Advanced Oxidation Processes (AOPs) for treatment of antibiotics in wastewater: A review

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Abstract. Antibiotics are a broad group of drugs that are used in human and veterinary medicine. Antibiotics are slow to be degraded, so they can live for a long time in water, and this leads to the possibility of bioaccumulation in the environment. After metabolism, antibiotics are released into the aquatic environment. These compounds can be removed in many different ways, but after reviewing the treatment by advanced oxidation process (AOPs), it was found that this treatment has the ability to completely remove antibiotics from wastewater. This paper provides an overview of the Advanced Oxidation Processes (AOPs) for treatment of antibiotics in wastewater and has focused on Nonphotochemical processes (Ozonation), Photochemical Processes (such as photo-Fenton), heterogeneous photocatalysis (TiO_2 / UV systems) were reviewed. These methods achieved very high removal efficiency of antibiotics from industrial wastewater.

Keywords: advanced oxidation processes; antibiotics; wastewater

1. Introduction
Antibiotics are among the most common types of medicine used all over the world. Antibiotics work very effectively, even at low doses. After the metabolism process, large quantities of antibiotics are thrown from anthropogenic sources to the aquatic environment, because the antibiotics are slow to degrade and some of them are not degradable, which leads to their stability for a longer period in wastewater. Among the damages caused by the accumulation of antibiotics in wastewater for a long period of time can cause resistance in bacteria as well as cause disruptive effects of the endocrine system when consumed by organisms [1,2,3].

Due to the development that took place in the field of antibiotics and the production of large quantities of them, which are considered one of the main sources of environmental pollution and their presence in water has become a great challenge and a very worrying matter because its serious negative effects that threaten the life of living organisms, so removing antibiotics from wastewater is an important challenge in wastewater treatment [4].

Antibiotics can be removed from wastewater by conventional treatment methods, but they are not able to remove them very efficiently [5]. During the past years, and through many studies conducted on (AOPs) to remove these pollutants from wastewater, it was found that this method is characterized by high efficiency for removing antibiotics. On the other hand, the reasons that led to the use of modern treatment methods such as advanced oxidation processes are the operational problems and the high costs of using traditional methods [6, 7, 8]. In this review, is aimed to present a review of the literature on the removal of antibiotics from wastewater by various treatments of advanced oxidation processes. The focus will be on reviewing three advanced oxidation processes, these methods are
Nonphotochemical processes (Ozonation), Photochemical Processes (such as photo-Fenton), And heterogeneous photocatalysis (TiO₂ / UV systems) to remove antibiotics.

2. Sources of antibiotics in the environment
In recent years, the development in the pharmaceutical industry, especially antibiotics, has led to the production of large quantities of antibiotics annually, and thus these compounds lead to increased water pollution [9]. These pollutants are constantly discharged into the water as compounds or decomposition products. There are several sources responsible for discharging these pollutants, as shown in Figure 1 [10].

![Figure 1. Antibiotic pathways in the environment](image)

Among the pollutants that lead to soil pollution are the fertilizers in the fields, which leads to the transmission of pollution to the surface water and then to the groundwater, and this occurs through surface runoff or percolation [11]. As well as antibiotics during their discharges, entry into sewage water and their arrival at wastewater treatment plants (WWTP). Micro-pollutants with high polarity cannot be completely removed by wastewater treatment plants [9], but can be transferred to surface water and to groundwater after the filtration process.

3. Advanced oxidation processes (AOPs)
Advanced Oxidation Processes (AOPs) are a chemical treatment method widely used in wastewater treatment. Due to its high ability to remove organic compounds, including antibiotics, it has been suggested as an important treatment method to remove these pollutants from wastewater. The fundamental principle of advanced oxidative stress processes is the production of (•OH), which is produced from H₂O₂, O₃, photocatalysis, or oxidants using (UV) or sunlight. The hydroxyl radicals is known as a strong, non-selective chemical oxidizer. After its production, it begins to attack the organic compounds, which leads to the collapse of these organic compounds completely [12]. The performance
of hydroxyl radicals in removing organic compounds can be described. The hydroxyl radicals attack the organic compound and take a hydrogen atom \((R - H)\), which leads to the formation of an organic radical \((\cdot R)\), as shown in Eq.1. To form many products and by products, this radical will go through a series of chemical reactions. In theory, AOPs should completely mineralized organic compounds (MOCs) to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) as shown [13].

\[
R - H + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \cdot R
\]  

(1)

Also, AOPs can be used in the simultaneous treatment of several pollutants because they have a fast reaction and non-selective oxidation.

AOPs are classified into two groups: (1) a non-photochemical group (2) a photochemical group. The non-photochemical group can be divided into several processes including ozone, Fenton, Fenton-like processes, moist air oxidation, etc. While the photochemical oxidation processes classify both homogeneous and heterogeneous processes [14].

3.1. Nonphotochemical oxidation processes

There are several methods for producing hydroxyl radicals without the use of ultraviolet rays for wastewater treatment, including \((\text{O}_3, \text{O}_3 / \text{H}_2\text{O}_2, \text{and Fenton})\). Among all the mentioned species, the focus is on the ozonation process [15].

Ozone is a powerful oxidant and is widely used in wastewater treatment [16]. In the ozone process, there are two ways to complete the oxidation mechanism, which are the direct method, which occurs due to the interaction of ozone with dissolved compounds, the other method is the radical method, which occurs by interaction between the reactions of radicals generated by the decomposition of ozone (hydroxyl radicals) with dissolved compounds. These two mechanisms depend on the decomposition of the compound on several factors, including the kind of the pollutant, the concentration of ozone, or the pH of the solution. The decomposition of ozone resulted in the formation of radicals \((\text{HO}_2^*\) and \(\cdot \text{OH})\) that react with organic matter including microorganisms, hydrogen and hydroxide ions. Ozone has other uses, including it is used as a strong disinfectant because of its high ability to remove odor and color and get rid of organic materials and toxic substances [17, 18]. This method can be used to treat wastewater that contains antibiotic residues to remove it. Of the common factors that affect the performance of the ozone process are temperature, pH, ozone dose, and impurity concentration. To obtain high removal efficiency in ozone treatment, it is preferable to have a pH higher than 8, because it leads to the decomposition of ozone at high speed into hydroxyl free radicals. The optimum pH for oxidation of all organic components including antibiotics is 8-10 [19]. The following are simplified reaction mechanisms for ozone at high pH; [20]

\[
3\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \cdot \text{OH} + 4 \text{O}_2
\]  

(2)

Table 1 reviews this treatment under several different conditions.

3.2. Photochemical Processes

Advanced photochemical oxidation processes (AOPs) are an effective treatment method because they have the high capacity to generate the \(\cdot \text{OH}\) radicals needed for ultraviolet rays. It is based on absorption of oxidant. Photochemical is classified into two types: isotropic processes (ozone / UV rays, hydrogen peroxide / ultraviolet rays, and photofenton) or complex and heterogeneous processes that include
photocatalysis [21]. This study focuses on the process of photo-Fenton.

Fenton treatment has been widely applied and effective in wastewater treatment to remove various organic compounds. The Photo-Fenton reaction consists of a combination of Fenton's reagent with ultraviolet light (UV) [22]. The aim of adding UV to the Fenton process is to produce \( \cdot \)OH hydroxyl radicals, which have a high ability to degrade organic compounds by attacking them [23]. The purpose of adding ferrous sulfate as a catalyst for this process is to give power to oxidize some of the pollutant particles in which the hydroxyl radicals are formed from \( \text{H}_2\text{O}_2 \). Next, is found that the cause of all this mechanism is the generation of free radicals, depending on the reaction shown in Eq.3.

\[
2 \text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{OH} + 3\text{O}_2
\]

The Fenton reaction, It is an easy to apply method that can be used to remove organic compounds, including antibiotics from wastewater. Also among the benefits of adding UV–visible light is that it significantly speeds up the dissolution of organic pollutants when added to the reaction [24]. The equations that explain the mechanism of the process are:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^{-}
\]
\[
\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \cdot \text{OH}
\]
\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}
\]

This treatment has other advantages including reducing the waste sludge formation that was formed in the original Fenton process. In an image like the Fenton process, \( \text{Fe}^{3+} \) ions are added to the \( \text{H}_2\text{O}_2/\text{UV} \) process. At an acidic pH, the \( \text{Fe(OH)}^{2+} \) [25] complex is produced as shown in (7):

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+
\]
\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH}
\]

Another advantage of adding UV rays is to recycle \( \text{Fe}^{2+} \) by reducing \( \text{Fe}^{3+} \). With this process, the \( \text{Fe}^{2+} \) concentration increases and speeds up the overall reaction [26].

\[
\text{Fe}^{3+} + \text{hv} \Leftrightarrow \text{Fe}^{2+}
\]

Table 1 reviews this treatment under several different conditions.

### 3.3. Heterogeneous Photocatalysis with TiO2

Heterogeneous photocatalysis is a widely used technique for treating aqueous pollutants. It can be defined as accelerating the photosynthesis reaction in the presence of the catalyst. In recent years, the interest of scientists and researchers in the use of semiconductor materials has increased because they can be used as photocatalysts to remove organic and inorganic species from the aqueous or gaseous phase. Since it has the ability to oxidize organic and inorganic substrates, it has been suggested in environmental protection [27].

Semiconductors consist of two power bands: one is a high-power conduction and the other is a low-power valence band. The purpose of using this type of photolytic chemical oxidation is to generate \( \cdot \text{OH} \) radicals in heterogeneous processes. \( \text{TiO}_2 \) has been used because it gives excellent results and is non-toxic and available. In a semiconductor material, the straightness and conduction bands are
characterized by an energy gap / bandgap [28]. In this review the focus is on the TiO₂ / UV process.

The titanium dioxide catalyst remains the ideal and standard catalyst among all other semiconductors. The titanium dioxide catalyst has the advantage of possessing a high resistance to light corrosion and a desired band-gap energy, which makes it an ideal photocatalyst [29]. On the other hand, it is considered that this catalyst is widely available in the market, and is chemically inert and non-toxic, so it is used in the decomposition of many organic and inorganic pollutants, including antibiotics [30,31].

In the heterogeneous photocatalysis process, the use of a semiconductor catalyst titanium dioxide is more important than conventional methods for removing organic pollutants in the environment. This is because the process works to break down the parts of the pollutant gradually forming, so it does not lead to the presence of residues of the original pollutant, and therefore no sludge is generated that needs to be removed. In addition, the surface of the catalyst is characterized by its high ability to attract the pollutant, and this will lead to the continuation and completion of the process at very low concentrations, and this feature is one of the important economic considerations [32].

The mechanism followed in this type of treatment is as follows: The first reaction to the photocatalytic process is the absorption of ultraviolet rays by the catalyst, with the generation of hollow electron pairs (h⁺ / e⁻), meaning that the heterogeneous photocatalysis process begins when the semiconductor absorbs the photons that are Its energy is probably equal to or greater than its beamwidth (eg = 3.2 eV for). The electron (e⁻) is able to upgrade from the valence band (VB) of the semiconductor to the conduction band (CB) through this absorption, which leads to (h⁺) holes in the valence band [33].

The electron is able to reduce the organic species as well as the interaction with O₂, and this either leads to its absorption on the surface of the semiconductor or its dissolution in water, and reduces it to the super anion (O₂⁻·). The hole has the ability to oxidize an organic molecule or react with .OH or H₂O, which leads to oxidation of the *OH molecules. The species that perform the photolysis of organic substrates such as antibiotics are the highly oxidized species that are produced during the photocatalysis process. The operation can be expressed according to the equations below [34].

\[
\begin{align*}
\text{TiO}_2 + h\nu (\text{UV}) & \rightarrow \text{TiO}_2 (e^-_{\text{CB}} + h^+_{\text{VB}}) \\
\text{TiO}_2 (h^+_{\text{VB}}) + \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + \cdot\text{OH} + \text{H}^+ \\
\text{TiO}_2 (h^+_{\text{VB}}) + \text{HO}^- & \rightarrow \text{TiO}_2 + \cdot\text{OH} \\
\text{TiO}_2 (e^-_{\text{CB}}) + \text{O}_2 & \rightarrow \text{TiO}_2 + \text{O}_2^- \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^-
\end{align*}
\]

There are a number of factors affecting the degradation of the organic substrate (pH, pollutants, concentration, etc.) [33].

Table 1 reviews this treatment under several different conditions.

| Antibiotic name         | AOP       | Concentration | Operation Conditions                  | Reference |
|-------------------------|-----------|---------------|---------------------------------------|-----------|
| Amoxicillin             | Ozonation | 5.0 × 10⁻⁴ M  | T= 25°C, pH< 5.5, flow rate= 361 h⁻¹, \text{synthetic wastewater} | [41]      |
| Chlortetracycline, doxycycline, oxytetracycline | Ozonation | 5 × 10⁻⁴ M  | T= -21°C, Flow rate= 80 cm³/min, pH 2 - 9, \text{synthetic wastewater} | [42]      |
Ciprofloxacin, erythromycin, ofloxacin, sulfamethoxazole, trimethoprim  
\[ \text{Ozonation} \]  
ERYC=346 ngL\(^{-1}\), CIP=5524 ngL\(^{-1}\), OFX=2275 ngL\(^{-1}\), SMX = 279 ngL\(^{-1}\), TMP=104 ngL\(^{-1}\)  
T=25°C, pH=8.5, gas flow rate=0.36 Nm\(^{-3}\)h\(^{-1}\), urban wastewaters  

Sulfamethoxazole and acetaminophen  
\[ \text{Ozonation} \]  
30 mg L\(^{-1}\)  
gas flow rate=20 Lh\(^{-1}\), 15-W black light lamps, 365-nm radiation, synthetic wastewater  

Sulfamethoxazole  
\[ \text{Ozonation} \]  
0.150 mM  
pH=2 and 8, flow=3.0 ml min\(^{-1}\), T=25°C, gas flow=8.5 gNm\(^{-3}\), synthetic wastewater  

Table 1: Several studies to remove antibiotics from wastewater using advanced oxidation processes. (continuo)

| Antibiotic name | AOP | Concentration | Operation Conditions | Reference |
|-----------------|-----|---------------|----------------------|-----------|
| Tetracycline    | Ozonation | 20–100 mgL\(^{-1}\) | T=25°C, O\(_3\) was generated from oxygen, synthetic wastewater | [46] |
| Oxytetracycline | Photofenton | 20 mg L\(^{-1}\) | T=25°C, I=500 Wm\(^{-2}\), wastewater | [47] |
| Amoxicillin, ampicillin, and cloxacillin | Photofenton | AMX, AMP, CLX: 104, 105, 103 mgL\(^{-1}\) | UV lamp, 230 V, 0.17 A, 6 W, 365 nm, synthetic wastewater | [48] |
| Flumequine, ofloxacin, and sulfamethoxazole | Photofenton | 100 μg L\(^{-1}\) | pH 5, Fe\(^{2+}\) conc.: 5 mg L\(^{-1}\), natural water | [49] |
| Ciprofloxacin   | Photofenton | 0.15 mM | T: 298 K, 125-W high-pressure lamp, photonic flux (9 × 10\(^{4}\) μEs m\(^{-2}\) s\(^{-1}\)), synthetic wastewater | [50] |
| Amoxicillin and cloxacillin | Photofenton | 150 mgL\(^{-1}\) | Solar intensity 0.85 kWm\(^{-2}\), pH=3, synthetic wastewater | [51] |
| Amoxicillin     | Photofenton | 0.1 mM | H\(_2\)O\(_2\) conc.=1–10 mmol L\(^{-1}\); pH=2.5; 15-W black-light fluorescent lamp (365 nm); flow rate=80 mL min\(^{-1}\); sewage treatment plant effluent | [52] |
| Sulfamethoxazole| Solar photofenton | 10 mg L\(^{-1}\) | T=25°C, 1100-W xenon arc lamp (below 290 nm); intensity =250 Wm\(^{-2}\), synthetic wastewater | [53] |

Table 1: Several studies to remove antibiotics from wastewater using advanced oxidation processes. (continuo)

| Antibiotic name | AOP | Concentration | Operation Conditions | Reference |
|-----------------|-----|---------------|----------------------|-----------|
| Moxifloxacin    | TiO\(_2\)/UV | 12.5, 24.9, 37.4, 49.9, 62.3 and 124.6 μM | T= 5-65°C, pH=7, volume of reactor=200 mL, catalyst conc =0.25–8 g L\(^{-1}\), light intensity UV-A at 3 cm, 485 W cm\(^{-2}\), synthetic wastewater | [54] |
4. Assessment of AOPs performance for antibiotic removal

In this review, (AOPs) were successfully applied for the purpose of removing antibiotics present in wastewater. Three types of AOPs have been highlighted. Ozone is a strong oxidant that is able to passivate antibiotics by disrupting their pharmacologically active functional groups [35]. Hydroxyl radicals are responsible for this mechanism. In ozonation treatment, antibiotics are effectively dissolved in water and wastewater, because this treatment is able to remove all pollutants through mineralization or converting them into products with little harm, so that they do not affect human health and the aquatic environment [36][37]. The ozonation method was found to have a high ability to remove all types of antibiotics [38].

The photo-Fenton process has also been reviewed for the purpose of degradation organic pollutants and antibiotics in particular. This system consists of hydrogen peroxide and iron salts in addition to ultraviolet radiation. UV radiation are known to accelerate Fenton reactions because they generate hydroxyl radicals, thus reducing H$_2$O$_2$ consumption compared to the traditional Fenton process, but it needs an acidic pH in order to give greater treatment efficacy. Thus, the photo-Fenton system is an important system for treating wastewater that contains organic pollutants, including antibiotics [39,40].

According to the literature, photo-Fenton is an economical, low cost, and easy to apply technique. A high antibiotic clearance was obtained through the use of this process.

Finally, the heterogeneous photocatalytic process with a TiO$_2$ semiconductor was reviewed by illumination of a suspension of TiO$_2$ in an aqueous solution with a photocatalytic energy greater than its bandgap energy. This leads to the generation of pairs of electronic holes that have high energy (e$^+$ + h$^+$), and may transfer to the catalyst surface and thus may lead to the production of thermal energy through recombination or may have a role in the redox reactions with the compounds that are absorbed On the surface of catalyst [35].

According to the literature, heterogeneous photocatalysis is the preferred method compared to the other methods. The TiO$_2$ catalyst is chemically stable, available and inexpensive, highly effective, easy to use and manufacture.

5. Conclusion

The intake of antibiotics is increasing worldwide by both human and veterinary uses. Antibiotics are one of the most common pollutants in the environment and they have been found in several places, including wastewater. The presence of antibiotics in wastewater has many disadvantages to the health of living organisms and may enhance the spread of resistant bacterial strains.

Advanced oxidation processes have proven their efficiency in removing antibiotics, according to the studies shown in Table 1 highlighting three advanced oxidation treatments, as in the ozonation process it is observed that there are several operational parameters that have a significant influence on O$_3$ and its subsequent conversion to OH radicals. Among these parameters, the chemical composition, pollutant concentration, effluent quality, pH, and temperature must be taken into consideration. However, ozone
treatment can be improved in combination with hydrogen peroxide and / or ultraviolet light (O₃ / UV, O₃ / H₂O₂, or O₃ / H₂O₂ / UV).

The photo-Fenton process is technically economical, and highly efficient for removing antibiotics from wastewater. The chemical compounds used in this method are available and cheap. Moreover, the use of UV radiation speeds up the generation of hydroxyl particles, thus reducing H₂O₂ consumption. The UV-TiO₂ system is very helpful in removing antibiotics from the water. However, it does have some disadvantages, including the use of large doses of the catalyst that reduces the efficiency of the process. Also, when applying this method, we may encounter difficulty separating and recycling an expensive photocatalyst such as TiO₂.

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