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Effects of metal oxide catalysts on the photodegradation of antibiotics effluent

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ABSTRACT

The current study examined the effect of metal oxide catalysts on the sorption and photocatalytic efficiencies for the removal of ciprofloxacin and ofloxacin in water. ZnO and TiO_2 catalysts are prepared using a suitable method based on the sol-gel process, which have a great change in structural and textural properties. The structure and surface area of the synthesized catalysts were characterized, and used as sorbents/catalysts to remove antibiotics from water. Results showed a high adsorption capacity for the Titania oxide related to its great surface area, it is about 280 m^2 g^{-1}, compared to that of ZnO catalyst with only 19 m^2 g^{-1}. However, both photocatalysts exhibit a difference in photocatalytic activity versus both drugs. Therefore, ZnO, as a competitor catalyst for the TiO_2, provides the most effective treatment of contaminated water with antibiotic pollutants to produce suitable reused water.

Keywords: ZnO, TiO$_2$, Catalysts, Antibiotics, Photocatalytic activity, Removal.

1. Introduction

The pharmaceutical compounds represent emerging pollutants due to their frequent use and persistence in the environment [1,2]. They are released to the environment through various human pharmaceutical uses, mainly hospital and industrial processes. Antibiotics with their metabolites are considered the most widely used drugs and detected drugs in groundwater and surface water and their disposal remains a major environmental issue [3]. It has been reported that supporting of nickel oxide onto clinoptilolite nanoparticles can degrade about 76% of cephalexin molecules. In addition, supported NiO onto NCP showed better degradation activity of cefixime than TiO_2 [4,5]. Among the available methods to remediate groundwater-containing pharmaceuticals, adsorption and photodegradation are some efficient alternatives because of their simplicity, sludge-free operation, easy regeneration of the separation agent and cost effectiveness [6-8]. Indeed, adsorption is the most conventional method, which is able to remove important pollutants in several media such as textile industry wastewater. Adsorption effect is crucial stage of pollutant removal. It is prior to photocatalytic experiment. Thus, adsorption is closely related to the degradation process because with higher adsorption sites, the photocatalyst amount increases [9]. Therefore, photocatalytic reactions significantly depend on the adsorption process and photodegradation yield is related to the adsorption on the catalyst surface [10]. A large variety of oxides has been evaluated to remove the pharmaceutical pollutants from aqueous solutions. Among them, TiO_2 and ZnO have been widely studied as catalysts for various photocatalytic reactions due to their high gap energies at UV range, knowing that the photocatalytic oxidation, under ultraviolet UV-light, is defined as a very interesting alternative way for the degradation of many organic pollutants [11-14]. During the photodegradation process, several reactions occurred.

(1) Metal oxide (TiO_2 or ZnO) + hν → MO (e^- + h^+)

(2) H_2O + h^+ → $OH^•$ + H^+

(3) $OH^•$ + antibiotic → CO_2 + H_2O (if the degradation was complete)
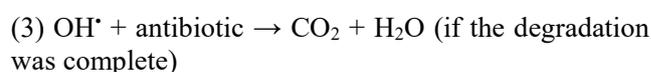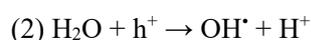
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However, many studies evaluated the photodegradation of environmental pollutants such as dyes (direct red 23, direct brown 166, MB, MO, RhB), an organophosphorus stimulant of chemical warfare agent (dimethyl methylphosphonate) and drugs (phenylephrine hydrochloride, ciprofloxacin) using titania [15-21] and zinc oxide [22-29]. Moreover, a relevant role is also played by the chemical structure and the surface area of catalysts and the consequence on their sorption and/or degradation of drugs, depend also on the chemical characteristics of antibiotic and the charge carriers generated by UV light absorption. Ciprofloxacin and ofloxacin antibiotics were selected for their excessive use and structural dissimilarity (Fig. 1), while ZnO and TiO$_2$ were prepared by a modified sol gel route and selected for their difference in their structures and surface areas. The present study aimed to compare the photodegradation efficiencies of the two drugs in aquatic solutions in relation to the chemical structure and the surface area of the used metal oxides.

2. Experimental

2.1. Synthesis of TiO$_2$ and ZnO catalysts using sol-gel process

Titanium dioxide TiO$_2$ was prepared by addition of concentrated ammonia (25 %) at pH 10 to tetraisopropyl orthotitanate (TIPT) in 1-propanol [30], while ZnO gel is commonly precipitated from zinc nitrates in ammonia medium to get closer to the TiO$_2$ operating conditions. The gel-like materials were filtered, dispersed in deionized water under sonication and filtered again; this procedure was repeated three times. The procedure of the ultrasound irradiation can increase the stability of the oxide phase affecting the cavitation phenomenon, it enhances the exchange reactions occurring at the particle surface and limits the particle aggregation. The resulting gel-like materials were dried overnight at 100 °C and calcined at 500 °C and 800 °C for 3 h.

2.2. Technique

The XRD patterns of the dried and calcined powders were obtained by means of Philips PW131 as the analytical device using monochromatic Cu-Kα radiation at an accelerating voltage of 40 kV and a current of 30 mA. XRD data were collected over an angular range from 10-70°. The porosity of ZnO and TiO$_2$ powders was studied by multi-point N$_2$ gas sorption experiments at 77 K using a micromeritics ASAP 2010 instrument. The specific surface areas were calculated according to the BET method using sorption data in the relative pressure range from 0.05 to 0.25 and the pore size distribution was obtained by the BJH method. The concentration of the residual drug in the solution was determined by HPLC using Alliance HPLC system equipped with barrette Diode PD A2998 with an Intersil C18 column (250 × 4.6 mm) and the 5 µm particle size was adjusted to the UV absorption detector. The conditions were (i) CIP using Agilient-Zorbax C18 SB (250 × 4.6 mm) 5 µm, the column temperature of 40 °C, the mobile phase: H$_3$PO$_4$-triethylamine (pH 3): acetonitrile (87:13), flow of 1.5 mL.min^{-1}, the injected volume of 50 µL, and (ii) OFL using GL Sciences Inc. Inertsil C18 (250 × 4.6 mm) 5 µm; the column temperature of 45 °C, mobile phase: CH$_3$COONH$_4$-NaClO$_4$-H$_3$PO$_4$ (pH 2.2): acetonitrile (85:15), the flow 2 mL min^{-1} and injected volume of 100 µL.

2.3. Antibiotic sorption and photodegradation experiments

Ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-yl-quinoline-3-carboxylic acid, named CIP) and ofloxacin ((R,S)-9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido [1,2,3-de]-1,4-benzoxazine-6-carboxylic acid, named OFL) are selected in this study. Solutions of CIP and OFL were prepared by dissolving 20 mg of the active ingredient of each antibiotic in 1 L of distilled water.
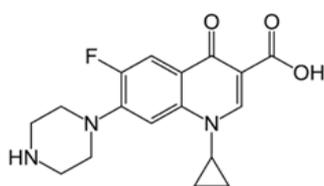
(a) Ciprofloxacin (CIP)

MW = 331.3 g mol-1

pka$_1$ = 6.1; pka$_2$ = 8.7; XlogP3 = -1.1
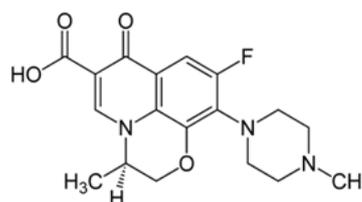
(b) Ofloxacin (OFL)

MW = 361.4 g mol-1

pka$_1$ = 6.0; pka$_2$ = 8.2; XlogP3 = -0.4

Fig. 1. Molecular structures of (a) ciprofloxacin and (b) ofloxacin.

The antibiotic degradation was carried out at room temperature under a 125 W UV A-B-C (200-600 nm) irradiation using a 200 mL water-cooled cylindrical glass reactor. 200 mg of catalyst was held in contact with 100 mL of the solution containing 20 mg L^{-1} as the initial concentration of each antibiotic at pH 5.6 and 6.5 for CIP and OFL solutions, respectively. Before every photocatalytic test and before the light was turned on, to determine the residual concentration of antibiotic in the solution based on kinetic sorption data, the mixture was kept in the dark for 30 min to ensure the adsorption-desorption equilibrium. After 30 min in the dark, the photodegradation experiments were performed. At the selected illumination time, the suspensions were filtrated using a 0.45 μm membrane filter and the concentration of antibiotics remaining in the solution C_e (mg L^{-1}) was measured by the HPLC technique. All sorption and photocatalytic results presented in this work are the mean of three replicates. The adsorbed amount of antibiotics q_t (mg g^{-1}) was measured by the difference between the initial and final concentrations as follows: $q_t = V.(C_0-C_t)/m$ [31], while the degradation rate was calculated using the following formula: $D(\%) = 100 \times (C_0-C_t)/C_0$ [32], where C_0 is the initial antibiotic concentration (mg L^{-1}), C_t is the equilibrium antibiotic concentration (mg L^{-1}), V is the volume of solution (L) and m is the adsorbent dose (g). The Langmuir-Hinshelwood (L-H) model was used to analyze the heterogeneous reactions occurring on the surface of catalysts. The rate law derived from the model was estimated by a simpler "pseudo-first order" model [33,34] represented by $\log(C_0/C_t) = (k_{app}/2.303).t$, where k_{app} is the apparent rate constant, C_0 is the initial solution and C_t is the concentration of the pollutant at time t.
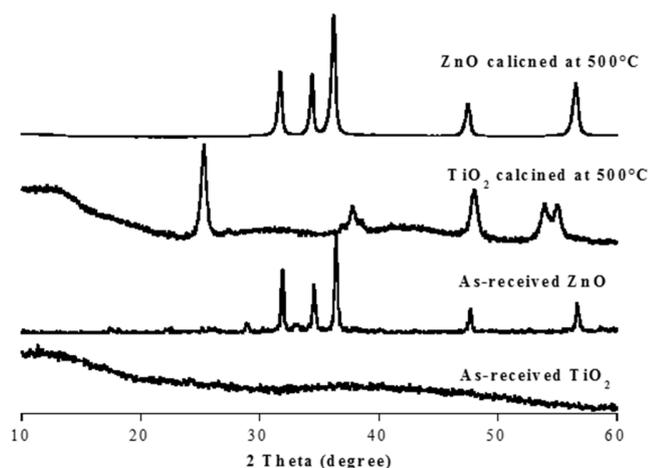
3. Results and Discussion

3.1. Characterization of catalysts

The X-ray diffraction (XRD) patterns of dried TiO$_2$ and ZnO at 100 °C and calcined at 500 °C are shown in Fig. 2. The as-received TiO$_2$ sample exhibits an amorphous crystalline phase but after treatment at 500 °C for 3 hours, it became a crystalline anatase phase (JCPDS 21-1272) with main peaks found at 24.8 (101), 47.6° (200), 53.5° (105) and 55.1° (211). In addition, the as-received ZnO material showed the main diffraction peaks of the zincite structure at ca. 32° (100), 34.5° (002), 36.5° (101), 47.5° (102) and 57° (110) (JCPDS 36-1451) and the heat treatment at 500 °C of ZnO sample did not affect the zincite structure.

Their sorption behavior can be described by an isotherm of type IV with a well identifiable sorption hysteresis (Fig. 3). The as-received ZnO and TiO$_2$ oxides have a specific surface area of 19 m^{2}g^{-1} and 280 m^2 g^{-1}, respectively, suggesting that the TiO$_2$ gel is more mesoporous catalyst than ZnO. As shown on Table 1, an analysis of the pore size distribution shows that these samples exhibit a similar pore population with a size of ca. 3.8 nm for ZnO and ca.3.5 nm for TiO$_2$. The thermal treatment of the powders at 500 °C led to a systematic decrease of the S$_{BET}$ values and a considerable enlarging of the average pore size but their heating to 800 °C led to a dramatic loss of the specific surface area of 10 m^{2}g^{-1} for typical Titania oxide. To preserve the surface properties of the powders, the current study was limited to the heat treatment at 500 °C, in this treatment, crystal growth was slightly affected, but the transformation of the amorphous phase to the TiO$_2$-anatase affects its crystallinity and the specific surface area, while ZnO retains its crystalline structure.

Fig. 2. XRD patterns of the dried and calcined ZnO and TiO$_2$ powders.
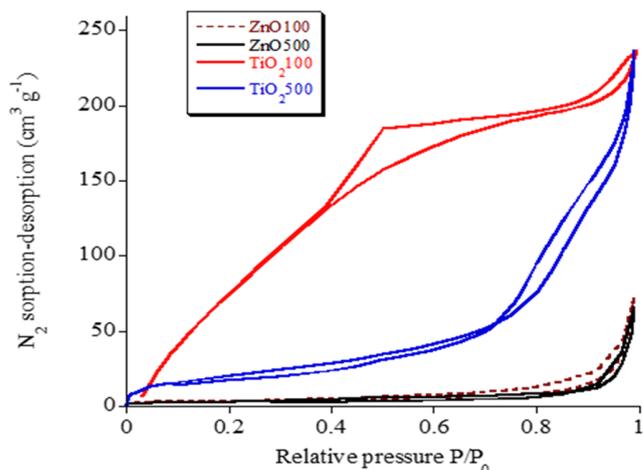
Fig. 3. N$_2$ adsorption-desorption isotherms of dried and calcined ZnO and TiO$_2$ catalysts.

Table 1. The specific surface area and pore diameter of prepared ZnO and TiO$_2$ catalysts.

Catalyst	$S_{BET}100$ (m^2 g^{-1})	$S_{BET}500$ (m^2 g^{-1})	D_p100 (nm)	D_p500 (nm)
ZnO	19	11	3.8	4.2
TiO$_2$	280	155	3.5	5.5

On the whole, these data suggest the difference in the structure and porosity between the prepared ZnO and TiO$_2$ catalysts and this difference can affect their sorption and photocatalytic behaviors.

3.2. Antibiotics sorption

Sorption tests were performed in a batch reactor equipped with a multi-stirrer. The antibiotic concentration in the supernatant was monitored using the HPLC technique. The instant quantity of antibiotic adsorbed on ZnO and TiO$_2$ powders (in mg g^{-1}) was calculated from the difference between the initial concentration C_0 and the measured concentration in the solution at time t. The sorption kinetics of ciprofloxacin and ofloxacin on both oxides after heating at 500 °C were studied using a moderately concentrated antibiotic solution (C_0 = 20 mg L^{-1}) (Fig. 4). The pH of solutions left at its initial state in the pH range from 5.6 to 6.5 without any adjustment in order to simulate the natural conditions. With 20 mg L^{-1} as initial concentration of each antibiotic, TiO$_2$ shows sorption capacities of ca. 6.0 mg g^{-1} and 5.2 mg g^{-1} for CIP and OFL respectively, higher amounts were displayed by ZnO (1.4 mg g^{-1} for CIP and 1.0 mg g^{-1} for OFL). The adsorption kinetics of TiO$_2$ heated at 500 °C for both antibiotics were quick in the beginning unlike ZnO.
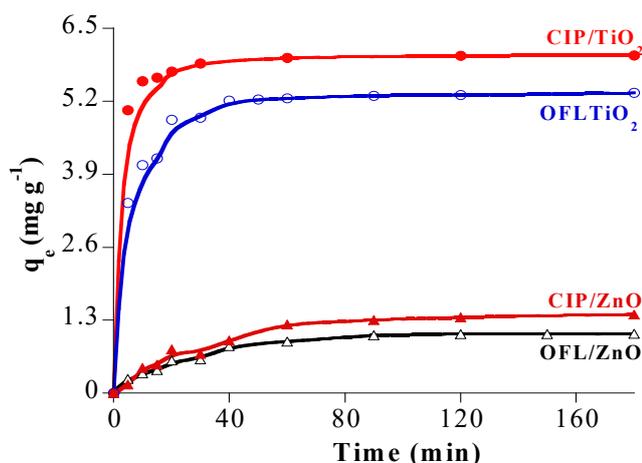
Fig. 4. Typical kinetics of antibiotic sorption on ZnO and TiO$_2$ heated at 500 °C (C_0 = 20 ppm, dose = 2 g L^{-1}, T = 25 °C, pH without adjustment).

Using TiO$_2$, the adsorption equilibrium was established in about 30 min for the CIP and 40 min for the OFL, but this time is increased to 60 min using of ZnO for the both antibiotics. After this period, the removal amount did not change significantly with time. Results suggest that antibiotic has specific interactions with Titania relating to its great porous surface compared to that of ZnO.

3.3. Kinetic of the photodegradation

The photochemical activity of these powders was evaluated and it became clear it has an advantage in removing all drug concentration from aqueous solutions. Fig. 5 shows the photodegradation of CIP and OFL antibiotics supported by ZnO and TiO$_2$ catalysts as a function of the time for 20 mg L^{-1} as the initial concentration of each antibiotic mixed with 2 g L^{-1} of catalyst dose. In comparison to the kinetic curves associated to the photocatalytic process, TiO$_2$ is faster than ZnO to degrade CIP and OFL antibiotics in water relating to its high sorption capacity in dark conditions.

The photocatalytic kinetics of many organic pollutants have often been modeled with the Langmuir–Hinshelwood equation [33,34]. The plot of log C_0/C_t versus time exhibit a straight line, where the values of the apparent first-order rate constant K_{app} are grouped in Table 2. The results show that the first-order kinetic model can describe the photocatalytic degradation of both drugs. It can be predicted that the significant difference in reaction rates might be due to the difference in surface properties between the both ZnO and TiO$_2$ catalysts. As shown in Table 2, K_{app} constants are larger with the TiO$_2$ catalyst calcined at 500 °C (K_{app} ≈ 0.69 min^{-1}), compared to those where ZnO was used (K_{app} between 0.02 and 0.15 min^{-1}). The results are in good agreement with the high porosity of TiO$_2$ compared to that of ZnO, which binds many drug molecules that facilitates the degradation process.

However, the photodegradation data confirm that zinc oxide also displays a closed efficiency to TiO$_2$ for ciprofloxacin, but needs more time for a complete degradation. Furthermore, the efficient photodegradative of ofloxacin requires a longer time for a complete degradation especially with dried catalysts. Noting that the photodegradative activity of dried ZnO shows optimal results despite its smaller specific surface area (19 m^2 g^{-1}) compared to that of dried titanium dioxide (280 m^2 g^{-1}). Nevertheless, the photocatalytic data show that the Titania catalyst calcined at 500 °C has a better degradation of both drugs than that of the dried sample, while those of dried and calcined ZnO sample have a small difference.
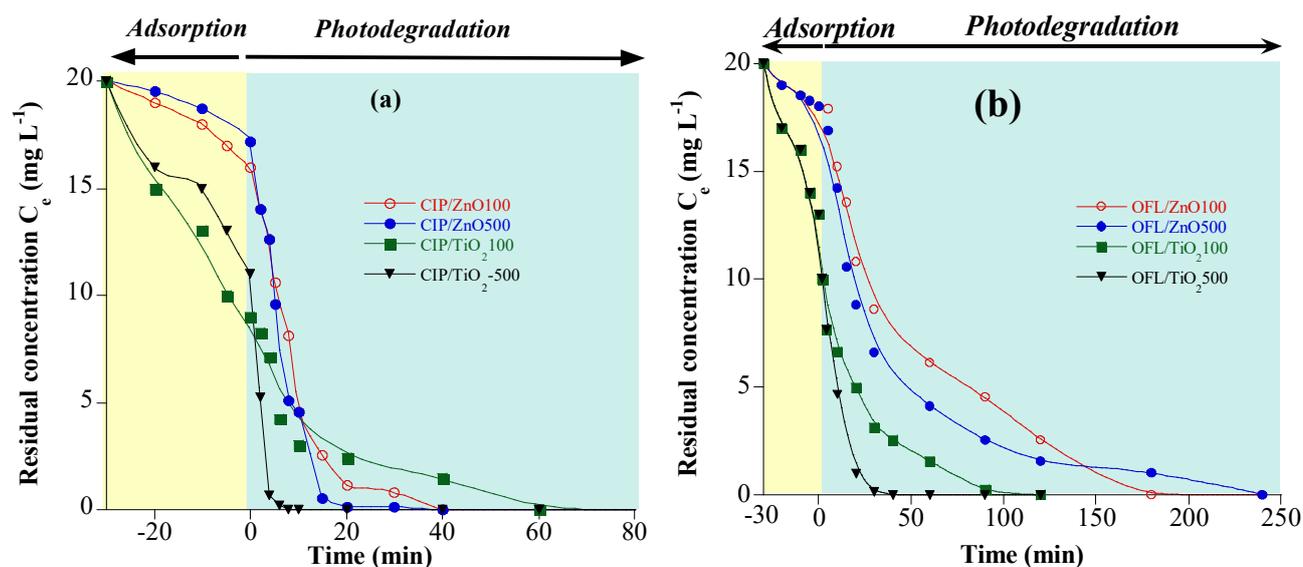
Fig. 5. Photodegradative efficiency of dried and calcined ZnO and TiO$_2$ catalysts versus (a) ciprofloxacin and (b) ofloxacin (C$_0$ = 20 ppm, dose = 2 g L^{-1}, T = 25 °C, pH without adjustment).

This is due to the amorphous phase of the as-received TiO$_2$ and the appearance of its anatase photoactive phase in calcining the powder at 500 °C, while the as-received ZnO powder is well crystallized and conserves its structure when the sample is heat-treated at 500 °C. The sorption capacity of antibiotic using ZnO and TiO$_2$ affects their photodegradation properties relating to the number of drugged molecules which are in direct contact with the photoactive surface. Each catalyst oxide provides a different template for the adsorption of antibiotic layer. With similar energy gap of ZnO (3.3 eV) and TiO$_2$ (3.2 eV) semiconductors [35], the acid/base character and their surface area can have a strong effect on the adsorbed molecules while their photocatalytic efficiency only differ in the illumination time.

On the other hand, the presence of each semiconductor under UV light may induce different reactions where the generated hydroxyl radicals (OH$^\bullet$) are the key agents responsible for the oxidation of various organic contaminants in water. Detailed reaction pathways have largely been described in most works published elsewhere [33,34].

3.4. Reusability of the photocatalysts

The regeneration of catalysts was realized at 500 °C for 6 h, in this condition, the organic matter was burned. In each regeneration, photodegradation was determined to see whether the photodegradative change occurred after the catalyst reuse. This regeneration process was repeated up to five times to investigate the effect of regeneration on photodegradative efficiency of each ZnO or TiO$_2$ catalyst and to determine the loss of the catalyst performance during the regeneration experiments. It was observed that there was no apparent change in adsorption capacity after 5 times and the average loss of particles during regeneration was about 2-5% per cycle for both TiO$_2$ and ZnO catalysts. For this, the use of the calcined catalysts at 500 °C is more useful for degradation of ciprofloxacin and ofloxacin antibiotics.

It is important to compare the photocatalytic activities of these oxides with those reported in the literature. The performance of CIP and OFL degradation by using TiO$_2$ calcined at 500 °C, is significantly higher than those found elsewhere [35-40], where their photocatalytic reactions are complete without any by-products.

Table 2. Maximum sorption capacities, rate constant and full degradation time of antibiotic degradation. C$_0$=20 mg L^{-1} of antibiotic, sorbent dose of 2 g L^{-1}, pH without adjustment, and ambient temperature.

	ZnO100		ZnO500		TiO$_2$100		TiO$_2$500	
	CIP	OFL	CIP	OFL	CIP	OFL	CIP	OFL
K$_{app}$ (min^{-1})	0.152	0.044	0.191	0.020	0.113	0.015	0.695	0.691
Full degradation time (min)	40	180	30	240	60	120	10	45

In addition, ZnO also degrades all antibiotic molecules, but it takes time. These data reveal that the photodegradation properties of ZnO depend on a complex interplay between the inter-molecular and molecule-catalyst interactions, while those of TiO_2 is due to its high surface area, preventing strong attractive electrostatic interactions with studied antibiotics. The effectiveness of photocatalytic processes using TiO_2 and ZnO depends on various parameters such as catalyst dose, light wavelength and intensity, initial pH, reaction time and initial concentration. Michael et al. [36] have indicated 60% of loxacin removal from wastewater samples using Titania dose of 3 g L^{-1}. In another study, Kaur et al. [37] have reported that the degradation of ofloxacin requited a longer time and the prepared silver modified ZnO exhibited higher photocatalytic activity compared to ZnO sample. In addition, El-Kemary et al. [38] showed that a significant degradation efficiency of ciprofloxacin (ca. 50%) was observed at pH 10 after 60 min but it is rather slow at pH 4. In accordance with these, the used photocatalysis process under UV- light has been applied using TiO_2 and ZnO prepared by the modified sol-gel process leading to a best and efficient treatment process for eliminating of CIP and OFL antibiotics.

As mentioned in the literature, the photocatalytic activity is dependent on the surface and structural properties of catalysts, which include the crystal composition, surface area, particle size distribution, porosity and band gap energy [39,40]. However, low-cost and easy-to-use heterogeneous catalysts such as ZnO with higher photocatalytic degradation are an important step in the remediation of waters especially for the degradation of antibiotic pollutants. Consequently, ZnO as a competitor of the TiO_2 provides the most effective treatment of contaminated water with antibiotic pollutants to produce suitable reuse water.

As a consequence, this study is devoted to investigate the relationships of structural and surface properties of ZnO and TiO_2 catalysts and compares their degradative power to remove the antibiotic effluents. To more details in this area, perspective studies should focus on the photoreactor design having a simple variation of the energy efficient UV/Vis light with low intensities.

4. Conclusions

In this study, ZnO and TiO_2 catalysts were prepared by using a modified sol-gel route at room temperature. Dried ZnO powders exhibit broad diffraction characteristic peaks of a zincite crystalline structure, while TiO_2 displays an amorphous phase. The heat treatment at 500 °C crystallizes the TiO_2-anatase phase, but retains the initial zincite structure for ZnO. A great difference in surface areas between the powders has been obtained. We also demonstrated a very high effectiveness of the prepared ZnO and TiO_2 catalysts as supports to degrade completely the ciprofloxacin and ofloxacin in water. Zinc oxide shows a kinetic degradation compared to that of titanium dioxide despite its small specific surface area, but needs more time to degrade the drug pollutant completely. Thermal treatment of Titania at 500 °C improves its photodegradative efficiency relating to the appearance of its anatase photoactif phase. The achieved results using the low-cost ZnO catalyst can be used to optimize the process and design appropriate reactor for potential large-scale applications in order to reduce the cost of water treatment.

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