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Review

The Potential of Constructed Wetland Systems and Photodegradation Processes for the Removal of Emerging Contaminants—A Review

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Abstract: The presence of emerging organic contaminants (EOCs) in the environment is increasing and requires the development of technologies for their effective removal. Therefore, a literature review on the behavior of EOCs during municipal wastewater treatment, both in major treatment systems and particularly in constructed wetlands (CWs), was carried out. The study also reviewed the behavior of EOCs in anaerobic digesters (ADs) and advanced oxidation processes, particularly in TiO_2-based photocatalysis, which are being proposed as promising pre- and post-treatments for combination with CW. The following ten compounds were screened: acetaminophen (ACE), ofloxacin (OFL), caffeine (CAF), carbamazepine (CBZ), ketoprofen (KET), ibuprofen (IBU), diclofenac (DCL), clofibric acid (ACB), bisphenol A (BPA), and sotalol (SOT). The degradation pathways of the selected EOCs are largely influenced by their physicochemical and biochemical properties. Sorption and biodegradation are the main elimination mechanisms found in AD and CW treatment systems, where the combination of anaerobic and aerobic environments improves the elimination efficiency of EOCs. However, various contaminants appear recalcitrant. In this sense, in combination with CWs, TiO_2-based photocatalysis emerges as a promising post-treatment for advanced EOC removal from wastewater.

Keywords: emerging organic contaminants; constructed wetlands; anaerobic digesters; photocatalysis; TiO_2; removal mechanisms; removal efficiency

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1. Introduction

In recent times, different organic compounds are gaining more and more presence in water bodies and soils, many of them newly incorporated into the market. These are the so-called emerging organic contaminants (EOCs), which remain unregulated and without regularly applied prevention and treatment actions but can affect the functioning of ecosystems and deteriorate the quality of aquatic resources.

The origin of EOCs has been mainly established in sources such as households, hospitals, industry, agriculture, or livestock. Consequently, EOCs and their metabolites enter the integral water cycle and are eventually detected in soil, the atmosphere, and water bodies [1]. Despite occurring in concentrations of ng/L or µg/L, most EOCs are considered highly toxic substances with the capacity to adversely affect human health, aquatic organisms, and the environment [2]. In fact, Khasawneh and Palaniandy [3] reported a dozen pharmaceuticals with a potential significant effect on the aquatic environment (risk quotient > 1, including ofloxacin, acetaminophen, ibuprofen, and diclofenac). The risk quotient is defined as the ratio of the measured environmental concentration to the predicted no-effect concentration (in organisms such as algae, invertebrates, and fish) for each target pollutant [3].

EOCs can be classified into a wide variety of groups depending on their chemical structures and end uses. A popular group of EOCs are pharmaceutically active compounds (PhACs). The growing use of PhACs is leading to persistence and prolonged exposure

of these compounds in the environment, which may eventually affect the enzymatic and metabolic mechanisms of living organisms. Examples are the chronic toxic effects of ibuprofen in humans and in the aquatic environment, the toxicity caused by ketoprofen in the aquatic environment, or the toxicity of diclofenac in bacteria and its risk to human health and the aquatic environment [4]. Regarding products used in industrial chemistry, it has been shown that bisphenol A can cause diseases such as cancer, diabetes, or premature sexual maturation in women, among others [5,6].

It should be noted that conventional wastewater treatment plants (WWTPs) cannot completely remove all influent pollutants [7–9]. For this reason, research has started in recent years on the ability to remove these new substances by means of other wastewater treatment technologies [10,11]. Constructed wetlands (CWs) have been presented as eco-friendly technologies, being part of nature-based solutions with high performance in terms of conventional treatment [12]. Hybrid CWs are those that combine two or more types of CWs in a series. These hybrid systems generally combine horizontal (HF) and vertical (VF) subsurface flow CWs, or even surface flow (SF) units [13,14]. These basic modes of CWs are differentiated by the oxygen transfer capacity, which is significantly higher in VF systems, where a more aerobic environment originates, compared to that of HF systems, where anaerobic conditions dominate. On the other hand, SF systems differ from the other two due to the exposure of the aquatic environment to sunlight and the atmosphere, which encourages photodegradation processes and volatilization.

In terms of EOC removal, early research reported a similar or even higher removal efficiency of PhACs by CWs compared to conventional WWTPs [15,16]. More than 60% removal of PhACs has been found in both CWs that act as primary or secondary treatment for municipal wastewater (MW) and in hybrid CW systems. Generally, most of the compounds showed overall removals of between 80 and 100%. Nevertheless, some PhACs are hardly degraded with removal rates below 60% overall, and even below 25% in certain single CW stage systems or in hybrid CW systems [16,17]. In CWs, removal mechanisms are complex and multiple and include sorption, sedimentation, aerobic biodegradation, anaerobic and anoxic biodegradation, photodegradation, phytoremediation, and volatilization [15,18,19]. Therefore, the most effective results are achieved by hybrid systems combining different aerobic and anaerobic environments and exposure to light.

However, CWs generally require pre-treatment of the wastewater that effectively removes suspended solids [20]. The most commonly used pre-treatment methods in combination with CW are septic tanks, Imhoff tanks, and anaerobic digesters (AD). On the other hand, considering the high land requirement for the implementation of CWs, the current trend is towards intensifying the treatment processes that take place in CWs [21], through measures such as artificial aeration, improvement in flow patterns, the use of specific bed substrates, or the predominant use of VF systems compared to HF and SF.

The use of ADs as pre-treatment is also an option for the intensification of CW systems. As highlighted by Fernández del Castillo [22], AD combinations with CW offer a highly sustainable and efficient option for the removal of pollutants compared to the individual units of AD, CWs, or conventional WWTPs. The treatment capacity of ADs is much higher than that of septic tanks and Imhoff tanks, so they favor the reduction of the surface area needed for the overall system. In hybrid systems with VF units, ADs can effectively replace HF units when denitrification of the final effluent is sought. This requires recirculation of the VF unit effluent [23]. On the other hand, the intensification of CWs systems has also led to a lower use of SF units, with the loss of photodegradation processes typical of these systems. A way to keep the photodegradation process present in intensified CWs consists of the use of small photodegradation units based on advanced oxidation processes (AOPs). The use of catalysts such as TiO_2 in combination with sunlight seeks to combine the natural character of SF systems while intensifying their own photodegradation processes. This formulation is represented by the hybrid system shown in Figure 1.

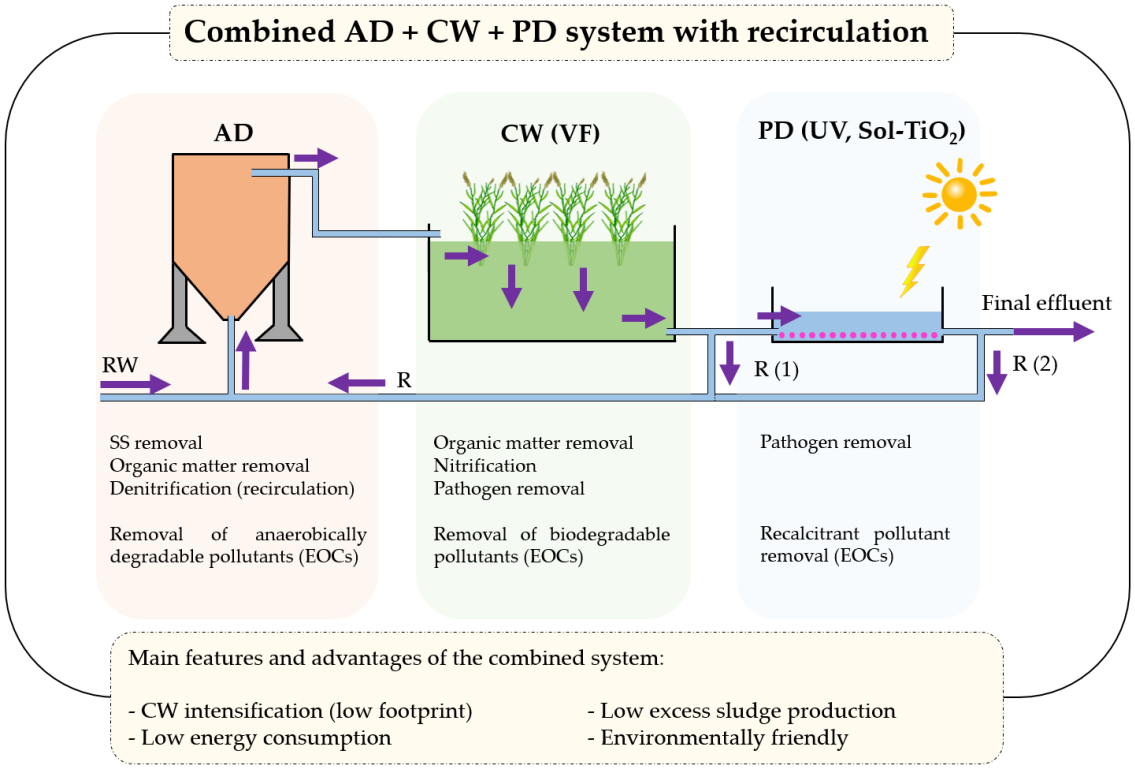


Figure 1. Combined anaerobic digester (AD), constructed wetland (CW), and photodegradation (PD) system with recirculation: The three technologies are complementary, requiring recirculation (two optional positions in the figure) to integrate treatment processes and achieve a true hybrid system with additional advantages to those of the multiple barrier concept.

AOPs are physicochemical processes capable of destroying or transforming EOCs resistant to conventional treatments, reducing toxicity and/or destroying pathogenic microorganisms [24–26]. The concept of AOPs was initially introduced by Glaze [27], referring to processes involving the generation of powerful transient species, mainly hydroxyl radicals ($HO^{\cdot}$), at near ambient pressure and temperature conditions. Some common examples of AOPs are the photo-Fenton process, ozonation, catalytic oxidation with H_2O_2, heterogeneous photocatalysis, electrochemical oxidation, or a combination of several of them [28].

Photodegradation (PD) includes photolysis and photocatalysis. Photolysis is a photochemical process in which UV radiation ranges between 200 and 400 nm. It is important to note that both direct and indirect photolysis can exist. Direct photolysis implies the transformation of an organic compound by the absorption of UV radiation without any other substance being involved and promotes the electronic excitation of the molecules. On the other hand, indirect photolysis occurs when UV radiation reacts with other substances present in the aqueous medium containing the EOC, generating reactive species (e.g., hydroxyl, sulphate, or chlorine radicals) capable of degrading that EOC.

The use of UV radiation during direct photolysis was highly effective in degrading many recalcitrant EOCs. The results of Gonzalo [29] indicate that the hybrid CW unit (HF-VF) removed most of ACE, CAF, and part of OFL (57% on average), IBU (69%), and KET (43%). Following PD post-treatment by the UVC-254 nm cell, IBU and KET were completely removed, being primarily responsible for the removal of SOT (79% on average) as well as ACB (75%), and BPA (77%). However, the UVC-254 nm cell did not show any effect on OFL. Similar results with the UVC-254 nm unit were reported by Sánchez [30,31] for these compounds, except for BPA, which was barely removed (below 20% on average). However, UV radiation was associated with high energy costs as well as risks for living organisms since it induced DNA damage. As a result of these major drawbacks, research into alternative photochemical processes is still in demand [32].

Photocatalysis is defined as a process in which the action of UV, Vis, or infrared radiation in the presence of a photocatalyst, such as TiO_2, varies the chemical kinetics and undergoes the transformation of a reactant [33]. From an environmental sustainability point of view, heterogeneous photocatalysis appears as an interesting technology because it allows the use of cheaper light sources (e.g., sunlight) together with harmless catalysts. However, the catalyst must be immobilized to avoid its loss in natural waters, due to economic considerations or, in the case of TiO_2 nanoparticle formulations, to the reported potential harmful effects [34]. Gonzalo [29] applied for the first time a UV light (UVC-254 nm) unit for the removal of EOCs in CW effluent, achieving interesting results that show the complementarity of these technologies.

Sánchez [30,31] studied the removal of various EOCs from raw urban wastewater in a three-stage AD-VF-PD system with recirculation. At the laboratory scale, they used a UVC-254 nm radiation unit as a PD unit [30], while at the pilot scale they experimented with three PD options: UVC-254 nm radiation, UVA-365 nm radiation with TiO_2 as catalyst (UVA + TiO_2), and sunlight with catalyst (Solar + TiO_2) [31]. The results of these studies highlighted the interest of these combinations, in which the AD carried out the retention and hydrolysis of the solids in suspension, and the elimination of nitrogen through the denitrification of the nitrate recirculated from the VF unit. Most of the COD was also removed in the AD unit since denitrification requires organic matter as electron acceptors. The VF unit completed the removal of organic matter and achieved advanced nitrification of the AD effluent, while the PD unit showed a negligible effect on the concentrations of organic matter and nutrients. The elimination of EOCs takes place at all stages, to a lesser extent in the AD, and in an advanced and complementary way in the VF and PD units [29–31]. The results of this combination for the removal of EOCs will be analyzed in detail in the following sections of this review.

Recently, Fernández del Castillo [22] reviewed the AD-CW system in relation to the removal of organic matter and nutrients, but not on the removal of EOC, which is pending as is the review of the combination of CWs and TiO_2 photocatalysis. Therefore, the main objective of this review of recent scientific literature was to evaluate the behavior of EOCs through wastewater treatment systems in general and through those systems whose core treatment phase consisted of CW in particular. Furthermore, considering the need for pre-treatment of CW influent, the behavior of EOCs in ADs was also reviewed. On the other hand, in view of the fact that some EOC recalcitrant to biological treatments can be effectively eliminated in compact TiO_2-based photocatalysis systems, the review included these systems and finally the combined AD-CW-PD system represented in Figure 1.

The review was carried out for a selection of ten specific EOCs that included pollutants that require different physicochemical conditions for their removal, some of which are difficult to remove in CWs. In Section 2, the methodology used for the selection of the scientific publications consulted was detailed. In Section 3, the main parameters defining the physicochemical and biochemical properties as well as the values of these properties for each selected EOC were introduced. In Section 4, the main degradation mechanisms and EOC removal efficiency in wastewater treatment systems and treatment technologies were assessed. Section 5 focused particularly on the removal of selected EOCs by CW and AD used as pre-treatment and hence on the combined AD-CW system. The potential of TiO_2-based photocatalysis as a post-treatment for the effluent from the combined AD-CW system was evaluated in Section 6. The overall comparison of these treatment technologies is addressed in Section 7, and the main research gaps are identified. Finally, the main conclusions of the review were presented.

2. Methodological Considerations

Two main criteria have been followed to select the EOCs to review: (1) EOCs that are hardly removed by CW, and (2) EOCs that require different physicochemical conditions for their degradation. Considering this criterion, the selected group of compounds provides an adequate evaluation of the EOC removal efficiency of a combined hybrid system

as that shown in Figure 1. A similar approach was followed in previous experimental studies. Another criterion used was to select compounds commonly used so that their presence in the aquatic environment is considered widespread. Ground-breaking literature reviews [15,16,35] and some complementary papers [17–19] were used to identify a list of compounds that presumably met some of the indicated criteria. Finally, after a discussion of the various aspects by the research team, the following contaminants were selected: acetaminophen (ACE), ofloxacin (OFL), caffeine (CAF), carbamazepine (CBZ), ketoprofen (KET), ibuprofen (IBU), diclofenac (DCL), clofibric acid (ACB), bisphenol A (BPA), and sotalol (SOT).

The search for scientific literature on the elimination of each of these compounds in ADs and CWs was carried out using Scopus. First, the most recent literature on the most common behavior of selected EOCs in WWTPs has been reviewed. Regarding CWs, the search methodology was as follows: keywords such as "constructed wetland", "treatment wetland", and "wastewater", were inserted in "Article title, Abstract, Keywords" and the name of each compound was inserted in "All fields". A larger number of publications were found in relation to CWs (Table 1), which made screening of them necessary. Initially, the total publication count was 390 papers. While applying a date limitation, from 2018 to 2021, 244 results were generated. Due to the difficulty of checking this number of papers, a preliminary qualitative screening was carried out with the aim of handling a minimum of 10 papers of interest for each EOC. Finally, because of the importance of the papers for the goals of this review as well as the fact that many publications deal with several EOCs, the total number of articles selected for each compound varied between 7 and 27, except for ACB and SOT, which had only 7 and 5 papers available, respectively. The review period ends in December 2021.

Table 1. Number of results obtained in the Scopus database until December 2021 dealing with each EOC in CWs and AD.

EOC	Acronym	CWs			ADs		
		Total No. [a]	2018–2021 Period	Included in This Review	Total No. [a]	2018–2021 Period	Included in This Review
Acetaminophen	ACE	89	43	11	7	2	2
Ofloxacin	OFL	42	35	10	7	2	1
Carbamazepine	CBZ	203	98	18	22	16	6
Caffeine	CAF	110	51	19	14	7	1
Ketoprofen	KET	61	22	13	4	3	2
Ibuprofen	IBU	214	114	27	18	13	6
Diclofenac	DCL	174	89	22	35	22	7
Clofibric acid	ACB	110	26	7	5	2	1
Bisphenol A	BPA	137	80	12	32	19	1
Sotalol	SOT	5	2	5	1	1	1
Total papers (without repeats)		392	220	76	89	46	17

[a] The period of literature review was from 2005 to 2021.

A similar search was carried out in Scopus for ADs (i.e., upflow anaerobic sludge bed (UASB) and hydrolytic anaerobic sludge bed). The search methodology was as follows: the terms "anaerobic digester", "upflow anaerobic sludge blanket", "hydrolytic upflow sludge bed" and "wastewater" were inserted in "Article title, Abstract, Keywords" and the name of each compound was inserted in "All fields". A relatively low number of scientific papers were obtained, of which only the 17 that actually related to the objectives of this study were included in the final review (Table 1).

During preliminary screening, the reported removal mechanisms for each selected EOC were identified and noted. This review provided the coverage of a wide range of different physicochemical conditions to determine the preponderance of these mechanisms. Figure 2 shows the recurrence of the identified mechanisms of EOC removal in CW based

on the research papers consulted. Details of these mechanisms and their respective paper references are given in Supplementary Information (Table S1). In addition, references to other aspects were also included. Regarding the main biological degradation processes that occur in CWs, i.e., aerobic and anaerobic biodegradation, three of them usually degrade under both aerobic and anaerobic conditions (ACE, CAF, and DCL), another three under aerobic but not anaerobic conditions (IBU, BPA, and, to a lesser extent, SOT), and two others under anaerobic conditions but not under aerobic conditions (OFL and KET). On the other hand, only one compound from each of these groups (DCL, SOT, and KET) was degraded by photodegradation. Finally, two of the compounds (CBZ and ACB) were very recalcitrant and were not significantly degraded by any of the indicated mechanisms but suffered from sorption on substrate and uptake by plants.

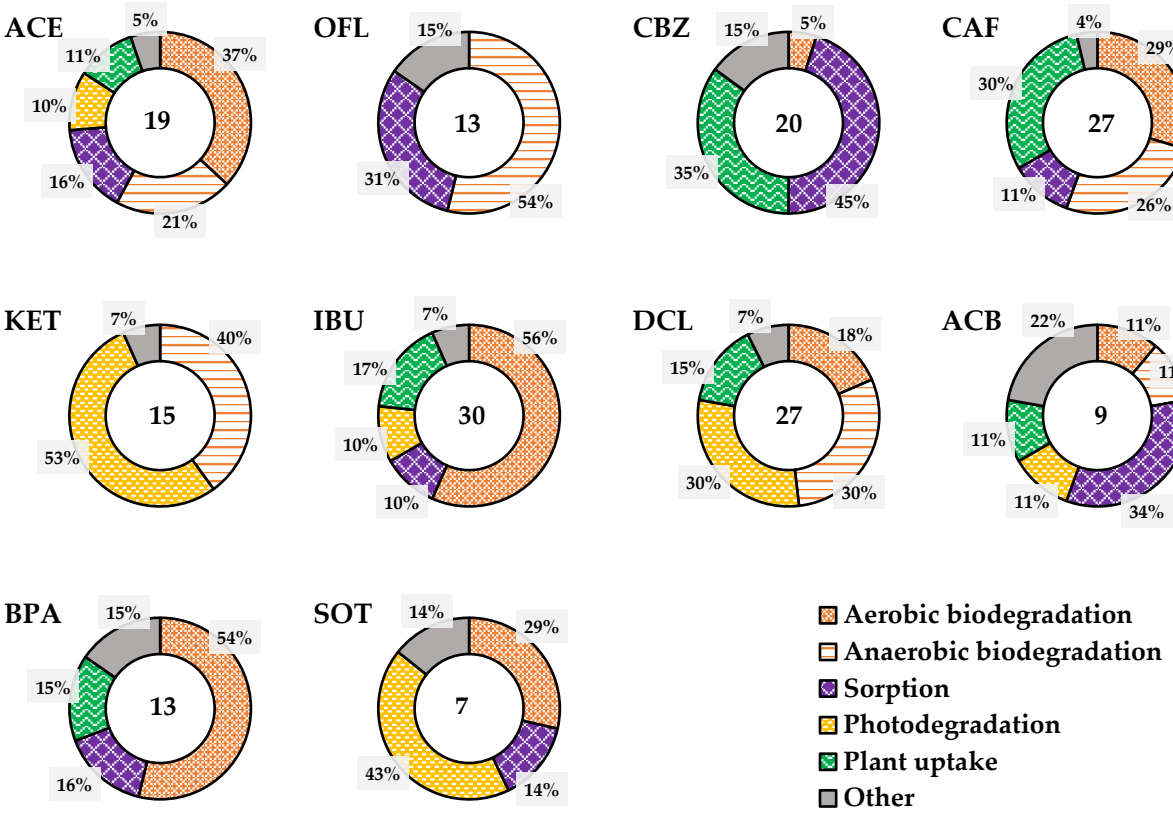


Figure 2. Recurrence of each removal mechanism over the total number of mechanisms (shown inside the pie chart) reported in the reviewed papers on the removal of each EOC in CW (For acronyms, see Table 1. Detailed information is given in Table S1).

3. General Characteristics and Physicochemical Properties of Selected EOCs

3.1. General Characteristics of Target EOCs

A diverse group of EOCs were investigated: four non-steroidal anti-inflammatory drugs (ACE, KET, IBU, and DCL), one antibiotic (OFL), one anticonvulsant (CBZ), one lipid regulator (ACB), one stimulant (CAF), one β-blocker (SOT), and one plasticizer (BPA). Their continued use by society is the common point between them.

The physicochemical properties of the selected EOCs are summarized in Table 2. ACE, which is usually known as paracetamol, is an analgesic used for pain relief and fever reduction. KET is commonly used to treat rheumatoid arthritis and osteoarthritis, as well as other non-rheumatic diseases. IBU is prescribed to treat mild to moderate pain, inflammation associated with arthritis and osteoarthritis, and to reduce fever. The fourth anti-inflammatory drug studied was DCL, which is generally used to reduce the pain of osteoarthritis and rheumatoid arthritis as well as pains associated with other causes [36]. ACB is a drug widely used for blood lipid regulation and was the first prescription drug

metabolite reported in environmental surveys [37]. OFL is a fluoroquinolone antibiotic that binds to enzymes involved in DNA replication and repair processes, leading to cell death in sensitive bacterial species. The anticonvulsant drug CBZ is a dibenzazepine derivative used for epilepsy and other psychiatric disorders. Finally, SOT is an ethanolamine derivative, which is classified as a β-blocker drug with antihypertensive and antiarrhythmic properties [36].

Table 2. Physicochemical properties of EOCs under review according to the references consulted on biological wastewater treatment processes [a].

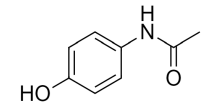
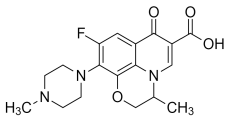
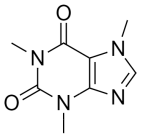
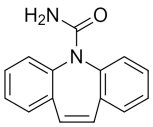
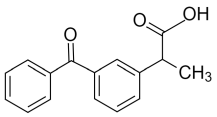
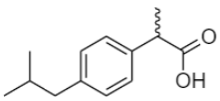
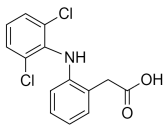
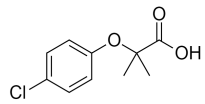
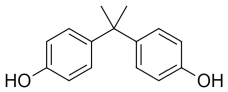
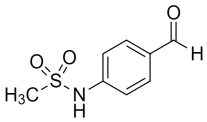
Name Acronym Chemical Composition	CAS MW [b] Formula	pK_a [a]	log K_{ow} [b]	log D_{ow} [c]	k_{bio} (L/gSS·d) [d]	k_d (L/kgSS) [d]
Acetaminophen **ACE** 	103-90-2 151.17 $C_8H_9NO_2$	9.5	0.46	0.9	58–240	1.5–1160
Ofloxacin **OFL** 	82419-36-1 361.37 $C_{18}H_{20}FN_3O_4$	5.97 9.28	−0.39	-	0.01–0.0933	12,000–22,100
Caffeine **CAF** 	58-08-2 194.19 $C_8H_{10}N_4O_2$	10.4	−0.07	−0.55	0.48–156.24	<30–140
Carbamazepine **CBZ** 	298-46-4 236.27 $C_{15}H_{12}N_2O$	13.9 15.96	2.45	2.77	0.005–0.389	<8–314
Ketoprofen **KET** 	22071-15-4 254.28 $C_{16}H_{14}O_3$	4.45	3.12	0.39	0.24–3.36	0.24–226
Ibuprofen **IBU** 	15687-27-1 206.28 $C_{13}H_{18}O_2$	4.85	3.5 3.97	-	3.24–38.7	6–103
Diclofenac **DCL** 	15307-86-5 296.15 $C_{14}H_{11}Cl_2NO_2$	4.2	4.98	2.26 0.86	0.02–8	1.9–321

Table 2. *Cont.*

Name Acronym Chemical Composition	CAS MW [b] Formula	pK_a [a]	log K_{ow} [b]	log D_{ow} [c]	k_{bio} (L/gSS·d) [d]	k_d (L/kgSS) [d]
Clofibric Acid **ACB** 	882-09-7 214.64 $C_{10}H_{11}ClO_3$	−4.9 3.2	2.57	-0.42	0.03–1	7–87.5
Bisphenol A **BPA** 	80-05-7 228.29 $C_{15}H_{16}O_2$	9.6	3.32	4.05	0.24–16.56	314–505
Sotalol **SOT** 	3930-20-9 272.37 $C_{12}H_{20}N_2O_3S$	8.3	0.85	-	-	-

[a] Values of the different physicochemical properties were extracted from: [a] [4,38,39]; [b] [4,38–40]; [c] [40,41]; and [d] [7,38]. [b] Molecular weight.

On the other hand, CAF is an alkaloid stimulant drug, which occurs naturally in coffee, tea, chocolate, and some painkillers, and is therefore widely consumed by the population for its stimulant effects on the central nervous system [42]. This review also included BPA, which is used as an industrial chemical in food packaging, dental veneers, plastics, etc., and its release into the environment can have a major impact on public health [5]. In fact, BPA is classified as an endocrine disruptor compound.

3.2. Physicochemical Properties of the Selected EOCs

The physicochemical properties of each EOC are closely linked to its environmental distribution in air, water, sediment, soil, and animals. In this respect, a minor change in their chemical structure can have significant effects [43].

The dissociation constant, pK_a, is used to compare either the relative acidity or basicity of weakly ionizing compounds in aqueous solutions of solvents or their miscibility in aqueous solutions. More acidic compounds have a lower pK_a and ionize easily in aqueous solutions, while the opposite is observed for less acidic or more basic compounds. The chemical speciation of contaminants is influenced by pK_a and pH, and generally, the protonated form exists when $pH < pK_a$ [44]. However, the deprotonated form of the compound can exist under the same condition of $pH < pK_a$, as is the case with the deprotonated nitrogen in CAF, leading to its lower water solubility [42].

To understand the behavior of EOCs in environmental matrices, the partition coefficient between n-octanol and water, known as log K_{ow}, is used. This coefficient is defined as the equilibrium ratio between the concentration of the non-ionized form of a compound in n-octanol and its concentration in water at constant temperature. However, it should be noted that the log K_{ow} values were obtained by adjusting the pH of the aqueous phase so that the non-ionized form of the contaminant would predominate. Log K_{ow} can predict the hydrophobicity of a compound: log K_{ow} values < 1 indicate a highly water-soluble compound, while log K_{ow} values > 4 imply a compound that is hydrophobic and tends to adsorb on organic matter [44,45]. Thus, log K_{ow} < 1 of ACE, OFL, CAF, and SOT means most of the total amount of these compounds are found in aqueous matrices (Table 2).

In some cases, however, the partition coefficient is a poor indicator of hydrophobicity, particularly for compounds that are ionizable at ambient pH conditions. For this reason,

the distribution coefficient of n-octanol in water, log D_{ow}, arises to account for the ionized and non-ionized form of a compound in each of the two phases. Thus, log D_{ow} values < 1 indicate a low probability of adsorption, while log D_{ow} values $\geq$ 3 suggest that a compound can adsorb on organic matter. For example, the log D_{ow} values of CBZ and BPA are 2.45 and 3.63, respectively, so these compounds have a high probability of adsorption (Table 2). Log D_{ow} is pH-dependent, using pH = 7 as a general standard for environmental risk assessment. For non-ionized compounds, it is assumed that log K_{ow} = log D_{ow} at any pH [44].

Sorption and biodegradation processes constitute the main EOC removal mechanisms during primary and secondary treatment in WWTPs [7,38]. These two processes are dependent on the physicochemical properties of the EOC, the characteristics of the medium and the environmental and operating conditions. In addition to the above-mentioned indicators (pK_a, log K_{ow}, and log D_{ow}), the tendency of EOCs to be absorbed can be estimated by the solid-water distribution coefficient (k_d). k_d is defined as the ratio of the concentration of the absorbed compound in sludge to its concentration in water (units L/kg SS in the liquor mixture). With k_d values < 300–500 L/kg SS, the sorption of EOC in sludge is negligible. According to values obtained in conventional sewage sludge (Table 2), DCL, OFL, CBZ, and BPA can be removed by sorption in sludge. Notably, OFL exhibits hydrophilic characteristics (log K_{ow} < 1 and log D_{ow} < 1) but often has a high sorption potential in sludge (k_d > 500 L/kg SS) due to electrostatic interactions. Biodegradability of EOCs can be estimated according to their biodegradation kinetic constant, known as k_{bio} (units L/g SS·d). EOCs with k_{bio} values < 0.01 indicate low biodegradability; values between 1 < k_{bio} < 10 show moderate biodegradability; and k_{bio} vales > 10 correspond to highly biodegradable compounds [7,46]. Thus, ACE and CAF are presented as compounds with a higher facility to biodegrade (Table 2).

4. Removal of EOCs from Municipal Wastewater: Technologies and Mechanisms

4.1. EOC Removal Technologies for Municipal Wastewater

Depending on the processes that may be involved, EOC removal technologies have been classified into three categories: physical, biological, and/or chemical processes (Figure 3). Over the last three decades, the main trends in PhACs removal were reported by Taoufik [47] through a systematic mapping study. Taoufik [47] concluded that adsorption was the most frequent process of PhACs' removal from the water phase, followed by photodegradation and biodegradation. Meanwhile, these authors also found that systems based on chemical processes were the most studied [47]. Some of the most applied physical processes use sorbents, such as activated carbon, or membrane technologies, such as nanofiltration, ultrafiltration, or reverse osmosis [48–50]. Chemical processes include AOPs such as photolysis, ozonation, Fenton or photocatalysis, among others, and chemical precipitation. However, the use of these physical and chemical technologies involves significant electricity consumption, investment, and operational costs.

Biological systems, on the other hand, were gaining popularity as several studies demonstrated their effectiveness in the degradation of many PhACs [51]. In addition, the use of biological technologies implies lower operating costs. Biological treatment of MW is due to the coexistence of different microenvironments that allow physical, chemical, and biological processes to take place. In terms of EOC removal, several studies support the effectiveness of biodegradation through systems such as: conventional activated sludge (CAS) in WWTPs, membrane bioreactors (MBR), sequencing batch reactors, trickling filters, or CW [2] (Figure 3). However, the complete removal of EOCs presented in MW by the above-mentioned technologies operating individually remains a challenge. Therefore, the combination of different technologies (e.g., hybrid systems based on biological+chemical, biological+physical, or biological+chemical+physical processes, Figure 3) emerged as the most effective approach to try to overcome the shortcomings of each specific treatment and attempt a global removal [48].

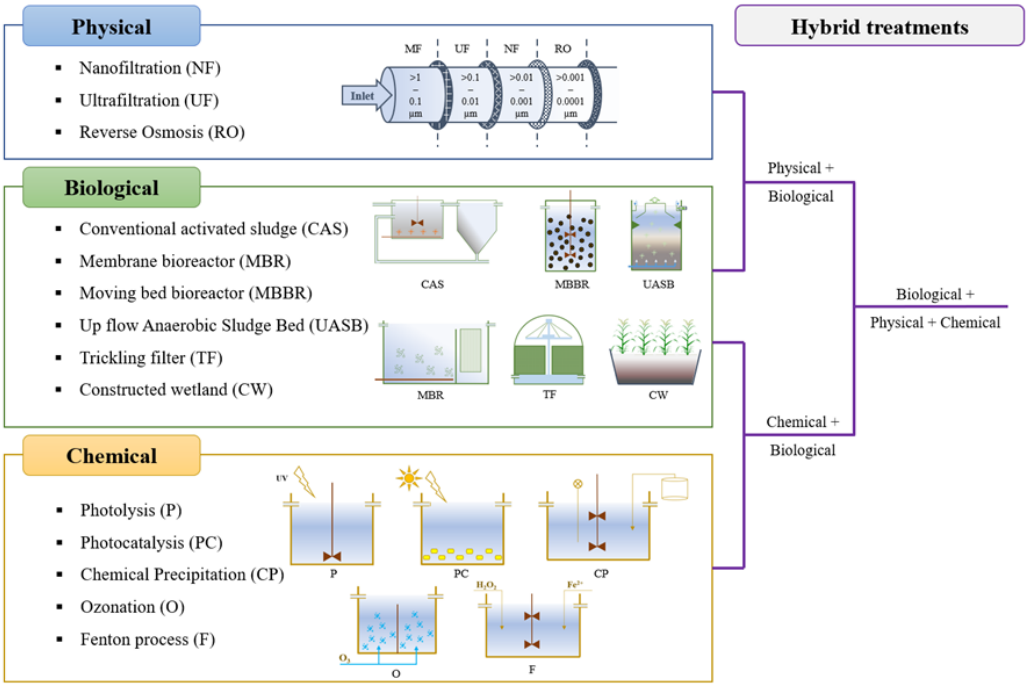


Figure 3. Main treatment methods for EOC removal from municipal wastewater.

The ranges of EOC removal efficiencies in WWTPs based on the reviewed literature are presented in Table S2. EOC removal efficiencies in conventional WWTPs typically range from 20–50% during primary treatment, 30–70% in systems that include primary and secondary treatment, and over 90% in systems that reach tertiary treatment [38]. EOCs that exhibit hydrophilicity (i.e., log D_{ow} < 1) were generally not well removed during primary treatment. Nevertheless, many hydrophobic EOCs (i.e., log D_{ow} > 3) showed a tendency to adsorb strongly onto primary sludge and were therefore partially removed from the dissolved phase after primary treatment [52–54]. In fact, Martín [52] observed that only 3 of the 16 studied EOCs were not detected in the sludge, while 11 of them were identified even in the final compost from sewage sludge.

Through biological processes (i.e., anaerobic and/or aerobic systems), certain EOCs can be degraded to a greater or lesser extent, leading to complete or partial mineralization and potentially generating by-products. In addition to sorption and biodegradation, volatilization may also contribute to the removal of volatile EOCs from the water phase.

4.2. EOC Removal by Sorption

The main mechanisms involved in the biological degradation of EOCs are sorption on sludge particles and aerobic or anaerobic biodegradation [39].

Sorption on sludge particles can occur through two mechanisms: absorption and adsorption. When the hydrophobic EOCs pass from the aqueous phase into the lipophilic cell membrane of the biomass, this is referred to as absorption. If the positively charged EOCs are retained by electrostatic interactions on the negatively charged surface of the sludge particle, adsorption takes place [55,56]. In general, sorption on EOCs is related to their physicochemical properties (log K_{ow}, log D_{ow}, pK_a, and k_d). Tiwari [39] previously estimated the sorption of pharmaceutical compounds in sludge from their log K_{ow} values and concluded that log K_{ow} and pK_a determine the affinity of EOCs to undergo sorption, so that EOCs with log K_{ow} > 3.5 (i.e., lipophilic compounds) are prone to sorption onto sediments. For example, BPA with log K_{ow} = 3.64 (Table 2) would have a high affinity for sorption.

The most relevant factors in terms of EOC sorption in sewage sludge are biomass composition and concentration, hydrodynamic parameters, and the use of sorbents [55].

Compared to granular biomass versus flocculent biomass, Alvarino [57] found that EOCs were absorbed more efficiently in flocculent biomass than in granular biomass due to a higher specific surface area available and lower mass transfer resistance. However, sorption was more important in UASB digesters than in CAS because of a higher concentration of accumulated biomass (7–30 g VSS/L in UASB vs. 1–2 g VSS/L in CAS).

In addition, EOCs with a low affinity to be retained in sludge may have a high affinity to interact with some adsorbents, such as activated carbon. For example, Alvarino [49] obtained 0% and 30% removal for DCL and CBZ, respectively, under biological treatment. It should be noted that DCL and CBZ (with 1 > log Dow < 3, Table 2) usually behave as recalcitrant to the biodegradation process. However, these authors improved the removals of DCL and CBZ to more than 80% and 90%, respectively, by adding activated carbon in a MBR. In contrast, these authors highlighted the progressive saturation of the active carbon, requiring new doses.

4.3. Biodegradation

Biodegradation is influenced by the concentration and chemical structure of EOCs. In addition, the type of metabolism would be determined by the concentration of the compound, while the degree and rate of biodegradation would be determined by the activity of the biomass [2,55]. Co-metabolism is the predominant mechanism in the degradation of EOCs contained in wastewater, due to the relatively low concentration of EOCs and the high concentrations of other substrates, such as easily biodegradable organic matter, acetate, ammonium, or nitrate. During co-metabolism, persistent EOCs are transformed into biodegradable intermediates within the overall metabolic pathways. A well-known example of co-metabolism is the nitrification process [58]. Ammonium oxidizing bacteria contain the enzyme ammonium monooxygenase, which is responsible for the degradation of certain EOCs [59]. For instance, an improvement in the degradation of recalcitrant ACB, CBZ, and DCL compounds was obtained by Tran [60] by increasing the ammonium concentration (from 20 mg to 200 mg NH_4^+-N/L) in a nitrifying activated sludge reactor compared to a CAS. Meanwhile, these authors found a high removal of IBU in the presence of allylthiourea (an ammonium monooxygenase inhibitor) and concluded that heterotrophic bacteria were also able to degrade IBU.

Aerobic metabolism and co-metabolism, on the other hand, appeared to be preferable to anaerobic or anoxic routes [61]. The redox potential and chemical structure of EOCs could also determine the metabolic pathway of degradation. According to Alvarino [55], most of the EOCs were transformed under aerobic conditions (such as IBU), and globally these authors, observed that aerobic systems were more efficient for a broad group of EOCs. However, due to their chemical structure, certain EOCs, such as naproxen or sulfamethoxazole, show higher degradation under anaerobic conditions [55]. These authors also highlighted that the combination of different redox conditions could be a feasible alternative to improve EOC removal efficiencies.

5. EOC Removal through CW-Based Systems

The treatment of raw wastewater in CWs usually requires a pre-treatment that is usually performed in septic tanks, Imhoff tanks, or in ADs such as UASB and hydrolytic upflow sludge beds. The predominant processes in these technologies are sedimentation, anaerobic hydrolysis, and digestion [20]. The combination of ADs as a biological pre-treatment with CWs as a central treatment stage is a promising alternative for the treatment of domestic, municipal, and industrial wastewater [13,62,63]. The AD pre-treatment unit is essential to prevent CW clogging. In addition, the application of recirculation allows the advanced removal of nitrogen in compact-intensified, CW-based systems [14].

The main elimination mechanisms and factors influencing the behavior of the ten selected EOCs (Table 1) in ADs and CWs were reviewed. The review was made from the recently published literature, as indicated in Section 2. The results are presented below.

5.1. Anaerobic Digesters

Up to now, EOC removal by the UASB reactor has been scarcely investigated. Data available for this review are presented in Table S3. The studies referenced below have mainly focused on the removal of musks, endocrine disrupting compounds, personal care products (PCPs), and PhACs contained in MW. Different operational characteristics have been tested to improve the removal of these compounds. Sorption and biodegradation processes were influenced by diverse factors such as temperature, HRT, and solids retention time (SRT) or even the substrate used for co-metabolism, among others [64]. For example, Carballa [65] investigated the removal of 13 PhACs and PCPs during anaerobic digestion, which occurred in sewage sludge, and tested the effects of temperature (under mesophilic conditions at 37 °C and thermophilic conditions at 55 °C) and SRT. These authors concluded that the studied EOCs were not influenced by neither temperature nor SRT. Furthermore, they observed a 69% removal of DCL and a 41% removal of IBU, while CBZ was not removed. The recalcitrant behavior of CBZ has already been observed by Stamatelatou [66] in both CAS and ADs. The recalcitrant behavior of CBZ could be related to the chemical structure. In fact, heterocyclic compounds (such as CBZ, Table 2) were resistant to anaerobic degradation, although substituted heterocyclic compounds were more prone to biodegradation [67]. Lahti and Oikari [68] investigated the behavior of DCL (plus naproxen and bisoprolol) under aerobic conditions (CAS) and anaerobic conditions (digested sludge) and concluded that DCL was recalcitrant in both aerobic and anaerobic biodegradation due to its physicochemical properties, since the addition of readily biodegradable C had no effect on its removal. Reyes-Contreras [19] reported between 20 and 40% removal of CAF, KET, and IBU through the UASB digester treating MW and observed a higher efficiency during winter for KET, where sorption was the most feasible removal mechanism. Faria [41] achieved almost 70% removal of KET under anaerobic conditions with an expanded granular sludge bed reactor and attributed this efficiency to the biodegradation process since KET showed a low sorption tendency (log D_{ow} = 0.39, Table 2). Butkovskyi [69] investigated the addition of granular activated carbon (GAC) in an UASB treating black water and grey water sludge plus EOCs (such as IBU and DCL) and reported that an UASB without GAC only removed 7% of DCL by sorption onto the sludge whereas IBU was not adsorbed. The low sorption tendency observed for IBU and DCL could be explained by the fact that these compounds were deprotonated at pH values between 6.5 and 8 and their anionic form prevailed, which involved an electrostatic repulsion between the compound and negatively charged particles of the sludge [70]. However, Butkovskyi [69] observed that UASB plus GAC improved IBU removal from 40 to 70% while DCL removal remained practically constant. Similarly, in other studies, UASB digesters operated at different HRT and SRT were not able to degrade DCL nor BPA [70], while a recalcitrant behavior was observed for DCL, CBZ, and IBU, which showed removal efficiencies below 15% [57]. Furthermore, methanogenic activity, upflow velocity, and HRT were parameters that influenced the biodegradation and adsorption processes of EOCs [57]. The results reported by Sánchez [30,31] for ADs used as MW pretreatment for CW were generally in the same trend as those reported above. These authors obtained better results at the laboratory scale than at the pilot plant scale, reporting mean values in the range from 60 to 80% removal for ACE, from 30 to 40% removal for DCL, KET, OFL, and CAF, and below 20% removal for IBU, CBZ, BPA, SOT, and ACB.

5.2. Constructed Wetlands

5.2.1. Main Factors Affecting the Removal of EOCs in CWs

The ranges of EOC removal efficiencies in CWs based on the reviewed literature are presented in Table S4, while Table 3 summarizes the data reviewed for each type of CW as well as for all CW types together. The mean removal values of the ten study EOCs were found to be 63.7%, 56.7%, and 52.2% for SF, HF, and VF CW types, respectively. Likewise, the maximum values were very similar, while the minimum values were different for the CW types, with the VF type showing the lowest. However, we should note the small

number of values for the SF CW type, only two in general (Table 3). Regarding all CW types, the number of values varies from 6 to 23, being then a better basis for co-comparison, as shown in Figure 4. VF systems showed the lowest removals for ACB and CBZ (and to a lesser extent for SOT), while they performed better for IBU. On the other hand, SF systems performed better than average for ACB, CBZ, SOT, and even KET. Finally, the HF systems showed removal values very close to the averages.

Table 3. Removal of EOC in all CW types together and separately in the different CW types.

	All CW Types			Mean (n) for Each Type of CW		
Pollutant	**Mean ± SD**	**n**	**CV (%)**	**SF**	**HF**	**VF**
ACB	43.0 ± 31.7	7	73.8	65.0 (2)	48.8 (3)	12.2 (2)
ACE	89.9 ± 10.2	11	11.3	94.0 (2)	86.7 (3)	90.2 (5)
BPA	53.3 ± 34.5	15	64.8	55.0 (2)	46.9 (7)	54.4 (5)
CAF	89.0 ± 13.4	16	15.1	78.0 (2)	91.3 (7)	89.8 (6)
CBZ	23.0 ± 22.0	13	95.6	40.5 (2)	26.7 (6)	7.0 (4)
DCL	52.1 ± 22.4	23	43.0	56.8 (5)	44.7 (9)	52.9 (8)
IBU	66.2 ± 29.7	23	44.8	49.7 (5)	59.8 (9)	80.8 (8)
KET	62.3 ± 27.3	13	43.9	73.2 (3)	58.9 (5)	51.6 (4)
OFL	81.3 ± 28.9	11	35.6	95.0 (1)	89.4 (4)	68.3 (5)
SOT	19.4 ± 14.0	6	71.9	29.5 (2)	13.8 (2)	15.0 (2)
All pollutants						
Minimum	19.4			29.5	13.8	7.0
Maximum	89.9			95.0	91.3	90.2
Mean	58.0			63.7	56.7	52.2

The data in Table 3 were obtained from the mean values of the ranges and the single values given in Table S4. Abbreviations: SD, standard deviation; n, data number; CV, coefficient of variation; SF, surface flow CW; HF, horizontal flow CW; VF, vertical flow CW. For pollutant abbreviations, see Table 2.

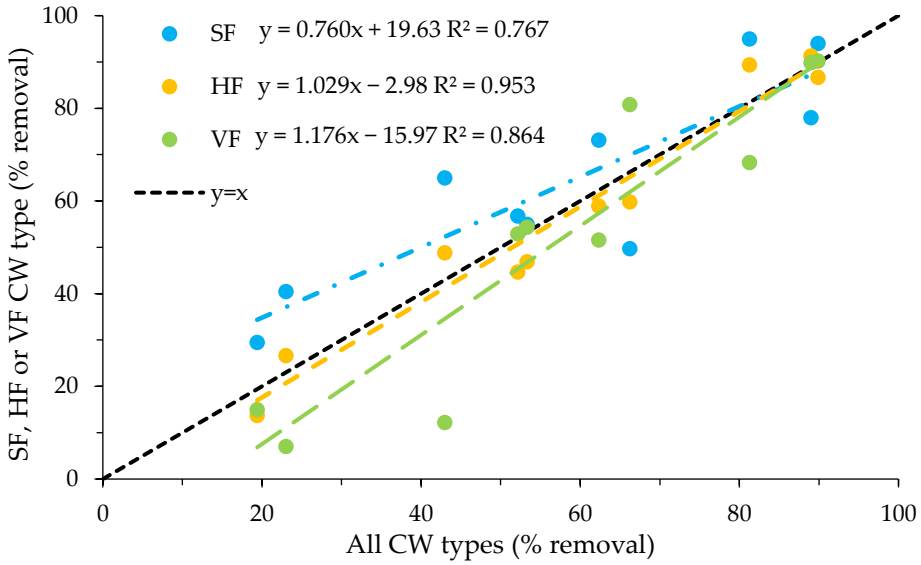


Figure 4. Correlations for EOC removal by each CW type versus EOC removal by all CW types (depicted values are from Table 3).

Figure 4 shows that the major differences between CW types correspond to those pollutants that are difficult to remove in CWs. The lower performance of VF CWs in this range (corresponding to ACB, CBZ, and SOT), as suggested in Figure 4, could be due to the application of higher loading rates, which would reduce the uptake potential of plants (important for the removal of CBZ, as shown in Figure 2). On the other hand, photodegradation processes are present in the SF CWs, which would explain the better performance of these systems with respect to SOT, KET, and DCL, in agreement with the data in Figure 2. An explanation is still missing for the behavior of the ACB, which could

be due to the reduced amount of data in all systems. Overall, Figure 4 shows that the three main types of CWs operate with very similar removal efficiencies despite typical differences in loading rates.

The main parameters influencing the elimination of EOCs in CWs are the type of CW, operating parameters such as loading rate or retention time, physicochemical characteristics of wastewater, presence and type of plants, and seasonality. Other parameters, such as the influence of primary treatment, evaporation and evapotranspiration, the type of granular material constituting the CW bed or the redox potential, could also have influenced the EOC removal performance [16]. CWs are able to remove EOCs due to the simultaneous presence of multiple mechanisms, including biodegradation, sorption, photodegradation, volatilization, plant uptake or hydrolysis [71,72]. It should be noted that, depending on the type of CW used, some mechanisms prevailed over others. For instance, Rabello [73] assessed the removal efficiency of CAF, CBZ, DCL, IBU, KET, and naproxen in different types of CWs, including SF, HF, and VF constructed wetlands. These authors found similar removal efficiencies for four EOCs (i.e., CBZ, DCL, KET, and naproxen) among the different CWs evaluated. However, CAF removal was higher with subsurface flow (57–80% removal) than with SF (41–76% removal), whereas IBU was better removed with SF (45–68% removal) than with subsurface flow (18–56% removal) [73]. As can be seen, the results of Rabello [73] are partly different from those reported here (Table 3, Figure 4).

In addition, the effect of diverse operational and physicochemical characteristics on EOC removal was also investigated. Ilyas and Van Hullebusch [74] reviewed the degradation efficiency of 26 PhACs in several CWs and concluded that there was no correlation between removal efficiency and a unique parameter since all parameters evaluated (including depth, hydraulic loading rate, HRT, and organic loading rate) directly or indirectly influenced their removal. Furthermore, pH was also considered as an important parameter since several biotic (e.g., plant uptake, nitrification, and heterotrophic microorganisms) and abiotic (e.g., ionizable PhACs fixation in sediment by ionic exchange) processes were controlled by pH. For example, KET removal efficiency had a significant correlation with pH and anaerobic biodegradation was the main degradation pathway [74]. On the other hand, these authors reported that temperature and dissolved oxygen (DO) were significantly correlated with the removal efficiency of most of the PhACs studied (e.g., DCL and KET), and the biodegradation process improved with higher values of temperature and DO. In addition, Liu [71] highlighted the importance of parameters such as temperature, HRT, SRT, and nitrification conditions on the removal efficiency of endocrine disrupting compounds such as BPA.

Regarding the role of plants in the degradation of EOCs, controversy is still present in the scientific community. For example, Cardinal [75] concluded that plants did not enhance PhACs and PCPs removal because other processes (e.g., photolysis) prevailed over the plant effect. Conversely, Zhang [76] reported the importance of the presence of macrophytes in the removal of DCL, IBU, KET, OFL, CAF, CBZ, and ACB. In a recent review by Hu [77], the influence of plant type was discussed. These authors found that emergent plants were more widely used for PhACs and PCPs removal due to their uptake potential to store these compounds, as emergent plants have a higher number of tissues than floating and submerged plants and floating leaves. Among the emergent plants, *Phragmites* ssp. and *Typha latifolia* were the most used. Rabello [73] reported a wide variation in EOC degradation depending on plant genus as well as on the presence or absence of plants, ranging from 81% removal of CAF with *Phragmites* ssp. to no removal of DCL in unplanted systems.

On the other hand, Hu [77] classified the effect of plants on EOCs removal into two categories, according to the role of the plant: direct effect (including uptake, translocation, and degradation by plants) and indirect effect (including the promotion of microbial and enzymatic activities, through the secretion of exudates and radial oxygen loss, and the production of humic acids, which increase the adsorption surface area). These authors reported that the direct effect of CW plants is relatively simple and insignificant compared

to the indirect effect, since uptake and transformation within the plant and precipitation on the roots represented only 0–20% of the overall removal of PhACs and PCPs by CWs. Although both hydrophilic and hydrophobic PhACs can be absorbed by plants, higher removal was found for the hydrophilic PhACs, according to Hu [77]. Furthermore, EOC removal could be improved by the indirect effect of plants because their microbial habitat could enhance the removal of PhACs and PCPs as well as an improvement of microbial activity as a consequence of secretion of root exudates. These indirect effects may have contributed to more than 70% of the overall removal of studied EOCs [77]. However, PhACs and PCPs removal by plants could be affected by multiple factors, such as low temperatures and the properties of EOCs.

Regarding seasonality, the processes of biodegradation, plant uptake, and photodegradation were influenced by changes in water temperature and oxygen solubility caused by differences between summer and winter. Ilyas and Van Hullebusch [74] reported higher removals of most of the studied PhACs during the summer compared to the winter. For instance, CAF showed seasonal differences that were statistically significant, as CAF was eliminated more efficiently in summer due to biodegradation and plant uptake, which were the predominant removal mechanisms, improving with higher temperatures. Moreover, some EOCs may also be degraded by natural photodegradation, i.e., by oxidation due to the absorption of UV radiation present in sunlight [78,79]. Mathon [79] investigated the removal of 23 EOCs by solar photodegradation that occurred in a SF in both winter and summer. These authors tested that the photodegradation process was most efficient in the first 10 cm of the water column. Furthermore, Mathon [79] reported insignificant differences in photodegradation between summer and winter, which they attributed to the fact that in their system the nitrate concentration was higher in winter than in summer and, consequently, the formation of hydroxyl radicals enhanced indirect photodegradation in winter.

The following sections present an in-depth analysis of the previously identified removal mechanisms (see Figure 2, Table S1) for each of the selected EOCs (Table 2) and their behavior in the CWs (Table S4).

5.2.2. Acetaminophen

In CWs, Chen [80] reached 95–100% removal of ACE in HF and concluded that biodegradation was the main removal mechanism, although sorption could also contribute to its degradation [80,81]. On the other hand, Ávila [82] worked with a hybrid VF-HF-SF system and observed that ACE was almost completely degraded in the first VF stage with 94% removal. De Oliveira [83] also reported an elevated removal of ACE (>90%). Analyzing other technologies with or without artificial aeration and comparing them with VF performance, Ilyas and van Hullebusch [84] reported high ACE removal efficiencies in all cases and concluded that both aerobic and anaerobic biodegradation can eliminate ACE. Vymazal [85] evaluated the performance of four HFs in terms of ACE removal and found high eliminations in the range of 86–99%. Other studies also reported that ACE could be removed to a lesser extent through sorption, plant uptake or photodegradation [80,82,86,87].

5.2.3. Ofloxacin

Zhu [88] recently reviewed the fate and removal of antibiotics through several biological technologies and reported that CWs were able to eliminate OFL by 63–92%. Chen [89] worked with an integrated system of five CWs and achieved 100% removal of OFL from the aqueous phase. In addition, these authors observed that OFL was accumulated in the solid phase of the five CWs and concluded that adsorption onto the medium was an important removal mechanism. On the other hand, OFL could also be biodegraded in CWs, as indicated by Yan [90], who reported more than 90% removal of OFL in a lab-scale HF. These authors observed that accumulation of OFL in plants was very restricted because of its weak lipophilic character (log K_{ow} = −0.39, Table 2). However, because its cationic form predominates at pH = 7, OFL may be adsorbable due to electrostatic inter-

actions [91,92]. Ávila [93] investigated antibiotic removal in an unsaturated and partially saturated VF, obtaining negative OFL removal and over 90% removal, respectively. These authors suggested that pH and ORP conditions (108 ± 34 mV) could affect the sorption process in unsaturated VF while varying the redox conditions in the partially saturated VF (−5 ± 41 mV) enhanced OFL removal. Conversely, other authors [94] found a negative correlation between OFL removal and DO and ORP values in conventional VF, up-flow VF, HF, and SF and concluded that anaerobic conditions improved OFL removal.

5.2.4. Carbamazepine

In general, CBZ appeared as a recalcitrant compound under biological treatment and even its concentration could be increased in the final effluent. This behavior could be explained by the return of existing metabolites in the wastewater to the parent compound by conversion reactions or by the splitting of the hydroxylated CBZ metabolite to CBZ by microbial activity [95,96]. Thus, the behavior of CBZ in CWs has also been presented as recalcitrant. Some elimination of CBZ in CWs could be attributed to sorption processes (such as adsorption onto available organic surfaces) and reductive transformation [97–99]. Kahl [97] observed that the HF was the only CW which achieved a constant removal in summer (46% removal on average), which they attributed to the reducing conditions of the medium, while rejecting a significant effect of plant uptake. Nivala [98] obtained 13% removal of CBZ in HF, a positive behavior that they explained by the predominantly anaerobic and reductive conditions. Park [99] proved that adsorption onto organic matter was the predominant mechanism of CBZ removal, achieving 50% removal in a HF acting as a tertiary treatment. On the other hand, Yan [90] suggested that CBZ could easily translocate and accumulate in leaves due to being a non-ionized compound with a molecular weight of <500 g/mol. Sorption on plants as well as on leaves added as extra organic matter to the CW bed was also reported by He [100].

5.2.5. Caffeine

The main removal mechanisms of CAF were biodegradation and photodegradation [101,102]. In subsurface flow CWs, CAF removal in the range of 85–100% was achieved, and biodegradation appeared as the dominant process [100,102–104]. According to Ilyas and van Hullebusch [84], the removal efficiency in VF was significantly higher compared to HF, SF, and even hybrid CWs. Other authors reported 97% and 94% CAF removal in VF and HF systems, respectively [83], and 93–99% removal in a HF system [80]. Even though aerobic biodegradation was presented as a dominant mechanism, anaerobic biodegradation, adsorption, and plant uptake also contributed to CAF removal [42,102].

5.2.6. Ketoprofen

According to the literature, photodegradation appears as the main removal mechanism of KET. Matamoros [105] verified its fast transformation by direct photolysis under sunlight in river water, seawater, and distilled water ($t_{1/2}$ = 2.4 min). The high performance under photodegradation processes could be explained by the fact that the C=O bond was easily broken under strong light intensity [78,106]. Therefore, KET was classified as a rapidly photodegradable compound by Mathon [79], both in the summer and winter campaigns. Zhang [107] also found the highest performance in SF (achieving between 51 and 91% removal of KET in the summer season), while the removals varied between 50 and 60% removal in HF and VF. However, biodegradation, which would improve with higher temperatures [108,109], has also been found to be a mechanism for KET removal. Chen [80] worked with three HF units and achieved between 47 and 91% KET removal. Other studies with HF systems obtained efficiencies in the range of 10 to 90% [101,110,111].

5.2.7. Ibuprofen

According to Ilyas and van Hullebusch [84], the most common mechanism found to explain the IBU removal in CWs was biodegradation, followed by processes such as

photodegradation, sorption, and plant uptake [17,80,82,92,98,107,112]. Hijosa-Valsero [113] classified IBU as an easily biodegradable compound (k_{bio} ranging from 3.2 to 38.7 L/g SS·d, Table 2), although aerobic biodegradation seemed to be the most important mechanism, so a higher removal efficiency was expected in VFs than in HFs [85]. The presence of the plants increased IBU degradation rates in a lab-scale VF [107], achieving 82–97% IBU removal. In addition, He [114] proved that a hydroponic culture of *Phragmites australis* was able to capture, translocate, and degrade IBU without significant phytotoxicity in terms of plant growth and enzyme activity. On the other hand, the photodegradation process was also found as a relevant removal mechanism in unplanted SFs [111,115].

5.2.8. Diclofenac

DCL was included in the moderately recalcitrant compounds under treatment by CWs and conventional WWTPs. This behavior could be explained due to the presence of chlorine in its chemical structure [116]. Ilyas and van Hullebusch [84] concluded that the efficiency of DCL removal was better in hybrid CWs than in VFs, SFs, and HFs separately. Zhang [115] found that the main removal mechanisms in CWs were photodegradation, biodegradation, and plant uptake. In fact, several studies suggested that DCL could be removed under both anaerobic and aerobic conditions [117,118], so the coexistence of both conditions explained the slightly higher efficiency obtained in hybrid CWs [17,97,98]. On the other hand, photodegradation, and plant uptake processes were also responsible for DCL removal [101,107,119]. For example, Zhang [107] achieved better removals in a SF (42–68% removal) than in a HF and a VF (42–52% removal) while the existence of plants had no significant effect on its elimination. Finally, Mathon [79] classified DCL as a fast-photodegradable compound.

5.2.9. Clofibric Acid

The low efficiency of ACB removal in CWs was due to its non-biodegradable and recalcitrant nature [102,110]. In addition, ACB was not degraded by direct photolysis in the natural environment as it could not absorb radiation above 290 nm [120]. Zhang [108] concluded that the presence of plants in CWs significantly improved the degree of ACB removal, achieving 39% removal at 4-days HRT in a HF compared to 33% removal in an unplanted HF. On the other hand, Dordio [121] added expanded clay to the CW bed and observed that sorption was the dominant mechanism for ACB removal. Dordio [92] obtained a moderate removal by sorption, whereas the authors observed that planted systems improved removal efficiencies. In addition, the authors tested the seasonal influence on ACB removal, achieving 75% removal in summer against 48% in winter [92].

5.2.10. Bisphenol A

According to the literature, biodegradation appeared as the main pathway to remove BPA, being more efficient under higher redox conditions [17,18,82,117]. However, it should be noted that Ávila [118] was able to remove BPA under anaerobic conditions (85–99% overall removal) and it could be associated with sorption onto organic matter and biodegradation. Ávila [82] obtained 44% removal in VF and 19% removal in HF, indicating that BPA degradation could be related to multiple simultaneous mechanisms. Dai [122] designed an assembled VF-HF system working from 6 to 24-h HRT with different plant species for the post-treatment of a WWTP effluent, achieving 45 ± 15% overall removal of BPA. On the other hand, Toro-Vélez [123] found that the planted HF removed a higher percentage than the unplanted HF (i.e., 70 ± 27% removal with *Phragmites australis* vs. 62 ± 33% without plants). The positive effect of plants has also been observed by Christofilopoulos [124] in a HF. Conversely, Papaevangelou [125] achieved 55% BPA removal in an unplanted HF while 50% removal was obtained in a HF with *Phragmites australis*. Meanwhile, Carranza-Diaz [126] was not able to remove BPA in a HF with *Phragmites australis* (5 ± 15%).

5.2.11. Sotalol

SOT removal by biological treatment presented low efficiencies in both conventional WWTPs [127] and CWs (removal range of 20–50% according to Li [15]). Verlicchi [128] used HF as a tertiary treatment and removed only 5% of SOT. Oulton [129] and Auvinen [112] classified SOT as a compound resistant to biodegradation. Auvinen [112] also tested different operational characteristics in a microcosm-scale batch experiment and found that SOT removal was dependent on artificial aeration at 2-days HRT whereas it was not dependent at 6-days HRT, showing a positive correlation with the DO effluent. On the other hand, Mathon [79] classified SOT as a moderate photodegradable compound in SF which was exposed to sunlight. Conkle [130] obtained an 82% overall SOT removal in a system that included aerated ponds, hybrid CW, and a natural wetland as the final stage.

6. Potential of Photodegradation with TiO_2 Catalyst as Post-Treatment of CW Effluents

6.1. Combining CWs and TiO_2-Based Photocatalysis

A combination of CWs and TiO_2-based photocatalysis was recently proposed to treat pesticide-polluted wastewaters [131] or textile wastewater [132]. Araña [131] used a photocatalytic reactor as pre-treatment and CW as post-treatment for degradation of two commercial pesticide mixtures and found that the combination of both methods proved to be the most successful option. Chen [133] investigated the feasibility of combining a TiO_2-photocatalytic process and a CW for treating polluted water for water reclamation, aiming to increase organic matter biodegradability through photocatalysis pre-treatment and improve the treatment efficiency and effluent quality of the CW system and thus shorten the HRT need. The study found that the combined system improved the treatment efficiency and effectively removed both trihalomethane and six haloacetic acid precursors. Li [134] treated greywater through CWs followed by TiO_2 photocatalysis, reaching water quality for bathing and other non-potable reuse purposes. However, Gulyas [135] reported insufficient quality of CW treated by TiO_2 photocatalysis and combined this treatment with activated carbon adsorption. Mahne [132] used the CW as pre-treatment to shorten the decolouration irradiation time for textile azo dyes in photocatalytic oxidation and photocatalytic ozonation experiments and found successful results with RRD22 and RBK5 azo dyes but not with RBL19 dye. Horn [136] investigated a combined CW-photocatalytic ozonation ($UV/TiO_2/O_3$) system for the treatment of university wastewater and reported total disinfection after 2 h of treatment. However, the authors observed an increase in COD and BOD after photocatalytic ozonation, probably due to saturation of the TiO_2 support, while ammonium values were not reduced sufficiently to remove wastewater acute toxicity. On the other hand, recently, other formulations and structures for wastewater treatment using TiO_2 photocatalysis have been developed with the aim of improving the efficiency of the photocatalytic treatment [137–139].

The order of treatment is crucial, with optimal configurations varying according to the nature of the contaminants [140]. Some researchers observed that the TiO_2 photocatalytic pre-treatment eradicated the activity of subsequent biological oxidation because some of the intermediates generated during photocatalysis were not biodegradable. Furthermore, higher degradation rates were found for the combined biological-photocatalytic treatment in comparison with the combined photocatalytic-biological treatment [140].

6.2. Removal of EOCs from CW Effluents Using TiO_2-Based Photocatalysis

Literature on EOC removal by the combined CW-TiO_2-based photocatalysis systems is scarce. The removal of EOCs combining CW and TiO_2-based photocatalysis was recently reported by Sánchez [31]. UVA + TiO_2 (UVA-365 nm) was more effective than Solar + TiO_2 in removing pollutants that had not been removed in the other units of the combined system. Thus, the UVA + TiO_2 unit achieved on average 90% ACE, 77% CBZ, 76% ACB, and 58% SOT removal, but only 6% BPA. Comparatively, the Solar + TiO_2 unit achieved 23% ACE, 61% CBZ, 67% ACB, 44% SOT, and 33% BPA removal, on average. These results

indicate that any of the options contributed to a significant increase in the elimination of EOCs in the overall system.

However, combining CW and TiO_2-based photocatalysis is a novel approach and most of the available literature on photocatalytic treatment concerns the removal of recalcitrant compounds from WWTP effluent. Regarding the EOCs subject to this review, Rueda-Márquez [141] treated WWTP effluents with solar (natural)/TiO_2 (33 Wh/m^2) and controlled irradiation/TiO_2 (55 Wh/m^2), reporting better results for solar irradiation, reaching 100% DCL removal, 85% OFL, and 22% CBZ. The authors [142] also found high removal efficiencies of DCL (100%), CBZ (76%), and IBU (74%), under solar/TiO_2 simulation after 96 h of irradiation. Available data for EOC removal by photolysis and TiO_2 photocatalysis from both WWTP and CW effluents are summarized in Table S5.

7. Overall Comparison and Some Research Gaps

Figure 5 compares the mean values obtained from the reviewed literature for the different types of treatment technologies. In general, CWs performed very similarly to other WWTPs, although the data reviewed here indicates lower removal percentages for some compounds. ADs showed approximately half the efficiency of EOC removal as compared to CWs. The elimination of EOC by these treatment technologies correlated with each other at least at a p-level of 0.05. Photodegradation by UVC irradiation or photocatalysis with TiO_2 showed a very different pattern for the removal of the studied EOCs. The general trend is that the worse the removal efficiency of the biological treatment systems, the higher the efficiency of the photodegradation technologies. This is the case for ACB, CBZ, DCL, and SOT. Thus, photodegradation appears as an interesting option to be included in combined systems that aim for the more complete removal of emerging pollutants. It is also in line with the current trend of intensifying CWs.

In a recent review, Cardoso-Vera [143] observed that only CWs as a biological treatment and photocatalysis as a photodegradation process have achieved high removal rates of antiepileptic drugs. These authors also pointed out that the efficiency of these technologies was closely dependent on the operating conditions. Thus, Cardoso-Vera [143] highlighted the combination of CWs with photocatalysis and photochemical post-treatment for the removal of recalcitrant compounds as a novel, environmentally friendly, and effective strategy. Generally, the implementation of TiO_2-based photocatalysis as post-treatment of CW effluent has resulted in higher effluent water quality [144]. For example, Nguyen [145] reported a successful reduction of organic matter and tetracycline through a free-water flow CW system coupled with a photocatalytic system consisting of a TiO_2/α-Al_2O_3 catalyst and UVA radiation. Felis [146] concluded that the coupling of an unsaturated downstream VF with TiO_2-photocatalysis induced by artificial sunlight could be a promising system to increase the removal efficiency of benzotriazole and benzothiazole.

Despite this, there are several research gaps related to PD options and their integration with CW or combined AD-CW systems. Among them are the effects of the presence of radical scavengers and photosensitizers, and the potential generation of toxic byproducts. These two aspects could be greatly affected by the position of the PD unit in the combined system or by the application and rate of recirculation. The power consumption of PD units should be minimized, and TiO_2-based photocatalysis combined with solar radiation appears as an interesting option, although it needs future development, as discussed below.

During photolysis, or photocatalysis, the water matrix is an important factor to be noted. If EOCs are contained in a wastewater matrix, the presence of both dissolved organic matter and inorganic species must be considered. These constituents, also known as radical scavengers, could play an inhibitory or promoting effect on the degradation of EOCs [147]. Thus, natural organic matter could be an inhibitory substance due to factors such as light-attenuating suspended solids, scavenging effect, or generation of by-products. The bicarbonate species was also found to inhibit the photolysis process [148]. Nevertheless, certain constituents present in wastewater, known as photosensitizers, could promote the production of reactive oxygen species by UV radiation, thus initiating the

process of indirect photolysis. Examples of photosensitizers were natural organic matter or nitrate ions [148]. The presence of radical scavengers and photosensitizers can be highly dependent on the position of the PD unit in the combined system. However, there are currently no experimental studies on this. Available studies for the combination of PD and CWs in MW treatment chose to use the PD stage as a post-treatment [29–31], with the aim of limiting solid deposition and biofilm formation on the surfaces of PD systems.

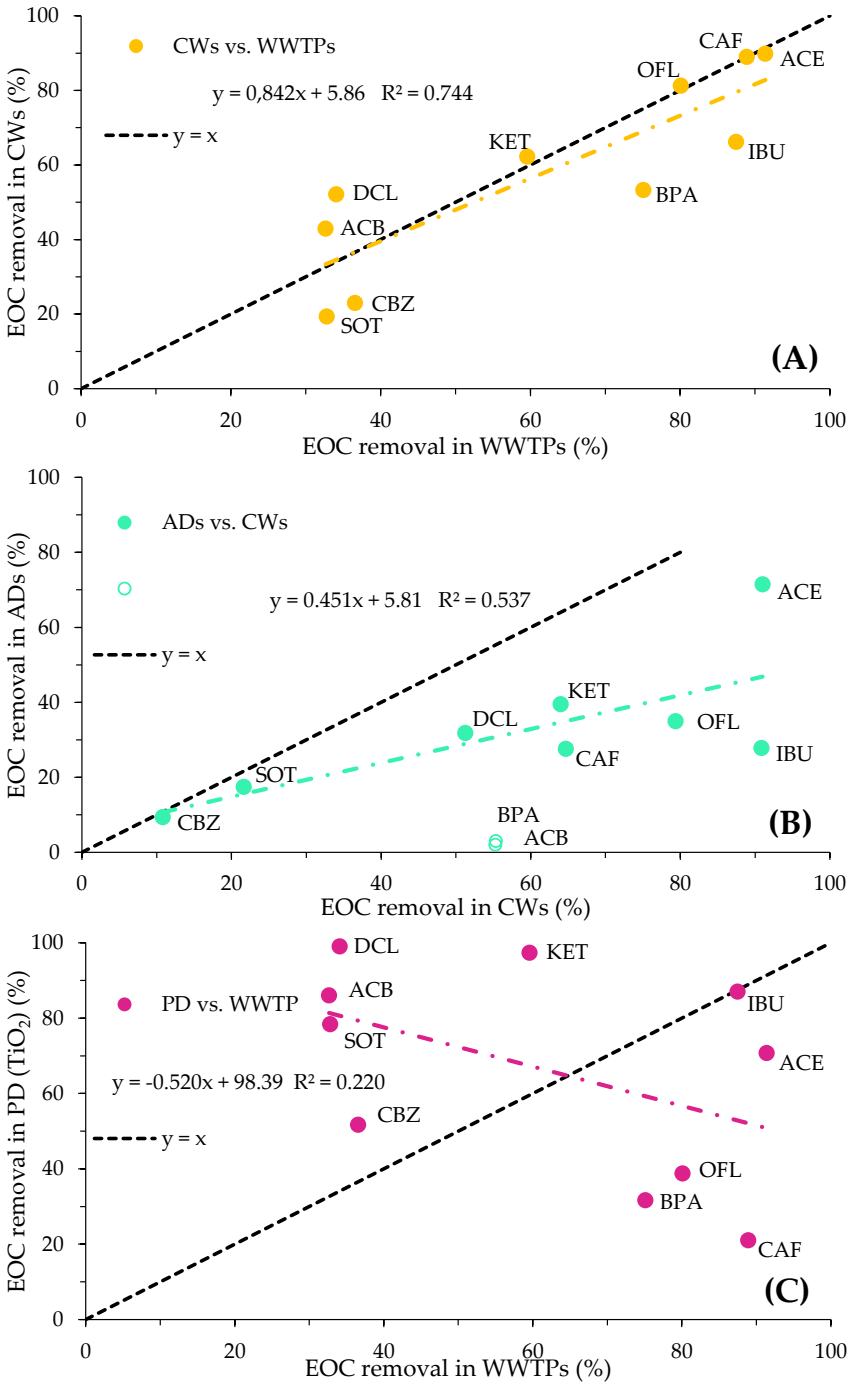


Figure 5. Graphical representation and correlations for EOC removal by different technologies: (**A**) EOC removal in CWs versus WWTPs, (**B**) EOC removal in ADs versus CWs, and (**C**) EOC removal in photodegradation systems (photolysis and photocatalysis with TiO_2) versus WWTPs (depicted values were obtained as mean values of the ranges and other values given in Tables S2–S5). Correlations are statistically significant at a *p*-level of 0.001 (**A**) and 0.05 (**B**), in this case excluding the data for BPA and ACB.

As for PD options, UVC radiation cells are currently available on the market. However, its high energy cost suggests looking for other options, such as photocatalysis with natural light. However, the TiO_2 catalyst needs improvement to increase its effectiveness when combined with solar radiation. It is still necessary to improve the design of the PD units that contain the catalyst, with the aim of facilitating their coupling with the rest of the units, especially for continuous flow systems, as well as the effective immobilization of the catalyst. Currently, the efficiency of TiO_2 catalysis clearly decreases in cloudy situations and during autumn and winter seasons. However, among other possibilities, the intensity and time of illumination can be increased by using artificial light obtained from renewable energy sources in situ.

On the other hand, the application of AOPs can result in more toxic by-products than the parent compounds. Some authors have proposed using CWs as a downstream stage of PD processes in order to remove possibly more biodegradable by-products [131,149–152]. As suggested by Gonzalo [29] for combined systems, recirculation could help for the integral treatment and complete mineralization of degradation intermediates.

8. Conclusions

CWs can act as a core treatment stage and can be combined with ADs as pre-treatment and PD as post-treatment to constitute hybrid wastewater treatment systems of great interest because of their more compact design and footprint reduction. Therefore, the present review has focused on the behavior of EOCs in CWs, Ads, and TiO_2 photocatalysis.

The main biological mechanisms involved were sorption and biodegradation (both aerobic and anaerobic/anoxic). However, physicochemical, and biochemical properties of EOCs (such as pK_a, log K_{ow}, log D_{ow}, k_{bio}, and k_d) determine the extent of these and other removal mechanisms. The high log K_{ow} of CBZ, DCL, and BPA shows their preference to adsorb onto organic matter and the potential to accumulate in the system. The opposite will occur for highly hydrosoluble compounds (low log K_{ow} value) such as ACE, OFL, CAF, and SOT. The tendency of EOCs to sorption on biological sludge and solid support is also determined by k_d, while the tendency to biodegrade can be estimated as a function of the value of k_{bio}. According to concentration values obtained in WWTP sludge, DCL, OFL, CBZ, and BPA compounds can be retained by sorption onto the sludge, favoring further removal of slowly biodegradable compounds. More easily biodegradable compounds such as CAF, IBU, ACE, and KET are efficiently removed in CWs.

As for CWs, the simultaneous presence of several mechanisms takes place, including sorption, biodegradation, hydrolysis, photodegradation, and plant uptake. ACE, CAF, IBU, and BPA were mainly removed by biodegradation, DCL by biodegradation, and other mechanisms, OFL by sorption and KET by photodegradation (which generally took place in SF). In contrast, CBZ, ACB, and SOT were presented as recalcitrant compounds in CWs, although CBZ and ACB may experience sorption and moderate plant uptake, and SOT may experience moderate photodegradation in SF units. Furthermore, it was concluded that aerobic biodegradation (the predominant mechanism in VF) was more efficient than the anaerobic route in removing CAF, IBU, and BPA, while ACE and DCL were able to biodegrade in both aerobic and anaerobic environments.

The results of this review indicate that CWs performed very similarly to other WWTPs, while ADs showed approximately half the efficiency of EOC removal as compared to CWs. The combination of ADs and VF units offers a compact and intensified treatment system that includes aerobic and anaerobic conditions, which can improve the removal of a large part of the EOCs contained in wastewater as well as organic matter and nitrogen. However, in such a system, photodegradation processes are virtually absent. Thus, the combination of an AD-VF system with post-treatment by photocatalysis gains advantages. The post-treatment by TiO_2 photocatalysis, among other AOPs, appeared as a potential solution to the recalcitrance and/or incomplete removal of certain EOCs by CW-based systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/environments9090116/s1, Table S1: Mechanisms of EOC removal in CW based on the research papers consulted and paper references; Table S2: Minimum and maximum (or mean) removal rates for each EOC and each technology evaluated in the literature on WWTPs; Table S3: Minimum and maximum (or mean) removal rates for each EOC and each technology evaluated in the literature on ADs; Table S4: Minimum and maximum (or mean) removal rates for each EOC and each technology evaluated in the literature on CWs; Table S5: Minimum and maximum (or mean) removal rates for each EOC and each technology evaluated in the literature on PD by UV photolysis and TiO_2–based photocatalysis (References [153–178] are cited in the supplementary materials).

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