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The Treatment of Wastewater Containing Pharmaceuticals

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Abstract

The massive production of pharmaceuticals and excessive consumption will lead to their leakage into various water sources. Conventional treatment methods have proven ineffective in the treatment of these contaminants. Thus, choosing the appropriate treatment method is extremely important to deal with these pollutants. This paper presents an overview of pharmaceuticals in wastewater and studies the difference between the conventional and advanced oxidation processes (AOPs) for pharmaceutical treatment. AOPs can be an ideal solution for the degradation of these contaminants. The factors that affect the removal efficiency for AOPs were discussed, such as type of catalyst, light intensity, initial concentration of contamination, catalyst dose, and pH of the solution. The degradation pathway for some pharmaceuticals has also been discussed.

Keywords: Pharmaceuticals; Advanced oxidation processes (AOPs); Antibiotics

1 Introduction

Wastewater treatment is a mechanism used to eliminate and transform pollutants from wastewater or groundwater into effluent that can be transferred to the water supply with acceptable environmental impacts or reused for other purposes [1-4]. Pharmaceuticals are among the most significant emerging classes of environmental contaminants. Pharmaceuticals are chemical compounds which frequently detected in the aquatic environment. Recent studies indicated that pharmaceuticals are introduced continuously in an incredibly vast amount into the aquatic environment. The growing production and usage of these products in hospitals, veterinary operations, and household has contributed to an increasing prevalence of such substances. Because of their widespread use, pharmaceutical products are already reported in potable water, surface water, and wastewater due to their extensive benefits [5,6]. During wastewater treatment, the incomplete removal of pharmaceuticals can contribute to their release into water sources. The disposal of pharmaceuticals effluents after treatment in sewage wastewater plants, through oceans, rivers, and lakes has resulted in measurable amounts of pharmaceuticals in many countries' marine ecosystems [7]. Pharmaceuticals categories include various groups as shown in Figure 1, such as hormones, β-blockers, antiulcer agents, non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, antiepileptics, blood-lipid regulators, antihistamines, anti-asthma drugs, and serotonin reuptake inhibitors.

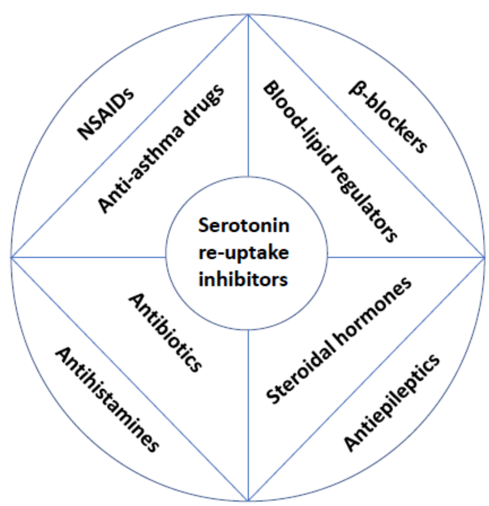

Figure 1: Classes of pharmaceuticals

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Their transformation/metabolites output mostly penetrate the marine system by effluents from sewerage wastewater treatment plants [8,9]. Consequently, before being discharged into water sources, the handling of pharmaceutical wastewater is desperately required for prior treatment to prevent severe environmental problems [10]. This study aims to concisely present the conventional treatment method and advanced oxidation process for pharmaceutical wastewater treatment.

2 Conventional treatment techniques

Conventional wastewater treatment plants consist of biological and physicochemical mechanisms [11]. However, their potential to eliminate pharmaceuticals from municipal sewage wastewaters is restricted. These pollutants cannot be digested as a carbon source by microorganisms and perhaps prevent the microorganisms' activity. Although more studies on this topic are required, it is understood that conventional WWTPs are not suitable to remove pharmaceuticals from wastewaters [12]. M. Zupanc et al. [13] studied using suspended activated sludge to degrade some pharmaceuticals. A limited degradation of clofibric acid, carbamazepine, and diclofenac were achieved. Simultaneously, the removal of ketoprofen, ibuprofen, and naproxen was higher than 74%. N. Delgado et al. [14] demonstrated a pilot-scale rotating biological contactor (RBC) for the degradation of methylparaben, carbamazepine, and sildenafl citrate. For methylparaben, the degradation efficiency was greater than 98%; however, carbamazepine and sildenafl citrate removal was less than 20%. S. Zorita et al. [15] studied a sewage plant with a tertiary treatment system located in Sweden containing a conventional system of activated sludge. By utilizing a chemical treatment, the removal efficiency was improved for various pharmaceuticals antibiotics. The study revealed that the removal efficiency was between 55 and 70%. Mckie et al. [16] used a conventional pilot plant to evaluate nine pharmaceutical compounds' removal efficiency. The steps of the treatment process included (flocculation, coagulation, sedimentation, and filtration). Also, the previous procedure was compared with biofilters. However, the removal efficiency of this method does not exceed 70%. From previous studies, it becomes clear that conventional treatment is not sufficient for pharmaceutical removal.

3 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are promising, relatively efficient, and ecological-friendly developments suitable for pharmaceuticals degradation [17-19]. Highly reactive oxidizing agents (ROS) species, including radical superoxide ($O_2^{\bullet-}$) and ($^{\bullet}OH$) hydroxyl radicals, could be generated in AOPs, and complicated organic molecules can be efficiently oxidized into more specific products [20, 21]. Heterogeneous photocatalysis is also widely utilized in AOPs to degrade various forms of recalcitrant organic contaminants, such as phenolic substances, pesticides, and pharmaceuticals [22, 23]. TiO_2 gets the most significant concern due to its elevated resistance in photo-corrosion, photocatalytic activity, biological resistance, and relatively cheap [24]. Also, several complex photocatalysts were studied in search of new semiconductors with reduced bandgap and broader light spectrum [25-27]. Fouad et al. [28] revealed a complete removal for sulfamethazine antibiotics after only 45 minutes of reaction time. An innovative photocatalytic reactor consisting of stainless-steel plates was designed. The plates were covered with W-TiO_2 catalyst. Also, the attached catalysts showed high stability and reusability even after five repetitive cycles. Samy et al.[29] demonstrated trimethoprim removal using fixed plates covered with S-TiO_2 and Ru/WO_3/ZrO_2. The results showed complete removal after 240 minutes of irradiation time. Catalyst dose was 0.5 g/L and at neutral pH. Gar Alalm et al. [30] revealed the removal of ampicillin under simulated solar light using synthesized WO_3/ZrO_2 nanoparticles. The results showed about 94% removal after 240 minutes of irradiation. Some examples of pharmaceutical removal efficiency using AOPs techniques are summarized in Table 1. Moreover, the chemical structure for some chosen pharmaceuticals is presented in Table 2.

3.1 Degradation Pathway

Tracking the compounds in the degradation process, their evaluation, and by-products degradation mechanism plays an essential part in determining the treatment method's success [31]. Identifying unknown products produced after degradation involve the collective usage of several analytical devices and techniques. LC/MS is an innovative version of mass spectrometry (MS) techniques with considerable benefits for the classification of by-products [32]. Yadav et al. [33] described removing an antibiotic sulfadiazine (SDZ) by using TiO_2 as a photocatalysis. For the examination of the samples, the LC/MS procedure was used for the investigation of samples, and intermediates produced during the degradation process were identified. SDZ was degraded until the formation of NO_3^-, H_2O, CO_2, CH_3COOH. Liu et al. [34] suggested a pathway for the degraded diclofenac (DCF) after degradation by using Ti-doped BiOI in the form of a microsphere. DCF was degraded until CO_2 and H_2O formation.

3.2 Parameters that affect the AOPs process

3.2.1 Composition and type of the catalyst

The photocatalytic process activity is based on the catalyst's structure characteristics and its surfaces, such as particle size distribution, bandgap, surface area, composition, porosity, and surface hydroxyl density [35].

Table 1: Degradation of pharmaceuticals using AOPs

Pharmaceutical	Treatment method	Initial concentration	Removal efficiency	Reference
Ibuprofen	AOPs	5 mg.L^{-1}	57%	[5]
Naproxen	AOPs	5-20 mg.L^{-1}	About 90%	[40]
Salicylic acid	AOPs	5 mg.L^{-1}	65%	[9]
Diclofenac	AOPs	0.1 mM	78.6%	[41]
Ciprofloxacin	AOPs	3 - 9 mg.L^{-1}	92.81%	[42]
Ciprofloxacin	AOPs	5 - 20 mg.L^{-1}	96%	[43]
Amoxicillin	AOP	105 mg.L^{-1}	92.3%	[44]
Sulfamethoxazole	AOPs	20 mg.L^{-1}	92%	[45]
Acebutolol; propranolol	AOPs	25 mg.L^{-1}	92% for acebutolol, and 75% for propranolol	[46]
Carbamazepine	AOPs	1 mg.L^{-1}	> 90%	[47]

These parameters may affect the adsorption activity of a contaminate or intermediates removal [36].

3.2.3 Light intensity

The quantity of absorbed light at a given length by the catalyst semiconductor is defined as the light intensity. The formation of the electron-hole and the initial speed for photocatalysis in the reaction are robustly affected by light intensity. The speed of the reaction revealed a square root dependence on the concentration of the light, while others found a direct relationship between the two factors [37]. Dillert et al. [38] studied nitrogen (II) oxide's oxidation using TiO_2 as a photocatalyst. The influence of light intensity on the oxidation process was achieved. The results revealed that photocatalytic oxidation is significantly affected by changing the light intensity.

3.2.4 Pollutant concentrations

The pollutants concentrations are a crucial factor that affects the kinetics and competence of removal [39]. In general, the degradation speed is enhanced with the increases in substratum amount and at low concentrations of contaminants. There are reasonable quantities of holes and oxidative radicals for the intense substrate concentration reaction with pollutants. Because of the inadequate concentrations of hydroxyl radicals ($OH^{\bullet}$), the degradation drops below the optimal concentration [48]. Increasing the number of pollutants leads to extra reactant particles adsorbed by the catalyst surface.

Reducing ($OH^{\bullet}$) production as a rare active position is available for the hydroxyl anions' adsorption. However, at higher concentrations of contaminants, the photons are absorbed before attainment of the catalyst surface. So, the light incorporation by the impurities reduces the photocatalytic activity [49]. The higher intensity of the substratum can moreover lead to catalyst deactivation. By the intensification in substrate amount, catalyst deactivation is extra prevalent for greater crystals in the catalysts. Some of this is attributed to the smaller specific surface area [49].

2.3.5 Influence of catalyst dose

Catalyst loading shows a vital function in the pollutant's concentration in the final removal results and the photocatalytic responses' removal speed. Usually, the degradation of such contaminants by the photocatalytic removal process increases with the catalysts' concentration until it approaches the optimal concentration. This behavior is detected because the rise in the catalyst's dosage provides a more significant number of active locations. Therefore, a more generation of electron-hole leads to improved superoxide and hydroxyl radicals that enable the removal of organic pollutants [50]. When the optimum level is reached, there is a direct correlation between the efficiency of removing and loading the catalyst. However, excess photocatalyst could decrease pollutants' degradation efficiency. This is because unfavorably light dispersion and reducing the penetration of light penetrating the solution [49]. The optimal catalyst concentration should, therefore, be used to avoid limiting process performance. The high catalyst concentration may also cause particle agglomeration and decrease suspension uniformity, thereby decreasing the active site's availability [51].

2.3.6 Influence the solution pH

The solution's pH is a significant parameter in the photocatalytic process because it regulates the size of the formed aggregates and the photocatalyst's surface charge properties [52]. Based on the pH of the solution, the catalyst surface may be negatively or positively charged. This is due to the most metal hydroxide surfaces amphoteric behavior. The following subsequent reactions are predicted to exist on the catalyst's surface, based on the pH [53]:

$$M-OH + H^{+} \rightarrow M-OH_2^{+} \quad pKa1 \quad (2.1)$$

$$M-OH + OH^{-} \rightarrow M-O^{-} + H_2O \quad pKa2 \quad (2.2)$$

where Ka is the acid dissociation constant, and (M-OH) equivalent metal hydroxyl groups.

Table 2: Chemical structure, and pharmaceutical classes

Pharmaceutical	Pharmaceutical class	Chemical structure
Ibuprofen	NSAIDs	$C_{13}H_{18}O_2$
Naproxen	NSAIDs	$C_{14}H_{14}O_3$
Salicylic acid	NSAIDs	$C_7H_6O_3$
Diclofenac	NSAIDs	$C_{14}H_{11}C_{l2}NO_2$
Sulfamethazine	Antibiotic	$C_{12}H_{14}N_4O_2S$
Ciprofloxacin	Antibiotic	$C_{17}H_{18}FN_3O_3$
Amoxicillin	Antibiotic	$C_{16}H_{19}N_3O_5S$
Sulfamethoxazole	Antibiotic	$C_{10}H_{11}N_3O_3S$
Acebutolol	b-blockers	$C_{18}H_{28}N_2O_4$
Propranolol	b-blockers	$C_{16}H_{21}NO_2$
Carbamazepine	Antibiotic	$C_{15}H_{12}N_2O$

The electric charge property of the pollutant is another vital factor in this process. When the pH is lower than the pollutant pKa, the contaminant is in molecular form, while at pH > pKa, the compound loses a proton and becomes negatively charged. However, because of the repulsion force between the base and the catalyst surface, while the dissociated pollutants and catalyst charges remain the same, the removal efficiency decreases. At pH < pKa, the water solubility is reduced, so the adsorption of organic contaminants on photocatalyst increases [54].

4 Conclusions

This research aims to study the treatment of wastewater containing pharmaceuticals. The AOPs treatment method has been confirmed to be effective in removing these pollutants. However, the conventional treatment method used in the wastewater treatment plant cannot remove these contaminants. Also, Pharmaceuticals degraded to sub-products after several stages. The role of AOPs parameters such as the composition of the catalyst, light intensity, catalyst loading, pH, and pollutant concentration was also discussed.

Ethical issue

Authors are aware of and comply with best practices in publication ethics, specifically concerning authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with research ethics policies. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice this scientific work's impartiality.

Authors' contribution

All authors of this study have a complete contribution to data collection, data analyses, and manuscript writing.

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