = 7–8, ET = <i>Eisenia foetida</i> , ED = 10,000	Earthworms/microorganisms degradation, biofilm adsorption, filter media sorption	-	[250]

Notes: [EC] = emerging contaminant concentration [mg/L], FR = flow rate [mL/min], HLR = hydraulic loading rate [cm/h], GAC = granular activated carbon, PT = plant type, ET = earthworm type, ED = earthworm density (worms/m<sup>3</sup>).

Likewise, the most used materials in the filter bed of filtration/biofiltration technologies are mostly gravel and sand (classified as conventional materials). However, in a few studies, other materials such as granular activated carbon, silica, and anthracite are used, showing to be very efficient. This makes it necessary to study other adsorbents such as agro-industrial residues, which have proved to be efficient in the removal of organic matter and nutrients.

#### 4.3. Outlook and Future Perspectives

Based on the findings of this bibliographical review, it is essential to continue researching/developing efficient adsorbents to remove Ecs. These adsorbents should be friendly to the environment, low cost, and available in the local market to reduce transportation costs and take advantage of resources/value waste. Moreover, the adsorbents will be biocompatible to be used in biofiltration technologies. This would imply, for example: i) Deepening the modification/regeneration of materials and the synthesis of nanomaterials using environmentally friendly substances. Ii) Analyzing the technical and economic feasibility of its production/synthesis on an industrial scale to be tested/used in technologies such as filtration/biofiltration. This is to remove contaminants from real wastewater. Iii) Investigating the efficiency, chemical/mechanical stability, and behavior (toxicity) of highly available materials (agro-industrial residues, industrial waste) when used in filtration/biofiltration technologies. In addition, it is necessary to deepen into how the presence of several ECs or their coexistence with other contaminants (e.g., metals, dyes, organic matter, nutrients) influences the behavior/efficiency of the adsorbents. Finally, the possible applications that the filter bed/adsorbent material may have once its useful life is over should be researched, since there is little to no evidence on the topic.

#### 5. Concluding Remarks

The removal of ECs is an emerging concern since adsorption and the technologies in which this process occurs are efficient and low-cost alternatives. However, finding an adsorbent with good adsorption characteristics for different ECs is challenging. Lipophilic (log  $K_{ow} > 4$ ) and poorly soluble in water ECs are the most easily removed (efficiency up to 100%), while hydrophilic ECs are more difficult to remove (greater amount of adsorbent/contact time). Therefore, it can be suggested that there is not yet an ideal adsorbent for the removal of all ECs. However, as observed in previous studies, when the optimal adsorption conditions are determined (adsorbent type, particle size/adsorbent dose, contact time, pH), the adsorption capacity of the material increases.

Undoubtedly, activated carbon has demonstrated to be the best adsorbent (up to 100%, >850 mg/g) for Ecs. Nevertheless, the challenge of this material is associated with the reduction of its costs, the use/exploitation of other materials for its production, the use of more environmentally friendly substances for its activation/regeneration, and maintaining its adsorption efficiency after regeneration. Nanomaterials also suggest being a promising alternative for the removal of Ecs, but it is necessary to produce them on a larger scale and improve their separation from the aqueous medium. In turn, industrial waste and agro-industrial residues (rice husks, coconut fibers, corn cobs, peanut shells, sugarcane bagasse, and fruit shells/seeds) are promising alternatives to replace activated carbon. This is due to its low/zero cost, high availability, and relatively high adsorption capacities (up to 300 mg/g). In addition, the reuse of agro-industrial waste would also solve its management problem and is aligned with the circular economy and the objectives of sustainable development. Furthermore, due to the low toxicity of agro-industrial residues (e.g., 14d-LC<sub>50</sub> = 82–97%), they could be used (alone/mixed) in biofiltration technologies.

Biofiltration technologies are characterized by their efficiency (up to 100%), low cost, and easy operation/maintenance, which are reasons why they are widely used in decentralized wastewater treatment systems in developing countries. However, research about this type of technology is limited to the use of gravel and sand, classified as conventional materials and representing between 50 and 60% of technological costs. Although adsorption is not the fundamental mechanism in biofiltration technologies, it does become representative (up to 20%). Furthermore, the role of the material is not only limited to the removal of contaminants but also has other functions that are essential for the performance/efficiency of biofilters. Thus, it is important to continue testing alternative materials that are capable of meeting these requirements.

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