Review

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Key Principles about Advanced Oxidation Processes: A Systematic Analysis on Current and Future Perspectives of the Antibiotics Removal from Wastewater

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Abstract: Simultaneously with the development of industrial society, wastewater with organic pollutants has caused various environmental problems. The most majority of organic pollutants in water and wastewater are persistent, reason which can cause serious problems for human health, animal health, and for the whole environment. Therefore, efficient treatment methods for wastewater with highly concentration of organic compounds are immediately necessary. During the last years, the prescribed and non-prescribed consumption of antibiotics has grown a lot worldwide. Big quantities of antibiotics are discharged into wastewater because their incomplete absorption by living organisms, but at small concentrations present in aquatic environments represents a major risk for the human health and environment protection. The paper presents the main advantages and disadvantages of advanced oxidation processes, but also current state and new perspectives in the field of environment protection. Advanced oxidation processes (AOPs) are often used in the field of treatment of different types of wastewater. AOPs are based on physicochemical processes that create significant structural changes in chemical species, their commercialization at a wide scale may result in cost reductions that are desirable for environmental applications. The majority of antibiotics may be eliminated using physicochemical processes, such as photo-Fenton, photolysis, ozonation, electrooxidation, heterogeneous catalysis, and other bio processes. In comparison to conventional chemical processes, AOPs provide superior oxidation efficiency, ideal operating costs, and zero secondary pollutants.

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1. Introduction

The most important natural resource which can be found on Earth is water. It is essential for human life and contribute to a good health of the environment. As it is well known, the water is unequal allocated in different parts of the world, and the quality is different in all the continents. On the other hand, the planet is home to an abundance of aquatic resources; however, the majority of these resources are either inaccessible to humans in their current state or are isolated from them. Some examples of these resources include the salty water found in oceans and seas, as well as glaciers [1,2]. However, a continuous access to water and energy is essential to guarantee the prosperity and the development of population worldwide. A good management of the two resources is also essential to sustain and improve the health of environment, respectively of the human population [3].

Lately, the availability of fresh water has become one of the biggest problems in the world, especially in the drinking water, and food and agriculture sectors amid a steady increase in the world's population. One of the major causes of this problem, especially in the case of developing countries, is the pollution of surface water by effluent discharges into surface water bodies from

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various sectors of activity such as chemical and petrochemical industry, pharmaceutical and cosmetics industry, electrical and electronic components manufacturing industry, etc. [4,5].

Among the many pollutants that reach these water bodies, persistent organic compounds have a strong negative impact on aquatic flora and fauna. These organic compounds are a threat not only to water resources, but also to human health [6,7]. Thus, a wide range of technologies have been developed and perfected to remove these organic compounds from effluents before they are discharged into surface water. Of these, the most widely used are advanced oxidation processes (AOPs) such as Fenton, photo-Fenton, photocatalysis, electrochemical and sonochemical advanced oxidation.

AOPs have the potential to be utilised in the treatment of hazardous effluents, such as those found in hospitals and slaughterhouses, in addition to industrial effluents, which include wastewaters from agrochemical and distillery operations, as well as wastewaters from oilfields, textile and pharmaceutical production, and metal plating. [1,7]. It is supposed that different contaminants of water, from hazardous contaminants of pesticides, herbicides, detergents and cosmetics products to pathogens agents, viruses, spores and coliforms are practically removed by photocatalytic processes [1,8].

2. Case studies on the Antibiotics Removal from Wastewater

Pharmaceutical compounds have been a growing concern in the last years due to their negative effects on the environment. In the recent years, such compounds like analgesics, antibiotics, and steroids have been detected in the public water systems worldwide. A lot of pharmaceutical compounds are used in human and veterinary medicine and finally these products are discharged in the environment through the metabolic processes. These compounds have been introduced in the category of emerging pollutants [8,9].

Antibiotics are produced by the pharmaceutical industry to treat infectious (microbial) and are used extensively in both human and veterinary medicine. The growing demand for antibiotics has led to an increase in their production, and implicitly of the effluents generated from it, especially wastewater with a high content of these compounds. In many cases, due to poor treatment of these wastewater, they end up into surface water in high concentrations [10,11]. Many antibiotics are not totally metabolized by humans and animals, leading to their release in sewage treatment plants, and finally in the environment [12,13].

In the last two years, it was observed that SARSCov-2 pandemic has contributed to a suddenly increasing of antibiotics consumption in the world [14]. Being a viral disease, for treatment of the bacterial co-infection that are in strong connection with COVID-19, there were used some antibiotics, especially azithromycin. Recent reviews identified that more of 50% of patients with COVID-19 receive antibiotics therapy, although less than 10% having a bacterial infection [15]. The fast pace of COVID-19 pandemic development represented a direct threat to patients safety and public health via over-prescribing with antibiotics [15].

Antibiotics could be considered to be persistent compounds due to the fact that the rate of elimination from the environment is much lower than the rate of their entry into it [16,17]. As well, the presence of the antibiotic residues in the environment is correlated with pharmacokinetic properties of the compounds. On the market, there are different types of antibiotics with oral administration, intravenous administration and antibiotics used for animals [16].

Several types of antibiotics have been founded in industrial, household wastewater, pharmaceutical and hospital wastewater from different countries worldwide. Depending on geographical region, seasonal changes, and demographic data it was founded that the concentration value of antibiotics in wastewater may fluctuate from ng/L to μg/L [14]. In consequence, numerous natural environments including groundwater, surface water, soil, and sediments, have been shown to contain antibiotics. The presence of antibiotics in water bodies for extended periods of time may pose a risk to the integrity of ecological systems since it can lead to the evolution of bacteria that are resistant to antibiotics (known as ARBs) as well as genes that are resistant to antibiotics (ARGs) [18,19].

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One of recent analyse estimated that in the last twenty years the antibiotics consumption expressed in definite daily dose (DDD) increased rapidly with more of 65%. It is estimated that in the next years, will be an increase up to 200%, if not major changes will be made soon. Numerous factors such as lack of information, poor health knowledge, pandemic situation, fear of disease drive to excessive use of antibiotics. Setting the quantity of antibiotic residues is very important in establishing relation between their presence in the environment and their biological effects and ecotoxicological evaluation [16].

Antibiotics can be classified in two basic categories based on type of action, as bacteriostatic (which inhibits the growth and reproduction of bacteria) and bactericidal (which caused the death of bacteria cell) [18]. The occurrence of antibiotics in different wastewaters is shown in Figure 1. Sulfamethoxazole, ciprofloxacin, and trimethoprim are antibiotics which are used to treat a lot of infections of urinary tract, respiratory system, and gastrointestinal tract. They were detected in hospital, urban and pharmaceutical wastewater often in high concentrations. Antibiotic degradation is a process of breaking down antibiotics into smaller, less harmful substances. This is important because antibiotics, which are designed to kill bacteria, can have unintended effects on the environment and human health. When antibiotics are not completely degraded, they can persist in the environment, leading to the development of antibiotic-resistant bacteria and other negative consequences.

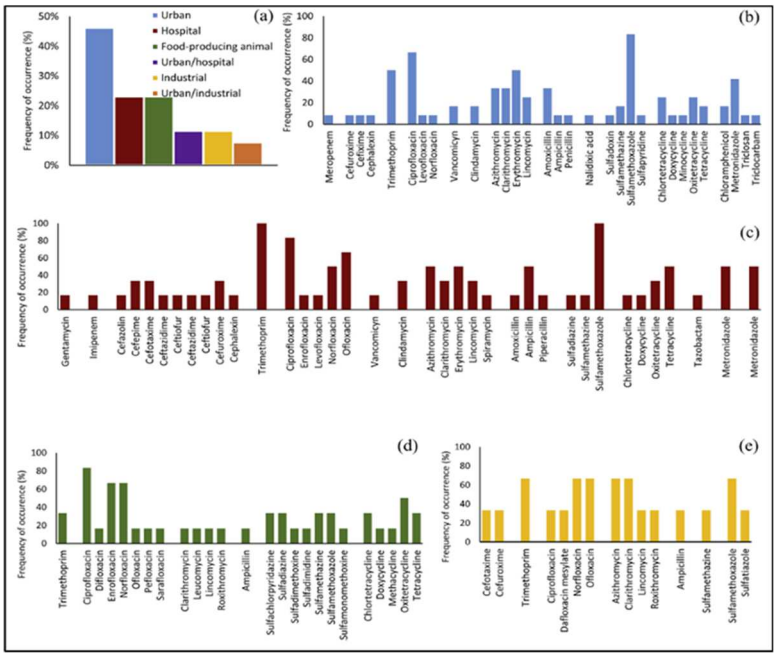

Figure 1. Occurrence of some antibiotics in different types of wastewaters [14].

There are several different mechanisms of antibiotic degradation, including chemical, physical, and biological processes. Chemical degradation of antibiotics occurs through reactions with other substances, such as sunlight or water, that can break down the chemical structure of the antibiotics. Physical degradation of antibiotics occurs when they are broken down into smaller particles through processes such as grinding or crushing.

Biological degradation of antibiotics, on the other hand, is the process by which microorganisms such as bacteria and fungi break down the antibiotics into smaller, less harmful substances. This is a crucial process because it helps reduce the amount of antibiotics that persist in the environment. Additionally, by breaking down antibiotics, these microorganisms can help reduce the risk of antibiotic resistance and the spread of antibiotic-resistant bacteria.

The degradation of antibiotics in the environment is a complex process that is influenced by many factors. Some of the most important factors that contribute to the degradation of antibiotics include the type of antibiotic, the presence of other substances in the environment, and the conditions

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of the environment, such as temperature, pH, and moisture. The effectiveness of antibiotic degradation is also influenced by the presence of other pollutants in the environment, as well as the presence of other microorganisms that may compete for the same resources.

Despite the importance of antibiotic degradation, there is still much that is unknown about this process. To better understand the degradation of antibiotics, researchers have developed a few methods for measuring and tracking the degradation of these compounds in the environment. Some of these methods include the use of bioreactors, which allow researchers to study the degradation of antibiotics in controlled environments, and the use of analytical techniques such as mass spectrometry and chromatography, which allow researchers to identify and quantify the products of degradation.

To help reduce the negative impact of antibiotics on the environment and human health, it is important to develop new methods for managing the degradation of antibiotics. This may involve developing new methods for removing antibiotics from the environment, such as through the use of bioreactors or other treatment technologies, as well as improving our understanding of the factors that contribute to antibiotic degradation. Additionally, it may be important to develop new antibiotics that are more biodegradable and less likely to persist in the environment, as well as to encourage the responsible use of antibiotics by healthcare providers and patients.

3. Advanced Oxidation Processes – Principles, Mechanism, and Their Applications

Advanced oxidation processes, often known as AOPs, are methods that generate extremely reactive radicals in order to destroy organic molecules, particularly resistant chemical compounds, that are found in aqueous environments. Degradation can be partial with the formation of organic intermediates, or complete when the mineralization of organic compounds takes place (Figure 2) [18]. So, by partial degradation are created some compounds that are more hydrophilic biodegradable, more electron-poorer and smaller in terms of molecular mass compared with the based pollutants. These compounds are more easily to be handled out in the next steps of treatment technology [21]. The advanced oxidation processes can be classified depending on the method of generation of reactive radicals like chemical, electrochemical, sonochemical, and photochemical, or depending on the reactive phase (homogeneous and heterogeneous) [8,22]. Recently, significant efforts have been made to use solar energy instead of ultraviolet or visible lamps to reduce reactors operating costs. However, the results obtained were not always as expected, thus highlighting the fact that important steps still need to be taken to achieve high efficiencies. In most cases, in order to achieve high efficiencies, advanced oxidation processes using solar energy are placed in ultrasonic or microwave fields, which increases the operating costs of the reactors [8,23]. Also, regarding the efficiency of the advanced oxidation processes, it must be taken into account that they are based on the strong reactivity of the radicals generated in the system. However, these radicals are non-selective and will act both on the target compounds in the system which are usually in low concentration and on the natural organic material in this system. Therefore, the degradation efficiency of the target compounds may be much lower compared to the overall degradation efficiency of the organic material present in the system.

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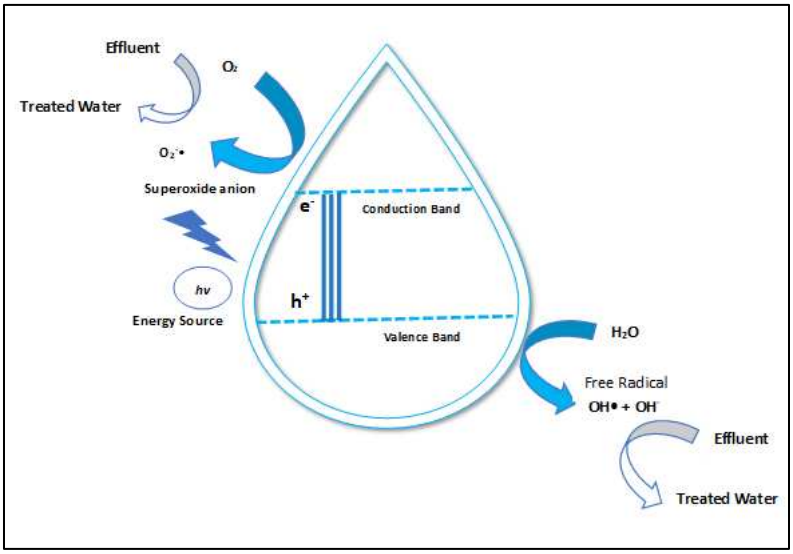

Figure 2. Advanced oxidation process – mechanism.

The advanced oxidation of low biodegradability, inhibitory, refractory, or high chemical stability organic pollutants involves the generation of reactive oxygen species (ROS) including hydroxyl radicals (•OH), superoxide radicals ($•O_2^-$), and sulphates radicals ($SO_4^{•-}$). All of these species are able to be derived from water by the use of hydrogen peroxide (H_2O_2), ozone (O_3), and peroxy-sulphates (PSs), with or without the application of a suitable catalyst or the utilisation of solar energy, electrical energy, or sound energy [1,18]. Generally, there are differences in the degradation efficiency of different AOPs for organic pollutants. The combination of different AOPs, including UV/H_2O_2, ultrasonic/photocatalytic oxidation, UV/O_3 and UV/Fe^{2+}/H_2O_2, and photo/sono/electro-assisted Fenton reaction processes, has been developed to address the limitations of a single AOP in terms of efficient ROS (reactive oxygen species) generation and operating parameters (Figure 3). Due to the synergistic effect of different substances, the combination of different AOPs can significantly improve the oxidation efficiency of contaminants compared with individual treatment technology [6]. The redox potentials of a selection of typical oxidants are shown in Table 1 as a summary in relation to the normal hydrogen electrode (NHE) [1].

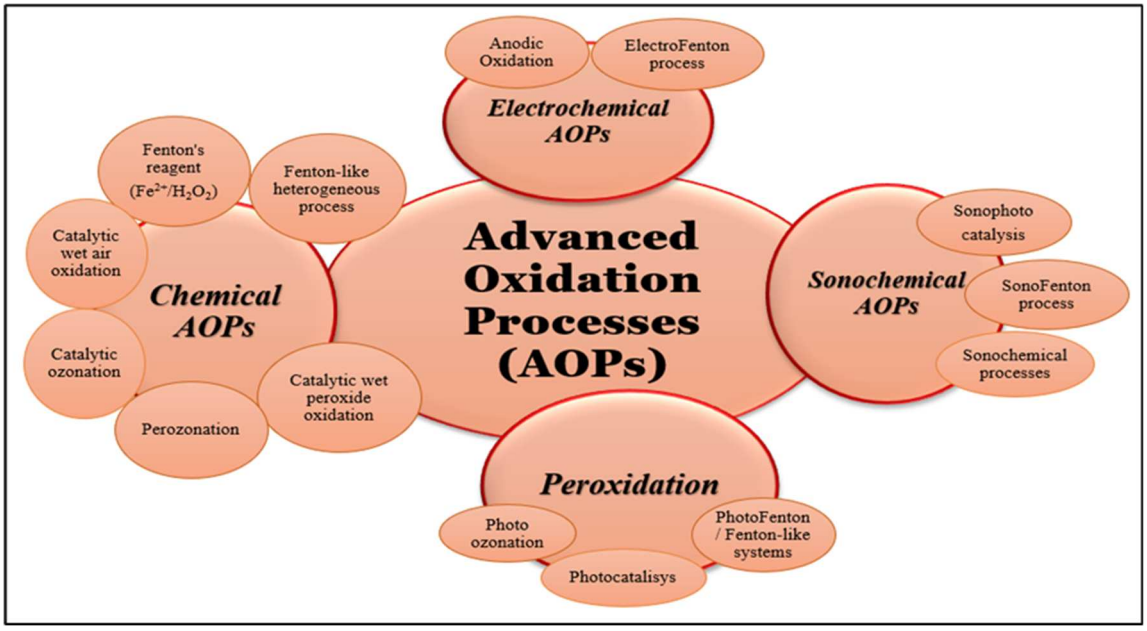

Figure 3. Advanced oxidation processes which generate reactive oxygen species.

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Table 1. Redox potentials of common oxidants referred to normal hydrogen electrode [1].

Redox potentials of some oxidants	Species E0 (V, t = 25°C)
fluorine (F_2)	3.03
hydroxyl radical (•OH)	2.80
sulphate radical ($SO_4^{\bullet-}$)	2.5 - 3.1
atomic oxygen (O)	2.42
ozone (O_3)	2.07
hydrogen peroxide (H_2O_2)	1.78
perhydroxyl radical ($HO_2^{\bullet}$)	1.70
permanganate (MnO_4^-)	1.68
chlorine dioxide (ClO_2)	1.57
hypochlorous acid (HOCl)	1.49
chlorine (Cl_2)	1.36
bromine (Br_2)	1.09
iodine (I_2)	0.54

When hydrogen peroxide comes into contact with active surfaces, such as catalysts, which typically have a large specific surface area, it is more likely to undergo a chain reaction that results in the release of oxygen in the form of a number of different free radicals. Some of these radicals include •OH and HO_2. Therefore, when combined with a catalyst that is effective, hydrogen peroxide demonstrates good reactivity and application efficiency, therefore lowering the high operating costs [1]. In general, the most important mechanisms involved in advanced oxidation are broken down and discussed in Figure 4.

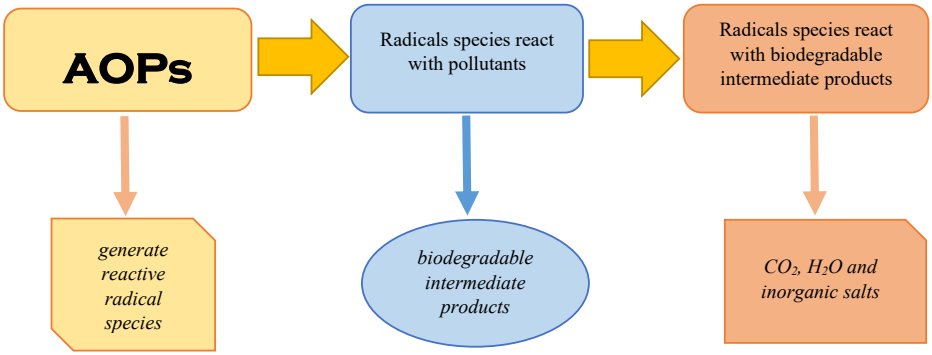

Figure 4. The processes involved in advanced oxidation processes.

Shortly, the main characteristics of the AOPs are presented below:

- the possibility of controlling the oxidation of inorganic chemicals and ions such chlorides and nitrates, as well as the mineralization of organic contaminants to CO_2 (carbon dioxide) and H_2O_2 (water).
- non-selective reactivity with practically all organic substances is necessary to avoid the existence of potentially hazardous intermediates produced from primary pollutants. This non-selective reactivity may be achieved using a variety of methods that do not entail the entire oxidation of the pollutant.
- one of the main disadvantages of AOPs is the high expense of employing expensive reagents (H_2O_2) and the increased energy usage (generation of O_3 or UV radiation) [21].

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4. Advantages and Disadvantages of AOPs

Advanced oxidation processes have some advantages, such as:

- Transformation of organic compounds to stable inorganic compounds such as carbon dioxide, water, and salts.
- High reaction rates [3];
- Potential to reduce toxicity and completely mineralize organic contaminants;
- No need to concentrate waste for further treatment like methods using membranes or activated carbon adsorption [24];
- Treatment of different organics at the same time.
- The cost is relatively low compared with other technologies.
- During oxidation processes, heavy metals could precipitate as hydroxides and can be removed in a subsequent stage [23,8].
- OH• radicals could help in the disinfection process during the wastewater treatment simultaneously with the organic compounds degradation [8].
- No new organic compounds with higher toxicity are formed [8,2].

In addition to these advantages, AOPs have some disadvantages, such as:

- A large consumption of acid and base is determined by the AOPs (Fenton oxidation), which is usually completed conducted in acid conditions [4];
- AOP system utilizing H_2O_2 can be dangerous for humans;
- The efficiency of the process depends on the dosage, so it is important to use the right amount in order to form an appropriate amount of hydroxyl radicals [4];
- The cost of AOPs can be high because of the need for chemicals and the high energy consumption, as well as the possibility of forming unknown, persistent by-products;
- AOPs are utilized for the elimination of radicals by non-target substances, but they are not effective for toxic compounds that resist hydroxyl radical involvement [8,4].

5. Fenton and Photo-Fenton Oxidation Processes

The first AOP which was considered throughout time is Fenton process. By using Fenton oxidation, it is possible to treat complex wastewater with the increasing of biodegradability of the effluent's recalcitrant organic compounds, decreasing the toxicity, and removing the remnant COD and the colour [25]. In the Fenton treatment process, a mixture of H_2O_2 and ferrous iron salts (Fe^{2+}) which forms the Fenton reagent, generates reactive (•OH) radicals causing the organic removal of wastewater by involving a complex reaction sequence [23]. The generation of •OH radicals is caused by the decomposition of H_2O_2 in acidic conditions initiated and catalysed by the Fe^{2+}. The mechanism of Fenton oxidation is presented in the next reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\bullet \quad (1)$$

According to Eq. (2), ferric ions can be reduced by hydrogen peroxide reaction to reconstruct ferrous ions but also to produce additional radicals. This type of reaction is called Fenton-like reaction.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \quad (2)$$

While iron is considered a catalyst, the consumption of hydrogen peroxide is continuous as it serves both as a generator of hydroxyl radicals and as a radical scavenger, as demonstrated in Eq. (3):

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (3)$$

In Figure 5 is illustrated a diagram of Fenton process. The primary advantages of this method are its ability to be performed under normal conditions (room temperature and atmospheric pressure) and the availability of readily accessible and easy to store and handle chemicals. Another advantage is that mass transfer is minimal due to its uniform structure, therefore reactor design is easy. However, this mechanism has two drawbacks: self-decomposition and oxidant loss due to the radical scavenging action of H_2O_2 (Eq. 4) [23].

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$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \quad (4)$$

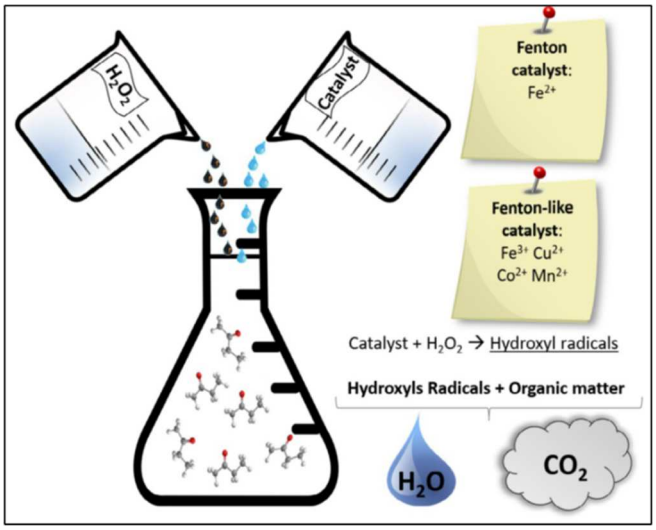

Figure 5. Diagram of Fenton process [23].

The second downside is referring to the pH conditions. The pH value has to be around value of 3 because the value of pH is dependent with the Fenton reaction. In the most cases, the pH must be decreased before the treatment because most of wastewaters do not have the value of pH around 3, and in the next phase it was observed that in order to precipitate the excess of iron, the pH have to be increase with the further solid sludge formation [10].

Concentration of hydrogen peroxide has a significative role in this process. It was highlighted that higher concentration of H_2O_2 leads to a higher organic compounds removal. However, care must be taken with the toxicity induced by high concentrations of hydrogen peroxide in aqueous systems. In this respect, for a proper control of the concentration, a continuous dosage of hydrogen peroxide during the oxidative treatment is preferred [23,2]. It was also highlighted that when the temperature is increased, the reaction rate could be increased too. On the other hand, for low organic concentrations the temperature could be increased with a few degrees because the reaction of H_2O_2 with the catalyst is an exothermal one. When organic contaminants are present in large quantities in the wastewater, hydrogen peroxide decomposition (Eq.4) might be expedited, resulting in increased consumption and higher operational costs [23,2]. It was observed that other three categories of processes derived from Fenton technology were used, like:

- Fenton-like
- Heterogeneous Fenton
- Zero-valent iron (ZVI).

5.1. Influencing Factors of the Fenton and Photo-Fenton Oxidation Processes

- Fenton catalysts

Even if Fenton oxidation process can degrade efficiently organic pollutants, in practical applications some problems may occur. Thus, if the utilization rate of H_2O_2 is low, it could cause a low decomposition rate of pollutants. Furthermore, as stated in the preceding chapters, the Fenton process requires a pH of 3, which is lower than the pH utilized in actual wastewater. As a conclusion, adjusting the pH value could increase the operational costs. Finally, the heterogeneous Fenton or Fenton-like process can be performed over a broad pH range and the catalyst can be reused repeatedly. These characteristics may help to reduce the development of iron sludge [10,2].

Heterogeneous Fenton catalysts can contain:

- Iron minerals, such as ferrite and magnetite.
- Zero-valent iron.

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- Metals and metal oxides such as MnO_2.
- Materials containing iron and iron oxide, typically used supports include activated carbon, alumina, silica, and zeolite.
- Metal-organic frameworks are crystalline functional materials made of a combination of transition metal ions and organic ligands [10].

- Catalysts dosage

The amount of catalyst used, which plays a major role in breaking down organic pollutants, is a crucial factor in the Fenton and Fenton-like oxidation process. Overuse of the catalyst may reduce the formation of hydroxyl radicals (•OH) and hinder the degradation of contaminants. As a result, overdosing on catalyst might raise operational expenses [25].

- Concentration of H2O2

H_2O_2 is the primary generator of hydroxyl radicals (•OH), and it plays a crucial role in the Fenton oxidation process. The reduction of the degradation efficiency it can be possible if an insufficient H_2O_2 dosage will lead to an insufficient amount of hydroxyl radicals (•OH). The actual added H_2O_2 concentration is frequently more than the estimated amount based on the chemical equations, which can be evaluated by preparatory tests [2,23].

- pH value

As shown above, in Fenton and Fenton processes pH value has a significant role and it is an important parameter for an efficient treatment of wastewater. The ideal pH value for the homogeneous Fenton process is 3, and the appropriate pH value in the Fenton process is contingent on the reaction system, especially when the reaction mechanisms depend on the catalyst's efficacy [27].

Table 2. Removal of antibiotics by Fenton and Fenton-like oxidation.

Antibiotics	Chemical formula and molecular weight, Mw (g/mol)	Catalyst (dosage); pH range	Removal efficiency (%)	References
Amoxicillin (AMX)	$C_{16}H_{19}N_3O_5S$ Mw = 365.4 g/mol	zero-valent iron (nZVI)-concentration between 0.2 - 2 g/L; pH range= 2 – 5 Fe(II) (0.32–24.3 mM); pH range= 2 - 4 H_2O_2/Fe^{2+} molar ratio = 2.0 - 50; pH range = 2 - 4 H_2O_2/Fe^{2+} molar ratio = 1 - 50; pH range = 1- 9	86.5 80 100 80.9	[28]
Ampicillin (AMP)	$C_{16}H_{18}N_3NaO_4S$ Mw = 349.406 g/mol	Fe(II) (53 - 87 lM); pH range= 2.3 - 5.7 Fe(II) (0.32–24.3 mM); pH range= 2 - 4 H_2O_2/Fe^{+} molar ratio = 2.0 - 150;	90.2 80 100	[10]

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		pH range= 2.0 - 4.0		
Azithromycin (AZT)	$C_{38}H_{72}N_2O_{12}$ Mw = 749.0 g/mol	H_2O_2/Fe^{2+} molar ratio= 1.75 mM; pH = 3	95	[29]
Ciprofloxacin (CPR)	$C_{17}H_{18}FN_3O_3$ Mw = 331.346 g/mol	Concentration of Fe_3O_4 between 1.0 - 2.5 g/L; pH range = 3 - 11 CNTs/FeS between 5–35 mg; pH range = 1 - 12 H_2O_2/Fe^{2+} molar ratio = 1.75 mM; pH range = 3	89 91.03 95	[30]
Tetracycline (TTR)	$C_{22}H_{24}N_2O_8$ Mw = 444.435 g/mol	Fe^0 (0.3 mM) CFO (0.05–0.2 g/L) Concentration of Fe^0/CeO_2 = 0.01 - 0.2 g/L) pH range = 3 – 7	100 84 93	[31]
Sulfadiazine (SDZ)	$C_{10}H_{10}N_4O_2S$ Mw = 250.278 g/mol	Fe^0 (0.3 mM)	100	[32]
Metronidazole (MTR)	$C_6H_9N_3O_3$ Mw = 171.16 g/mol	$FeNi_3/SiO_2$ nanocomposite, concentration between 0.005 - 0.1 g/L; pH range = 3 - 11	95.3	[33]
Metacycline (MTC)	$C_{22}H_{22}N_2O_8$ Mw = 442.419 g/mol	spinel copper cobaltate $CuCo_2O_4$ (0.1 - 0.3 g/L)	95.1	[34]

There are several strategies for optimizing Fenton technology. To avoid sludge production, the operation conditions have to be near a neutral pH value, to bypass the neutralization acidification and to operate with a low iron concentration. On the other hand, this technology might be placed in microwave or ultrasound fields. Regarding operation conditions, several strategies are described below:

1. One of the strategy is to use some chelating agents like oxalate, citrate, EDDS (ethylenediamine-N,N'-disuccinic acid) or EDTA (ethylenediaminetetraacetic acid) in order to build some iron ligand complex that can continue to be at neutral pH in the solution.
2. Copper, manganese, and cobalt are other metals that can be a good alternative to ferrous iron. These ones derive in the Fenton-like processes.
3. Another strategy is to immobilize the ferrous iron on the mesoporous materials, which can conduct to some heterogenous Fenton process [23].

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The Fenton process contributes to the generation of reactive species by having Fe(II) and H_2O_2 in solution, which also leads to the elimination of organic pollutants through the photolysis of H_2O_2 to produce hydroxyl radicals. It was observed that the photo-Fenton technology is taking place when these three elements are applied [23]. Also compared with the classical Fenton process, the main improvement integrated is the continuous generation of the catalyst as it is described in the Eq. (5). The key results are that a lower amount of iron salt is needed, and a smaller amount of iron residue is produced. Both factors lead to cost reductions and improved process efficiency [23].

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad (5)$$

Solar energy, on the other hand, is appealing from a sustainability viewpoint. Also, it was observed that when the $Fe(OH)^{2+}$ is present in the solution the pH is around the value of 3.0 because of the photoactivity of the $Fe(OH)^{2+}$ and the process is very efficient [23]. However, the pH adjustment cannot be avoided due to the implications of higher reagent costs, and in these circumstances, pH limits remain a concern. It is also suggested that various catalysts be developed that are more efficient at pH levels near to neutrality. An alternative to using humic acids are chelating agents like EDTA (ethylenediaminetetraacetic acid), citrate, and oxalate. Furthermore, if sunlight is employed as a source of radiation, the wavelength might shift closer to the visible range depending on the chelating agent. However, the costs will be increased if a chelating agent will be used, but the value of TOC (total organic carbon) will be increased [23,35].

A less efficiency is obtained when some excess of H_2O_2 concentration is used, causing a scavenging effect. Also, some undesirable results can be obtained in the improbable case of using a catalyst that can decrease the efficiency. As a conclusion, all these variables have to be studied for every single case [23]. Under appropriate irradiation, solid iron oxides such as hematite might behave as semiconductors, creating electron hole pairs. Additionally, their zero-point charge might vary, leading to substantial differences in their effectiveness at various pH levels.

Adding ultrasound to the system leads to a further increase in hydroxyl radical production, resulting in the sono-photo-Fenton process. In this case, the intermediate species produced with Fe3+ can be converted to Fe^{2+} not only through photolysis, but also through sonolysis. However, the energy needed for ultrasonic generation would raise the process's energy consumption when using this technique [2,23].. The entire energy consumption can be lowered when solar light is utilized. However, if the treatment time is too long or if geographical limitations exist, research might consider alternative parameters, such as the electrical energy per order (EEO) [23,25]. Figure 5 shows a typical SWOT analysis for a photo-Fenton process.

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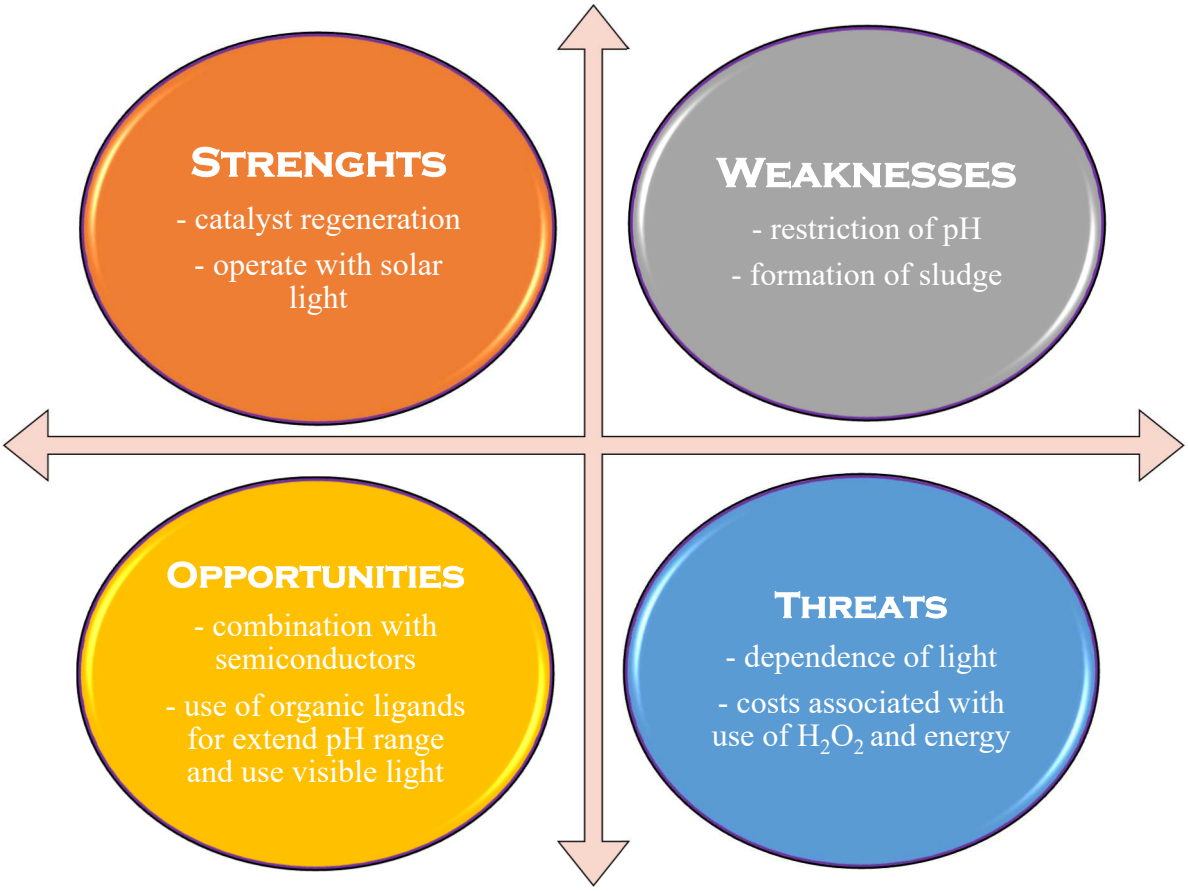

Figure 5. SWOT analysis for photo-Fenton.

6. Photochemical Advanced Oxidation Process

In photochemical accelerated oxidation processes, light energy is the principal source of transient species production. Compared to previous AOPs, this procedure is clean, reasonably inexpensive, straightforward, and much more efficient. In photochemical AOPs, UV/Visible Light radiations are linked with potent oxidants such as O_3 and H_2O_2 and catalysts such as titanium dioxide (TiO_2). These photochemical reactions may destroy pollutants via three distinct mechanisms: photodecomposition in the presence of O_3 under UV irradiation, photooxidation in the presence of H_2O_2, and oxidation by photocatalysis [1].

6.1. Photo-Peroxidation (H_2O_2/UV)

H_2O_2 can be photolyzed by UV radiations at different wavelengths ranging from 200 to 300 nm. Homolytic fission of the O–O bond of the H_2O_2 molecule is possible and leads to the formation of •OH radicals through a series of successive reactions following in the next equations.

$$H_2O_2 + hv \rightarrow 2{\bullet}OH \quad (6)$$

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad (7)$$

$$HO_2\bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2 \quad (8)$$

$$\bullet OH + HO_2^- \rightarrow HO_2\bullet + OH^- \quad (9)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (10)$$

$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2 \quad (11)$$

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$$2\bullet OH \rightarrow H_2O_2 \quad (12)$$

The reaction rate is faster in alkaline medium at a value of pH >10, as the UV radiations can produce the free radicals, $HO_2\bullet$ and $\bullet OH$. However, the molar absorption coefficient of H_2O_2 in the UV area is quite low, therefore a higher concentration of hydrogen peroxide is required for the safe destruction of target contaminants [1,2].

6.2. Photo-Ozonation (O_3/UV)

Ozone dissolved in water effectively absorbs UV radiation in the range of 200-360 nm, with the highest absorption occurring at 253.7 nm. This absorption is measured by the molar absorption coefficient, εmax, which has a value of 3600 L $mol^{-1}cm^{-1}$. Due to this high εmax value, the process of ozone photolysis in water is more efficient than the photolysis of hydrogen peroxide. The photolysis of ozone in water leads to the formation of $\bullet OH$ radicals, which are highly reactive and effective oxidizing agents. These radicals can participate in a series of chemical reactions as shown in the following equations [23].

$$O_3 + H_2O + hv \rightarrow 2\bullet OH + O_2 \quad (13)$$

$$O_3 + \bullet OH \rightarrow HO_2\bullet + O_2 \quad (14)$$

$$O_3 + HO_2\bullet \rightarrow \bullet OH + 2\,O_2 \quad (15)$$

$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2 \quad (16)$$

The use of nanoparticles made from ZnO and TiO_2 as catalysts in the photo-ozonation process has yielded significant results. These materials have proven to be effective in producing oxidizing agents when they are exposed to light [1].

6.3. Heterogeneous Photocatalysis

Photocatalysis is a process in which a chemical reaction is accelerated by a catalyst that is activated by the absorption of photons with energy above its bandgap. The term heterogeneous refers to the fact that pollutants are present in a fluid phase while the catalyst is in a solid phase [41]. Various methods of this technique have been attempted, resulting in the development of a new Advanced Oxidation Process (AOP) technology for environmental and energy applications based on semiconductor photocatalysis [1].

When a semiconductor is exposed to light with ultra-band-gap energy, a valence band electron is excited to the conduction band, leaving a photogenerated hole (h^+) in the valence band [37]. The e^-/h^+ pairs can then migrate to the surface of the semiconductor and participate in redox reactions that generate hydroxyl radical ($\bullet OH$), h^+, and superoxide ion radical ($\bullet O_2^-$) in the photocatalytic degradation of pollutants in wet conditions, as shown in Figure 6 [38]. The photogenerated h+ is considered an oxidant that directly degrades organic contaminants, and its effectiveness is determined by the catalyst used and the oxidation states [1].

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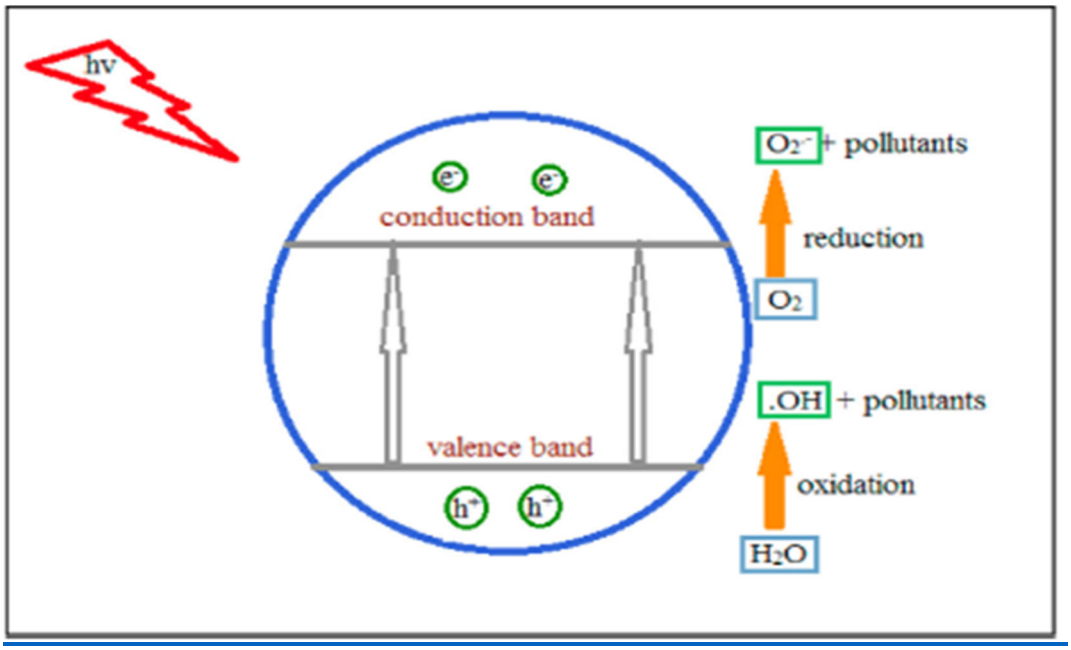

Figure 6. Mechanism of photocatalysis. Super oxide anions and hydroxyl radicals produced by electron-hole pairs get a complete degradation of pollutants [1].

In this process, when the catalyst surfaces are exposed to photoirradiation, valence band holes and conduction band electrons are generated. When the valence band holes react with water, •OH radicals are generated, while when they react with molecular oxygen absorbed on the catalyst surface, superoxide radical anions are generated.

Different classes of therapeutic drugs such as analgesics, antibiotics, anticonvulsants, and psychiatric drugs, are oxidized by the UV/TiO_2 photocatalyst. Different operational parameters such as initial concentration of the substrate, catalyst loading, type of TiO_2 photocatalyst, wavelength/light intensity, pH of the solution, and the water matrix influences the degradation kinetics for pharmaceutical pollutants.

Heterogeneous photocatalysis requires some items to be fulfilled, such as:

(a) Emitted a photon at the suitable wavelength.

(b) A semiconductor material as a catalyst.

(c) A strong oxidizing agent.

The main challenge is connected to the growth of new types of catalysts with improved quality. There are some restrictions that need to be detailed:

1. Band gap regulation for getting a type of catalyst which has activity in the visible range.
2. Morphology improvement which can optimize shape and size.
3. Delay or avoidance recombination of electron-hole [23].

Forwards, in Figure 7 is shown a typical SWOT analysis for heterogeneous photocatalysis process.

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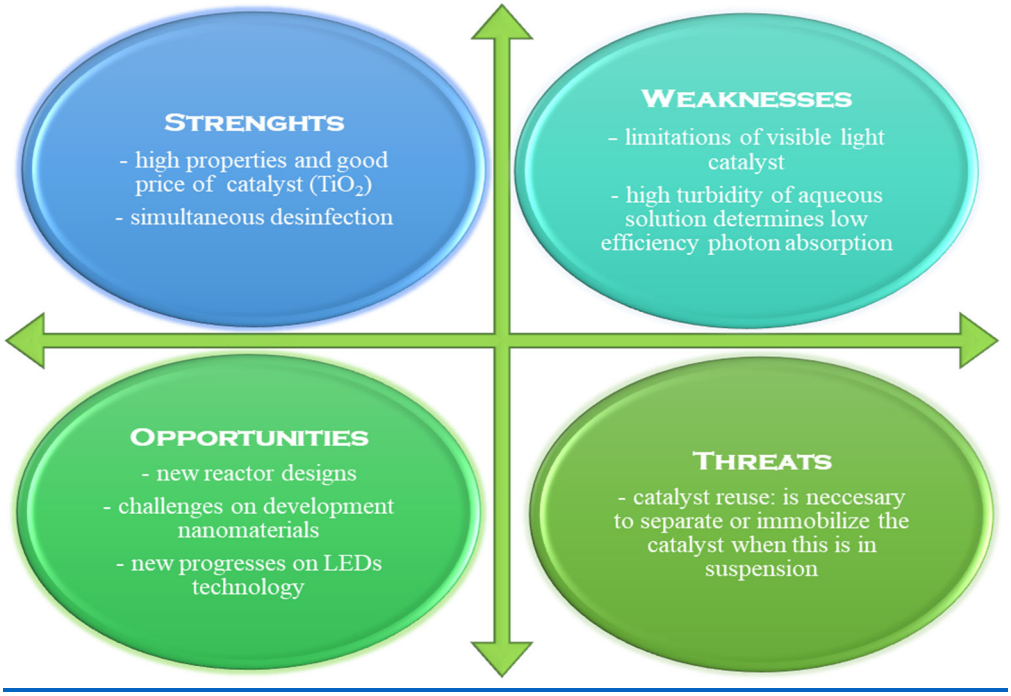

Figure 7. SWOT analysis for heterogeneous photocatalysis process.

The current trend is to develop a new mixt advanced oxidation processes which combine microwaves or ultrasounds. Some preliminary results shows that the reaction rate can be grown to an acceptance level and a successful rate of removing organic substrate can be reached. The solar energy could be used, in association with some photovoltaic panels, to reduce the operation costs regarding the implementation of the AOPs on the large scale. This system has some major advantages like the reduced costs of operation and maintenance, it is considered to be a clean energy and the process of energy generation it is noiseless, and it can be close to the final consumer. It was observed that, this system has still significant problems like the limited of the ability of the system, the high rate initial cost, a large area of a land is required for the system to be installed and the system cannot be installed in some geographical area which has a low rates of solar radiation [23].

6.4. TiO_2/UV System

The process of photocatalytic oxidation is a widely recognized technique for eliminating a variety of organic compounds. This process involves the combination of UV light, a photocatalyst (typically TiO_2), and air or oxygen. However, it is not widely implemented due to the need for separating the photocatalyst, despite its relatively simple application. TiO_2 is highly effective when used in powder form with particle sizes in the tens of nanometers range. Also, the light that reaches the photocatalyst surface must have low energy for the promotion of electrons from the semiconductor's valence band to the conduction band, thus creating hole-electron pairs, to be possible [2]. In this case of, TiO_2 radiation in the near-ultraviolet is absolutely needed. Because of its relatively broad bandgap, TiO_2 may absorb up to 5% of the solar spectrum (UV radiation with a wavelength of 380 nm) [39]. Consequently, researchers have given more attention to the catalytic activity of TiO_2 within the visible zone of the solar spectrum in recent years [40].

In this respect, efforts were made to improve the photocatalytic properties of TiO_2 under visible irradiation, like surface modification with organic molecules or nanoparticles, or doping with metal and non-metal ions [41]. Table 3 summarizes the results, and it can be stated that the UV-TiO_2 system is effective at removing antibiotics from wastewater. However, when significant catalyst dosages are utilized, the process efficiency drops. However, probably the most significant impediment to the adoption of this technology is the difficulty in separating and reusing a costly photocatalyst, such as TiO_2 [2].

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Table 3. Removal efficiency of antibiotics from wastewaters by TiO_2/UV.

Antibiotic	Matrix	Operation Conditions	Removal Efficiency	Observations	References
Ciprofloxacin $C_{17}H_{18}FN_3O_3$	Ultrapure water	Graphitized mesoporous carbon and TiO_2 nanocomposite used as a catalyst (0.35 g/L) UV lamp (λ = 254 nm)	Maximum efficiency (100%) in 45 minutes	Complete mineralization realized in 90 minutes. The primary degradation processes are hydroxylation and decarboxylation.	[42]
Cloxacillin $C_{19}H_{18}ClN_3O_5S$	Ultrapure water Synthetic solutions of pharmaceuticals	Concentration of TiO_2 = 2.0 g/L UV light = 150W	Efficiency was approximate 100%	TiO_2 photocatalysis it has higher degradation and mineralization efficiencies than other processes.	[43]
Metronidazole $C_6H_9N_3O_3$	Complex aqueous Matrix solutions (include anions and cations)	Concentration of TiO_2 = 1.5 g/L UV light = 6.5 mW cm-2	Efficiency was approximate 88% in 30 minutes	Except of glucose, the presence of common water matrix components interferes with medication degradation.	[44]
Norfloxacin $C_{16}H_{18}FN_3O_3$	Ultrapure water	Concentration of TiO_2 = 0.3 g/L Low-pressure UV lamp (λ= 254 nm)	Efficiency was approximate 90%	TiO_2 photocatalysis is the second most efficiency process for the removal of norfloxacin, after photo-Fenton	[45]

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				(efficiency was approximate 96%).	
Oxacillin $C_{19}H_{19}N_3O_5S$	Ultrapure water	Concentration of TiO_2 = 0.5 g/L Mercury high-pressure lamp UV lamp = 150 W	Efficiency was approximate 100% in 45 minutes	Efficiency was ~90% mineralization realized in 135 minutes.	[46]
	Synthetic solutions of pharmaceuticals wastewater	Concentration of TiO_2 = 0.5 g/L High-pressure mercury lamp (λ =365 nm)	100% in 45 min (without additives) 100% in 60 min (with additives)	The additives had the least effect on TiO_2 photocatalytic treatment.	[43]

7. Sustainable Photocatalytic Wastewater Treatment

To increase the biodegradability of dangerous and non-biodegradable contaminants, like persistent organic pollutants and antibiotics, photocatalytic degradation can be used which is an efficient and advantageous treatment technology for wastewater. This technology allows the transformation of chemical pollutants into less toxic compounds with structural features that are much more readily biodegradable. Photocatalytic treatment process consists of the combination of oxidizing agents with an appropriated catalyst and/or light [10,43]. For treatment of effluents containing toxic compounds for which biological process are not efficient, photocatalytic oxidation process may be used. Photoexcitation of a semiconductor that is solid sometimes due to the absorption of electromagnetic radiation, but not always in the near UV spectrum is the basic stage of photocatalysis [25].

Over the years, several photocatalytic oxidation processes that could be effective for the degradation of various types of organic contaminants have been investigated. As an example, some semi-conductor materials, including TiO_2, ZnS, WO_3, and SnO_2 are utilized as photocatalysts. A photocatalyst must absorb energy in order to produce electrons (e^-) with strong reducing capacity, according to numerous research. Also, the excited electrons (e^-) could be used to reduce the quantity of O_2 to form superoxide radical ($\bullet O_2^-$). While holes (h^+) go to the photocatalyst surface where they will oxidize water to generate hydroxyl radical ($\bullet OH$) will begin to break down the organic contaminants. After then, either the superoxide radical ($\bullet O_2^-$) or hydroxyl radical ($\bullet OH$). It was found that titanium dioxide, due to its high catalytic efficiency and stability, is the most significant catalyst [10,48].

The mechanisms of photocatalytic oxidation using TiO_2 as catalyst are presented in Figure 8 and it is described by the following equations:

$$TiO_2 + hv \rightarrow TiO_2 + h^+ + e^- \quad (17)$$

$$h^+ + OH^- \rightarrow \bullet OH \quad (18)$$

$$h^+ + H_2O + O_2 \rightarrow \bullet OH + H^+ + \bullet O_2^- \quad (19)$$

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$$O_2 + e^- \rightarrow O_2^- \quad (20)$$

$$O_2^- + H^+ \rightarrow HO_2^- \quad (21)$$

$$2HO_2^- \rightarrow O_2 + H_2O_2 \quad (22)$$

$$H_2O_2 + {}^{\bullet}O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (23)$$

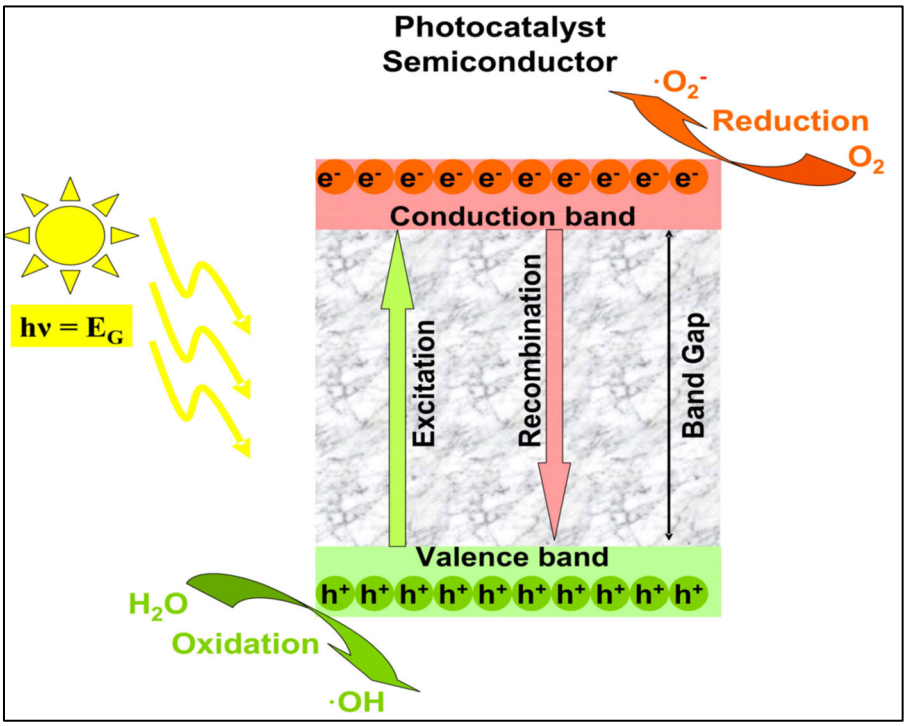

Figure 8. Mechanism of oxidative radicals development [49].

7.1. Photocatalytic Materials

A photocatalytic reaction is a redox process and a photochemical reaction that takes place between a photocatalyst and the substrates on its surface, such as hydrogen peroxide, oxygen, and target pollutants, when light is applied. Photocatalysts are relevant components in photocatalytic process. The photocatalysts can be classified in two main categories:

- Oxide photocatalysts: TiO_2-based photocatalyst, Bi_2O_3-based photocatalyst and other oxide photocatalyst such as ZnO, WO_3, Fe_2O_3.
- Non-oxide photocatalyst: CdS series photocatalyst, CuS series photocatalyst, ZnS series photocatalyst and nitride series photocatalyst.

To enhance the efficiency of photodegradation process, some photocatalysts, such as metal oxides (i.e. titanium dioxide, zinc oxide), metal sulfides (i.e. CdS), precious metal semiconductors (i.e. BiOBr, BiOCl, $BiVO_4$, Ag_3O_4, $SmVO_4$, $GdVO_4$); non-metallic semiconductors (i.e. g-C_3N_4) have been tested in photochemical oxidation process [10,50].

TiO_2 photocatalysts were utilized in the living world and wastewater treatment for the elimination of hazardous organic pollutants, notably antibiotics, due to a higher photocatalytic activity, non-toxicity, and high photo-stability [50]. Another important photocatalyst, zinc oxide (ZnO) has been studied in the literature for the degradation of a series of antibiotics (such as ciprofloxacin, norfloxacin, sulfamethoxazole, cefixime trihydrate, and tetracycline hydrochloride), due to its reduced cost, non-toxicity, raised redox potential, and environmentally-friendly properties [10].

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7.1.1. Photocatalysts Preparation Methods

All the types of photocatalyst are obtained by different techniques. Along the time, there were developed a lot of methods to prepare a photocatalyst. For example, solid phase method, electrospinning method, vapor phase method, and liquid phase method are the most commonly methods used in obtaining photocatalysts.

Electrospinning method

The electrospinning method is used to produce polymer nanofibers directly. This technique has been utilized to make a variety of nanofibers, including organic and inorganic composites. The electrospinning process requires several components: a nozzle, a liquid supply device, a fiber receiving device, and a high voltage power source. The high voltage power supply, which uses a direct current, produces thousands of volts and generates an electromagnetic field to polarize and charge the liquid. The fiber receiving device, which may take the form of a rotating metallic roller, is located on the opposite side of the nozzle, grounded with a thread and connected to the negative electrode of the high voltage power supply. The most important factors that contribute to a highly efficient electrospinning process include the voltage, surface tension, solution viscosity, conductivity, and solvent evaporation rate [51,52].

Solid Phase method

The solid phase method is a process where the reactant ingredients are ground and blended together in a specified ratio, and then calcined at a specific temperature to yield the desired product [51]. This method has many benefits such as a simple setup, low cost, ease of use, uniform particle size, and controlled reaction conditions [53]. The absence of a solvent also minimizes the formation of hard agglomerates and reduces environmental pollution. However, this method also has some drawbacks such as a tendency for particle aggregation, a coarser powder, and a higher likelihood of ion oxidation, as well as easy impurity contamination [51,53].

Gas Phase method

The gas phase method involves directly using gas or converting a substance into gas to allow it to react either physically or chemically in the gas phase. During the cooling process, the nanoparticles can then aggregate and form [51]. This method results in high-purity nanoparticles with desirable properties, but it requires advanced techniques and equipment. It encompasses various vapor phase methods, including physical vapor deposition, chemical vapor deposition, and molecular beam epitaxy.

The Chemical Vapor Deposition (CVD) process involves the use of chemical reactions between vapor phase components to produce thin films on a substrate surface. This technique can be used to deposit various materials such as metals, nitrides, and oxides. CVD can be further divided into four categories, namely atmospheric pressure CVD, low pressure CVD, plasma pressure CVD, and laser pressure CVD, depending on the conditions under which it is performed. However, there are certain limitations to the CVD process, such as inconsistent surface roughness and particle size (ranging from 50-150 nm) [51,54].

The Physical Vapor Deposition (PVD) technique involves vaporizing a paint physically to create a film on the surface of a substrate. This method has advantages over conventional vacuum deposition techniques, such as ion beam deposition, ion plating, and ion beam assisted deposition. Additionally, the PVD process operates at low deposition temperatures and does not result in substrate deformation or cracking. This process has been used to deposit ceramic compounds, polymer films, as well as metal and alloy films [51,55].

The Molecular Beam Epitaxy (MBE) method is a cutting-edge film production process that allows for the creation of single crystal films. In this process, a hot beam of atoms or molecules is directed onto the surface of a heated substrate under vacuum conditions. The MBE technique offers several benefits, such as the ability to precisely control beam intensity and shape the surface of the epitaxial material, which can be transformed into a multi-layer structure with various compositions [51].

Liquid Phase method

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The Liquid Phase Method, also referred to as the wet chemical method, is a process for producing material. To start, a soluble metal salt must be selected based on the desired composition of the material. The metal ions in the solution must then be precipitated or crystallized using appropriate agents. Finally, the desired raw material powder is produced through thermal decomposition of the precipitate [56].

Sol-Gel method

The sol-gel method is a common technique for preparing photocatalysts. It involves dissolving a precursor in a solvent to form a sol via hydrolysis. The sol-gel process is influenced by various parameters such as the pH of the solution, concentration, reaction time, and temperature. The sol-gel process has numerous benefits, including high purity and homogeneity, low synthesis temperature, and easy control of reaction parameters. However, it also has some drawbacks, such as the high cost of titanium alkoxide raw material, the use of a large amount of organic solvent, high cost of film production due to high-temperature heat treatment, low film adhesion, and weak transparency [51].

Precipitation method

The precipitation method is a commonly used technique for synthesizing nanomaterials. In this method, a precipitant is added to form a precursor precipitate which is then mixed with other substances having varied chemical components. However, some heavy metals introduced during the precipitation process may not react in solution and could potentially introduce impurities into the solution, affecting the usage of this approach. The reaction temperature, duration, pH value, and titration rate all have an effect on the material manufacture throughout this method's operation. Some advantages of the precipitation method are the low cost of operation, simple and safety process [57,58].

Liquid deposition method

In this method an uniform film is putted into the substrate, before that the substrate is diving into an reaction solution. For this method it is not needed a high temperature during film formation or an expensive equipment. This approach may also be used to create composite oxide films, multicomponent oxide films, metal fine particle dispersion oxide films, and laminated oxide films [51,59]. One of the most significant advantages is that environmental pollution is minimal, and the benefit-to-cost ratio is high. It does not have these advantages because all of them have been solved, which sustain that liquid deposition method have a broad application area [59].

Hydrothermal method

In this method, an enhanced inorganic material is created by combining an inorganic or organic component with water under high pressure at temperatures ranging from 100°C to 300°C. The inorganic compound that results is filtered, washed, and dried to produce ultrafine particles of high purity. Some advantages of the hydrothermal method are mild conditions, stable system, easy process, low cost, and small environmental pollution. Another advantage is that films obtained using this method have a good uniformity and are not limited by the shape and size of the substrate [51]. On the other hand, by adjusting the amount of the product using the hydrothermal approach, homogenous nanocomposites may be obtained.

7.2. Factors which Influencing the Photocatalytic Oxidation Process

- pH value

An important parameter of photocatalytic oxidation processes is the pH of the aqueous solutions. It was discovered that the charge on the surface of the catalyst can vary depending on whether the pH is above or below the potential of zero charge. Likewise, if the pH is higher or lower than the pKa (acid dissociation constant), the substrates may exhibit a different charge form [60]. In certain studies, a UV-A/TiO_2 photocatalyst was used to degrade amoxicillin, and it was discovered that the degradation was unaffected by the rise in pH from 5.0 to 7.5. This rise may be ascribed to both the ionisation states of the catalyst and the pollutant. The mineralization of amoxicillin reduced from 95% to 75% when the pH increased from 5 to 7. Also was studied the photocatalytic degradation of cefotaxime in various aqueous solutions employing TiO_2 and ZnO as photocatalyst. It was discovered that, when the pH of cefotaxime was elevated from 4 to 6.2 using TiO_2 as a catalyst, the

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removal rate rose, but reduced when the pH was increased from 6.2 to 7.6. Other results were remarked in scientific papers in the case of the cefotaxime degradation using ZnO as catalyst [10,61].

- Catalyst dosage

Another significant parameter in photocatalytic oxidation process is photocatalyst dosage. It has been discovered that having a higher amount of photocatalyst in the system can result in more active sites and improved ability to remove pollutants through oxidation and mineralization. However, having too much catalyst can also obstruct light energy from reaching the system and reduce the effectiveness of light energy due to reflection, scattering and light blockage caused by solid particles [2,10].

- Mineralization of antibiotics

Frequently, it was remarked that the degradation efficiency due to formation of some short time organic intermediates which are formed during the photocatalytic process, is higher than the mineralization efficiency [62]. In this respect, it was found that for the oxytetracycline degradation under UV irradiation for 10 hours, the total organic carbon (TOC) removal was of only 9.5%. It was also found that in the case of tetracycline under UV radiation for 5 hours with the addition of 0.2 g/L (multi-walled carbon nanotube) MWCNT/TiO_2, TOC removal reached 83%. Flumequine's mineralization ratio reached 74% after 15 minutes of UV irradiation, and it remained unchanged after 60 minutes, or even extended irradiation times. It was observed that some aromatic organic intermediates remained intact after they were exposed for longer time to irradiation, for several times [10,63].

Table 4. Removal of several antibiotics by photocatalytic oxidation.

Antibiotics	Chemical formula and molecular weight, Mw (g/mol)	Photo-catalysts	Removal efficiency (%)	References
Amoxicillin (AMX)	$C_{16}H_{19}N_3O_5S$ Mw = 365.4 g/mol	UV-A/TiO_2	100%	[64]
Ampicillin (AMP)	$C_{16}H_{18}N_3NaO_4S$ Mw = 349.406 g/mol	UV/TiO_2/PLA/Fiberglass fabric plain woven-type membrane	95.2%	[65]
		UV/TiO_2/PLA/Fiberglass mat-type membrane	83%	
		UV/TiO_2/PLA/Fiberglass fabric one fold edge-type membrane	79.7%	
Cefixime (CFX)	$C_{16}H_{15}N_5O_7S_2$ Mw = 453.452 g/mol	Nitrogen doped titanium dioxide/ graphene oxide (N-TiO_2/GO)	80%	[66]
Cefixime trihydrate	$C_{16}H_{21}N_5O_{10}S_2$ Mw = 507.50 g/mol	Zinc oxide/iron oxide (ZnO/a-Fe_2O_3)	99.1%	[67]

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Cefotaxime (CFT)	$C_{16}H_{17}N_5O_7S_2$ Mw = 455.47 g/mol	Titanium dioxide/zinc oxide (TiO_2/ZnO)	84.2%	[68].
Chloramphenicol (CHL)	$C_{11}H_{12}Cl_2N_2O_5$ Mw = 323.132 g/mol	Titanium dioxide (TiO_2)	85%	[69]
Ciprofloxacin (CPR)	$C_{17}H_{18}FN_3O_3$ Mw = 331.346 g/mol	TiO_2/carbon dots Reduced graphene oxide (rGO)/bismuth vanadate ($BiVO_4$) Ag/AgBr/$BiVO_4$ photocatalyst Zinc oxide (ZnO) Cadmium sulfide (CdS)/strontium titanate ($SrTiO_3$) Ternary photocatalyst, graphitic carbon nitride (g-C_3N_4), iron oxide) Fe_3O_4/g-C_3N_4	91.1% 68.2% 91.4% 100% 93.7% 100%	[66,70,71,72,73,74]
Enrofloxacin (ENF)	$C_{19}H_{22}FN_3O_3$ Mw = 359.4 g/mol	Cadmium sulfide/ strontium titanate CdS/$SrTiO_3$ g-C_3N_4, Fe_3O_4/g-C_3N_4	93.7% 100%	[73,74]
Norfloxacin (NRF)	$C_{16}H_{18}FN_3O_3$ Mw = 319.331 g/mol	Bismuth vanadate/tungsten trioxide ($BiVO_4$/WO_3) Zinc oxide ZnO/CuOx	70% >80%	[75,76]
Oxytetracycline (OXY)	$C_{22}H_{24}N_2O_9$ Mw = 460.434 g/mol	Titanium dioxide (TiO_2) Multi-walled carbon nanotube/ Bismuth vanadate (MWCNT/$BiVO_4$) Titanium dioxide (TiO_2)	100 88.8 100 80	[77,78,79,80,81]
Penicillin (PNC)	$C_9H_{11}N_2O_4S$ Mw = 334.4 g/mol	Cadmium sulfide/ strontium titanate (CdS/$SrTiO_3$) Bismuth vanadate ($BiVO_4$)	93.7 100	[82]

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Sulfamethazine (SMZ)	$C_{12}H_{14}N_4O_2S$ Mw = 278.33 g/mol	Graphene modified anatase/titanate nanosheets (G/A/TNS)	96.1	[83]
Sulfamethoxazole (SLF)	$C_{10}H_{11}N_3O_3S$ Mw = 253.279 g/mol	UVC lamp (10 W)	95.8	[84]
Sulfaquinoxaline (SLQ)	$C_{14}H_{12}N_4O_2S$ Mw = 300.366 g/mol	Titanium dioxide	100	[85]
Vancomycin (VAN)	$C_{66}H_{75}C_{12}N_9O_{24}$ Mw = 1.449.3 g/mol	Titanium dioxide (TiO_2)	95	[86]

7.3. Photocatalysis – Challenges and Opportunities

In many applications area, such as environmental remediation, energy production, chemical engineering, medicine/biochemistry, and agriculture the heterogeneous photocatalysis has shown his great efficiency [87]. The applicability of the photocatalytic technology for wastewater treatment is constrained by some important technical issues that need more research in the near future, for example:

- The first issue would be if the photocatalytic process is a pre-treatment or is a separate system.
- The photocatalytic process cand be used as a pre-treatment step for improve the biodegradation of recalcitrant organic pollutants before to biological wastewater treatment due to the non-selective reactivity of the non-biodegradable wastewater soluble pollutants [88]. For try obtaining significant results of efficiency of this process, is necessary to be considered another technical aspect, from the catalyst development to reactor design and process optimization, such as:
- The improvement of catalyst for a high photo-efficiency.
- Catalyst immobilization for ensure a cost-effective solid-liquid separation.
- Improve of photocatalytic operation for a wider pH range and for the minimize the addition of oxidant additives.
- A new integrated or coupling system for improved photo-mineralization or photo-disinfection kinetics.
- Efficient design of reactor photocatalytic system or use of solar energy to reduce the electricity costs [88].

So, a photocatalytic wastewater treatment process with a large-scale applicability, with high efficiency, with use of solar energy, with low costs of operation cand be realized in order to rapid evaluation of different possible issues and ambiguities that may appear.

Nevertheless, the applicability of heterogeneous photocatalysis based on ZnO and TiO_2 is still on doubtful due to some limitations:

- The quantum efficiency is reduced under the sunlight because of utilization a large bandgap energy.
- e-/h+ pair is generated by a high energy consumption.
- the photocatalytic activities are decreased due to reactive oxidative species reduction of a rapid e-/h+ pair recombination.
- Limited ability to extend due to a complexed modification process needed to increase the photocatalysis.
- The kinetic reaction rate is getting down due to a fast active surface site the activation by interaction with intermediate secondary products.
- A low photocatalyst stability is reducing its reusing its lifetime services.

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- Elimination of the solid photocatalyst as a secondary solid waste.
- A low photocatalytic efficiency against high concentrations of pollutants at high air and water flow rates [87].

As a remark, the water can also be considered as a solvent or a chemical component because the water properties are changed due to the rapidly increases of the temperature or the applied pressure. The operation and synthesis costs depend by many factors involved in the utilization of catalyst like energy consumption, regeneration process, the long-term stability, and the individual component costs [89].

8. Opportunities and Future Perspectives

In the recent years, the scientists were involved looking for a strategy to allow a total removal of the low concentration of contaminants founded in the wastewater that was already treated with conventional removing techniques. Furthermore, it was observed that using AOPs it is a proper option in which the pollutants are adsorbed in a porous material that is removed by some following in situ AOPs reactions; these reactions could take place on the surface of the exhausted adsorbent [90,91].

Advanced oxidation processes could be considered suitable technologies that can used to treat wastewaters when they include recalcitrant or toxic organic compounds. In some cases, an excellent option could be when the full mineralization can be obtained with a good costs and time. These processes are efficient and some of them could be seen as “green” technologies. The combination of two or three methods can increase the mineralization efficiencies in eliminating pesticide pollutants. This approach not only transforms organic compounds into non-toxic by-products, but also proves to be cost-effective as it requires minimal space, chemicals, and generates little to no sludge.

It was observed that most of the heterogeneous photocatalysis research were conducted using bench setups in unrealistic conditions that there are too far from the real conditions. Only some limited efforts have been made testing the real performance of the heterogeneous photocatalysis using water and air feed streams. On the other hand, it was discovered that are many inconsistent data in the existing research regarding heterogeneous photocatalysis application for the environment [91].

Moreover, the scalability of the heterogeneous photocatalysis technology has barely been implemented for industrial purposes like wastewater treatment or air purification. The most recent studies suggest that the photocatalytic water splitting to hydrogen, that could be used as a renewable energy, is impractical, because it requires expensive sacrificial agents or electron donors, for example, methanol, glucose or isopropanol.

9. Conclusions

Antibiotics are widespread contaminants found in a wide range of surface waters, wastewaters, WWTPs (wastewater treatment plants), and hospital effluents. Furthermore, the presence of antibiotics in wastewater may have negative consequences for human health and may enhance bacterium resistance to antibiotics. Advanced oxidation processes have frequently proved their great efficacy in the removal of a wide range of contaminants, including antibiotics.

The high efficiency and non-selectiveness of AOPs have made them a highly sought-after method for removing organic pollutants in various matrices, as evidenced by the high removal rates, effective remediation of water, and low energy consumption. Therefore, it is important to consider harnessing the full potential of AOPs in future developments by implementing them on an industrial scale for removing organic pollutants. These techniques show great promise as effective tools for wastewater treatment and further research should focus on improving the stability of solid catalysts, as well as evaluating the cost-effectiveness and long-term efficacy of large-scale AOP applications. From the point of view of the photochemical properties, some AOPs like UV/H2O2 can be considered undisguised, and its development will be in straight line with the new UV light sources such as LEDs. In some places with high insolation, solar-powered photo-Fenton and heterogeneous photocatalysis may be advantageous for future implementation of the technology. In the next perspectives, it is

visible that a huge effort is taking apart in order to develop new catalysts for heterogenous photocatalysis, in order to increase the efficiency of this technology and to reach the commercial stage.

AOPs have the potential to effectively eliminate a wide range of stubborn organic compounds due to their high oxidation capability, which can be further enhanced by pairing with various oxidants and catalysts. One of the promising advanced oxidation process technologies for industrial applications, such as wastewater treatment, is photocatalysis. Selecting an appropriate photocatalyst and optimizing conditions can result in high degradation rates of persistent organic contaminants from wastewater. Therefore, the principal provocations of AOPs are using some renewable energy sources to reduce the costs and maybe to substitute the electricity with them. An area of future research that could prove to be of interest is the utilization of solar energy on a large scale, which has the potential to significantly reduce the environmental impact by over 90%.

Future developments will have to be in straight participations of engineers, analytical chemists, and electrochemists to create and make research for an efficient application and operations of advanced oxidations processes. AOPs could represent efficient, important, and environmental-friendly methods to remove or to degrade a series of organic pollutants from wastewaters.

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