

Advanced Oxidation Processes II: Removal of Pharmaceuticals by Photocatalysis

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Abstract In this chapter, basic concepts of advanced oxidation processes (AOP) are cited, such as photolysis, photocatalysis, and semiconductors used as photocatalysts. This is important since the wastewater pollution with drugs, coming from domestic use, hospitals, and industry is not only an environmental problem but social too. Pharmaceutical case study is shown to exemplify the photocatalytic degradation of different drugs contained in wastewater taken directly from some currents in the pharmaceutical industry, such as diclofenac, acetaminophen, naproxen, and ibuprofen, using modified TiO₂ catalysts with different tin contents.

Keywords Heterogeneous photocatalysis, Photodegradation of NSAIDs

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1 Introduction

In recent years, the issue of water pollution has increased and, above all, the need to purify wastewater using environmentally friendly techniques to comply with regulatory standards regarding water quality has become mandatory [1]. The aquifers are polluted mainly by chemical compounds, such as pesticides, herbicides, dyes, drugs, dissolved organic matter and microorganisms, the pharmaceutical pollutants will be emphasized in this chapter, which come mainly from industrial, household, and hospital wastewaters. The pharmaceutical molecules that stand out for the amount in which they are found in wastewater and for their toxicity are mainly non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen, naproxen, diclofenac, and acetaminophen; these resilient molecules have been previously reported causing damage to aquatic flora and some species of aquatic fauna. The increase of pollutants in the aquifer mantles is mainly due to the fact that drugs are discharged as hospital waste, as well as the increasing consumption of these drugs by people in general, because it can be acquired and consumed without medical prescription.

It is well known that drugs consumed by humans are only used in a small proportion in the body and a percentage greater than 60% is excreted via urine and feces as well as through the sweat glands contributing also to the pollution of domestic water.

Different methods have been proposed for the removal of these organic pollutants from wastewater prior to being discharged to rivers. Among these methods, absorption, biological and chemical processes such as chlorination are of common use. There are also some promising, modern, and environmentally friendly methods such as the advanced oxidation processes on which this chapter focuses on.

1.1 *Advanced Oxidation Processes*

Nowadays, the preservation of aquifers without pollutants mainly of organic nature is an issue that has maintained many research groups proposing alternative solutions from different perspectives such as environmental, chemical and from the science and materials engineering. It is important to note that resilient organic pollutants cannot be removed using the traditionally available procedures as they are inadequate to achieve the degree of purity required by regulatory environmental pollution laws. The use of advanced oxidation processes (AOP) has been applied rarely and is little known in the countries of emerging economies such as these in Latin America. These processes are used to remove organic pollutants prior to discharge into aquifers. It is considered that the advanced oxidation processes are based on physicochemical processes that are capable of inducing deep changes in the chemical structure of the organic molecules. The concept was initially introduced by Glaze et al. [2] who stated that these processes involve the generation and use of highly reactive transient species such as the hydroxyl (OH^{\bullet}), superoxide ($\text{O}_2^{\bullet-}$), and hydroperoxyl ($^{\bullet}\text{OOH}$) radicals. These are species with high oxidation potential that

Table 1 Oxidation potential of different species

Oxidizing agent	Oxidation potential (V)
Fluorine (F)	3.06
Hydroxyl radical (\bullet OH)	2.80
Atomic oxygen (O)	2.42
Ozone (O ₃)	2.08
Hydrogen peroxide (H ₂ O ₂)	1.78
Chlorine (Cl ₂)	1.36
Molecular oxygen (O ₂)	1.23

can oxidize many organic compounds in a non-selective manner and with high reaction rate; these characteristics are used to achieve the complete mineralization of the pollutants to CO₂, water, and mineral acids or, under appropriate conditions, can transform them in molecules easier to be biodegraded. These reactive species can be generated by photochemical processes using UV and visible light or other forms of energy, particularly, the hydroxyl radical has a great oxidizing power of organic matter being the second powerful oxidant only after fluorine as shown in Table 1 [3]. It is important to emphasize that it is required a significant amount of steady state hydroxyl radicals in a degradation reaction to optimize the process.

1.2 Advantages of Advanced Oxidation Processes

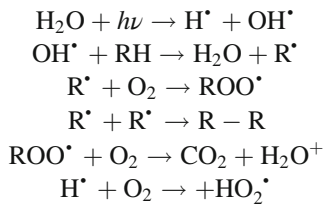
In these processes, it is important to emphasize that the organic compounds are eliminated from water, and are not transferred from one medium to another. The main characteristic of AOP is that the degradation of organic compounds occurs until the complete mineralization and usually does not generate sludges that require another stage in the process for its removal [4]. These processes are useful for the removal of resilient organic compounds that cannot be removed by other methods, especially by biological ones. It is possible to remove very small amounts up to parts per million, requiring less energy than other methods as the thermal treatments and generating lower amounts of toxic metabolites becoming environmentally friendly.

It is important to note that there are advanced non-photochemical oxidation processes and photochemical processes. Among the non-photochemical processes can be mentioned electrochemical processes, ozonization, and combined processes using ozone with hydrogen peroxide, Fenton, and some other chemicals. The photochemical processes are ozone with UV-light, hydrogen peroxide with UV-light, ozone with hydrogen peroxide and UV-light, and photo-Fenton using ferrioxalate. Photocatalytic methods can be performed in the homogeneous or heterogeneous phase, the latter is environmentally friendly and is applied for the study of degradation of organic pollutants present in wastewater such as pharmaceutical drugs from industrial, domestic, and hospital wastewaters.

1.3 Photolysis

Organic pollutants contained in wastewaters can be degraded directly just by irradiation with some energy source, such as the sunlight, which is absorbed by the organic molecules reaching the required excited states to carry out their degradation; although that natural process is thermodynamically feasible, it is too slow taking from several hours to days [5].

Photolysis of a variety of organic compounds can be carried out with UV-C radiation (210–230 nm) and is based on the formation of free radicals. The degradation of organic molecules by photolysis depends to a great extent on the absorption capacity of radiation by the molecule to be degraded and on the presence of other compounds that absorb at the same wavelength. It has already been reported by other authors the use of mercury lamps in these processes [6], and has been proven useful in the disinfection and purification of some pollutants in water. In order to efficiently carry out photolysis, it is necessary to apply radiation with lower wavelengths, that is, with higher energies as the ultraviolet radiation to break the bonds in the organic molecules. The degradation degree can be estimated from the measurement of the absorbed light through the quantum yield, which can be defined as the number of molecules that react with respect to the number of photons that are absorbed. It has been reported that oxygen has great importance in these oxidation reactions, by studying the effect of distance from the source of irradiation due to the different concentration of oxygen in the environment [7]. To resume the photolysis process, the following reactions are considered to take place:



When the free radicals (R^\bullet) react with oxygen, they can form peroxy radicals (ROO^\bullet). If dissolved oxygen is absent or is not sufficient, these free radicals can react by recombination or dismutation.

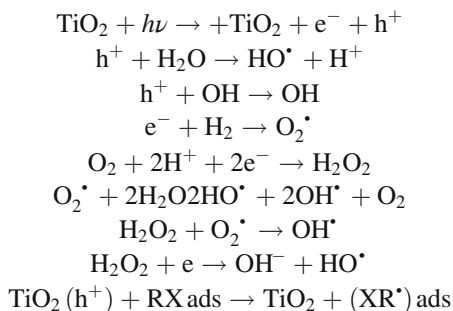
1.4 Photocatalysis

Photocatalysis has acquired importance for its energy and environmental applications; this process involves a chemical reaction that starts when photons irradiate a catalyst material. If the catalyst is in the same phase of the reaction system, the process is called homogeneous photocatalysis, on the contrary, when the catalyst is in a different phase of the reaction system, is called heterogeneous photocatalysis.

Then the photocatalytic process involves the light absorption by the photocatalyst generating electron-hole pairs; these photogenerated charges promote the formation of radicals such as hydroxyl ($\cdot\text{OH}$), hydroperoxyl ($\cdot\text{OOH}$), and superoxide ($\text{O}_2\cdot$). These radicals react through oxidation and reduction reactions, oxidizing organic compounds and reducing inorganic ions and other organic compounds. A very important point to remark in the heterogeneous photocatalysis process is that the material employed as photocatalyst is a semiconductor, usually an oxide or sulfide with a bandgap energy suitable to promote the transition of electrons from the valence band (VB) to the conduction band (CB) by the irradiation source. When an electron leaves the valence band a positive empty site is generated. This empty site in the valence band is known as a hole (h^+). The photogenerated electron-hole pairs can recombine, in the bulk or in the material surface, returning to the initial state and dissipating the energy as heat, can also be trapped in the metastable surface states or react with the molecules adsorbed on the surface of the semiconductor by accepting or donating electrons.

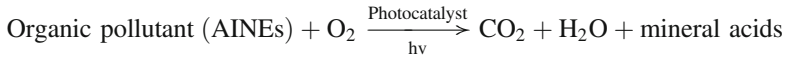
It is important that the materials used as photocatalysts can be excited with cheaper available energy sources such as sunlight. However, the majority of commercially available materials require higher energies than the naturally available sources such as the solar light because of their higher bandgap energies as in the case of TiO_2 with bandgap energy of 3.2 eV for the anatase phase. Nowadays, there are a wide variety of photocatalysts such as V_2O_5 , ZnO , Fe_2O_3 [8, 9], the most commonly used is TiO_2 , the so-called Degussa P25 is its commercial version composed by a mixture of phases, anatase/rutile (70/30). Degussa P25 is the most utilized photocatalyst because of its increased photocatalytic activity, non-toxic, stable in aqueous solutions, and low cost. It is worth mentioning that different proportions of the anatase/rutile phases have already been evaluated with good results.

It is important to note that the penetration depth of the radiation does not exceed 50 nm and only the materials surface is catalytically accessible. On the surface holes react with both the adsorbed water and the OH groups to form hydroxyl radicals ($\text{OH}\cdot$). On the other hand, the electrons react with the oxygen (O_2) in the environment to form superoxide radicals ($\text{O}_2\cdot$) and under suitable conditions hydrogen peroxide (H_2O_2). The superoxide radicals and the hydrogen peroxide react generating a greater proportion of hydroxyl radicals as indicated below:



Among the main advantages of using heterogeneous photocatalysis as a method for cleaning of wastewaters, this is one method capable of truly cleaning the water,

since the toxic organic compounds present can be completely mineralized to form CO₂, water, and simple inorganic acids. From this point of view, the photocatalytic method can degrade toxic and dangerous compounds such as biphenyl dioxins, phenols, solvents, pesticides, dyes, and others in a safe way. The organic molecules are eliminated in a one-stage process without needing of extraction from the medium in which they are dissolved before or after the treatment.



1.5 Factors that Influence the Photocatalytic Response

Among the factors that affect the rate of photocatalytic reactions, it can be mentioned the wavelength of the radiation source, the nature of the photocatalyst, the amount of oxygen present in the environment, the temperature and pH of the reaction system, as well as the presence of additional factors such as turbidity, suspended solids, dissolved organic matter, and the existence of microorganisms in the system. One of the most important factors that influence strongly the photocatalytic process is the wavelength emitted by the radiation source. It is well known that the wavelength determines the kind of semiconductor that can be used. In general terms, the energy corresponding to the wavelength must be greater or at least equal to the bandgap energy of the semiconductor material. For example, titania in its anatase phase has a bandgap of 3.2 eV, this implies that only wavelengths lower than 387 nm can promote an electron from the valence to the conduction band. These wavelengths are provided by energetic sources that radiate ultraviolet light as mercury lamps and even xenon lamps in a low fraction. Therefore, numerous efforts have been focused to develop photocatalysts susceptible to be activated using light sources cheaper or even available for free as is the sunlight. In this line, numerous research works have been aimed at reducing bandgap energies to take advantage of a greater fraction of the solar spectrum. In spite of the foregoing, for tests at laboratory-level, there is a drawback of using naturally available light to evaluate the photocatalysts, because natural solar radiation has changes in intensity and wavelengths received during the day and between the different days. In a simple way, there are cloudy days, rainy days, and sunny days, therefore, the radiation reaches the surface of the earth with some changes in the photon density and in the proportion of the different wavelengths, making the evaluation of photocatalysts difficult with this source of natural radiation. For this reason, it is very important to have a source of simulated solar radiation, which emulates the solar spectrum that the sun would emit in different conditions, for example, at the midday, with the sun in the zenith, or simulate the solar spectrum of a day with clouds, or including both direct light from the sun and the diffuse light that is scattered by the atmosphere or by trees and buildings. A solar simulator provides a controllable and reproducible solar light source.

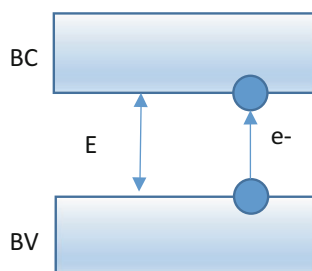
1.6 Photocatalytic Materials

It has been mentioned earlier in this chapter that a photocatalyst is a semiconductor material with a bandgap energy susceptible to being excited by photons to generate charge carriers, the hole-electron pairs, as the bands model indicates (Fig. 1). In recent years, emphasis has been placed on the traditional use of titania-based materials as photocatalysts, which have developed their potential application by commercializing them in environmental applications, such as odor reduction in the refrigerators, stain-resistant fabrics, self-cleaning walls, and germicidal properties in hospital walls. Semiconductor-based photocatalysts can be found in the form of colloids, powders, porous granules, thin films, or bulk solids, which can be used in liquid phase or gas transformations. It is important to emphasize that each heterogeneous photocatalytic process is different in terms of its kinetics and the superficial reactions involved; the photocatalytic reactions begin with the photoexcitation of the electrons in the material, in this case in the TiO_2 .

As mentioned before, a key issue in the development of photocatalytic materials is the narrowing of the bandgap of materials commonly employed for this purpose in order to extend their absorption to longer wavelengths of the solar spectrum; for example, decreasing the bandgap energy of 3.2 eV characteristic of the TiO_2 in its anatase crystalline phase to have a photocatalyst sensitive under solar light. To achieve this, several strategies have been proposed by researchers around the world, focused on the modification of TiO_2 . The first successful modification reported was the mixture of the anatase and rutile crystalline phases, giving rise to the commercially available Degussa-P25 which is a nanostructured material with particle sizes around 25 nm. In this mixture, the coupling of the crystalline phases achieves a synergic effect increasing the photocatalytic activity; however, it is important to note that this photocatalyst has the drawback of not being easily removed from the reaction system, losing a large amount of catalyst or resorting to the addition of one more stage in the process for their separation.

Other researchers have reported the synthesis of TiO_2 doped with metals (Ni, Ag, Co, Cu, Fe, Au, Sn, among others) [10–12], either by introducing these metals into the crystalline lattice of the anatase phase, that sometimes achieved reduction of bandgap energy to values as low as 2.8 eV, or by immobilizing metallic nanoparticles on the titania, thus achieving that the metals function as charge carrier centers in an

Fig. 1 Schematic bands model in a semiconductor



electron trap, thus decreasing the recombination rate of the hole-electron pair [13]. Coupled semiconductors have been reported to promote synergistic effects increasing the photocatalytic activity due to the decrease of the recombination rate of the electron-hole pairs, allowing the catalytically active sites remain accessible during longer times [14].

Another proposal by some researchers is the study of alternative materials with bandgap energy small enough to be activated under visible light so to make better use of the solar spectrum, this is the case of Bi_2O_3 and its polymorphs that exhibit reduced bandgap energies such as 2.8 eV ($\alpha\text{-Bi}_2\text{O}_3$), 2.48 eV ($\beta\text{-Bi}_2\text{O}_3$), and 3.01 eV ($\delta\text{-Bi}_2\text{O}_3$) [15]. Regarding these polymorphs, Cheng et al. reported that the photocatalytic capacity of this semiconductor mainly depends on two factors, which are the separation efficiency of the photoinduced carriers (electron-hole pair) and the light absorption range. Authors in that research work also conclude that the photocatalyst with the lowest photocatalytic activity was due to the many defects on the surface or in the volume, which leads to a high recombination rate of the electron-hole pairs. Additionally, Cheng et al. provide theoretical and experimental evidence for the synergistic effects of the crystallite and electronic structures on the photocatalytic properties, which could be applied to other semiconductor photocatalysts with polymorphs, such as WO_3 , In_2O_3 , CdS , and so on. This data gives an idea for selection of a photocatalyst as a function of the molecule to degrade.

Once it was known the importance of crystallite and electronic structures that influence the photocatalyst efficiency, it is reported within this chapter, the degradation of some NSAIDs, ibuprofen, naproxen, diclofenac, and acetaminophen using some photocatalysts based on TiO_2 modified with different atomic contents of Tin (Sn) in the form of powder obtained by the sol gel technique, which showed satisfactory results in the degradation of these drugs from various wastewater streams from a pharmaceutical industry.

Additionally, it must be emphasized that photocatalysts can be used to increase the reaction rate of other chemical reactions, for example, breakdown of the water molecule in H_2 and O_2 ; the dehydrogenation of alcohols in H_2 and aldehydes or ketones, the oxidation of inorganic substrates such as water in H_2O_2 , NO_2 in NO , CN , and CON and partial oxidation of other molecules with O_2 such as the benzene in phenol and toluene in methylphenol; complete oxidation or hydrocarbons mineralization; reduction of CO_2 with H_2O in CH_3OH and $\text{C}_2\text{H}_5\text{OH}$; nitrogen fixation, $\text{N}_2 + 3\text{H}_2\text{O} \sim 2\text{NH}_3 + 3/2 \text{O}_2$; synthesis of amines, oligomerization and polymerization; structural isomerization reactions of hydrocarbons; and hydrogenation and cracking of alkynes with H_2O or alcohols.

1.7 Photocatalytic Degradation of NSAIDs

In the last 10 years with the increase in the demand and especially in the waste of pharmaceutical products in the aquifer mantles, it has become a necessity their

elimination to have clean water. These pharmaceutical products that pollute wastewater are mainly non-steroidal anti-inflammatory drugs (NSAIDs), such as ibuprofen, diclofenac, naproxen, and acetaminophen [16, 17]. These are released in higher quantities due to their excessive use in treatments against pain and inflammation as well as for their antipyretic action; because they can be obtained without medical prescription, becoming a public health problem; these pharmaceutical products are released to the environment from domestic wastewaters polluted with human and animal excretions. Other sources are the disposal of hospital waters and wastewaters from the process of manufacturing of these pharmaceuticals without any treatment; becoming a dangerous pollutant for the aquatic flora and fauna. Some harmful effects have been observed in some endemic species, such as renal failure, death, and resistance to these drugs in some species. There is not enough evidence that these harmful effects can be extrapolated to human beings. Nevertheless, their detrimental effect on aquatic biota is not arguable.

At this time, there are already some reports about extinction of some bird species due to the indirect consumption of medicines. Particularly, reports of vulture poisoning by diclofenac, a drug that is used by veterinarians to treat pain, inflammation, and fever in domestic animals and also used by humans for the same purposes. The animals known as vultures accidentally ingest diclofenac by feeding on a putrefied body of cattle that has been treated with this anti-inflammatory prior to its death. Vulture mortality causes an ecological imbalance becoming perhaps a potential threat to human health. This ecological imbalance is the most dangerous effect that promotes the water pollution by pharmaceutical products, and due to the difficulty of its regulation, the proposal goes in the sense of pretreating the wastewater before being thrown into the different aquifers. It is important to promote environmental regulation standards for water emissions from the different pharmaceutical industries, as well as from domestic and hospital wastewaters, so that the respective treatments can be applied, such as the advanced oxidation process proposed in this chapter, as heterogeneous photocatalysis, using as catalysts the Tin-modified TiO_2 .

In this case study, wastewaters collected from a pharmaceutical industry, from different streams, containing separately, diclofenac, ibuprofen, naproxen, and acetaminophen in high concentrations as is shown in Table 2. In Table 3 it can be seen the main physicochemical data of these wastewaters, data analyzed from waters collected in the place of discharge to the aquifers.

These wastewaters were photocatalytically treated using TiO_2 -Sn powders synthesized by the sol gel technique. The reaction system used was a Q-200

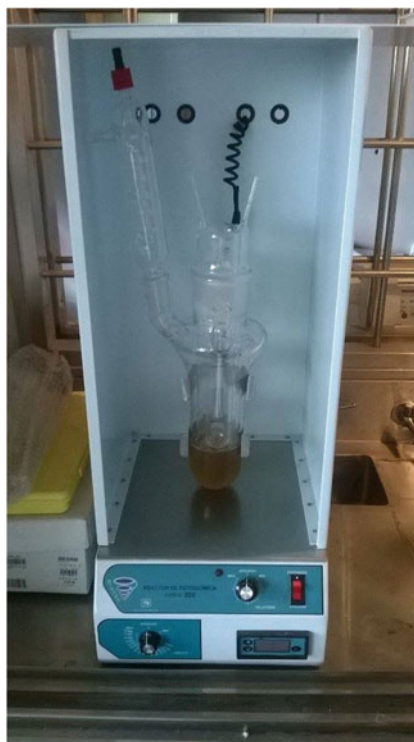
Table 2 NSAIDs concentration in the different assessed streams of wastewaters from a pharmaceutical industry

	Units	Acetaminophen	Naproxen	Diclofenac	Ibuprofen
Concentration	mg/L	195	85	3.6	2.8
TOC	ppm	10,770	2,194	1,649	26,998
OQD	mg/L DBO	18,212	159	1,943	26,972
Fecal coliforms	NMP/100 mL	<2	<2	<2	<2

Table 3 Physicochemical characterization of wastewaters in the pharmaceutical industry

Industrial effluent	
Temperature ($^{\circ}\text{C}$)	16
Solved oxygen (mg L^{-1})	12
Conductivity ($\mu\text{S cm}^{-1}$)	143
pH	6.3
Chlorides (mg L^{-1})	101
Fluorides (mg L^{-1})	4
Hardness (mg L^{-1})	247
Ammonium (mg L^{-1})	0.73
Total suspended solids (mg L^{-1})	36
Total phosphorus (mg L^{-1})	7
Total nitrogen (mg L^{-1})	18
Oxygen chemical demand (mg L^{-1})	33
Sodium hypochlorite (mg L^{-1})	1.0

Fig. 2 The photochemical reactor used to test the photocatalytic response of $\text{TiO}_2\text{-Sn}$ powders



photochemical reactor, Prendo brand (Fig. 2), with 200 ml of solution containing each of the NSAIDs (acetaminophen, diclofenac, ibuprofen, and naproxen), separately; 0.5 g of photocatalyst was added and afterwards, the reaction was irradiated with a light source with emission at 366 nm wavelength.

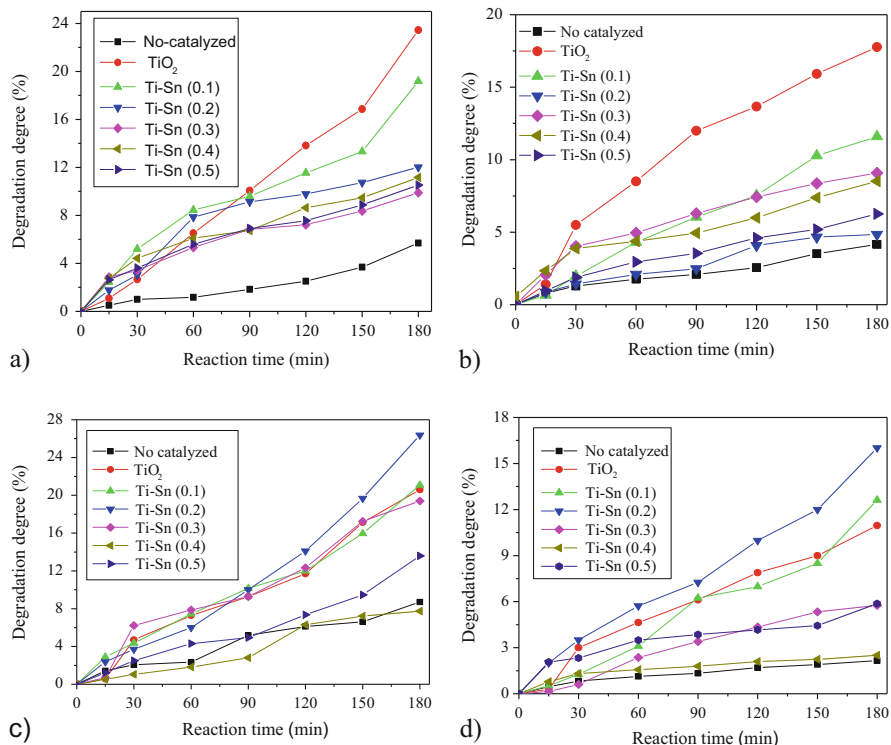


Fig. 3 Photocatalytic degradation of (a) diclofenac, (b) acetaminophen, (c) ibuprofen, (d) naproxen

The degradation degree of each $\text{TiO}_2\text{-Sn}$ powder was determined by following the change in the concentration of each drug in the reaction solution as a function of time; for this purpose, calibration curves were determined to establish the correlation between the drug concentration with the intensity of the characteristic absorption band, located at 222 nm for ibuprofen, 243 nm for acetaminophen, 262 nm for naproxen, and 275 nm for diclofenac. Drug degradation was followed through the decrease in each characteristic absorption band as a function of the reaction time under irradiation at 366 nm, taking aliquots each 15 min the first hour and each 30 min until the ending time until 180 min. Figure 3a shows the results obtained for the degradation of diclofenac, it is clearly observed that a maximum degree of degradation, of approximately 23%, is reached, after 180 min using the TiO_2 without Tin; as the Sn is incorporated to the TiO_2 and also with the Sn content increase, the degree of degradation is reduced to values of around 19%, 12%, 10%, 10%, and 5% for the samples that contain molar ratios $x = 0.1, 0.2, 0.3, 0.4,$ and 0.5 , respectively. The photolysis reaction was taken as reference, showing the lower catalytic activity than the catalyzed reactions. It is worth noting that for irradiation times lower than 60 min, the samples containing Sn are more photoactive than the TiO_2 alone. In

Fig. 3b is shown the acetaminophen photocatalytic degradation; when the reaction system is catalyzed by the TiO_2 , a degradation percent of 18% is obtained, higher than the degradation percent observed for the Tin-modified catalysts; in this case, the TiO_2 photocatalyst produces the best result. The photocatalytic degradation of ibuprofen showed a different behavior, after 180 min of reaction time, the catalytic formulation with a molar ratio $x = 0.2$ achieved the highest degradation degree, 26%, whereas the Tin-free sample only reached 18%, as shown in Fig. 3c.

The photocatalytic degradation of naproxen was the lowest among all NSAIDs (Fig. 3d), which allows to suppose a greater resistance of this molecule to be degraded, besides being the most concentrated pollutant of the four; in this case, the photocatalyst that achieved the highest degradation degree (16%) was the molar ratio $x = 0.2$, as in the degradation of ibuprofen. It is important to note that even when the maximum photocatalytic conversion reached for each of these drugs is low, between 16 and 26%, the results seem to be good, since in this case the treated wastewaters contain, on the one hand, high concentrations of drugs and, on the other hand, the treated solutions are real wastewaters with a high degree of turbidity due to the high amount of dissolved solids and the other components listed in Table 3.

2 Conclusions

Heterogeneous photocatalysis is a promising advanced oxidation process to remove polluting NSAIDs drugs from wastewater from the pharmaceutical industry. The process variables affecting the efficiency removal of pollutants are initial concentration and chemical nature of pollutants; optical, structural, morphological, and textural characteristics of the used photocatalyst, photoreactor configuration, and hydrodynamics and characteristics of the radiation source. Some important challenges that this process currently faces are the use of catalysts able to be activated by visible radiation and the immobilization of such catalysts onto structured supports to ease the separation process and to allow the reuse of such catalysts. This aims to decrease the cost of the whole process. Regarding the former, the addition of metals to TiO_2 has been one of the mainly assessed approaches by different research groups around the globe. In this context, TiO_2 -Sn powders have been demonstrated to improve the removal efficiency of not nitrogen containing NSAIDs (ibuprofen and naproxen) under 366 nm radiation when compared to the extensively used TiO_2 Degussa P25. Through the presented case study it can also be concluded that such removal efficiency strongly depends on the Sn content.

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