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Recent nano-based technologies in the removal of pharmaceutical compounds from aquatic environment

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Abstract

Nowadays, pharmaceutical compounds have been recognized as emerging contaminants in water sources. The presence of these compounds, even in very small quantities, has been illustrated undesirable effects on the environment and living organisms. In light of this global problem, many studies have been conducted in respect of the distinguishing of occurrence, impacts, fate, and removal procedures of pharmaceutical residues from aqueous media. Up until now, the availability of pharmaceutical contaminants in surface waters, groundwater, wastewaters, soils, and sludge has been proved and well documented. In this sense, the current review has been investigated the fate of pharmaceutical compounds in aqueous solutions first. Afterward, different treatment methods were investigated and compared, such as conventional techniques, membrane processes, advanced oxidation processes, and combined methods of adsorption. In this study, it was found that the conventional water treatment methods have been recognized to be insufficient for the removal of pharmaceuticals. However, advanced oxidation processes have been exploited the most for the mineralization of the contamination with some restrictions, especially secondary contaminates. Also, it was found that the processes of ozonation, sonication, Fenton/photo-Fenton, and semiconductor photocatalysis are better compared to other methods. Furthermore, advanced oxidation processes are considered to be secured as they use non-toxic chemicals. Composed processes seem to be an excellent solution for water and wastewater treatment containing pharmaceutical contaminants, especially those that use renewable energy and by-products materials.

Keywords: Pharmaceutical pollution; Removal technologies; Advanced oxidation processes; Wastewater.

Introduction

During the last years, many organic contaminants have been recognized as potential emerging pollutants in the environment with limited existing literature [1]. Industrialization and excessive use of resources and consumer goods have led to destruction in terms of contamination and energy utilization [2]. An enormous number of pharmaceutical products are used around the world to treat humans and animals. Although the concentration of pharmaceuticals in the environment

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is low, its uninterrupted entry into the environment may pose a long-term threat to aquatic and terrestrial organisms. In recent years, pharmaceutical compounds ranging from a few nanograms to a few micrograms have been identified in surface water, groundwater, and wastewater treatment plants [3]. Pharmaceuticals are considered harmful because they are not degraded by various biological treatment methods in wastewater treatment plants. They residual untreated even after these treatments for a long time and are toxic to the environment in both low and high concentrations [4]. Many researchers have indicated the existence of pharmaceuticals in drinking water. Active pharmaceutical compounds in surface and groundwater with 100 ng L−1 concentration in drinking water [5]. Pharmaceuticals are excreted after application in their natural form, in their chemical structures, or metabolites. These compounds enter water frameworks via the pharmaceutical industry, hospitals, treatment centers, and landfill leachates [6]. Pharmaceuticals usually do not get completely eliminated in a conventional wastewater treatment plant. Therefore, the water containing these pharmaceuticals is released in the treated effluent and pollutes lakes, rivers, and eventually returns to drinking water. Pharmaceuticals in water can threaten the quality of drinking water resources, can lead to spread of drugs resistance, and can be toxic to aquatic organisms [7]. The fate and presence of these Pharmaceuticals compounds have caused growing global concern for politicians and the general public [8]. Hence, the development of efficient techniques is required to improve the removal of traces of pharmaceuticals. The purpose of the present paper is to review the occurrence and fate of pharmaceuticals compounds in water and wastewater. Afterward, the performance of different water treatment systems in the removal of pharmaceuticals, especially advanced oxidation technologies, will be investigated.

Attendance and the fate of pharmaceutical compounds in the environment

Pharmaceuticals are persistent human substances intended for medical purposes to treat human or animal disease [9]. Although originally designed as a pharmaceutical to treat a variety of diseases in humans and animals, but in fact, it has been found that due to their overuse, they have a negative impact on the environment, surface water, groundwater, urban wastewater, and drinking water [10]. United States Environmental Protection Agency (USEPA) has placed three drugs and eight artificial hormones, along with disinfectants and pesticides, on its current Infectious Diseases List (CCL-3) [11]. The European Union (EU) and the United States of America (USA) have also paid close attention to the fight against drugs in the environment [12-14]. For this purpose, several guidelines and frameworks have been approved that including the Community Research Program on Drug Compounds and Environmental Hormones (COMPREHEND), ecotoxicological assessments and waste disposal technologies (REMPHARMAWATER), and environmental risk assessment of veterinary drugs (ERAVMIS) [14,15]. These efforts clearly indicated that drugs are an environmental threat to the future, and therefore methods to remove them from the environment are essential. Table 1 displays the most commonly detected Pharmaceutical groups in the aquatic environment, which includes: (1) Anti-inflammatory and non-steroidal anti-inflammatory drugs (Ibuprofen, Acetaminophen, Diclofenac, and Naproxen), (2) Antibiotics (Penicillins, Tetracyclines), (3) Antidepressants (benzodiazepines), (4) Antiepileptics, (5) Lipid-lowering drugs, (6) Beta-blockers (Propranolol and atenolol), (7) Anticoagulants and antihistamines (Ranitidine and Famotidine) [16,17]. About 30 to 90% of these Pharmaceutical compounds are not degradable in humans and animals' bodies after consumption and enter aquatic environments as active compounds [18]. Most of these Pharmaceutical compounds are detected in hospital effluents, wastewater treatment plants, surface water, drinking water, and groundwater [19,20].

Table 1: Common Pharmaceuticals in water and wastewater and their concentrations [21-23].

Group of pharmaceutical	Therapeutic use	Name of pharmaceutical
Antibiotics	Antibiotics	Ofloxacin (6–52 ng/L) sulfamethoxazole (0.02–0.58 (μg/L) Penicillin G (b0.025 μg/L) Ciprofloxacin (6–60 ng/L)
Analgesic, antipyretic Nonsteroidal anti-inflammatory drugs (NSAIDs)	Analgesic/Antipyretics	Acetaminophen (10–23.33 μg/L) Naproxen (0.5–7.84 μg/L), Carbamazepine (0.1–1.68 μg/L), Diclofenac (0.01–510 μg/L), ketoprofen (0.13–3 μg/L), Ibuprofen 0.49–990 μg/L),
Antiepileptics CNS stimulant	CNS (Central nervous system) drugs	Caffeine (3.2–11.44 μg/L),

Beta blockers Cholesterol and Triglyceride reducers	Cardiovascular drugs	Atenolol (10–730 ng/L), Propranolol (0.05 µg/L), metoprolol (10–390 ng/L), gemfibrozil (0.3–3 µg/L), clofibric acid (0.47–170 µg/L) clofibric acid (0.47–170 µg/L),
Steroid hormones	Endocrinology treatments	17α-ethinylestradiol (1 ng/L), 17β-estradiol (10 ng/L), , estriol,
Iodinated X-ray contrast media	Diagnostic aid-adsorbable organic halogen compounds	Iomeprol (1.6 µg/L), Iopromide (0.026–7.5 µg/L)

Pharmaceuticals contaminants are continuously discharged by various input sources into the environment as indicated in Figure 1. The fate and behavior of Pharmaceuticals in aqueous media are not yet sufficiently understood. However, pharmaceutical compounds can be decreased by processes and reactions initially in the dilution phase [24]. The removal efficiencies of pharmaceutical compounds in treatment plants are different in various countries due to climate, the nature of organic compounds, geography [25], and operating conditions [26]. Chemical reactions in an aqueous medium are capable to change the main combination of drug compounds. Complete mineralization of compounds may occur in the form of carbon dioxide, sulfate, nitrate, and other mineral compounds [27]. In these cases, the final products may be more stable than the original compound, which is more or less toxic. However, due to their stability and resistance to degradation, these compounds have the potential to cause side effects in aquatic organisms and can directly affect human health [28]. Regarding this, researchers recommended the use of various advanced technologies to reduce drugs in aquatic environments. Liu and Wong [29]. Reported a comprehensive survey of drug contamination in China and emphasized that precautions should be taken to prevent the diffusion of drug compounds into water, soil, humans, and animals. After identifying contaminants from the pharmaceutical industry, extensive research has been conducted to reduce the effect or remove these substances in pharmaceutical wastewater. The following measures were taken to purify and reduce drug contaminants.

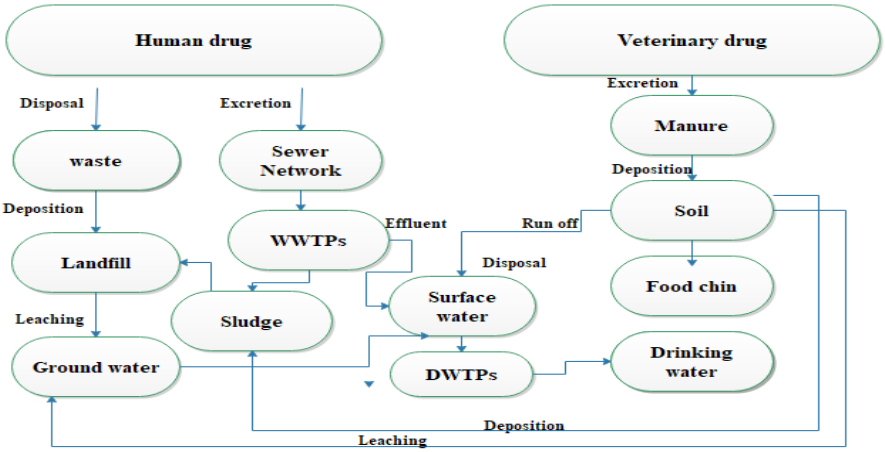

Figure 1: Main sources and pathways of drug pollutants in the environment [19].

Table 2: Composition of Pharmaceutical wastewater [30].

Fermentation processes wastewaters				Chemical processes wastewaters			
parameters (mg/L)	Maximum value	Minimum value	Average compounds	parameters (mg/L)	Maximum value	Minimum value	Average compounds
COD	32500	375	8854	COD	12380	180	4670
BOD_{50}	6000	200	2344	BOD_{50}	6000	2.5	2150
BOD50/COD	0.6	0.1	0.32	BOD50/COD	0.6	0.2	0.4
TOC	4940	860	2467	TOC	760	190	440
TDS	9320	675	6.9	TDS	7130	57	1200

Methods of pharmaceutical wastewater treatment

Since a conventional treatment system is not designed to remove these polar contaminants [31]. So far, various methods have been applied to remove pharmaceutical contaminants from water and wastewater. Since the effluents of these industries are different in quantity, the initial composition of drug, season, and time, so a special treatment system cannot be considered for these industries. This section provides an overview of the methods used for the removal of drug compounds to 2020 year.

Chlorination

Chlorine is one of the materials used in water disinfection. A study on the removal of acetaminophen from wastewater noticed that chlorine treatment produced different products that identified two toxic compounds [32]. Among the chemical oxidants used in water treatment, chlorine dioxide (ClO_2) is one that has the potential to be further investigated for the removal of pharmaceutical compounds in wastewater. ClO_2 is a very strong oxidant compared to chlorine and can degrade many organic compounds by oxidation. Compared to ozone, ClO_2 reacts more slowly and with fewer compounds, also compared to chlorine, with sulfonamides groups, estrogens and macrolides react faster [33]. ClO_2 is not able to degrade diclofenac as a non-steroidal anti-inflammatory drug because it has been reported at concentrations above the gram per liter of water [33]. ClO_2 was also able to remove wastewater containing steroidal estrogens and estrogen industrial chemicals as well as personal care products with low doses of ClO_2 between 1.25 and 3.75 mg/L [34]. It has also been reported that several antibiotics in water and wastewater have been completely degraded by ClO_2 [35].

Surface adsorption using activated carbon

Adsorption is a mass transfer process in which components in a solution are collected on a suitable contact surface. In the adsorption process, activated carbon can be used to remove many pharmaceuticals from water [36]. The effectiveness of this process depends on the adsorbent properties such as the physiochemical structure, the specific surface area, the porosity, however, the adsorbate characteristics comprising the size, shape, and surface hydrophobicity. There are many studies dealing with the adsorption of pharmaceutical compounds from water and wastewater but the involved mechanisms must be considered in the judgment of adsorbents superiority. The advantage of using activated carbon as an adsorbent in the removal of drugs is that it does not produce toxic products and has a high capacity to absorb drug compounds [37,38]. In regard to the activated application, in primary treatment effluent, some drugs are removed during the adsorption process, while others remain in the water, including naproxen, iopromide, sulfamethoxazole, and ibuprofen [25]. In a study concerning the adsorption of nitroimidazole using activated carbon, the results showed that by increasing the percentage of oxygen and enhancing the hydrophobicity of carbon, a significant increment in the nitroimidazole uptake occurred. This achievement obviously illustrated that the adsorption process is notably influenced by the chemical properties of carbon [39]. Also, the efficiency of adsorption of drugs by activated carbon significantly depends on pH, initial concentration of the contaminant, temperature, and the presence of other ions in the solution [40]. It should be noted that if the activated carbon adsorption process is used in wastewater treatment, it may compete with the dissolved organic matter in the wastewater to adsorb active sites, thus reducing the capacity of activated carbon leads to decreasing the drug contaminants adsorption [41]. Adsorption can reduce the concentration of organic matter in wastewater, improve the biochemical process, and recover useful substances, even if the cost of the adsorbent is predominantly high. Another major problem of using activated carbon is the separation of the adsorbent from the treated water, which is partially solved by integrating this process with another treatment unit [42].

Membrane filters

Removal of drug contaminants in membrane processes occurs through several processes [43]. Membrane separation processes include diffusion process, reverse osmosis, ultrafiltration, nanofiltration, in which these methods usually use external energy or chemical potential difference as a driving force to separate pollutants from wastewater [44]. These processes and mechanisms depend on the physicochemical properties of the contaminant (hydrophobicity or hydrophilicity of the contaminant compound), solution pH, type of membrane materials, surface morphology, and pore size [36]. Separating by membrane filters deals with the wastewater properties that whether is difficult to treat with conventional methods or not. Besides, in this technique, changing the water quality will not have much effect on the treatment process. In this regard, because the pores used in the ultrafiltration approach for the passage of drug contaminants are very small, nowadays, reverse osmosis and nanofiltration methods are mainly substituted. A study of pharmaceutical wastewater treatment plants demonstrated that sulfonamides were effectively removed by nanofiltration and reverse osmosis [24]. Lee et al [45] noticed

that 92% of oxytetracycline at an initial concentration (1000 mg/l) was removed using a membrane filter. The advantages of this method are easy operation, simplicity of operation, and change in the nature of wastewater. However, in recent years, due to the high cost of the membrane module and membrane deposition and susceptibility to use, its utilization has been limited.

Biological treatment

Biological methods are commonly applied for the management of pharmaceutical wastewater. Typically, bacteria, fungi, and algae perform biological treatment of wastewater containing pharmaceutical contaminants, which can reduce pollution of natural ecosystems via a cost-effective and sustainable manner. In general, the main purpose of biological treatment processes is the decomposition of organic matter pollutants by a dense mass of microorganisms, which is capable to remove or reduce organic pollutants like the available drugs in wastewater.

Biodegradation of pharmaceutical wastewater using bacterial strains

Microbial communities are essential for ecosystems. Microbial organisms, especially bacterial ones, can decompose drug contaminants through the biodegradation process [46]. Some drugs, particularly antibiotics, are toxic for some bacterial strains while some special bacterial strains in the environment have the potential to biologically degrade these contaminants. These bacterial strains use drugs as a source of carbon and nitrogen, and by consuming them, they reduce these pollutants in the environment. In a study, the biodegradation potential of different drugs by *Achromobacter denitrif icans PR1* strain was evaluated. The results elucidated that this strain removed 100% of sulfamethazine and sulfapyridine, and 98% of sulfamethoxypyridazine and sulfasalazine in 56 hours, while its efficiency for Sulfamatoxin and sulfathiazole drugs was not considerable [47]. Paje et al [48] reported that biofilms composed of a combination of algal and bacterial species were exposed to 100 µg/L diclofenac for 4 weeks. The results illustrated that some species of *cytophage* bacteria (gram-negative, rod-shaped bacteria) survived after 6 weeks and were capable to biodegrade Diclofenac up to 97%. In another study, *Pseudomonas* bacteria were able to remove a high percentage of paracetamol at initial concentrations up to 2500 mg/L in 70 hours of incubation [49].

Biodegradation of pharmaceutical wastewater using fungi

Numerous studies have shown the effectiveness of microorganisms in removing drug contaminants through the mechanism of biodegradation and production of some enzymes [50]. Table 3 illustrated some of the most important studies concerning the biodegradation of different drugs by various organisms. Some fungal species produce extracellular enzymes that lead to the degradation of drug contaminants even with low solubility in water. These fungal strains contain strong oxidation enzymes (including peroxidases, ligninolytic, and intracellular enzymes such as cytochrome P-450) that can attack contaminants [51]. Buchicchio et al [52] removed carbamazepine by the fungal species i.e. *Trametes versicolor* over 7 days exposure. They reported a 72% of the drug removal occurred mainly influenced by the production of intracellular enzymes of manganese peroxidase. Complete degradation of Ibuprofen with an initial concentration of 10 mg/l was achieved by four white fungi namely *Irpex lacteus, Pryerochaete chrysoporium, Ganoderma lucidium,* and *Trametes versicolor* after 7 days of incubation [53]. However, *Trametes versicolor* removed clofibric acid (91%) and carbamazepine (58%) with high efficiency. These studies have shown that both intracellular and extracellular enzymatic activities are responsible for the degradation of drug contaminants [53].

Table 3: Biodegradation of different drugs by various organisms.

Organism	Species	Drug compound	Removal (%)	References
Algae	*Scenedesmus dimorphus*	Estrone	8 days 85%	[49]
	Chlamydomonas reinhardtii	17b-estradiol	100%, 7 days	[54]
	Nannochloris sp.	Sulfamethoxazole	32%, 14 days	[55]
	Scenedesmus	Obliquus	79.09%, 9 days	[56]
	Chlorella sp.	7-amino cephalosporanic acid	100%, 5 days	[57]
	Chlorella vulgaris and Spirulina platensis	penicillin	100%, 100%	[58]
	Chlamydomonas mexican	Carbamazepine	37%, 10 days, k = 0.0424/day	[59]
	Chlorella vulgaris	Diclofenac	21.58%, 9 days	[60]

	Chlorella sorokiniana	Diclofenac Ibuprofen	60, 100	[59]
Bacteria	*bacteria Paucibacter Filomicrobium*	Sulfamethoxazole	89%	[60]
	Starkeya sp. C11	Diclofenac	90	[61]
	Pseudomonas sp. CE21	Cefalexin Sulfamethoxazole Caffeine	46.7% 87.5 67.9%	[62]
	Delftia tsuruhatensis Pseudomonas aeruginosa	Paracetamol	99.9%	[63]
	Rhizobium sp. C12	Carbamazepine,	32	[61]
	Bacillus thuringiensis B1	Ibuprofen Naproxen	44–57%	[64]
Fungi	*P. chrysosporium*	Diclofenac Ibuprofen	99 75–99	[65]
	T. versicolo	17β-estradiol (E1)	95	[66]
	P. ostreatus	Triclosan 17-α ethinylestradiol	98 62	[67]
	B. adusta	17-α ethinylestradiol	78	[67]
	T. versicolor	Ranitidine, Crimetidine	90, 100	[68]
	T. versicolor	Erythromycin	90	[69]
	Trametes versicolor	hydrochlorothiazide	93	[70]

Biodegradation of pharmaceutical wastewater using microalgae

Recently, microalgae-based technology has been used as an effective method in industrial wastewater treatment. This technology has advantages such as stabilizing carbon dioxide, removing pollutants, saving nutrient inputs, and the potential of developing microalgae-derived products. The use of microalgae-based technology has also been reported for the treatment of water or effluents containing pharmaceutical products. Studies have shown that microalgae can effectively remove wastewater containing drugs from the wastewater [71]. The microalgal species *Scenedesmus obliquus* and *Chlamydomonas mexicana* were used to remove carbamazepine, which achieved 28% and 35% removal at a concentration of 1 mg/l, while at higher concentrations it inhibited the growth of algae. *Chlorella sorokiniana* was also used for the biodegradation of metoprolol, diclofenac, paracetamol, and ibuprofen, which were capable to remove 60-100%[59]. Microalgae also have the ability to effectively remove various types of emerging contaminants such as analgesic and anti-inflammatory drugs greater than 95% at a concentration level of 1 mg/l [50]. Therefore, this method is a low-cost and efficient technique to remove food, metals, and other contaminants from aquatic ecosystems [72,73].

Advanced oxidation processes (AOP)

In recent years, the use of Advanced Oxidation Methods (AOPs: Advance Oxidation Processes) has been increased in the removal of organic contaminants, especially drugs [74]. Based on the number of publications obtained from the Google Scholar and Scopus databases, studies on AOPs have increased annually, so that from 2000-2020 we have witnessed a multiplication of this process (Figure 2). In this process, free radicals such as $HO^{\bullet}$, $O_2^{\bullet}$, and $HO_2^{\bullet}$ are produced, which are very effective in the degradation of pollutants and by-products, as well as the mineralization of compounds. These reactions can be briefly described as follows: First, Hydroxyl radicals ($HO^{\bullet}$) react with the removed hydrogen from organic compounds through electron-transferring from donor orbital to acceptor orbital or the formation of two bonds, and organic radicals are formed (Eq. 1). Then, the produced organic radicals react with the available oxygen in the solution to form peroxides, which lead to decomposition (Eq. 2). Eventually, the mineralization of drug contaminants will be occurred (Eq. 3), resulting in the removal of organic compounds [75].

$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$ (Eq. 1)

$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$ (Eq. 2)

$HO^{\bullet} + RX \rightarrow RX^{\bullet+} + HO^{\bullet}$ (Eq. 3)

Advanced oxidation systems used to remove drug contaminants include ozone (O_3), UV/O_3, UV/O_3/hydrogen peroxide, Fenton, Photo-Fenton, Ultraviolet photolysis, and Photocatalysis [76,77]. Addressing literature [18,22], the process of AOPs has resulted in the removal of almost (90%) drugs from aqueous compounds.

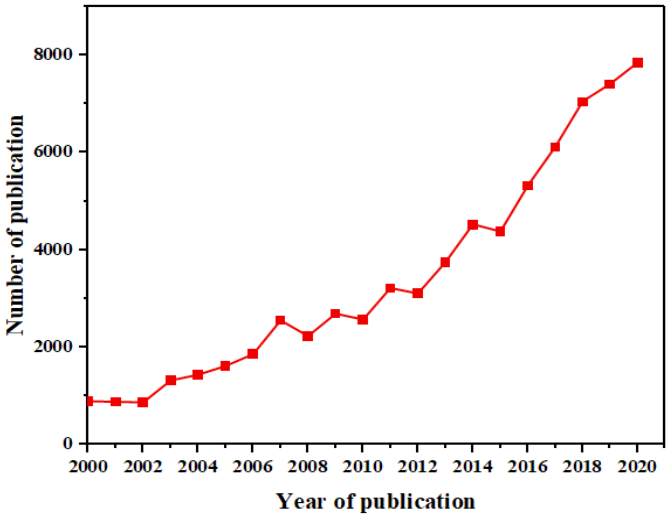

Figure 2: Number of publications on AOPs between 2000-2020 (Obtained from Google Scholar and Scopus databases, December 20, 2020).

Chemical oxidation process with ozone (O_3)

Ozone is the most common advanced oxidation treatment currently used in wastewater treatment. Ozone is usually utilized for disinfection, taste and odor management, and removal of organic compounds from water and wastewater [78]. No formation of by-products accompanied by the independence of performance from the pH of solution are the most advantages of disinfection by O_3 [79]. It is noteworthy to mention that due to the amide-bonded compounds are resistant to ozone degradation, this disinfection approach is not recommended for a highly saturated solution with these compounds. To solve this problem, the combination of O_3 with hydrogen peroxide (H_2O_2) can be used as an alternative process. As a result of the simultaneous addition of H_2O_2 and O_3, ozone decomposes and the production of hydroxyl radicals increases. In this case, the reaction of ozone and hydrogen peroxide will be as follows [80].

$O_3 + OH^- \rightarrow O_2 + HO_2^-$ (Eq. 4)

$O_3 + OH^- \rightarrow HO_2^{\circ} + O_3^{\circ-}$ (Eq. 5)

$HO_2^{\circ} \rightarrow H^+ + O_2^{\circ-}$ (Eq. 6)

$HO_3^{\circ} + H^+ \rightarrow HO_3^{\circ}$ (Eq. 7)

$O_2^{\circ-} + O_3 \rightarrow O_2 + O_3^{\circ-}$ (Eq. 8)

$HO_3^{\circ} \rightarrow HO^{\circ} + O_2$ (Eq. 9)

$HO^{\circ} + O_3 \rightarrow HO_2^{\circ} + O_2$ (Eq. 10)

Addressing Pal et al [81] the concurrent application of H_2O_2/O_3 has introduced an appropriate option for removing Naproxen and Ibuprofen. The degradation of antibiotic compounds by O_3 application has been strongly recommended [33,82]. In this process, various agents such as pH, the concentration of drugs, the dose of O_3, and the amount of H_2O_2 affect the process of ozone oxidation and removal of pollutants. Figure 3 schematically depicted the possible points for the ozonation and AOPs application to remove the pharmaceutical compounds from wastewater.

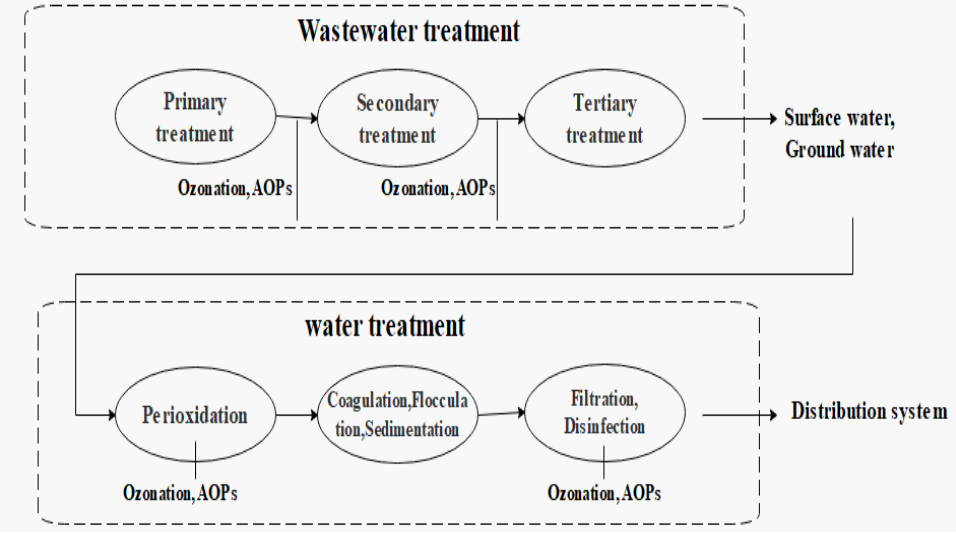

Figure 3: Possible points to apply ozonation and AOPs for the degradation of pharmaceuticals [83].

Fenton process

Fenton is another method of AOPs that produces hydroxyl radicals using H_2O_2 and iron ions. This is a heterogeneous catalytic reaction process in which iron ions act as reducing agents and hydrogen peroxide acts as oxidants. This method has been used in the degradation of penicillin, metronidazole and Gemfibrozil, and other organic compounds [84]. Some of the advantages of this method are outstanding efficiency, degradation rate, and mineralization degree. During the Fenton process, the enhanced oxidative potential of H_2O_2 along with the Fe ions as a catalyst under acidic conditions lead to the degradation of organic pollutants as follows (Eq. 11-16).

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + HO^{\bullet} + HO^{-} \quad \text{Eq. (11)}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad \text{Eq. (12)}$$

$$Fe^{+2} + HO^{\bullet} \rightarrow Fe^{+3} + HO^{-} \quad \text{Eq. (13)}$$

$$Fe^{+3} + HO_2^{\bullet} \rightarrow Fe^{+2} + O_2 + H^{+} \quad \text{Eq. (14)}$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad \text{Eq. (15)}$$

$$Organic\ pollutant + HO^{\bullet} \rightarrow Degraded\ products \quad \text{Eq. (16)}$$

The Fenton process depends on pH, drug contaminant properties, iron concentration, Fenton reagents, hydrogen peroxide content, and reaction time. However, the disadvantages of this method are practicality under the limited range of pH and a large amount of iron precipitation. However, this method can be used in the pretreatment process as a technology to convert non-biodegradable pharmaceutical wastewater into safe materials [85,86].

Photo-Fenton process

This process is the inverse of the Fenton process, however, an irradiation light in the photo-Fenton process uses a combination of UV radiation and the Fenton reactor [87]. The degradation rate of organic pollutants by the photo-Fenton process is significantly higher than the Fenton process because of more hydroxyl radicals generation. Contrary to the Fenton process, the regeneration of consumed ferric ions is taken place under the photo irradiation and Fe^{+3} ions are again converted to Fe^{+2} to continuous these cyclic reactions. The Fenton and photo-Fenton reactions can be formulated as follows:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad \text{Eq. (17)}$$

$$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad \text{Eq. (18)}$$

This method has many applications to remove contaminants from aqueous solutions. Numerous drugs including diclofenac, dipyrone, tetracycline, and amoxicillin have been degraded by this process with notable mineralization efficiencies [88,89]. In another study, complete degradation of ibuprofen was obtained using the photo-Fenton oxidation method [90]. The Fenton and photo-Fenton processes cannot be used in wastewater containing high concentrations of carbonate, bicarbonate, chloride, and nitrate, as these compounds scavenge hydroxyl radicals [87]. Table (4) is summarized some of the recent investigations regarding the different applications of various AOP processes for pharmaceutical removal from aqueous solutions.

Table 4: The application of various AOP processes for encountering with the different pharmaceutical-derived contamination.

AOP Process	Types of pharmaceutical	Summery	References
Ozonation	Amoxicillin	The highest degradation of Amoxicillin was obtained by the ozonation process at pH =10. The reaction kinetics followed the pseudo-first order kinetics, and the highest reaction rate was 1.970 min^{-1}.	[91]
	Diclofenac, Trimethoprim, Carbamazepine, Sulfamethoxazole	Diclofenac, Carbamazepine, sulfamethoxazole, and Trimethoprim were completely degraded at low doses of ozone, while sulfamethoxazole was degraded only at high concentrations of ozone due to the competition with intermediate reaction products.	[92]
	Ibuprofen, acetyl sulfamethoxazole and metoprolol	In this study, in optimal conditions, it was shown that the removal of metoprolol is faster than acetyl sulfamethoxazole and ibuprofen.	[78]
	Propranolol	The complete removal of propranolol was achieved in 8 minutes, while propranolol degradation decreased with decreasing ozone concentration.	[93]
	Paracetamol	The complete removal of paracetamol was occurred within 20 minutes, while mineralization was within 30 minutes (30%). In this study, by-products and reaction pathways were also identified.	[94]
	Penicillin	The degradation of penicillin increased with the increment of pH. However, due to the ozonation process, the BOD_5/COD ratio significantly increased.	[82]
	Sulfamethoxazole	The complete degradation of Sulfamethoxazole by ozonation was achieved after 60 minutes. The ozonation performance increased with the enhancement of pH, while its mineralization potential was low. In addition, by-products of the reaction were identified.	[94]
	drug contaminants	A 90% of drug contaminants was removed from wastewater using ozonation. At dosage less than 0.1 mg_{O_3}/mg_{COD} could not able to removed drug contaminants, while at a dosage of 0.5 mg_{O_3}/mg_{COD}, more than 70% of the contaminants were removed.	[95]
Fenton & Photo-Fenton	Amoxicillin	Complete oxidation of Amoxicillin was achieved under Fenton ($FeSO_4$) conditions for 5 minutes, while in the presence of sunlight oxidized for 15 minutes.	[96]

	Antipyrine	Complete degradation of Antipyrine was achieved using photo-Fenton in the presence of UVA-LED light in 2.5 minutes, which is attributed to •OH radicals in the system, and TOC was removed at optimal conditions and in 60 minutes at a rate of 93%.	[97]
	Ciprofloxacin	Degradation of ciprofloxacin using Photo-Fenton process in the presence of two different concentrations (25 and 1 mg/l) of iron citrate and iron oxalate and two pH i.e. 2.5 and 4.5 showed that at a concentration of 1 mg/l and pH 2.5 ciprofloxacin was degraded within 10 minutes.	[98]
	Nalidixic acid	Complete removal was achieved for nalidixic acid, while the degradation and mineralization were slower in a synthetic industrial effluent and saline water with a compound parabolic collector.	[99]
	Ofloxacin and trimethoprim	Degradation of Afloxacin and trimethoprim using photo-Fenton in the presence of sunlight in acidic and neutral conditions showed that in acidic conditions, the rate of drug degradation was higher but performed at a slower rate.	[43]
	Sulfamethoxazole	Drug degradation increased at a ratio of 1:1.5 H_2O_2: Fe^{+2}. In addition, as the H_2O_2 concentration increased, the degradation and mineralization of drugs and enhanced.	[100]
	Fluoxetine, Ciprofloxacin	80% and 36% Fluoxetine was removed at pH 4.5 after 20 minutes with Fecit and $Fe(NO_3)_3$, respectively. While Ciprofloxacin degradation was obtained 86% with Fecit and 75% with Fe $(NO_3)_3$, at the same time.	[101]
	Tetracycline	A 99% of Tetracycline degradation was obtained after 2 h and TOC achieved 43.7% within 120 minutes.	[102]
	Dipyrone	Dipyrone degradation was achieved by the process of Fenton (94.1%) and Photo-Fenton (96.4%), while the removal of TOC by these processes was 49.3% and 58.%2, respectively.	[103]
	Chloramphenicol, Ciprofloxacin, and Dipyrone	Degradation of chloramphenicol, ciprofloxacin, and dipyrone by Fenton and photo-Fenton processes showed that the degradation efficiency due to the production of common ions such as NH_4^+, NO_3^-, Cl_2, and FN may be hindered and reaction pathways were determined.	[104]
	Mitoxantrone	The results indicated that the degradation efficiency of Mitoxantrone using Fe (III), FeOx, and photo-Fenton processes were 77%, 82%, and 90%, respectively.	[105]
	flutamide	Removal of the anticancer drug flutamide by the photo-phantom process showed that the use of 5 ml/L Fe^{+2} and 50 mg/L H_2O_2 caused a 20% initial degradation and only a 3.05% mineralization, while 5 mg/L Fe^{+2} with an initial H_2O_2 concentration of 150 mg/L yielded a 58% initial degradation, along with a 12.07% mineralization. Eventually, thirteen transformation products were created	[106]
Sonication	Sulfadiazine	In this study, H_2O_2 demonstrated an undesirable effect on Sulfadiazine sonodegradation in comparison with sonolysis alone, while an optimal H_2O_2 concentration might exist when the oxidant is added to the sonochemical process.	[107]
	Fluoxetine	Fluoxetine sonodegradation demineralized water was insignificantly different than that in natural mineral water, and the degradation Fluoxetine was obtained under helium (%20), air (%80), and argon (>99%).	[108]

	Naproxen	The highest degradation was obtained under w/TiO_2-NT/US irradiation (72.4%). The sonocatalytic removal was decreased in the presence of radical scavengers. In these conditions, the •OH radicals illustrated a predominant role to control the mechanisms dealt with the US irradiation reactions.	[109]
	Antiepileptic Carbamazepine	In the early stages where the removal was high, probably due to the chemical effects, similarly led to the mass transfer and fluid flow improvement that increased adsorption. The highest elimination was obtained under the optimal conditions at 99.5% (35 kHz) and 98% (130 kHz).	[110]
	Tetracycline	The optimal tetracycline removal by US/TiO_2/H_2O_2 was attained at an acidic pH, TiO_2 (250 mg/l), and H_2O_2 (100 mg /L).	[111]
	Ibuprofen	In the sonophoto-Fenton process, the IBP degradation (95%) and mineralization (60%) were attained. The presence of ultrasonic irradiation slightly improved the iron catalytic activity. However, total degradation of IBP and removal of more than 50% of dissolved organic carbon were noticed by photocatalysis using TiO_2 in the presence of ultrasound irradiation.	[90]
	Acetaminophen	This study presents optimal conditions (580 kHz, 0.18 W, and 60 minutes) for the degradation of Acetaminophen under US irradiation. At 580 kHz and 227 W, a high rate of Acetaminophen degradation and H_2O_2 production were noticed.	[112]
	Ibuprofen	The highest Ibuprofen removal was 92.58 % obtained at 35 kHz frequency, pH =3 and 90 minutes retention time. Also, In the optimal conditions, the highest total organic carbon degradation was achieved by the sonocatalyst approach (77% at 90 minutes).	[113]
	Ciprofloxacin	Degradation of Ciprofloxacin was performed under optimal conditions (frequency 544 kHz, temperature 25 °C, and pH 7). The study showed that the addition of t-butanol reduced the rate of degradation due to radical ·OH reduction.	[114]
	Sulfamethoxazole, Diclofenac and Carbamazepine	The combined ultrasound/ozonation process reduced the degradation of drugs namely Diclofenac and sulfamethoxazole. Carbamazepine was also degraded by adding O_3 to the stream (3.3 g/h) over 20 minutes.	[115]
	Amoxicillin	The combined process of ozonation and US irradiation resulted in the degradation of amoxicillin in 2.5 minutes under optimal conditions. In addition, the TOC removal of 45% was obtained under similar conditions.	[91]
	Ibuprofen	The findings indicated that Pd-GO nanocomposite had higher sonocatalytic activity for the Ibuprofen degradation than sonicates alone. The higher Ibuprofen degradation rate was obtained at pH (3), Ibuprofen concentration (30 mg/L), catalyst dosage (2 g/L), and ultrasonic irradiation time (50 minutes). The kinetics of the degradation of Ibuprofen pursued pseudo-first-order reaction kinetics.	[71]
Photocatalyst	Diclofenac and Amoxicillin	In this study, the complete mineralization for amoxicillin and diclofenac was obtained by the utilization of TiO_2/photocatalytic and ozonation after 30 and 120 minutes, respectively. The non-toxicity of treated water was also confirmed using the growth of *Escherichia coli* and *Staphylococcus aureus.*	[116]

	Metoprolol and Propranolol	The highest degradation of Metoprolol and Propranolol was acquired by a concentration of 0.4 g/L TiO_2. The removal of TOC and COD after 360 minutes of light irradiation was 55%.	[117]
	Naproxen and Diclofenac	Photodegradation of Naproxen and Diclofenac by TiO_2 was showed that the photodegradation efficiency of drugs in river water reduced from 0.21 minutes when phosphate and chloride anions were added into river water samples, respectively. Also, the degradation rate of drugs was followed from the first-order kinetics.	[75]
	Methotrexate	In the presence of HCO_3^-, the Methotrexate photodegradation efficiency increased and the half-life of Methotrexate in a dose of 100 mg/L in the photocatalytic treatment was 13.8 minutes. By-products and reaction pathways were also detected.	[118]
	Ibuprofen	The rate of complete degradation of Ibuprofen by TiO_2 photocatalyst enhanced by increasing the number of LED-UV lamps within 30 minutes of the treatment period.	[119]
	Paracetamol	Complete degradation of paracetamol was achieved by increasing the concentration of TiO_2 over 20 minutes. The drug degradation was reduced at the high concentrations of TiO_2. Because it resulted in the decline of light penetration due to the increment of the solution turbidity.	[120]
	Diclofenac	The photodegradation of Diclofenac by TiO_2 under an irradiation level of 400 W/m^2 was achieved 96%, while the photodegradation under the photolysis process was attained 80%.	[121]
	Tetracycline	The photodegradation of Tetracycline in drinking water was higher than in ultrapure water. However, the degradation of Tetracycline by adding H_2O_2 to the TiO_2 solution was increased. Furthermore, the required time to degrade 100% of the Tetracycline drug was significantly reduced.	[122]
	Trimethoprim	The photocatalytic degradation of Trimethoprim using TiO_2 under solar light in the distilled water was greater than the simulated water. Also, the synthesis of degradation did not follow the first-order kinetics.	[123]
	Venlafaxine	Complete degradation of Venlafaxine was attained at optimal condition (0.4 g/L TiO_2, 2.5 mg/L venlafaxine) after 20 minutes. In addition, Venlafaxine photodegradation efficiency was enhanced by increasing TiO_2 concentration up to 0.8 g/L.	[124]
	Acetaminophen	In this study, the photodegradation of acetaminophen by TiO_2 nanotubes at different pH (3, 7, and 9) was illustrated that the increase of Reynolds during anodization led to an enhancement in the achieved photocurrents. Because a part of the initiation layer formed over the tubes under the hydrodynamic position was removed.	[125]

Ultrasonic radiation method

Recently, many studies have used the sonochemical process to improve the degradation performance of organic pollutants, especially drugs in water and wastewater. The ultrasonic method alone is capable of degrading contaminants, but this process, in combination with other AOP methods, degrades at a high rate. Therefore, the ultrasonic process (the act of applying sound energy to agitate particles in a sample, for various purposes) can also be an excellent option for organic contaminant degradation [113]. Ultrasonic reactions are caused by high-intensity ultrasound radiation from liquids (a frequency range of 20-1000 kHz) that produce cavitation. In this case, cavitation is a means of concentrating the energy emitted by ultrasound into the micro-reactor, which acts along with the simultaneous release of reactive radicals [43]. During this process, H_2O_2 is formed, which is associated with the catalyst leads to the degradation of drug contaminants

[126]. Advantages of this method compared to other methods are no production of toxic and carcinogenic compounds, no need to use chemicals, ease of use, short contact time, and no problems with odor and taste [127]. Equations (19-22) indicate the degradation of water and other molecules in water by the sonochemical process, hydroxyl radicals (OH) and hydroperoxy radicals (HO_2) are the main species that oxidize organic compounds existent in the aqueous medium [128].

$$H_2O + US \rightarrow H^{\cdot} + {}^{\cdot}HO \qquad \text{Eq. (19)}$$

$$O_2 + US \rightarrow 2O^{\cdot} \qquad \text{Eq. (20)}$$

$$N_2 + US \rightarrow 2N^{\cdot} \qquad \text{Eq. (21)}$$

$$H^{\cdot} + O_2 + US \rightarrow HO_2^{\cdot} \qquad \text{Eq. (22)}$$

In one study, the effect of sonolysis on the degradation of Diclofenac, Ibuprofen, and Dicloxacillin was investigated and the results showed that the rate of degradation increased linearly with increasing sonolysis power [129,130]. Another study of sonodegradation of Carbamazepine and Amoxicillin and Acetaminophen showed that the most removal efficiency occurred at a temperature range of 24-40 °C [112,131]. It was also found that the use of ultrasonic methods alone leads to a reduction in the rate of degradation, for this reason, it is recommended to use combined methods such as sonofiltration, sonoelectrochemical, sonophthalysis or catalysts [113,132].

Photocatalytic process

The term photocatalysis has been emerged since the 1920s. A photocatalyst is a substance that is activated by the initial absorption of photons and leads to an increase in the reaction rate. In fact, by irradiating light to the photocatalyst, electron-hole pairs (e^-, h^+) are produced, which increases the reaction rate [133]. A photocatalytic reaction depends on the energy of light (photon) the catalyst and wavelength. Generally, semiconducting materials are used as catalysts. The use of semiconductor metal oxides such as SnO_2, WO_3, ZnO, CuS, ZnS, TiO_2, etc. as photocatalysts for the oxidation of contaminants in the degradation of drug compounds has been applied. In the photocatalytic process, organic matter, including dyes and Pharmaceutical compounds, is converted to carbon dioxide and water in the presence of UV or solar light [134]. As mentioned, photocatalysts, which are mostly semiconductor materials with suitable energy band gaps, are activated in the presence of light, which leads to the degradation of pollutants and their conversion into harmless materials [7]. There is a conduction and valence band in semiconductor materials, which is called the bandgap energy, and when the photon energy is proportional to or more than the bandgap energy of the semiconductor, it leads to the excitation of an electron and its transfer from the valence band to the conduction band. As the electrons moved, there are created holes in the semiconductor valence band. These holes react with water atoms to generate hydroxyl radicals (OH), which have oxidizing power and are responsible for the degradation of pollutants. The conduction band electrons react with disintegrated oxygen species to form superoxide species, a process called reduction [135,136]. These electrons begin the redox reactions (figure 4).

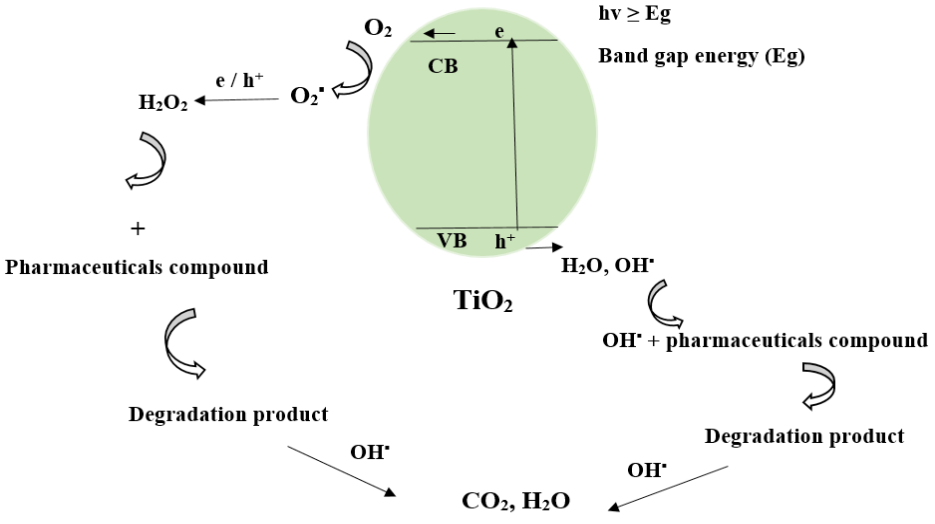

Figure 4: Schematic diagram illustrating the basis of TiO_2 photocatalysis.

In the mid-1920s, the ZnO semiconductor attracted much attention as a sensitizer for the optical decomposition of minerals and organics, and then the TiO_2 semiconductor was investigated for its optical degradation properties. However, this photocatalyst is one of the most effective AOPs for the treatment of pharmaceutical wastewater. In principle, stable compounds such as micropollutants can be removed via photocatalytic in advanced wastewater treatment processes [133,135]. In fact, photocatalysts, which are mostly semiconductor materials with appropriate energy band gaps, are activated in the presence of light, which leads to the degradation of pollutants and their conversion into harmless materials [137]. Figure 5 illustrated the mechanism of the number of published literature from 2000 to 2020, respectively, regarding the utilization of different approaches to remove different pharmaceuticals from aqueous media.

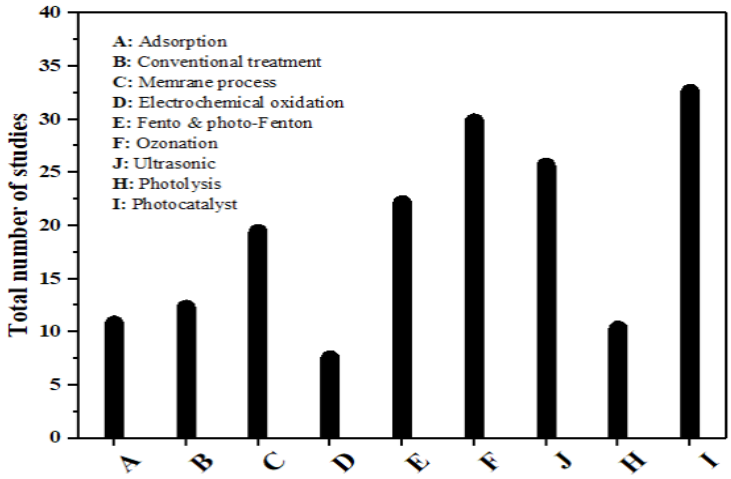

Figure 5: The number of documents concerning the application of different approaches towards the different pharmaceuticals removal from various aqueous media from 2000-2020 (December 20, 2020).

Conclusion and final recommendations

Although pharmaceuticals have been discharged into water bodies for years, their levels in the environment have only recently been measured and are recognized as potentially dangerous contaminants in surface water and groundwater for humans and other organisms. However, despite their unknown impacts on the environment and human health, there is currently no legal maximum concentration of drugs in most countries in the world. Besides, since the majority of conventional wastewater treatment systems are not capable to completely remove large amounts of these emerging pollutants from the municipal wastewater, more effective and specific treatment approaches are needed to reduce the environmental impacts of these pollutants. Various methods including adsorption by activated carbon, biological methods, membrane filters, and advanced oxidation processes (AOPs) have been developed to remove these contaminants from water and wastewater. TiO_2-based photocatalysts have been considered as one of the most prevalent AOP approaches due to their various advantages over other methods, and are also the most promising and appropriate options for the optical degradation of drug contaminants in water. Studies have shown that AOPs are highly effective in the degradation of pharmaceuticals compounds, thus the recognition of degradation products and toxicity levels are equally important because these products can be more toxic or biologically active than their parent compounds, so it may be imposed more risks to the environment. Although water solutions or synthetic wastewater samples have mostly been used for pharmaceuticals degradation studies, further studies using real wastewater samples are recommended. Although the matrix of the actual wastewater specimens is intricate due to the existence of inorganic and organic compounds as well as changes in the wastewater properties, an authentic AOP protocol to be required to ensure its efficiency. Moreover, the intricate nature of wastewater specimens makes the recognition of degradation products challenging and difficult. In addition to single AOP methods, hybrid methods are also becoming popular to achieve high removal efficiencies. Future studies should focus on the development of AOP degradation protocols in drug mixtures, given that they do not present exclusively in water bodies. Also, environmental planning (contaminant concentration, type of aquatic matrix) should be considered when planning for experimental drug degradation designs.

Moreover, the production of wastes (sludge in the Fenton process or exhausted or toxic catalysts in the photocatalysis process) should be reduced and possible options for e valorization of such wastes should be considered. The application of renewable energy is necessary for these processes. AOPs driven by solar light irradiation have an apparent through start not only for industrial wastewater treatment but also for the generation of energy simultaneously. This is the more economical solution for the problem of water treatment and its reuse. Therefore, it is not possible to replace accessible water and

wastewater treatment methods with AOPs from an economic viewpoint. But this problem can be resolved by using the composition of AOPs processes with the ancient treatment technologies. Therefore, combination use is feasible and cost-effective compared to a fully AOP application.

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