



Emerging Pollutants in Wastewater, Advanced Oxidation Processes as an Alternative Treatment and Perspectives

Alexis Rubén Bracamontes-Ruelas ¹, Luis Alberto Ordaz-Díaz ², Ana María Bailón-Salas ³, Julio César Ríos-Saucedo ⁴, Yolanda Reyes-Vidal ⁵ and Liliana Reynoso-Cuevas ^{6,*}

- ¹ Departamento de Ingeniería Sustentable, Centro de Investigación en Materiales Avanzados, S.C., Calle CIMAV 110, Ejido Arroyo Seco, Durango 34147, Mexico; alexis.bracamontes@cimav.edu.mx
- ² Departamento de Ingeniería en Tecnología Ambiental, Universidad Politécnica de Durango, Carretera Durango-México Km. 9.5, Durango 34306, Mexico; luis.ordaz@unipolidgo.edu.mx
- ³ Facultad de Ciencias Forestales y Ambientales, Universidad Juárez del Estado de Durango, Río Papaloapan, Valle del Sur, Durango 34120, Mexico; bailon_anna@hotmail.com
- ⁴ Campo Experimental Valle del Guadiana, Instituto Nacional de Investigaciones Forestales Agrícolas y Agropecuarias, Km. 5 Carretera Durango-El Mezquital, Durango 34170, Mexico; rios.julio@inifap.gob.mx
- ⁵ Cátedras CONACYT, Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S.C., Parque Tecnológico Querétaro s/n, Pedro Escobedo, Querétaro 76703, Mexico; mreyes@cideteq.mx
- ⁶ Cátedras CONACYT, Centro de Investigación en Materiales Avanzados, S.C., Calle CIMAV 110, Ejido Arroyo Seco, Durango 34147, Mexico
- * Correspondence: liliana.reynoso@cimav.edu.mx

Abstract: Emerging pollutants are present in wastewaters treated by conventional processes. Due to water cycle interactions, these contaminants have been reported in groundwater, surface water, and drinking waters. Since conventional processes cannot guarantee their removal or biotransformation, it is necessary to study processes that comply with complete elimination. The current literature review was conducted to describe and provide an overview of the available information about the most significant groups of emerging pollutants that could potentially be found in the wastewater and the environment. In addition, it describes the main entry and distribution pathways of emerging contaminants into the environment through the water and wastewater cycle, as well as some of the potential effects they may cause to flora, fauna, and humans. Relevant information on the SARS-CoV-2 virus and its potential spread through wastewater is included. Furthermore, it also outlines some of the Advanced Oxidation Processes (AOPs) used for the total or partial emerging pollutants removal, emphasizing the reaction mechanisms and process parameters that need to be considered. As well, some biological processes that, although slow, are effective for the biotransformation of some emerging contaminants and can be used in combination with advanced oxidation processes.

Keywords: emerging pollutants or contaminants; SARS-CoV-2; advanced oxidation processes (AOPs); mineralization; biological processes

1. Introduction

Conventional processes to treat wastewater, such as activated sludge and aeration lagoons, are usually designed to stabilize and remove readily biodegradable contaminants, such as nutrients and other microbiological pollutants. However, according to recent research, other constituents are present in wastewater at low concentrations (ng/L– μ g/L), termed as emerging contaminants. Emerging contaminants are chemicals or substances that have the power to, directly and indirectly, harm humans, flora, and fauna [1].

Emerging pollutants can be mainly divided into the following groups: pharmaceuticals, personal care products, pesticides, and hormones; also, they can be natural or synthetic substances that are not fully regulated at a global level [2,3].

On the other hand, the list of these emerging pollutants is very long since it is increasing according to the requirements that human beings demand to improve their quality



Citation: Bracamontes-Ruelas, A.R.; Ordaz-Díaz, L.A.; Bailón-Salas, A.M.; Ríos-Saucedo, J.C.; Reyes-Vidal, Y.; Reynoso-Cuevas, L. Emerging Pollutants in Wastewater, Advanced Oxidation Processes as an Alternative Treatment and Perspectives. *Processes* 2022, *10*, 1041. https://doi.org/ 10.3390/pr10051041

Academic Editors: Maria Jose Martin de Vidales, Dimitris Zagklis and Georgios Bampos

Received: 8 April 2022 Accepted: 19 May 2022 Published: 23 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of life as the years go by [4]. So the number of organic and inorganic substances is in the millions, which has directly impacted the increase of emerging pollutants [1,5]. Moreover, since the water cycle interrelates the distribution of emerging pollutants discharged in domestic wastewater with other types of water, these emerging contaminants have also been quantified in surface water, groundwater, and drinking water [2,6,7].

Therefore, it is necessary to investigate and study the emerging pollutants based on their origin and transformation to recommend some processes that effectively treat them. Nevertheless, the conventional processes used to treat wastewater often cannot degrade some of them [8], as mentioned above.

In this sense, advanced oxidation processes (AOPs) have been of great interest in treating a wide diversity of pollutants, including emergent pollutants, present in wastewater [9]. AOPs are oxidation treatments based on the generation of potent oxidizing agents for organic compounds degradation, a clear example of which is the hydroxyl radical (HO°), which has an oxidation potential of 2.80 V. Hydroxyl radicals are equivalent to conventional oxidants such as chlorine, oxygen, and ozone [10,11]. The advantage that hydroxyl radicals show over other types of radicals is that they can react with most organic and inorganic substances [11]; therefore, AOPs promote the degradation of emerging pollutants favorably.

A general classification of AOPs that can remove emerging contaminants is shown in Figure 1. The classification was made based on that reported by Miklos et al. [10]. In addition, AOPs were classified according to the energy source (UV, chemical, and electrochemical) required to initiate the pollutant degradation reaction. Finally, it should be mentioned that the AOPs are described in more detail in the following sections.

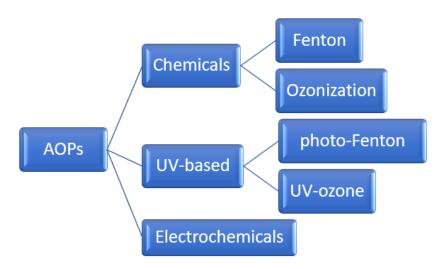


Figure 1. Most common advanced oxidation processes (AOPs) general classification, adapted and modified from [10].

In this context, the leading review objective is to suggest the consideration of the advanced oxidation process as an alternative for the removal of the emergent contaminants from wastewater due to their prevalence, hazardous, and the potential risk that they represent to the human health and the environment if their removal is not achieved until innocuous levels.

Although biological processes are currently the most widely used for wastewater treatment, several studies have shown that they have failed to adequately remove emerging pollutants [12,13]; therefore, it is necessary to attract the scientific community's attention to the need for the implementation and incorporation of other alternatives in the treatment processes, such as AOPs.

2. Emerging Pollutants and Their Relationship with the Water Cycle

Emerging contaminants are distributed throughout the water cycle, as shown in Figure 2. It should be noted that the primary inputs of emerging contaminants to surface

water, groundwater, and drinking water is wastewater from households, followed by wastewater generated in industry, hospitals, livestock, and finally, wastewater produced in agriculture (Figure 2). Water from different activities converges at a certain point in the water cycle and distributes the emerging pollutants in the natural water reservoirs until they reach the drinking water (Figure 2) [14].

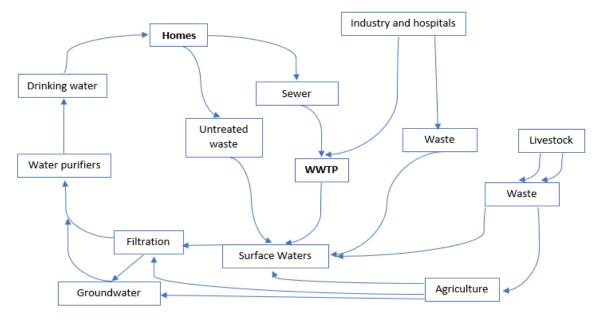


Figure 2. Distribution of emerging pollutants throughout the water cycle, adapted and modified from [14].

Emerging contaminants can cause problems for flora and fauna even in low concentrations [15]. A clear example of this is the research reported by Lee et al. [16], where the accumulation of some emerging contaminants was determined in selected fish species in the Tamsui River (Taiwan). According to the research, these fish accumulated the emerging contaminants and were then consumed by humans, causing problems to human health. Note that, to a certain extent, emerging contaminants can also reach human consumption through the trophic chain through species that have had contact with emerging contaminants and on which humans feed. In addition, it was also determined that the main source of discharge of the emerging pollutants analyzed came from products used in the home and effluents from wastewater treatment plants [16].

One of the main inputs of emerging contaminants into wastewater and the aquatic environment is through direct discharge of substances used in households, industry, hospitals, livestock, and agriculture into sewers (Figure 2). Another route is human excretion; emerging pollutants are consumed by humans and then excreted in parent compound form or as metabolites, which sometimes are not degraded or altered in wastewater treatment plants (WWTPs) [17].

The following subsections describe the significant groups of emerging contaminants.

2.1. Pharmaceuticals

Previous research on 212 medicines for human consumption has proposed that 35% of them are excreted via feces, and 64% are excreted in the urine. However, it is essential to mention that 42% of the total medicines excreted via urine are metabolites [2].

Human pharmaceuticals are considered on the official list of emerging pollutants reported by the United Nations Educational Scientific and Cultural Organization [18]. The medicines found in aqueous systems belong to the following classification groups: analgesics and anti-inflammatory drugs, antibiotics, antidepressants, antiepileptics, cardio-vascular medicines, and cytostatics, among others [19,20].

Due to their characteristics, microorganisms are the leading taxonomic group affected by antibiotics. However, this has a double effect. One is that if antibiotics reach aquatic reservoirs in adequate concentrations, the population of both pathogenic and non-pathogenic microorganisms can be reduced. Nevertheless, on the other hand, if they arrive in low concentrations, they could cause resistance of some pathogenic microorganisms to antibiotics. This factor could cause severe problems for humans and health [21,22], which makes antibiotics assigned special attention among the other groups of pharmaceuticals to be treated urgently.

Table 1. Aquatic toxicity of major drug groups, adapted and modified from [20].

Group	Extremely Toxic $EC_{50} < 0.1 mgL^{-1}$	Highly Toxic EC ₅₀ 0.1–1 mgL ^{–1}	Toxic EC ₅₀ 1–10 mgL ^{–1}	Harmful EC ₅₀ 10–100 mgL ^{–1}	Non-Toxic EC ₅₀ > 100 mgL ⁻¹
Analgesics			D*	D*, E*	
Antibiotics	A*	B*			
Antidepressants		D*			
Antiepileptics			C*		D*, E*
Cardiovascular medicines		D*			
Cytostatics		A*		D*, E*	

 $Most \ sensitive \ taxonomic \ groups: \ A^* = Microorganisms; \\ B^* = Algae; \\ C^* = Cnidaria; \\ D^* = Crustaceans; \\ E^* = Fish. \\ C^* = Crustaceans; \\$

Figure 3 illustrates the behavior and distribution of pharmaceutical drugs in aqueous systems, the primary and secondary production sources, and how humans can consume them. In Figure 3, wastewater generated in hospitals is indirectly included in treating human and animal diseases. However, the pharmaceutical industry and hospitals are the main generators of wastewater contaminated by these pollutants [23].

In the pharmaceutical industry, in the generation of pharmaceutical compounds, water is used at the different points of operation of the process for the washing of equipment and extraction of the medicine of interest. It is worth mentioning that the wastewater generated in pharmaceutical manufacturing (Figure 3) processes contains both the medicine in its parent form and a wide variety of toxic compounds that are harmful to humans, flora, and fauna in general [23].

Also, since pharmaceuticals are designed to increase their biological activity at low concentrations because they are used for diseases treatment in both animals and humans, their unintended presence risk in the environment and drinking water increases; thus, they should be removed from wastewater (Figure 3) and drinking water [24]. In addition, there is concern about the unintentional consumption of pharmaceuticals in drinking water, which can cause long-term adverse effects on human health [25].

To conclude this subsection, the most commonly used and consumed medicines may vary from country to country, and the level of contamination caused by their incidence in drinking water and the danger they represent to people [26]. Therefore, it is urgent to treat or remove this group of emerging contaminants (pharmaceuticals) that are present in aquatic systems.

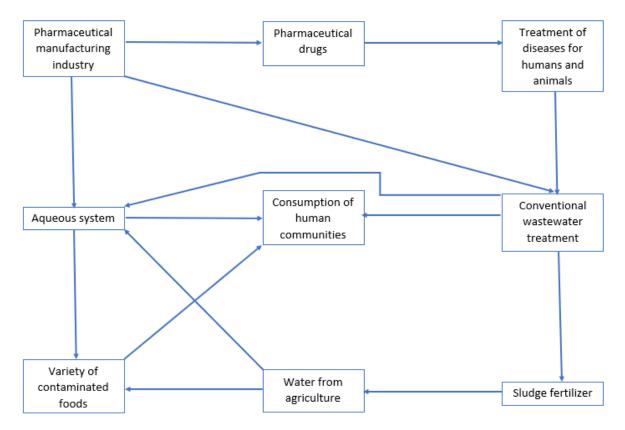


Figure 3. Pharmaceuticals distribution via aquatic routes, primary and secondary production sources, adapted from [23].

2.2. Personal Care Products

The group of emerging contaminants referred to as personal care products, also abbreviated as PCPs, can be purchased without a prescription and are commonly available in department stores and pharmacies in the health and beauty sections [27].

PCPs, like any other emerging pollutant, reach the aquatic environment through wastewater treatment plants [21]. PCPs may include mosquito repellents, surfactants, antifungal agents, antimicrobial agents, fragrances, and sunscreens, which are widely used in urban sites [21,28].

The PCPs and pharmaceuticals concentration vary according to the region and season of the year [29]. PCPs, unlike pharmaceuticals, do not have a significant change in their molecular structure, as most are designed for external use and are not metabolized by human consumption, e.g., fragrances and sunscreens [3].

Now, the PCPs toxicity will depend directly on the concentration of the emerging contaminant and the length of time the organism is exposed to the contaminant in general [30]. It is worth mentioning that plants can accumulate and metabolize PCPs, affecting them in a certain way and harming the organisms that consume them, such as humans (Figure 4) [31].

Figure 4 shows the interrelationship between wastewater contaminated by PCPs and the food chain.

It should be noted that PCPs have also been found in sludge generated in wastewater treatment plants [32]. However, there has been an increase in knowledge about PCPs commonly found in sediments, water, and biota [33]. However, there is still a lack of knowledge and information on these emerging contaminants and the possible treatments for their removal from wastewater.

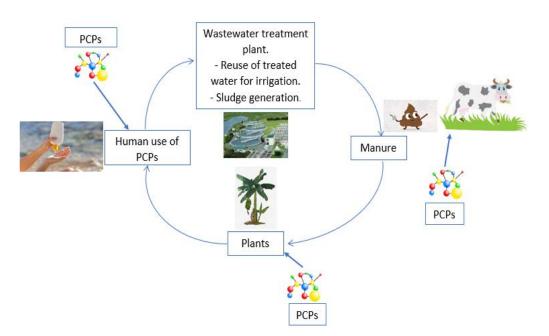


Figure 4. Distribution of personal care products (PCPs) via wastewater in the environment and the food chain, adapted and modified from [31].

2.3. Pesticides

Pesticides are a group of chemical compounds used in agriculture, mainly to regulate plant growth and eliminate insects and diseases (undesirable organisms) that may attack plants [34,35]. Pesticides can be natural or synthetic compounds [34]. Moreover, pesticides in waters can be a significant problem because they affect both ecosystems and human beings [35]. Therefore, an assessment of pesticide exposure is necessary to safeguard aquatic ecosystems [36].

The pesticides with a broad market are organophosphates, carbamates, organochlorines, neonicotinoids, triazoles, and amides [37]. Pesticides are also used in residential areas, specifically on lawns and gardens, which can cause these substances to reach the sewage system and groundwater through runoff caused by rainfall. In addition, pesticides can enter the human body through skin contact, inhalation, the eyes, or swallowing [38].

On the other hand, Rezaei Kalantary et al. [39] reported the presence of 16 pesticides in river water and drinking water; it was established that the concentration of some pesticides was very high and therefore unacceptable, as it could cause harm to people using the river water. It should be emphasized that the research presented the pesticide aldrin, which can be a danger due to the carcinogenic risk it presents to children and adolescents, a factor that promotes its long-term consumption when it is found in drinking water [39].

In addition, Mojiri et al. [40] showed that maximum pesticide concentrations in water bodies amounted to 1.21×10^5 ng/L in the Karun River in Iran, with respective bioaccumulation of pesticides in fish of up to 26.1×10^3 g/Kg, affecting both fish and the food chain.

However, the challenges in pesticide removal from wastewater are the influent composition, the pesticide molecular structure, and the pH of the pesticides contaminating the water, which varies from 0.5 to 14 [41]. Therefore, it is necessary to investigate methods that can feasibly promote their degradation and removal and counteract the abovementioned problems.

2.4. Hormones

Hormones are biochemical substances that come from the endocrine glands of humans and animals [42]. In humans, hormones are produced in the individual cells of the testes, adrenal cortex, ovaries, and placenta. The testes generate (androgen) testosterone, and the adrenal cortex aldosterone, cortisol, and dehydroepiandrosterone. The ovaries generate estrogens, generally divided into estradiol, 4-androstene-3, 17-dione, and progesterone, and finally, the placenta also generates estradiol, progesterone, and a substance called estriol [43]. Hormones are transported through the bloodstream and cause the activation of functions, including growth, reproduction, and general metabolic functions [42].

Currently, synthetic and natural hormones in water have gained a great deal of attention, attributed to the effects they can cause to organisms even though they are in low concentrations (μ g/L or ng/L). In addition, hormones are known to be endocrine disruptors [44]. The arrival of endocrine disruptors in surface waters depends mainly on the efficiency, capacity, and technology of wastewater treatment plants to treat them [45].

As a result, natural and synthetic hormones reach aquatic systems through wastewater discharges from households, hospitals, agriculture, livestock, and industrial effluents [44]. For example, Lei et al. [46] found a total concentration (468 \pm 27 ng/L) of estrogens such as estrone, 17 β -estradiol, estriol, 17 α -ethinylestradiol, and diethylstilbestrol in treated wastewater and 219 \pm 23 ng/L in river water in the Beijing-Tianjin-Hebei region, China. Moreover, Aris et al. [47] concluded that the presence of synthetic estrogenic compounds, detected in various aquatic environments, has currently received much attention due to their high bioactivity, toxicity, and persistence; because they can cause health problems, such as reduced fertility and carcinogenic problems, by ingesting water and food contaminated with it [47].

In addition, they also indicated that environmental pollution caused by estrogenic compounds leads to an imbalance in the aquatic environment, where fish are the main affected since the changes generated in the characteristics of male fish cause the fish population to decrease. Similarly, it was identified that prenatal and postnatal development in women and men must have an adequate relationship between estrogens and androgens since, if not, a complete formation of the reproductive organs will not be achieved [1].

Also, Jarošová et al. [48] defined, based on 15 in vitro tests, the level of estrogenic activity (concentration) that can be safe in municipal wastewater (effluent), whereby they indicated that for extended exposure times of more than 60 days a concentration of 0.4 ng/L was safe. For exposure times of less than 60 days, a concentration of 0.5–2 ng/L was safe in terms of safe levels of estrogenic equivalents (SEQ-SSEs) to know if the effluents can be discharged into the receiving bodies.

It is worth mentioning that synthetic hormones such as ethinylestradiol (birth control pills) and drospirenone, a synthetic progestin, were the 98th most prescribed hormones in the United States [49]. Therefore, it is highly relevant to urgently quantify, treat, and remove hormones from wastewater.

2.5. SARS-CoV-2, an Important Factor in Wastewater Today

Although COVID-19 is not an emerging contaminant but an emerging disease [50], SARS-CoV-2 has also been found in wastewater from treatment plants in some countries, e.g., the USA, Australia, Spain, Japan, France, India, and the Netherlands. However, although there is no evidence that the presence of SARS-CoV-2 in wastewater is related to virus transmission, the detection of SARS-CoV-2 in wastewater may serve as an indicator to follow up on COVID-19 cases [51]. In addition, researchers such as Cao & Francis [52] have concluded a strong correlation between the SARS-CoV-2 concentration in wastewater and the cases that exist in a given community.

However, it is imperative to say that the SARS-CoV-2 virus resides in wastewater from asymptomatic, presymptomatic, and symptomatic individuals. In addition, it should be added that samples taken from different wastewaters from different sewers in Ohio in the United States of America showed different SARS-CoV-2 strain patterns due to the diversity of strains that exist today [53].

Figure 5 shows, in general, how the COVID-19 disease can be contracted through wastewater. It should be mentioned that SARS-CoV-2 can survive from hours to seven days, depending on the type of matrix in which it is found [50].

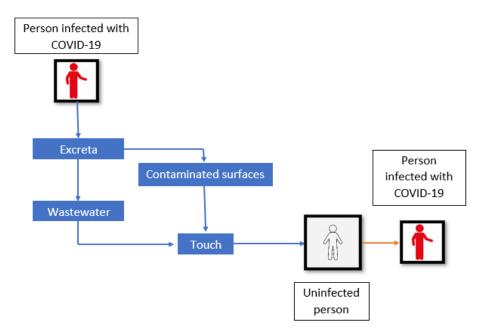


Figure 5. Possible human transmission of the COVID-19 disease through human excreta and sewage, adapted and modified from [50].

Therefore, based on the information gathered in this section, it is essential to note that SARS-CoV-2 may be a quality parameter measured in wastewater discharges soon. This may lead humans to employ new wastewater treatment methods or modifications to existing conventional methods that eliminate SARS-CoV-2.

Additionally, the SARS-CoV-2 virus is not thriving at hydrogen potential (pH) levels of 2–3 and 12–13 in a day [54]. Consequently, treatment methods that work at extreme pH can be used for SARS-CoV-2 virus removal, an example being AOPs that work in acidic ranges.

3. Emerging Pollutants Treatments in Wastewater

Some technologies applied to treat emerging pollutants are adsorption, use of membranes, advanced oxidation processes (AOPs), and biological processes. Where efficiency depends on multiple parameters, highlighting the type of technology and the pollutant concentration [55]. However, it is essential to mention that more emphasis will be placed on advanced oxidation processes (AOP) and biological treatments in this section.

3.1. Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are recognized methods because they offer a great diversity of processes that generate hydroxyl radicals (HO°). This factor allows coupling and adapting a specific AOP based on the treatment requirements [56]. AOPs are often used when conventional wastewater treatment cannot remove or treat certain pollutants [57]. A clear example of this is some organic pollutants that show a high chemical balance and low biodegradability [58], the most recognized are emerging pollutants. In addition, it has already been shown that AOPs have high efficiency in removing trace level organic compounds compared to other water treatment technologies [59].

AOPs commonly work with an oxidizing agent, e.g., ozone (O₃) and hydrogen peroxide (H₂O₂), a catalytic agent such as Fe²⁺, TiO₂, and other types of catalysts [60,61]. It is worth mentioning that catalysts can be modified to solve a given problem. For example, Dai et al. [61] in their research modified a catalyst to remove chlorinated volatile organic compounds.

In addition, in some cases, an external energy source such as UV radiation is included in order to degrade certain emerging pollutants that according to their molecular structure are susceptible to photocatalytic degradation [60,62]. For example, Chen et al. [62] in their research showed that some emerging contaminants present in saline wastewater tend to degrade photocatalytically. This is evidence that advanced oxidation processes can be modified and adapted depending on the molecular composition of the emerging pollutant that needs to be removed.

However, it must be ensured that the addition of external energy to the advanced oxidation process is necessary, since if the emerging contaminant of interest to be removed is not amenable to photocatalytic degradation, this would only lead to increased operating costs.

Therefore, in the following subsections, some of the most commonly used AOPs for treating emerging contaminants in wastewater are described in more detail. Emphasis will be placed on the reaction mechanisms and operating parameters (pH, catalyst dosage, oxidant dosage, among others) of the AOPs.

3.1.1. Chemicals

Fenton

AOP Fenton was named in honor of Fenton H.J.H. Fenton., who observed that tartaric acid could be oxidized by the reaction of ferrous (Fe^{2+}) salts with hydrogen peroxide (H_2O_2). Classical reactions, or Fenton reaction mechanisms, produce hydroxyl radicals (HO°) at pressure and room temperature at an acidic pH level in aqueous solution when hydrogen peroxide and ferrous ions come into contact.

Equation (1) shows how ferrous ions react with hydrogen peroxide giving hydroxyl radical as the main product. On the other hand, if there is hydrogen peroxide remaining in the process, through Equation (2), the ferric ions produced in Equation (1) will be reduced to ferrous ions again, generating protons and perhydroxyl radicals [63]. However, it should be noted that perhydroxyl radicals have less oxidative power than hydroxyl radicals [63,64]. Therefore, it is advisable to start the Fenton AOP with reagents containing ferrous ions instead of ferric ions.

It is necessary to mention that, if there is no remaining hydrogen peroxide, which can react with the ferric ions generated in Equation (1), the ferric ions generated in Equation (1) will precipitate in the form of amorphous ferric oxyhydroxides when the pH of the aqueous solution is increased from acidic to neutral [65].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\circ + OH^-, k_1 = 40-80 \text{ M}^{-1}\text{s}^{-1}$$
 (1)

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\circ} + H^+, k_2 = 9.1 \times 10^{-7} M^{-1} s^{-1}$$
 (2)

However, some side reactions may be negatively involved in the Fenton AOP (Equations (3)–(6)) [11]. For example, the (3)–(6) side reactions can decrease the pollutant removal performance of the Fenton AOP due to the loss of hydroxyl radicals.

$$Fe^{2+} + HO^{\circ} \rightarrow Fe^{3+} + OH^{-}$$
(3)

$$H_2O_2 + HO^{\circ} \rightarrow HO_2^{\circ} + H_2O \tag{4}$$

$$HO_2^{\circ} + HO^{\circ} \rightarrow O_2 + H_2O \tag{5}$$

$$\mathrm{HO}^{\circ} + \mathrm{HO}^{\circ} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{6}$$

The appropriate pH to manage the Fenton AOP has been indicated in several articles, which should be approximately 3 [8,9]. The pH set required for the degradation of a specific pollutant may also vary based on the nature of the pollutant and the wastewater in which it is found.

The optimal dosage of hydrogen peroxide (H_2O_2) to treat wastewater needs to be determined by experimentation since a lack of hydrogen peroxide may decrease the performance of the Fenton-type AOP to treat wastewater [9]. Some publications [9,66–69] have used Equation (7) (chemical reaction) to define the theoretical amount of hydrogen peroxide required to treat the emerging contaminant.

$$C_aH_bN_cO_d + (2a + 0.5b + 2.5c - d)H_2O_2 \rightarrow aCO_2 + (2a + b + 2c - d)H_2O + cHNO_3$$
 (7)

In Equation (7) (2a + 0.5b + 2.5c - d) are the moles of hydrogen peroxide that are required to degrade one mole of a molecule of the type $C_aH_bN_cO_d$. It should be clarified that if the wastewater contains more contaminants and not only the emerging target pollutant to be treated, the other contaminants may decrease the removal performance of the target pollutant since Fenton AOP is a non-selective treatment process. Therefore, the following Equation (8) can be used [70,71] instead of Equation (7).

Quantity
$$H_2O_2 = \frac{17}{8}COD$$
 (8)

where the amount of hydrogen peroxide to treat the wastewater can be calculated as a function of the amount of chemical oxygen demand (COD) that is present in a certain volume of the wastewater to be treated. The concentrations of both hydrogen peroxide and COD should be in mg/L units.

It is important to mention that the load of all the pollutants present in the wastewater to be treated by the Fenton AOP is considered in the total COD of the wastewater in Equation (8).

The theoretical amount of ferrous ions, which in this case are the most common catalysts of the AOP, Fenton type, can be calculated by means of Equation (1), and the results obtained by means of Equation (7) or Equation (8), as the case may be.

Currently, Fenton-type AOP carried out in the absence of light can be classified into two major branches, which are: Homogeneous Fenton and Heterogeneous Fenton.

The difference from one method to the other is that in homogeneous Fenton, which is the process just described in more detail in this section, its catalytic process occurs throughout the liquid phase, whereas in the heterogeneous Fenton method, it occurs on the surface of the catalyst [9]. The AOP heterogeneous Fenton type emerged to solve the problems presented by the homogeneous Fenton type AOP, since some of the catalysts used are solids [72]. However, there are still more challenges for both processes.

Some examples of emerging contaminants that have been treated by the Fenton method are presented in Table 2. It should be noted that the experimentation (Table 2) was carried out in real water (wastewater) and synthetic solutions. As can be seen in Table 2, all the emerging contaminants that were treated with the AOP Fenton type, had good removal percentages in synthetic water and wastewater.

The commonly handled pH's were around the value of 3, and in what refers to the amounts of ferrous ion and hydrogen peroxide, in this case, they were very variants according to the pollutant that needed to be treated. Therefore, the AOP Fenton type, according to the information gathered, is effective in the treatment of emerging pollutants.

	1 1					
Contaminant	Type of Water	Hydrogen Potential (pH)	Catalyst Dose and Oxidant Dose	% Removal	Reference	
Amoxicillin	Synthetic	3.5	$[H_2O_2] = 255 \text{ mg/L}$ $[Fe^{2+}] = 25 \text{ mg/L}$	100%	[73]	
Bisphenol A	Synthetic	3	$Fe^{2+}/H_2O_2 = 0.012$	100% (maximum)	[74]	
Estrogens *	Activated sludge waste	3	$Fe^{2+}/H_2O_2 = 0.167$	70–98%	[75]	
Paracetamol	Synthetic	3	$H_2O_2/Fe^{2+} = 2$	70.37%	[76]	

Table 2. Examples of emerging contaminants treated by the Fenton advanced oxidation process and process parameters.

* Estrogens: include estrone, 17β -estradiol, estriol and 17α -ethinylestradiol.

Ozonization

Ozone has been used as an oxidant and disinfectant in water treatment. However, ozone as such (direct form) used as an oxidant is very selective and, therefore, potentially attacks groups that are rich in electrons, for example, amines and activated aromatic rings, among others [10,77]. On the other hand, ozone can be used to generate hydroxyl radicals (HO°) and indirectly carry out the oxidation of organic compounds [77] because hydroxyl radicals (HO°) are formed by the decomposition of O₃ are non-selective oxidants [78], as compared to the O₃. So it is better, from an oxidative point of view, to use ozone (O₃) to generate hydroxyl radicals because they are not selective instead of using ozone (O₃) directly to carry out the oxidation.

It is worth mentioning that in order for ozone to generate hydroxyl radicals (HO°), there must first be a considerable amount of hydroxide ions, which promote the generation of these radicals. The pH for the generation of hydroxyl radicals is a crucial factor since the pH of the wastewater to be treated must be maintained at a level approximately higher than 8 [10], but this may change depending on the nature of the contaminants to be treated and the matrix in which they are found.

The process that generates hydroxyl radicals by means of ozone mentioned above and which will be emphasized in this section, is known as indirect ozonation. The reaction mechanisms of indirect ozonation, also known as indirect reactions or hydroxyl radical pathways, are divided into initiation reactions, propagation reactions, and termination reactions [79,80].

According to Malik et al. [80], in the initiation reactions (Equations (9) and (10)), first, ozone decreases when ozone and hydroxide ions react to give a superoxide anion as a product (O_2^-) and a perhydroxyl radical (HO₂°).

$$O_3 + OH^- \rightarrow O_2^- + HO_2^\circ \tag{9}$$

$$HO_2^{\circ} \leftrightarrow O_2^{-} + H^+ \tag{10}$$

Subsequently, in the propagation reactions (Equations (11)–(13)), the superoxide anion reacts with ozone to generate oxygen and O_3^- . Hydroxyl radicals (HO°) are then generated via hydrogen trioxide (HO₃°). It should be noted that hydrogen trioxide (HO₃°) is produced through the reaction of the protons generated in Equation (10) with the O_3^- produced in Equation (11) [80].

$$O_3 + O_2^- \to O_3^- + O_2$$
 (11)

$$\mathrm{HO_3}^\circ \to \mathrm{O_3}^- + \mathrm{H}^+ \tag{12}$$

$$\mathrm{HO_3}^\circ \to \mathrm{HO}^\circ + \mathrm{O_2} \tag{13}$$

Likewise, hydroxyl radicals react with ozone and produce HO_4° in Equation (14), which are transformed into perhydroxyl radicals (HO_2°) in Equation (15) [80].

$$\mathrm{HO}^{\circ} + \mathrm{O}_3 \to \mathrm{HO}_4^{\circ} \tag{14}$$

$$\mathrm{HO_4}^\circ \leftrightarrow \mathrm{O_2} + \mathrm{HO_2}^\circ$$
 (15)

It should be noted that hydroxyl radicals (HO $^{\circ}$) in the propagation reactions (Equation (16)) can also react with an organic molecule R, which can produce an interaction between the hydroxyl radical and an organic radical R $^{\circ}$ [80].

$$H_2R + HO^\circ \to HR^\circ + H_2O \tag{16}$$

Another situation that can also occur if oxygen is present is that peroxyl radicals (ROO°) are generated and start a chain reaction (Equations (17)–(19)) [80].

$$\mathrm{HR}^{\circ} + \mathrm{O}_2 \to \mathrm{HRO_2}^{\circ} \tag{17}$$

$$HRO_{2}^{\circ} \rightarrow R + HO_{2}^{\circ} \tag{18}$$

$$HRO_2^{\circ} \rightarrow RO + OH^{\circ}$$
 (19)

Now, as a final phase, it is essential to say that some organic and inorganic molecules can be involved in a reaction with HO^o and produce secondary radicals, which do not produce superoxide radicals, but rather HO₂^o y O₂⁻. These molecules commonly terminate the chain reaction and thus ozone depletion. It is worth mentioning that carbonate and bicarbonate can also act as scavengers of hydroxyl radicals (Equations (20) and (21)) [80].

$$\mathrm{HO}^{\circ} + \mathrm{CO}_{3}^{2-} \to \mathrm{CO}_{3}^{-\circ} + \mathrm{OH}^{-}$$

$$\tag{20}$$

$$HO^{\circ} + HCO_3^{-} \rightarrow HCO_3^{\circ} + OH^{-}$$
 (21)

A situation that can also occur is that the hydroxyl and perhydroxyl radicals react (Equation (22)) and stop the process (Equation (22)) [80].

$$HO^{\circ} + OH_2^{\circ} \to O_2 + H_2O \tag{22}$$

It should be mentioned that the degree of solubility of ozone in water is temperature dependent, as well as its reaction rate [81].

However, since ozone is an unstable gas and therefore, its production must be carried out at the wastewater treatment site, the corona discharge process can be used for its generation, which is based on the principle of discharging a high voltage into a dry or cooled gas phase, which is constituted by oxygen or air, if any [82].

On the other hand, Equation (23) indicates the exposure of hydroxyl radicals (HO°) per unit of ozone used in the process, and it should be clarified that this kinetic parameter has been proposed to characterize the ozone process [78,83] and can also be used to measure the production of hydroxyl radicals with respect to the ozone consumption in the ozonation process [83].

$$R_{OH,O3} = \frac{\int \left[HO^{\circ} \right] dt}{\Delta O_3}$$
(23)

Table 3 shows some examples of emerging contaminants reported by Mathon et al. [84] that can be removed by direct and indirect ozonation. It should be added that some of the data presented in Table 3 are obtained by means of mathematical modeling. Emerging contaminants were added to the wastewater by means of synthetic solutions (spike), and the process was generally operated in a range of pH = 6.7–7.2, a temperature of 21 °C, and ozone dosing (O₃) of 1.6 gO₃/gCOD per gram of dissolved organic carbon. It is necessary to add that, in the research, paracetamol and estrogens were considered as easily oxidized emerging pollutants, the only estrogen that was considered as a pollutant of medium oxidation difficulty was estriol in conjunction with the antibiotic ofloxacin, and metformin was considered as a pollutant of difficult oxidation. In addition, the research showed that 34 of the total emerging contaminants studied were mostly oxidized by indirect ozonation [84]. This indicates the feasibility of using indirect ozonation generates hydroxyl radicals with a higher oxidative potential than ozone (O₃) [64], which is also selective.

Table 3. Examples of emerging pollutants treated by direct and indirect ozonation.

Contaminant	Type of Water	Direct Ozonation (O ₃). % Removal	Indirect Ozonation (HO°). % Removal	% Large-Scale Removal	Reference
Paracetamol	Wastewater	97%	3%	ND*	[84]
Estrogens *	Wastewater	17–99%	1-83%	87–96%	[84]
Ofloxacin	Wastewater	7%	93%	80-92%	[84]
Metformin	Wastewater	1%	99%	ND*	[84]

* Estrogens: include estrone, 17β -estradiol, estriol and 17α -ethinylestradiol and ND*: is undetermined.

3.1.2. UV-Based

Photo-Fenton

The photo-Fenton process is an advanced oxidation process (AOP) that generates hydroxyl radicals (HO°) through the use of hydrogen peroxide (H₂O₂), iron salts, and UV-visible light [85]. In this case, the reactions are accelerated by light; the wavelength needed to perform the photo-Fenton AOP must be $\lambda < 580$ nm [86].

The pH level to be managed in the photo-Fenton AOP must be acidic to keep the iron in the solution [87]. Gou et al. [88], based on the information gathered in their article, the optimum pH value for operating the photo-Fenton AOP in research should be between 3 to 3.5, very similar to that of the traditional Fenton AOP. However, this may change depending on the type of contaminant to be treated and the wastewater in which it is found.

On the other hand, the literature review by Clarizia et al. [89] analyzed the feasibility of employing chelators to extend the pH range to more conveniently work the homogeneous photo-Fenton AOP and concluded that chelators increase the concentration of total organic carbon (TOC) in water, and also indicated that the biodegradability and ecotoxicity of the species formed should be evaluated. This is a field that should be studied further.

It should be clarified that the photo-Fenton AOP can also be classified into homogeneous and heterogeneous, just like the traditional Fenton AOP, and just like the photo-Fenton AOP, chelating agents can also be used in the traditional Fenton, an example of which is the research carried out by Sánchez Proaño & García Gualoto [90].

However, it is of utmost importance to mention that in both Fenton and photo-Fenton processes, problems are solved by means of heterogeneous processes or the use of chelating agents, etc., and others arise.

Now, in the reaction mechanisms of homogeneous photo-Fenton, the power of UV-visible radiation is added to the reagents used in traditional Fenton (Equations (24)–(26)) [91].

$$H_2O_2 + Fe^{2+} \to Fe^{3+} + HO^\circ + OH^-$$
 (24)

$$\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O} \xrightarrow{hv} \mathrm{Fe}^{2+} + \mathrm{HO}^\circ + \mathrm{H}^+ \tag{25}$$

$$H_2O_2 \xrightarrow{n_0} 2HO^\circ \ (\lambda < 400 \text{ nm}) \tag{26}$$

Most of the hydroxyl radicals (HO $^{\circ}$) in the photo-Fenton AOP are generated by Equation (24) from the traditional Fenton AOP and by the photolysis of the ferric ion carried out by Equation (25). Equation (25) also indicates that oxidation by irradiation is promoted by the photoreduction of ferric ions to ferrous ions, which can react again with hydrogen peroxide if there is any remaining hydrogen peroxide [92].

As for Equation (26), hydrogen peroxide at a wavelength of less than 400 nm can also produce hydroxyl radicals in the process for the degradation of pollutants in wastewater.

The dosage of hydrogen peroxide (H_2O_2) and iron salts has to be defined experimentally as in the traditional Fenton AOP for the removal of the target pollutants. As for the theoretical doses of hydrogen peroxide and ferrous ions, they can also be calculated by means of Equations (1), (7) and (8) as in the traditional Fenton method. It should be added that the photo-Fenton AOP has been considered to disinfect water from resistant microorganisms [93].

Some examples of emerging contaminants that have been treated by photo-Fenton AOP are shown in Table 4 below. As can be seen in Table 4, the photo-Fenton process was operated at pH = 3 in the two different investigations. It should be noted that the pH used is very similar to that used in the conventional Fenton AOP since this AOP is a derivative of it. Moreover, the dosages of the catalyst (Fe²⁺) and oxidant (H₂O₂) also varied from one investigation to another. In addition, all the removals shown amounted to 100% in both wastewater and synthetic water, which leads to establish the feasibility of this advanced oxidation process to treat and remove emerging contaminants that might be present in wastewater.

Contaminant	Type of Water	Hydrogen Potential (pH)	Catalyst Dose and Oxidizer Dose	% Removal	Reference
Amoxicillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%	[94]
Ampicillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%	[94]
Cloxacillin	Synthetic	3	$H_2O_2/Fe^{2+} = 20$	100%	[94]
17α -ethinylestradiol	Wastewater with spike	3	$[Fe^{2+}] = 5 \text{ mg/L}$ $[H_2O_2] = 4.3-15 \text{ mg/L}$	100%	[95]

Table 4. Examples of emerging contaminants treated by the photo-Fenton advanced oxidation process (AOP) and process parameters.

UV/O_3

In UV-ozone AOP, the wavelength to be handled should be $\lambda < 300$ nm so that dissolved ozone can be split and a fast reaction of atomic oxygen (O) with water (H₂O) takes place, and thermally excited hydrogen peroxide (H₂O₂) is generated [10].

In the following Equations (27)–(31), the process that occurs to generate thermally excited hydrogen peroxide (H_2O_2) and hydroxyl radicals (HO°) is captured. It needs to be emphasized that there are two spin reactions allowed (Equations (27) and (28)) and that the quantum yield of the ozone decomposition is only 0.64 [96].

$$O_3 + hv \to O(^1D) + O_2(^1\Delta g)$$
⁽²⁷⁾

$$O_3 + hv \rightarrow O(^{3}P) + O_2(3\sum_{g})$$

$$(28)$$

The low quantum yield of ozone decomposition can be attributed to the recombination that takes place in the solvent (Equation (29)) [96]. As can be seen, in Equation (29), the atomic and diatomic oxygen produced in Equation (27) react again, generating ozone.

$$O(^{1}D) + O_{2}(^{1}\Delta g) \rightarrow O_{3}$$
⁽²⁹⁾

On the other hand, in order to generate thermally excited hydrogen peroxide, oxygen $(O(^{1}D))$ reacts rapidly with water to generate it, as denoted in Equation (30) [96].

$$O(^{1}D) + H_{2}O \rightarrow H_{2}O_{2} \text{ (hot)}$$

$$(30)$$

It is worth mentioning that not all of the hydrogen peroxide generated decomposes into hydroxyl radicals (HO°) (Equation (31)) [96].

$$H_2O_2(hot) \rightarrow 2HO^\circ$$
 (31)

At the end of the UV/O₃ process, the quantum yield of free hydroxyl radicals (HO $^{\circ}$) is 0.1 [96].

Now, regarding the operating pH of the UV/O_3 AOP, Souza & Féris [97] found in their research, which focused on mineralizing caffeine in synthetic solution, that to obtain high mineralization of caffeine, the pH levels and reaction time must be kept high. The levels of pH and time used in the experimental design of this research ranged from 3 to 11 for pH and from 15 to 30 min for reaction time, respectively.

On the other hand, in another investigation by Chang et al. [98] for the removal of mefenamic acid, they established that pH plays an important role because in the first 5 min at pH levels of 4, 7, and 9, mefenamic acid remnants of 62, 53, and 50% were found. However, after 40 min of exposure, at pH levels of 4, 7, and 9, 37.5, 42.5, and 45.8% of mefenamic acid remained, so it was concluded that when the pH decreases, the removal of mefenamic acid increases, and the UV/O_3 process showed a higher removal power than the traditional ozonation process [98]. With this, as mentioned above, it is evident from the references [97,98] and their changing pH levels that pH levels can vary drastically in

the UV/O_3 AOP depending on the type of emerging contaminant that needs to be treated since in one investigation the pH level should be kept high and in the other investigation, it should not. In addition, the optimum ozone dosage and radiation exposure must be calculated experimentally, in conjunction with pH, depending on the pollutants to be treated in the wastewater.

Table 5 below shows additional data that were not mentioned in the previous description of the referenced research [97,98]. Additional research is also presented [99]. The maximum removals by the UV/O₃ process ranged from 60–95%, and the water commonly used for the experimentation was synthetic water, based on the information compiled in Table 5. It should be noted that although the UV/O₃ AOP presents good removal percentages, Miklos et al. [10] point out that the AOP presents problems such as the UV lamps and the ozone generator demands large amounts of electrical energy and the efficiency of generation of hydroxyl radicals is low. Therefore, based on this information, it can be said that the UV/O₃ AOP is expensive.

Table 5. Examples of emerging contaminants treated by UV/O₃ advanced oxidation process (AOP).

Contaminant	Type of Water	% Maximum Removal	Reference	
Caffeine	Synthetic	95%	[97]	
Mefenamic acid	Synthetic	60-80%	[98]	
Ketoprofen	Synthetic	95% (mineralization)	[99]	

3.1.3. Electrochemicals

In this section, a brief description of the advanced electrochemical oxidation processes will be given since they are diverse. It is worth mentioning that some of the electrochemical AOPs, such as anodic oxidation, and the electro-Fenton process, among others, are relatively new processes that have been studied with the purpose of removing recalcitrant emerging contaminants [100].

Electrochemical AOPs are basically considered methods whose main objective is the remediation of wastewater contaminated by organic compounds (emerging pollutants) through the in situ production of reactive oxygen species such as hydroxyl radicals (HO°). One of the most studied electrochemical AOP is the electrochemical AOP of anodic oxidation; in general, in this process, a high current density (*j*) is applied to the anode (M) of the cell in order to produce physisorbed hydroxyl radicals on the anode surface M(HO°) [101]. The transfer of electrons, M(HO°) and M = O, or the combination of both, are part of the water cleaning process [102]. However, the oxidation capacity of electrochemical AOPs will depend on the electrochemical system used, the cell type, the electrodes, and the additional equipment used [103].

It should be added that in electrochemical AOPs, hydrodynamic parameters must be taken into account. As far as costs are concerned, the energy used to pump the water must also be considered since it could contribute to most of the energy consumption in these processes. This applies greatly if the current intensities used in the electrochemical AOP are low in order to increase the production of hydroxyl radicals (HO°) since the duration of the treatment and, therefore, the pumping time would be prolonged which would significantly increase costs [10].

On the other hand, Seibert et al. [104] concluded that, with respect to the application for industrial wastewater treatment, the costs generated by the use of electrochemical AOPs could be higher compared to those generated in conventional processes. However, if the operating conditions and parameters are optimized, they are more efficient in removing emerging pollutants.

Examples of emerging contaminants that have been removed by electrochemical AOPs in an aqueous solution are shown in Table 6. In the research reported by Brillas et al. [105], it was found that the mineralization of paracetamol in an aqueous solution is independent of pH, and it increases when the applied current and temperature are increased but decreases

when the concentration of paracetamol increases more than 315 mg/L. A boron-doped diamond electrode was used in this research because anodic oxidation was performed.

Now with regard to the research of Domínguez et al. [106], it was found in the experimental design used that for the 100% oxidation of ketoprofen in synthetic solution, the most important variable was the influence of the current intensity, followed by the electrolyte concentration, the flow rate and finally the pH. In this research, pH was also considered a parameter of minor importance. The electrodes used in this research were also made of boron-doped diamond.

On the other hand, Donoso et al. [107] found that the most important factor for the removal of tartrazine in synthetic solution was also the current intensity in the anodic oxidation. Boron-doped diamond electrodes were also used in this research. It is worth mentioning that, in this case, tartrazine is an artificial colorant used in the food industry.

Therefore, based on the information gathered, electrochemical methods are efficient for removing emerging contaminants (Table 6). However, they are very expensive due to the electrical energy used to carry them out, as in the case of anodic oxidation.

Table 6. Examples of emerging contaminants treated by electrochemical advanced oxidation processes (AOP).

Contaminant	Type of Water	Important Notes	Electrochemical Method Used	% Removal	Reference
Paracetamol	Synthetic	pH independent	Anodic oxidation	100% (mineralization)	[105]
Ketoprofen	Synthetic	pH variable of minor importance	Anodic oxidation	100%	[106]
Tartrazine	Synthetic	-	Anodic oxidation	57.85–99.97%	[107]

3.2. Biological Treatments

The biotechnological use of enzymes, plants, and microorganisms such as bacteria, fungi, cyanobacteria, and microalgae have been used effectively in the bio-transformation of emerging pollutants [108].

Microorganisms, which participate in biogeochemical processes, are capable of degrading organic compounds [109] due to the ability to modify their metabolic pathways when exposed to various contaminants [110]. Bacillus cereus, a bacterial isolated from petroleum sludge, has been shown to be effective in the degradation of prometryn, fluometuron, and sulfamethoxazole [111]. On the other hand, microalgae have the ability to bioabsorb, bio-adsorb, and biodegrade emerging pollutants [112]. Removing parabens [113], fungicides such as triclosan, compounds related to the manufacture of plastics such as bisphenol A, 17-ethinylestradiol, a synthetic steroid, and analgesic as tramadol and diclofenac. In addition, they are capable of removing metals and heavy metals such as mercury and lead. [114]. The use of algae for the treatment of emerging contaminants is considered profitable [115], and it can be applied in developing countries since energy and economic resources are the main limitation in reducing micropollutants and bacteria in urban wastewater [114,116]. On the other hand, wetlands have been shown to be effective in reducing many emerging organic pollutants [117]. Wetlands successfully removed (81–99.9%) compounds present in plastics such as diethyl phthalate, di-isobutyl phthalate, di-n-octyl phthalate, bis(2-ehtylxexyl) phthalate, tris(1-chloro-2-propyl) [118]. Oxidoreductases, enzymes capable of degrading varied organic compounds, including phenolic compounds, have also been used [119].

However, the use of microorganisms for emerging contaminants removal is still limited. Being the specific biological processes and difficult to scale. Some contaminants exert selective pressure on some microorganisms, for example, bactericides and fungicides [120]. The case of algal-based systems has limitations such as microbiological contamination that can affect the efficiency of the system. On the other hand, it is possible to use microalgaebacteria that form biofilms that work in synergy to improve the process [121]. The enzymes used are immobilized on various supports. However, it has been found that the enzymes are denatured, thus losing their catalytic activity [119,122]. Furthermore, the production of biomass for application at the industrial level is very low, so they have been genetically modified [123]. These strategies, called synthetic biology, allow for obtaining better results since they use the editing of sequences responsible for the degradation of compounds [124]. Considering genetically modified microorganisms as bioremediation factories [125].

Due to all these disadvantages, it has been suggested to use a combination of processes. As is the use of bioremediation, nanotechnology, and physicochemical treatments (AOPs included) to ensure that they are efficient and fast [110]. Taoufik et al. [126] state that biological processes have many advantages such as operability under mild conditions, economic feasibility, and ease of automation, such as activated sludge and oxidation ponds conventional processes used worldwide for wastewater treatment. However, these fail to remove recalcitrant or toxic contaminants such as emerging pollutants [126].

On the other hand, advanced oxidation processes present high operating costs, but meet the objective of removing recalcitrant or toxic contaminants such as emerging pollutants [126].

Therefore, Taoufik et al. [126] recommend in their research the use of hybrid processes, which employ both biological and advanced oxidation processes, in order to minimize the AOP costs by eliminating easily biodegradable pollutants through biological processes and guaranteeing the removal of emerging pollutants through advanced oxidation processes. This would be of great benefit, since most countries have conventional biological processes to treat wastewater, for example, oxidation ponds and activated sludge processes, which could be used.

4. Conclusions

Based on the information presented in this article, the following conclusions can be drawn. First, it is concluded that the main entry of emerging contaminants into the environment is through wastewater because the conventional processes commonly used to treat wastewater in different regions of the world do not have the capacity to degrade emerging contaminants in their entirety. In addition, it was also concluded that the distribution of emerging contaminants in the environment takes place primarily through the water cycle.

Now, it is of great importance to mention, according to the information gathered, that emerging contaminants affect the environment (flora, fauna, and human health) drastically, as can be seen in the subsection on pharmaceuticals, which affect several taxonomic groups in aquatic systems, such as microorganisms, algae, cnidaria, crustaceans, and fish. Also, some hormones have been reported as endocrine disruptors which can affect the poblational reproductive behavior, mainly in some aquatic species.

Moreover, emerging contaminants such as personal care products and pesticides, tend to bioaccumulate and be consumed through the food chain and the water cycle, affecting flora, fauna, and human health. In addition, pesticides have been detected in river water and drinking water at unacceptable concentrations due to their persistent, recalcitrant, and bioaccumulative characteristics; thus, they represent a global problem that must be urgently addressed.

It should be emphasized that the SARS-CoV-2 virus in the very near future could be a factor that defines the quality of water since its presence has been found in the wastewater of different countries, but this will be defined when the research on this subject is expanded, which by the way is of urgency. It should also be mentioned that the COVID-19 disease can possibly be contracted through human contact with contaminated wastewater containing the active virus (SARS-CoV-2). Therefore, it is of great importance to start looking for processes that can eliminate it, a clear example of which the advanced oxidation processes (AOP) represent.

Regarding advanced oxidation processes (AOP), it was concluded that they have good removal percentages of emerging contaminants and can be used for this purpose. However, there is still a lack of information and experimentation in real wastewater to verify the

18 of 23

potential of these processes to remove emerging contaminants that could be present in wastewater since most of the research is carried out with synthetic solutions. On the other hand, it is ruled that as different removal parameters are added to the AOP, their cost and difficulty of operation increase, as in the case of electrochemical AOPs.

However, current research on the oxidation and removal of emerging contaminants should also focus on identifying the oxidation products that are obtained through the oxidation of the target emerging contaminants, as the oxidation products may sometimes be more toxic than the parent emerging contaminant.

Finally, it sounds tentative to suggest that hybrid processes should be formed between biological and advanced oxidation processes in order to remove emerging pollutants and address the shortcomings of such processes when used alone. This is in order to remove emerging contaminants of interest and take advantage of conventional wastewater treatment processes that are already installed in the countries, as mentioned at the end of Section 3.2 in this manuscript.

Author Contributions: Conceptualization, A.R.B.-R., Y.R.-V. and L.R.-C.; methodology, A.R.B.-R. and L.R.-C.; validation, A.R.B.-R., L.A.O.-D., A.M.B.-S. and L.R.-C.; formal analysis, A.R.B.-R., L.A.O.-D., A.M.B.-S., J.C.R.-S., Y.R.-V. and L.R.-C.; investigation, A.R.B.-R., L.A.O.-D., A.M.B.-S., J.C.R.-S., Y.R.-V. and L.R.-C.; resources, A.R.B.-R., L.A.O.-D., A.M.B.-S. and L.R.-C.; data curation, A.R.B.-R. and L.R.-C.; writing—original draft preparation, A.R.B.-R., L.A.O.-D., A.M.B.-S., J.C.R.-S., Y.R.-V. and L.R.-C.; writing—review and editing, A.R.B.-R., L.A.O.-D., A.M.B.-S., J.C.R.-S., Y.R.-V. and L.R.-C.; writing—review and editing, A.R.B.-R., L.A.O.-D., A.M.B.-S., J.C.R.-S., Y.R.-V. and L.R.-C.; visualization, A.R.B.-R. and L.R.-C.; supervision, L.R.-C.; project administration, L.R.-C.; funding acquisition, Y.R.-V. and L.R.-C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Council of Science and Technology (CONACYT) with the scholarship grant number 805457, and the project number CF-2019/102967.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: To M.S.A. Luis A. Torres-Castañón from CIMAV-DGO, for his valuable technical support and collaboration.

Conflicts of Interest: The authors declare that they have no conflict of interest. The National Council of Science and Technology, which provide the scholarships grants, were not involved at any stage of the study.

Abbreviations

The following abbreviations are used in this manuscript:

AOP Advanced Oxidation Process

EC Emerging Contaminants or Pollutants

References

- Ramírez-Sánchez, I.M.; Martínez-Austria, P.; Quiroz-Alfaro, M.A.; Bandala, E.R. Efectos de los estrógenos como contaminantes emergentes en la salud y el ambiente. *Tecnol. Cienc. Agua* 2015, 6, 31–42.
- Tejada, C.; Quiñonez, E.; Peña, M. Contaminantes emergentes en aguas: Metabolitos de fármacos. Una revisión. *Rev. Fac. Cienc.* Básicas 2014, 10, 80–101. [CrossRef]
- 3. Rodriguez-Narvaez, O.M.; Peralta-Hernandez, J.M.; Goonetilleke, A.; Bandala, E.R. Treatment technologies for emerging contaminants in water: A review. *Chem. Eng. J.* 2017, 323, 361–380. [CrossRef]
- Sánchez-Ramírez, J. Contaminantes emergentes en nuestros sistemas acuáticos: Enemigos invisibles. *Ing. Reg.* 2018, 19, 18–21. [CrossRef]
- 5. American Chemical Society. Available online: https://www.cas.org (accessed on 18 August 2021).
- 6. Caviedes Rubio, D.I.; Delgado, D.R.; Olaya Amaya, A. Normatividad ambiental dirigida a regular la presencia de los productos farmacéuticos residuales en ambientes acuáticos. *Rev. Juríd. Piélagus* **2017**, *16*, 121–130. [CrossRef]

- 7. Babuponnusami, A.; Muthukumar, K. A review on Fenton and improvements to the Fenton process for wastewater treatment. *J. Environ. Chem.* **2014**, *2*, 557–572. [CrossRef]
- 8. Vorontsov, A.V. Advancing Fenton and photo-Fenton water treatment through the catalyst design. *J. Hazard. Mater.* **2019**, 372, 103–112. [CrossRef]
- Wang, N.; Zheng, T.; Zhang, G.; Wang, P. A review on Fenton-like processes for organic wastewater treatment. J. Environ. Chem. 2016, 4, 762–787. [CrossRef]
- 10. Miklos, D.B.; Remy, C.; Jekel, M.; Linden, K.G.; Drewes, J.E.; Hübner, U. Evaluation of advanced oxidation processes for water and wastewater treatment-A critical review. *Water Res.* **2018**, *139*, 118–131. [CrossRef]
- 11. Bautista, P.; Mohedano, A.F.; Casas, J.A.; Zazo, J.A.; Rodriguez, J.J. An overview of the application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biotechnol.* **2008**, *83*, 1323–1338. [CrossRef]
- 12. Deblonde, T.; Cossu-Leguille, C.; Hartemann, P. Emerging pollutants in wastewater: A review of the literature. *Int. J. Hyg. Environ. Health* **2011**, 214, 442–448. [CrossRef]
- 13. Zhou, Y.; Meng, J.; Zhang, M.; Chen, S.; He, B.; Zhao, H.; Li, Q.; Zhang, S.; Wang, T. Which type of pollutants need to be controlled with priority in wastewater treatment plants: Traditional or emerging pollutants? *Environ. Int.* **2019**, *131*, 104982. [CrossRef]
- 14. Contaminación y Calidad Química Del Agua: El Problema de Los Contaminantes Emergentes. Available online: https://fnca.eu/phocadownload/P.CIENTIFICO/inf_contaminacion.pdf (accessed on 19 August 2021).
- Saidulu, D.; Gupta, B.; Gupta, A.K.; Ghosal, P.S. A review on occurrences, eco-toxic effects, and remediation of emerging contaminants from wastewater: Special emphasis on biological treatment based hybrid systems. *J. Environ. Chem.* 2021, *9*, 105282. [CrossRef]
- 16. Lee, C.C.; Hsieh, C.Y.; Chen, C.S.; Tien, C.J. Emergent contaminants in sediments and fishes from the Tamsui River (Taiwan): Their spatial-temporal distribution and risk to aquatic ecosystems and human health. *Environ. Pollut.* **2020**, *258*, 113733. [CrossRef]
- 17. Malmborg, J.; Magnér, J. Pharmaceutical residues in sewage sludge: Effect of sanitization and anaerobic digestion. *J. Environ. Manag.* **2015**, 153, 1–10. [CrossRef]
- Castillo-Zacarías, C.; Barocio, M.E.; Hidalgo-Vázquez, E.; Sosa-Hernández, J.E.; Parra-Arroyo, L.; López-Pacheco, I.Y.; Barceló, D.; Iqbal, H.N.M.; Parra-Saldívar, R. Antidepressant drugs as emerging contaminants: Occurrence in urban and non-urban waters and analytical methods for their detection. *Sci. Total Environ.* 2021, 757, 143722. [CrossRef]
- 19. Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. *Toxicol. Lett.* **2002**, *131*, 5–17. [CrossRef]
- 20. Jones, O.A.H.; Voulvoulis, N.; Lester, J.N. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water Res.* 2002, *36*, 5013–5022. [CrossRef]
- Stuart, M.; Lapworth, D.; Crane, E.; Hart, A. Review of risk from potential emerging contaminants in UK groundwater. *Sci. Total Environ.* 2012, 416, 1–21. [CrossRef]
- Scott, L.C.; Wilson, M.J.; Esser, S.M.; Lee, N.L.; Wheeler, M.E.; Aubee, A.; Aw, T.G. Assessing visitor use impact on antibiotic resistant bacteria and antibiotic resistance genes in soil and water environments of Rocky Mountain National Park. *Sci. Total Environ.* 2021, 785, 147122. [CrossRef]
- 23. Zaied, B.K.; Rashid, M.; Nasrullah, M.; Zularisam, A.W.; Pant, D.; Singh, L. A comprehensive review on contaminants removal from pharmaceutical wastewater by electrocoagulation process. *Sci. Total Environ.* **2020**, *726*, 138095. [CrossRef] [PubMed]
- Teixeira-Lemos, E.; Teixeira-Lemos, L.P.; Oliveira, J.; Pais do Amaral, J. Pharmaceuticals in the Environment: Focus on Drinking-Water. In *Encyclopedia of Analytical Science*, 3rd ed.; Worsfold, P., Poole, C., Townshend, A., Miró, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 325–335. [CrossRef]
- Mohd Nasir, F.A.; Praveena, S.M.; Aris, A.Z. Public awareness level and occurrence of pharmaceutical residues in drinking water with potential health risk: A study from Kajang (Malaysia). *Ecotoxicol. Environ. Saf.* 2019, 185, 109681. [CrossRef] [PubMed]
- Kondor, A.C.; Molnár, E.; Vancsik, A.; Filep, T.; Szeberényi, J.; Szabó, L.; Maász, G.; Pirger, Z.; Weiperth, A.; Ferincz, A.; et al. Occurrence and health risk assessment of pharmaceutically active compounds in riverbank filtrated drinking wáter. *J. Water Process Eng.* 2021, 41, 102039. [CrossRef]
- 27. Figueiredo, L.; Erny, G.I.; Santos, L.; Alves, A. Applications of molecularly imprinted polymers to the análisis and removal of personal care products: A review. *Talanta* 2016, 146, 754–765. [CrossRef]
- Pal, A.; He, Y.; Jekel, M.; Reinhard, M.; Gin, K.Y.-H. Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. *Environ. Int.* 2014, 71, 46–62. [CrossRef]
- Delgado, N.; Bermeo, L.; Hoyos, D.A.; Peñuela, G.A.; Capparelli, A.; Marino, D.; Navarro, A.; Casas-Zapata, J.C. Occurrence and removal of pharmaceutical and personal care products using subsurface horizontal flow constructed wetlands. *Water Res.* 2020, 187, 116448. [CrossRef]
- 30. Pemberthy, M.D.; Padilla, Y.; Echeverri, A.; Peñuela, G.A. Monitoring pharmaceuticals and personal care products in water and fish from the Gulf of Urabá, Colombia. *Heliyon* **2020**, *6*, e04215. [CrossRef]
- 31. Bartrons, M.; Peñuelas, J. Pharmaceuticals and Personal-Care Products in Plants. Trends Plant Sci. 2017, 22, 194–203. [CrossRef]
- 32. Pérez-Lemus, N.; López-Serna, R.; Pérez-Elvira, S.I.; Barrado, E. Analytical methodologies for the determination of pharmaceuticals and personal care products (PPCPs) in sewage sludge: A critical review. *Anal. Chim. Acta* 2019, 1083, 19–40. [CrossRef]
- 33. Meng, Y.; Liu, W.; Liu, X.; Zhang, J.; Peng, M.; Zhang, T. A review on analytical methods for pharmaceutical and personal care products and their transformation products. *J. Environ. Sci.* **2021**, *101*, 260–281. [CrossRef]

- 34. He, B.; Ni, Y.; Jin, Y.; Fu, Z. Pesticides-induced energy metabolic disorders. Sci. Total Environ. 2020, 729, 139033. [CrossRef]
- 35. Hassaan, M.A.; El Nemr, A. Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *Egypt. J. Aquat. Res.* **2020**, *46*, 207–220. [CrossRef]
- 36. Chow, R.; Scheidegger, R.; Doppler, T.; Dietzel, A.; Fenicia, F.; Stamm, C. A review of long-term pesticide monitoring studies to assess surface water quality trends. *Water Res.* 2020, *9*, 100064. [CrossRef]
- Zhou, Y.; Wu, J.; Wang, B.; Duan, L.; Zhang, Y.; Zhao, W.; Wang, F.; Sui, Q.; Chen, Z.; Xu, D.; et al. Occurrence, source and ecotoxicological risk assessment of pesticides in surface water of Wujin District (northwest of Taihu Lake), China. *Environ. Pollut.* 2020, 265, 114953. [CrossRef]
- 38. Md Meftaul, I.; Venkateswarlu, K.; Dharmarajan, R.; Annamalai, P.; Megharaj, M. Pesticides in the urban environment: A potential threat that knocks at the door. *Sci. Total Environ.* **2020**, *711*, 134612. [CrossRef]
- Rezaei Kalantary, R.; Barzegar, G.; Jorfi, S. Monitoring of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers using Monte Carlo simulation in Behbahan City, Iran. *Chemosphere* 2022, 286, 131667. [CrossRef]
- 40. Mojiri, A.; Zhou, J.L.; Robinson, B.; Ohashi, A.; Ozaki, N.; Kindaichi, T.; Farraji, H.; Vakili, M. Pesticides in aquatic environments and their removal by adsorption methods. *Chemosphere* **2020**, 253, 126646. [CrossRef]
- 41. Saleh, I.A.; Zouari, N.; Al-Ghouti, M.A. Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches. *Environ. Technol. Innov.* **2020**, *19*, 101026. [CrossRef]
- 42. Sacdal, R.; Madriaga, J.; Espino, M.P. Overview of the analysis, occurrence and ecological effects of hormones in lake waters in Asia. *Environ. Res.* **2020**, *182*, 109091. [CrossRef]
- Hormonas Esteroides. 7. Hormonas Esteroidesnivel 3—Participación Plástica y Funcional (Biopsicologia.net). Available online: https://biopsicologia.net/nivel-3-participaci%C3%B3n-pl%C3%A1stica-y-funcional/7.-hormonas-esteroides (accessed on 28 August 2021).
- 44. Sta Ana, K.M.; Espino, M.P. Occurrence and distribution of hormones and bisphenol A in Laguna Lake, Philippines. *Chemosphere* **2020**, 256, 127122. [CrossRef]
- Jálová, V.; Jarošová, B.; Bláha, L.; Giesy, J.P.; Ocelka, T.; Grabic, R.; Jurčíková, J.; Vrana, B.; Hilscherová, K. Estrogen-, and rogenand aryl hydrocarbon receptormediated activities in passive and composite samples from municipal waste and surface Waters. *Environ. Int.* 2013, 59, 372–383. [CrossRef] [PubMed]
- Lei, K.; Lin, C.Y.; Zhu, Y.; Chen, W.; Pan, H.Y.; Sun, Z.; Sweetman, A.; Zhang, Q.; He, M.C. Estrogens in municipal wastewater and receiving waters in the Beijing-Tianjin-Hebei region, China: Occurrence and risk assessment of mixtures. *J. Hazard. Mater.* 2019, 389, 121891. [CrossRef] [PubMed]
- 47. Jarošová, B.; Bláha, L.; Giesy, J.P.; Hilscherová, K. What level of estrogenic activity determined by in vitro assays in municipal waste waters can be considered as safe? *Environ. Int.* **2014**, *64*, 98–109. [CrossRef] [PubMed]
- Aris, A.Z.; Shamsuddin, A.S.; Praveena, S.M. Occurrence of 17α-ethynylestradiol (EE2) in the environment and effect on exposed biota: A review. *Environ. Int.* 2014, 69, 104–119. [CrossRef]
- Ojoghoro, J.O.; Scrimshaw, M.D.; Sumpter, J.P. Steroid hormones in the aquatic environment. Sci. Total Environ. 2021, 792, 148306. [CrossRef]
- Ahmad, J.; Ahmad, M.; Usman, A.R.A.; Al-Wabel, M.I. Prevalence of human pathogenic viruses in wastewater: A potential transmission risk as well as an effective tool for early outbreak detection for COVID-19. *J. Environ. Manag.* 2021, 298, 113486. [CrossRef]
- 51. Hu, L.; Deng, W.J.; Ying, G.G.; Hong, H. Environmental perspective of COVID-19: Atmospheric and wastewater environment in relation to pandemic. *Ecotoxicol. Environ. Saf.* 2021, 219, 112297. [CrossRef]
- 52. Cao, Y.; Francis, R. On forecasting the community-level COVID-19 cases from the concentration of SARS-CoV-2 in wastewater. *Sci. Total Environ.* **2021**, *786*, 147451. [CrossRef]
- 53. Ai, Y.; Davis, A.; Jones, D.; Lemeshow, S.; Tu, H.; He, F.; Ru, P.; Pan, X.; Bohrerova, Z.; Lee, J. Wastewater SARS-CoV-2 monitoring as a community-level COVID-19 trend tracker and variants in Ohio, United States. *Sci. Total Environ.* 2021, 801, 149757. [CrossRef]
- 54. Chan, K.H.; Sridhar, S.; Zhang, R.R.; Chu, H.; Fung, A.Y.; Chan, G.; Chan, J.F.; To, K.K.; Hung, I.F.; Cheng, V.C.; et al. Factors affecting stability and infectivity of SARS-CoV-2. J. Hosp. Infect. 2020, 106, 226–231. [CrossRef]
- Rempel, A.; Gutkoski, J.P.; Nazari, M.T.; Biolchi, G.N.; Cavanhi, V.A.F.; Treichel, H.; Colla, L.M. Current advances in microalgaebased bioremediation and other technologies for emerging contaminants treatment. *Sci. Total Environ.* 2021, 772, 144918. [CrossRef]
- 56. Cheng, M.; Zeng, G.; Huang, D.; Lai, C.; Xu, P.; Zhang, C.; Liu, Y. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review. *Chem. Eng. J.* **2016**, *284*, 582–598. [CrossRef]
- Aleksić, M.; Kušić, H.; Koprivanac, N.; Leszczynska, D.; Božić, A.L. Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water—The application of zeolite assisted AOPs. *Desalination* 2010, 257, 22–29. [CrossRef]
- Oller, I.; Malato, S.; Sánchez-Pérez, J.A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. Sci. Total Environ. 2011, 409, 4141–4166. [CrossRef]
- 59. Liu, Z.; Demeestere, K.; Hulle, S.V. Comparison and performance assessment of ozone-based AOPs in view of trace organic contaminants abatement in water and wastewater: A review. *J. Environ. Chem. Eng.* **2021**, *9*, 105599. [CrossRef]

- 60. Rubio-Clemente, A.; Chica, E.; Peñuela, G.A. Procesos de tratamiento de aguas residuales para la eliminación de contaminantes orgánicos emergentes. *Rev. Ambient. Água* 2013, *8*, 93–103. [CrossRef]
- 61. Dai, Q.; Shen, K.; Deng, W.; Cai, Y.; Yan, J.; Wu, J.; Guo, L.; Liu, R.; Wang, X.; Zhan, W. HCl-Tolerant H_XPO₄/RuO_X-CeO₂ Catalysts for Extremely Efficient Catalytic Elimination of Chlorinated VOCs. *Environ. Sci. Technol.* **2021**, *55*, 4007–4016. [CrossRef]
- 62. Chen, C.X.; Yang, S.S.; Ding, J.; Wang, G.Y.; Zhong, L.; Zhao, S.Y.; Zang, Y.N.; Jiang, J.Q.; Ding, L.; Zhao, Y.; et al. Non-covalent selfassembly synthesis of AQ2S@rGO nanocomposite for the degradation of sulfadiazine under solar irradiation: The indispensable effect of chloride. *Appl. Catal. B* 2021, 298, 120495. [CrossRef]
- 63. Cai, Q.Q.; Jothinathan, L.; Deng, S.H.; Ong, S.L.; Ng, H.Y.; Hu, J.Y. Fenton- and ozone-based AOP processes for industrial effluent treatment. In *Advanced Oxidation Processes for Effluent Treatment Plants*, 1st ed.; Maulin, P.S., Ed.; Elsevier: Singapore, 2021; Volume 11, pp. 199–254. [CrossRef]
- 64. Legrini, O.; Oliveros, E.; Braun, A.M. Photochemical processes for water treatment. Chem. Rev. 1993, 93, 671–698. [CrossRef]
- 65. Pignatello, J.J.; Oliveros, E.; MacKay, A. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84. [CrossRef]
- 66. Zhang, A.; Wang, N.; Zhou, J.; Jiang, P.; Liu, G. Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash. *J. Hazard. Mater.* **2012**, 201–202, 68–73. [CrossRef] [PubMed]
- 67. Wang, N.; Zheng, T.; Jiang, J.; Lung, W.; Miao, X.; Wang, P. Pilot-scale treatment of p-Nitrophenol wastewater by microwaveenhanced Fenton oxidation process: Effects of system parameters and kinetics study. *Chem. Eng. J.* 2014, 239, 351–359. [CrossRef]
- 68. Pastrana-Martínez, L.M.; Pereira, N.; Lima, R.; Faria, J.L.; Gomes, H.T.; Silva, A.M.T. Degradation of diphenhydramine by photo-Fenton using magnetically recoverable iron oxide nanoparticles as catalyst. *Chem. Eng. J.* 2015, 261, 45–52. [CrossRef]
- 69. López, N.; Plaza, S.; Afkhami, A.; Marco, P.; Giménez, J.; Esplugas, S. Treatment of Diphenhydramine with different AOPs including photo-Fenton at circumneutral pH. *Chem. Eng. J.* **2017**, *318*, 112–120. [CrossRef]
- Carmona, P.B. Tratamiento de Aguas Residuales de la Industria Cosmética Mediante el Proceso Fenton y con el Sistema Fe/γ-Al₂O₃/H₂O₂. Ph.D. Thesis, Universidad Autónoma de Madrid, Madrid, Spain, 2008.
- 71. Taco Ugsha, M.; Mayorga Llerena, E. Aplicación del proceso Fenton en la disminución de materia orgánica en aguas residuales de la industria termoeléctrica. *Quím. Cent.* **2013**, *3*, 25–30. [CrossRef]
- 72. Lai, C.; Shi, X.; Li, L.; Cheng, M.; Liu, X.; Liu, S.; Li, B.; Yi, H.; Qin, L.; Zhang, M.; et al. Enhancing iron redox cycling for promoting heterogeneous Fenton performance: A review. *Sci. Total Environ.* **2021**, 775, 145850. [CrossRef]
- 73. Ay, F.; Kargi, F. Advanced oxidation of amoxicillin by Fenton's reagent treatment. J. Hazard. Mater. 2010, 179, 622–627. [CrossRef]
- Escalona, I.; Fortuny, A.; Stüber, F.; Bengoa, C.; Fabregat, A.; Font, J. Fenton coupled with nanofiltration for elimination of Bisphenol, A. Desalination 2014, 345, 77–84. [CrossRef]
- 75. Zhang, A.; Li, Y. Removal of steroid estrogens from waste activated sludge using Fenton oxidation: Influencing factors and degradation intermediates. *Chemosphere* **2014**, *105*, 24–30. [CrossRef]
- 76. Van, H.T.; Nguyen, L.H.; Hoang, T.K.; Nguyen, T.T.; Tran, T.N.H.; Nguyen, T.B.H.; Vu, X.H.; Pham, M.T.; Tran, T.P.; Pham, T.T.; et al. Heterogeneous Fenton oxidation of paracetamol in aqueous solution using iron slag as a catalyst: Degradation mechanisms and kinetics. *Environ. Technol. Innov.* 2020, *18*, 100670. [CrossRef]
- Zhu, S.; Dong, B.; Yu, Y.; Bu, L.; Deng, J.; Zhou, S. Heterogeneous catalysis of ozone using ordered mesoporous Fe₃O₄ for degradation of atrazine. *Chem. Eng. J.* 2017, 328, 527–535. [CrossRef]
- Kwon, M.; Kye, H.; Jung, Y.; Yoon, Y.; Kang, J.W. Performance characterization and kinetic modeling of ozonation using a new method: R_{OH,O3} concept. *Water Res.* 2017, 122, 172–182. [CrossRef]
- 79. Ikehata, K.; Li, Y. Ozone-Based Processes. In *Advanced Oxidation Processes for Waste Water Treatment*, 1st ed.; Ameta, S.C., Ameta, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; Volume 5, pp. 115–134. [CrossRef]
- 80. Malik, S.N.; Ghosh, P.C.; Vaidya, A.N.; Mudliar, S.N. Hybrid ozonation process for industrial wastewater treatment: Principles and applications: A review. J. Water Process Eng. 2020, 35, 101193. [CrossRef]
- 81. Egbuikwem, P.N.; Mierzwa, J.C.; Saroj, D.P. Evaluation of aerobic biological process with post-ozonation for treatment of mixed industrial and domestic wastewater for potential reuse in agriculture. *Bioresour. Technol.* **2020**, *318*, 124200. [CrossRef]
- 82. Rekhate, C.V.; Srivastava, J.K. Recent advances in ozone-based advanced oxidation processes for treatment of wastewater—A review. *Chem. Eng. J. Adv.* 2020, *3*, 100031. [CrossRef]
- Yang, Y.; Liu, Z.; Demeestere, K.; Van Hulle, S. Ozonation in view of micropollutant removal from biologically treated landfill leachate: Removal efficiency, •OH exposure, and surrogate-based monitoring. *Chem. Eng. J.* 2021, 410, 128413. [CrossRef]
- Mathon, B.; Coquery, M.; Liu, Z.; Penru, Y.; Guillon, A.; Esperanza, M.; Miège, C.; Choubert, J.M. Ozonation of 47 organic micropollutants in secondary treated municipal effluents: Direct and indirect kinetic reaction rates and modelling. *Chemosphere* 2021, 262, 127969. [CrossRef]
- 85. Polo-López, M.I.; Sánchez Pérez, J.A. Perspectives of the solar photo-Fenton process against the spreading of pathogens, antibioticresistant bacteria and genes in the environment. *Curr. Opin. Green Sustain. Chem.* **2021**, 27, 100416. [CrossRef]
- Oller, I.; Malato, S. Photo-Fenton applied to the removal of pharmaceutical and other pollutants of emerging concern. *Curr. Opin. Green Sustain. Chem.* 2021, 29, 100458. [CrossRef]
- 87. Cabrera-Reina, A.; Miralles-Cuevas, S.; Sánchez Pérez, J.A.; Salazar, R. Application of solar photo-Fenton in raceway pond reactors: A review. *Sci. Total Environ.* **2021**, *800*, 149653. [CrossRef]

- Gou, Y.; Chen, P.; Yang, L.; Li, S.; Peng, L.; Song, S.; Xu, Y. Degradation of fluoroquinolones in homogeneous and heterogeneous photo-Fenton processes: A review. *Chemosphere* 2021, 270, 129481. [CrossRef] [PubMed]
- 89. Clarizia, L.; Russo, D.; Di Somma, I.; Marotta, R.; Andreozzi, R. Homogeneous photo-Fenton processes at near neutral pH: A review. *Appl. Catal. B* 2017, 209, 358–371. [CrossRef]
- Sánchez Proaño, R.G.; García Gualoto, K.J. Tratamiento de aguas residuales de cargas industriales con oxidación avanzada en sistemas convencionales. Granja 2018, 27, 103–111. [CrossRef]
- 91. Xavier, S.; Gandhimathi, R.; Nidheesh, P.V.; Ramesh, S.T. Comparative removal of Magenta MB from aqueous solution by homogeneous and heterogeneous photo-Fenton processes. *Desalin. Water Treat.* **2015**, *57*, 12832–12841. [CrossRef]
- 92. Huang, Y.H.; Tsai, S.T.; Huang, Y.F.; Chen, C.Y. Degradation of commercial azo dye reactive Black B in photo/ferrioxalate system. *J. Hazard. Mater.* **2007**, 140, 382–388. [CrossRef]
- 93. O'Dowd, K.; Pillai, S.C. Photo-Fenton disinfection at near neutral pH: Process, parameter optimization and recent advances. *J. Environ. Chem. Eng.* **2020**, *8*, 104063. [CrossRef]
- 94. Elmolla, E.S.; Chaudhuri, M. Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process. *J. Hazard. Mater.* **2009**, *172*, 1476–1481. [CrossRef]
- Frontistis, Z.; Xekoukoulotakis, N.P.; Hapeshi, E.; Venieri, D.; Fatta-Kassinos, D.; Mantzavinos, D. Fast degradation of estrogen hormones in environmental matrices by photo-Fenton oxidation under simulated solar radiation. *Chem. Eng. J.* 2011, 178, 175–182. [CrossRef]
- 96. Von Sonntag, C. Advanced oxidation processes: Mechanistic aspects. Water Sci. Technol. 2008, 58, 1015–1021. [CrossRef]
- 97. Souza, F.S.; Féris, L.A. Degradation of Caffeine by Advanced Oxidative Processes: O₃ and O₃/UV. *Ozone Sci. Eng.* **2015**, 37, 379–384. [CrossRef]
- Chang, E.E.; Liu, T.Y.; Huang, C.P.; Liang, C.H.; Chiang, P.C. Degradation of mefenamic acid from aqueous solutions by the ozonation and O₃/UV processes. *Sep. Purif. Technol.* 2012, *98*, 123–129. [CrossRef]
- Illés, E.; Szabó, E.; Takács, E.; Wojnárovits, L.; Dombi, A.; Gajda-Schrantz, K. Ketoprofen removal by O₃ and O₃/UV processes: Kinetics, transformation products and ecotoxicity. *Sci. Total Environ.* 2014, 472, 178–184. [CrossRef]
- Raj, R.; Tripathi, A.; Das, S.; Ghangrekar, M.M. Removal of caffeine from wastewater using electrochemical advanced oxidation process: A mini review. CSCEE 2021, 4, 100129. [CrossRef]
- Flores Tapia, N.E.; Roman Rodríguez, M.; Coba Cabrera, R.L.; Vélez Ortiz, J.J.; Sirés Sadornil, I.; Brillas Coso, E. Procesos Electroquímicos de Oxidación Avanzados en la degradación de los ácidos trans-cinámico y trans-ferúlico. *Cienc. Digit.* 2019, 3, 49–60. [CrossRef]
- 102. Ganiyu, S.O.; Martínez-Huitle, C.A.; Oturan, M.A. Electrochemical advanced oxidation processes for wastewater treatment: Advances in formation and detection of reactive species and mechanisms. *Curr. Opin. Electrochem.* 2021, 27, 100678. [CrossRef]
- Brillas, E. Recent development of electrochemical advanced oxidation of herbicides. A review on its application to wastewater treatment and soil remediation. J. Clean. Prod. 2021, 290, 125841. [CrossRef]
- 104. Seibert, D.; Zorzo, C.F.; Borba, F.H.; de Souza, R.M.; Quesada, H.B.; Bergamasco, R.; Baptista, A.T.; Inticher, J.J. Occurrence, statutory guideline values and removal of contaminants of emerging concern by Electrochemical Advanced Oxidation Processes: A review. *Sci. Total Environ.* 2020, 748, 141527. [CrossRef]
- 105. Brillas, E.; Sirés, I.; Arias, C.; Cabot, P.L.; Centellas, F.; Rodríguez, R.M.; Garrido, J.A. Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode. *Chemosphere* **2005**, *58*, 399–406. [CrossRef]
- Domínguez, J.R.; González, T.; Palo, P.; Sánchez-Martín, J. Anodic oxidation of ketoprofen on boron-doped diamond (BDD) electrodes. Role of operative parameters. *Chem. Eng. J.* 2010, *162*, 1012–1018. [CrossRef]
- Donoso, G.; Domínguez, J.R.; González, T.; Correia, S.; Cuerda-Correa, E.M. Electrochemical and sonochemical advanced oxidation processes applied to tartrazine removal. Influence of operational conditions and aqueous matrix. *Environ. Res.* 2021, 202, 111517. [CrossRef]
- 108. Agrawal, K.; Bhatt, A.; Chaturvedi, V.; Verma, P. Bioremediation: An effective technology toward a sustainable environment via the remediation of emerging environmental pollutants. In *Emerging Technologies in Environmental Bioremediation*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 165–196. [CrossRef]
- Azaroff, A.; Monperrus, M.; Miossec, C.; Gassie, C.; Guyoneaud, R. Microbial degradation of hydrophobic emerging contaminants from marine sediment slurries (Capbreton Canyon) to pure bacterial strain. J. Hazard. Mater. 2021, 402, 123477. [CrossRef] [PubMed]
- Meganathan, B.; Rathinavel, T.; Rangaraj, S. Trends in microbial degradation and bioremediation of emerging contaminants. *Phys. Sci. Rev.* 2021, 000010151520210060. [CrossRef]
- 111. Alhefeiti, M.A.; Athamneh, K.; Vijayan, R.; Ashraf, S.S. Bioremediation of various aromatic and emerging pollutants by Bacillus cereus sp. isolated from petroleum sludge. *Water Sci. Technol.* **2021**, *83*, 1535–1547. [CrossRef] [PubMed]
- Sutherland, D.L.; Ralph, P.J. Microalgal bioremediation of emerging contaminants-Opportunities and challenges. *Water Res.* 2019, 164, 114921. [CrossRef]
- Vale, F.; Sousa, C.A.; Sousa, H.; Santos, L.; Simões, M. Parabens as emerging contaminants: Environmental persistence, current practices and treatment processes. J. Clean. Prod. 2022, 347, 131244. [CrossRef]
- Singh, D.V.; Bhat, R.A.; Upadhyay, A.K.; Singh, R.; Singh, D.P. Microalgae in aquatic environs: A sustainable approach for remediation of heavy metals and emerging contaminants. *Environ. Technol. Innov.* 2021, 21, 101340. [CrossRef]

- Gondi, R.; Kavitha, S.; Kannah, R.Y.; Karthikeyan, O.P.; Kumar, G.; Tyagi, V.K.; Banu, J.R. Algal-based system for removal of emerging pollutants from wastewater: A review. *Bioresour. Technol.* 2022, 344, 126245. [CrossRef]
- Kumar, V.; Jaiswal, K.K.; Verma, M.; Vlaskin, M.S.; Nanda, M.; Chauhan, P.K.; Singh, A.; Kim, H. Algae-based sustainable approach for simultaneous removal of micropollutants, and bacteria from urban wastewater and its real-time reuse for aquaculture. *Sci. Total Environ.* 2021, 774, 145556. [CrossRef]
- 117. García-Galán, M.J.; Day, J.W.; Boopathy, R.; White, J.R.; Wallace, S.; Hunter, R.G. A review of emerging organic contaminants (EOCs), antibiotic resistant bacteria (ARB), and antibiotic resistance genes (ARGs) in the environment: Increasing removal with wetlands and reducing environmental impacts. *Bioresour. Technol.* 2020, 307, 123228. [CrossRef]
- Gikas, G.D.; Papaevangelou, V.A.; Tsihrintzis, V.A.; Antonopoulou, M.; Konstantinou, I.K. Removal of Emerging Pollutants in Horizontal Subsurface Flow and Vertical Flow Pilot-Scale Constructed Wetlands. *Processes* 2021, 9, 2200. [CrossRef]
- 119. Zdarta, J.; Jankowska, K.; Bachosz, K.; Degórska, O.; Kaźmierczak, K.; Nguyen, L.N.; Nghiem, L.D.; Jesionowski, T. Enhanced wastewater treatment by immobilized enzymes. *Curr. Pollut. Rep.* **2021**, *7*, 167–179. [CrossRef]
- 120. Gomes, I.B.; Maillard, J.Y.; Simões, L.C.; Simões, M. Emerging contaminants affect the microbiome of water systems—Strategies for their mitigation. *NPJ Clean Water* **2020**, *3*, 39. [CrossRef]
- Sousa, H.; Sousa, C.A.; Simões, L.C.; Simões, M. Microalgal-based removal of contaminants of emerging concern. J. Hazard. Mater. 2022, 423, 127153. [CrossRef]
- 122. Al-Maqdi, K.A.; Elmerhi, N.; Athamneh, K.; Bilal, M.; Alzamly, A.; Ashraf, S.S.; Shah, I. Challenges and Recent Advances in Enzyme-Mediated Wastewater Remediation—A Review. *Nanomaterials* **2021**, *11*, 3124. [CrossRef]
- Xiong, J.Q.; Kurade, M.B.; Jeon, B.H. Can microalgae remove pharmaceutical contaminants from water? *Trends Biotechnol.* 2018, 36, 30–44. [CrossRef]
- 124. Jaiswal, S.; Shukla, P. Alternative strategies for microbial remediation of pollutants via synthetic biology. *Front. Microbiol.* 2020, 11, 808. [CrossRef]
- 125. Bilal, M.; Iqbal, H.M. Microbial bioremediation as a robust process to mitigate pollutants of environmental concern. *Case Stud. Therm. Eng.* **2020**, *2*, 100011. [CrossRef]
- Taoufik, N.; Boumya, W.; Achak, M.; Sillanpaa, M.; Barka, N. Comparative overview of advanced oxidation processes and biological approaches for the removal pharmaceuticals. J. Environ. Manag. 2021, 288, 112404. [CrossRef]