



Sorption and photocatalytic degradation of ciprofloxacin and ofloxacin in aqueous suspensions of TiO₂ and ZnO catalysts

C. El Bekkali¹, H. Bouyarmane¹, S. Laasri², M. El Karbane³, A. Saoiabi¹, A. Laghzizil^{1*}

¹Laboratoire de Chimie Appliquée des Matériaux, Université Mohamed V, Faculté des Sciences, BP.1014, Rabat, Morocco

²Laboratoire des Sciences de l'Ingénieur Pour l'Énergie, École Nationale des Sciences Appliquées-El Jadida-Morocco

³Laboratoire National de Contrôle des Médicaments, Rabat-Morocco

Received 13 Aug 2017,

Revised 21 Sep 2017,

Accepted 28 Sep 2017

Keywords

- ✓ Antibiotics
- ✓ Photocatalysis
- ✓ Degradation
- ✓ Water treatment

laghzizi@fsr.ac.ma

Phone: +212537775440

Fax: +212537775440

Abstract

Pharmaceuticals are often present in wastewaters at low concentration and their removal is largely dependent on their physical and chemical properties. The current study examined the comparative sorption and photocatalytic efficiencies of ciprofloxacin and ofloxacin in aqueous solutions supported on ZnO and TiO₂ catalysts under UV-light irradiation. The selected catalysts are prepared using a suitable method based on the sol-gel process, which have a great change in structural and textural properties. The results showed high adsorption capacity for the titania oxide related to its great surface area compared to that of ZnO powder. However, the both photocatalysts exhibit a specific difference in photodegradative efficiency versus the both drugs related to their difference in sorption process and specific surface areas. Results of this work are of great significance for the environmental application of TiO₂ and ZnO oxides for the removal of pharmaceuticals from wastewaters.

1. Introduction

The pharmaceutical compounds represent an 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 used drugs and largely detected in ground and surface waters and their remediation removal is a major environmental issue [3]. Among the available method to remediate groundwater containing pharmaceuticals, adsorption and photodegradation are an efficient alternatives because of their simplicity, sludge-free operation, and easy regeneration of the separation agent and cost effectiveness [4-6]. A large variety of oxides has been evaluated to remove the pharmaceutical pollutants from aqueous solutions. In this context, TiO₂ and ZnO oxides have been widely studied for photocatalytic reactions due to their gap energies [7-9]. However, few studies evaluate the photodegradation of pharmaceutical pollutants using titania [10, 11] and zinc oxide [12-13]. Ciprofloxacin and ofloxacin were selected to test the prepared TiO₂ and ZnO catalysts using a modified method based sol-gel process. This study discusses the influence of the nature of catalyst (TiO₂ or ZnO), illumination time and antibiotic formula on the sorption and photodegradation performance.

2. Materials and methods

Titanium dioxide TiO₂ was prepared by addition of concentrated ammonia (25 w%) at pH 10 to tetraisopropyl orthotitanate (TIPT) in 1-propanol, while ZnO gel is commonly precipitated from Zinc nitrates in ammonia medium to get closer to the TiO₂ operating conditions. The gel-like materials were filtered, redispersed in deionized water under sonication and filtered again; this procedure being repeated three times, which the ultrasound irradiation can increase the stability of oxide phase affecting the cavitation phenomenon and enhances the exchange reactions occurring at the particle surface and limits the particle aggregation. The obtained gel-like materials were dried overnight at 100°C and calcined at 500°C and 800°C.

Ciprofloxacin and ofloxacin antibiotics were selected for their excessive use and structural dissimilarity (Figure 1). To study the effect of the catalyst nature, sorption and photocatalytic degradation supported on TiO₂ and ZnO catalysts— were realized in batch experiments conducted at 25°C. The antibiotic degradation was carried out at room temperature under a 125W UV A-B-C (200-600 nm) irradiation using a water-cooled cylindrical 200 mL glass reactor. 200 mg of catalyst was held in contact with 100 mL of solution containing 20

mgL⁻¹ as the initial concentration of each antibiotic at pH 6. Before every photocatalytic test and from kinetic sorption data, the mixture was kept in the dark for 30 min to ensure that the adsorption-desorption equilibrium was reached before the light was turned-on in order to determine the residual concentration of antibiotic in solution. After 30 min in the dark, the photodegradation experiments were started. At selected illumination time, the suspensions were filtrated using a 0.45 μm membrane filter and the concentration of antibiotic remaining in solution C_e (mg L⁻¹) was measured by HPLC technique. All the photocatalytic results presented in this work are the mean of three replicates.

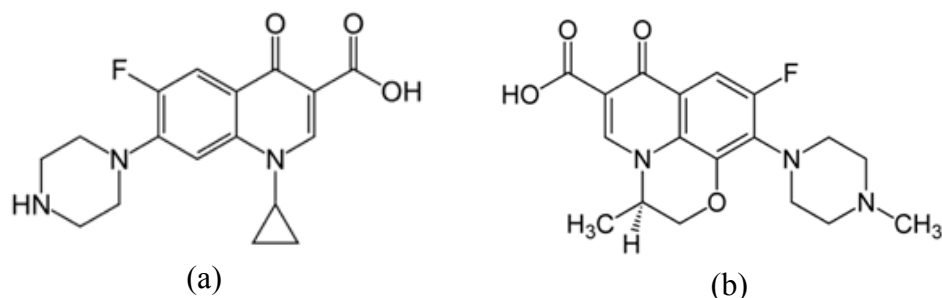


Figure 1: Molecular structures of (a) ciprofloxacin and (b) ofloxacin.

3. Results and discussion

3.1. Characterization of catalysts

The X-ray diffraction (XRD) patterns of dried ZnO and TiO₂ at 100°C and calcined at 500°C are shown in Figure 2. The as-received TiO₂ sample exhibits an amorphous crystalline phase but after treatment at 500°C for 3 hours, it became a crystalline anatase phase while the heat treatment of ZnO did not affect its crystalline structure.

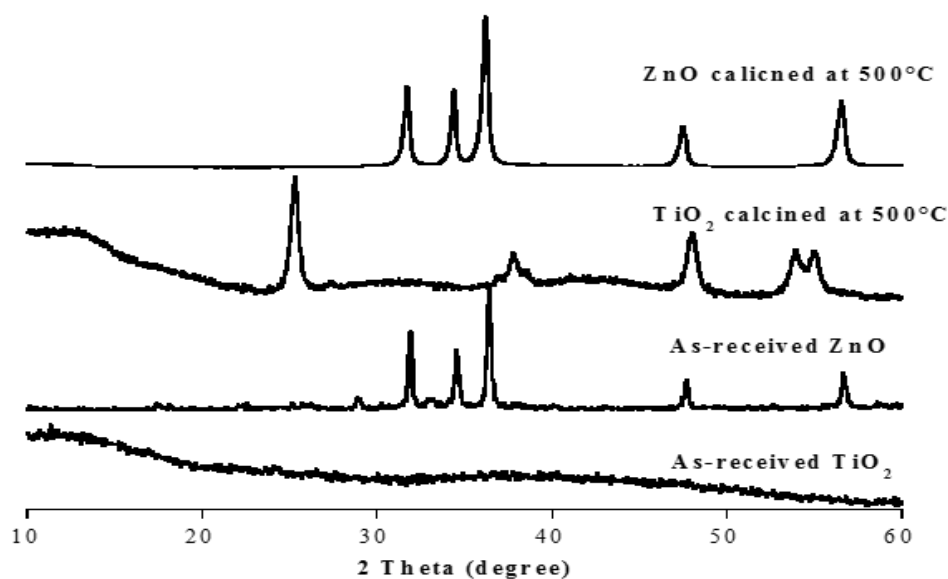


Figure 2: XRD patterns of the dried and calcined ZnO and TiO₂ powders.

The porosity of ZnO and TiO₂ powders was studied by multi-point N₂ gas sorption experiments at 77K using a micromeritics ASAP 2010 instrument. Their sorption behavior can be described by an isotherm of type IV with a well identifiable sorption hysteresis (Figure 3). The specific surface area was 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 as-received ZnO and TiO₂ oxides have a specific surface area of 19 m²g⁻¹ and 280 m² g⁻¹, respectively, suggesting that the TiO₂ 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 TiO₂.

Thermal treatment of the powders at 500°C leads 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 specific surface area of 10 m²g⁻¹ for typical titania oxide. Altogether these data suggest the difference in structure and porosity between the prepared ZnO and TiO₂ catalysts can affect their sorption and photocatalytic behaviors.

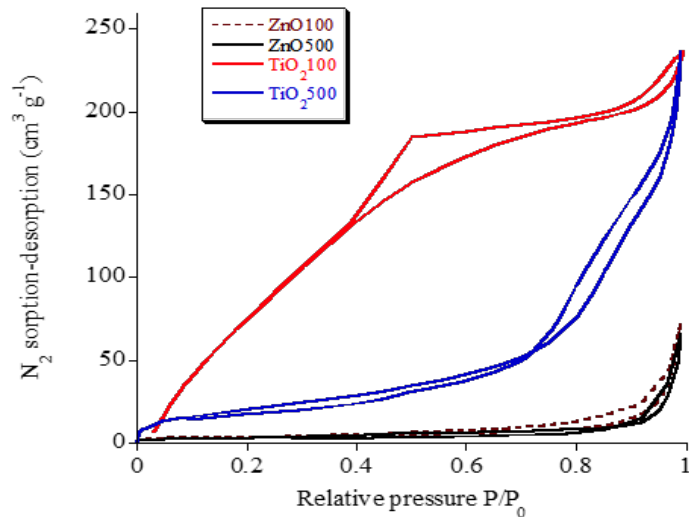


Figure 3: N₂ adsorption-desorption isotherms of dried and calcined ZnO and TiO₂ catalysts.

Table 1: Specific surface area and pore diameter of prepared ZnO and TiO₂ catalysts.

Catalyst	S _{BET} 100 (m ² g ⁻¹)	S _{BET} 500 (m ² g ⁻¹)	D _p 100 (nm)	D _p 500 (nm)
ZnO	19	11	3.8	4.2
TiO ₂	280	155	3.5	5.5

3.2. Adsorption and photodegradation experiments

Sorption tests were performed in a batch reactor equipped with a multi-stirrer. The antibiotic concentration in the supernatant was monitored using a high performance liquid chromatography (HPLC). The instantly quantity of antibiotic adsorbed on ZnO and TiO₂ powders (in mg g⁻¹) was calculated from the difference between the initial concentration C₀ and the measured concentration in 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 (C₀ = 20 mg L⁻¹) (Figure 4). The pH of solutions was left at its initial state in pH 5.6-6.5 range without any adjustment in order to simulate the natural conditions. Contrary to ZnO material, a good sorption is achieved almost instantaneously for TiO₂ powder. With 20 mg L⁻¹ as initial concentration of each antibiotic, TiO₂ shows sorption capacities of ca. 6.0 mg g⁻¹ and 5.2 mg g⁻¹ for CIP and OFL respectively, higher that displaying by ZnO (1.4 mg g⁻¹ for CIP and 1.0 mg g⁻¹ for OFL). Results suggest that antibiotic has specific interactions with titania related to its great porous surface compared to that of ZnO. Thus, the photochemical activity of these powders was evaluated to have an advantage in removing all drug concentration from aqueous solutions.

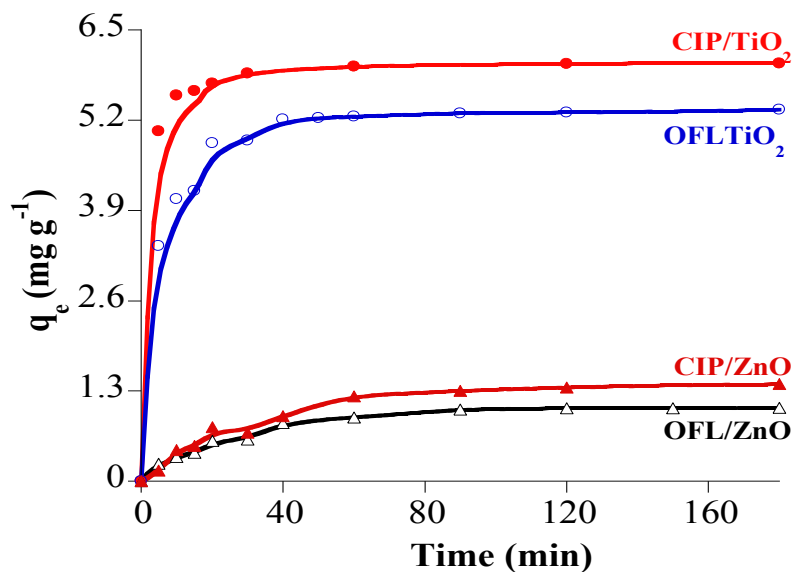


Figure 4: Typical kinetics of antibiotic sorption on ZnO and TiO₂ heated at 500°C.

Figure 5 shows the photodegradation of CIP and OFL antibiotics supported by ZnO and TiO₂ catalysts as a function of the time for a 20 mg L⁻¹ as initial concentration of each antibiotic mixed with 2 g L⁻¹ of catalyst dose. In comparison of the kinetic curves associated to the photocatalytic process, TiO₂ is faster than ZnO to degrade CIP and OFL antibiotics in water related to its high sorption capacity in dark conditions. However, the photodegradation data confirm that zinc oxide also displays a closed efficiency to TiO₂ for ciprofloxacin, but needs more time for a complete degradation. Furthermore, the photodegradative efficiency 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 m² g⁻¹) compared to that of dried titanium dioxide (280 m² g⁻¹). Nevertheless, the photocatalytic data show that the titania catalyst calcined at 500°C has a better degradation of the both drugs than that of the dried sample, while those of dried and calcined ZnO sample are similar. This is due to the amorphous phase of the as-received TiO₂ and the appearance of its anatase photoactive phase from 500°C, while the as-received ZnO powder is well crystallized and conserve its structure at 500°C. For this, the use of the calcined TiO₂ catalyst is more useful for degradation of ciprofloxacin and ofloxacin antibiotics.

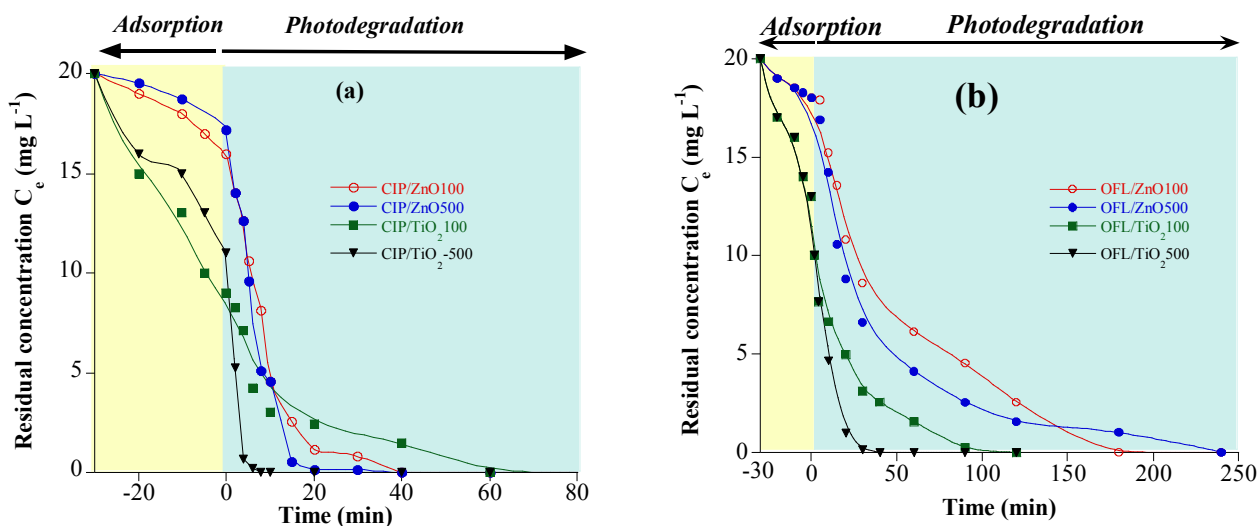


Figure 5: Photodegradative efficiency of dried and calcined ZnO and TiO₂ catalysts versus (a) ciprofloxacin and (b) ofloxacin.

The difference in sorption capacity of antibiotic by ZnO and TiO₂ affects their photodegradation properties related to the amount of druged molecules that 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 TiO₂ (3.2 eV) semiconductors [14], the acid/base character and area of their surface can have a strong effect on the adsorbed molecules while their photocatalytic efficiency only differ of the illumination time. The effectiveness of photocatalytic processes using TiO₂ and ZnO depends on the various parameters such as the catalyst dose, light wavelength and intensity, initial pH, reaction time and initial concentration [8-9,15]. Therefore, the different experimental conditions can lead to the dissimilar removal efficiencies of antibiotics using photocatalysis processes. In fact, Michael et al. [16] have reported 60% ofloxacin removal from wastewater samples using titania dose of 3 g L⁻¹. In other study, Kaur et al. [17] have reported that the degradation of ofloxacin required a longer time and the prepared silver modified ZnO exhibited higher photocatalytic activity compared to ZnO sample. In addition, El-Kemary et al. [18] showed that a significantly 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-visible light has been applied using TiO₂ and ZnO prepared by modified sol-gel process leading a best and efficient treatment process for eliminating completely of CIP and OFL antibiotics.

The regeneration of catalysts was realized at 500°C for 6 h, which altogether the organic matter was burned. 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 and TiO₂ 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 TiO₂ and ZnO materials. In comparing the recycling behavior of TiO₂ and ZnO catalysts, we noticed that TiO₂ is more rigid than ZnO to degrade CIP and OFL antibiotics related to its structure and surface properties.

As described in the literature, the photocatalytic activity is dependent on the surface and structural properties of catalyst, which include crystal composition, surface area, particle size distribution, porosity and band gap energy [19-20]. However, low-cost and easy-to-use heterogeneous catalysts as ZnO with higher photocatalytic degradation is an important step in the remediation of waters especially for the degradation of antibiotic pollutants. As consequence, this study provides an overview on the structural and photocatalysis properties of ZnO and TiO₂ materials and discusses the effect of specific variables affecting the performance of degradation of ciprofloxacin and ofloxacin pollutants in water. To more details in this area, future studies should focus on the photoreactor design able to have simply variation of the energy efficient UV/Vis light with low intensities.

Conclusion

In this study, we demonstrated a very high effectiveness of the prepared ZnO and TiO₂ powders, which can be used as photocatalysts to degrade completely the ciprofloxacin and ofloxacin in aqueous solutions. Zinc oxide shows a kinetic degradation comparable to that of titanium dioxide despite its small specific surface area, but needs more time to degrade completely the drug pollutant. Thermal treatment of titania catalyst at 500°C improve its photodegradative efficiency related 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. Further research to investigate the degradation of antibiotics containing in the wastewaters is required to better comprehend the process applications.

References

1. V. Homen, L. Santos, *J. Envir. Manage.* 92 (2011) 2304-2347.
2. M. Amini, M. Khanavi, A. Shafiee, *Iran. J. Pharm. Res.* 2 (2004) 99-101.
3. E. Zuccato, S. Castiglioni, R. Fanelli, G. Reitano, D. Calamari, Risk Related to the Discharge of Pharmaceuticals in the Environment, edited by K. Kümmerer, *New York: Springer-Verlag*, 2004.
4. L. Ellselami, N. Hafidhi, F. Dappozze, A. Houas, C. Guillard, *Chinese J. Catal.* 36 (2015) 1818-1824.
5. A.M. Ferrari-Lima, R.P.D Souza, S.S. Mende, R.G. Marques, M.L. Gimenes, N.R.C. Fernandes-Machado, *Catal. Today* 241 (2015) 40-46.
6. G.S. Pozan, A. Kambur, *Chemosphere* 105 (2014) 152-159.
7. D. Li, H. Haneda, *Chemosphere* 51 (2003) 129-137.
8. V. Srikant, V., D. R. Clarkea, *J. Appl. Phys.* 83 (1998) 5447-51.
9. E. Elmolla, M. Chaudhuri, *J. Hazard. Mater.* 173 (2011) 445-449.
10. G. H. Safari, M. Hoseini, M. Seyedsalehi, H. Kamani, J. Jaafari, A. H. Mahvi, *Int. J. Environ. Sci. Technol.* 12 (2015) 603-616.
11. R.A. Palominos, M.A. Mondaca, A. Giraldo, G. Penuela, M. Perez-Moya M, H.D. Mansilla, *Catal. Today* 144 (2009)100-105.
12. M.M. Khan, S.A. Ansari, D. Pradhan, M.O. Ansari, D.H. Han, J. Lee, *J. Mater. Chem. A* 2 (2014) 637-644.
13. R. Nosrati, A. Olad, R. Maramifar, *Environ. Sci. Pollut.* 19 (2012) 2291-2299.
14. D. Li, W. Shi, *Chinese J. Catal.* 37 (2016) 792-799.
15. L. Dong, S. Zhu, L. Zhang, M. Huo, X. Yang, *Catal. Comm.* 16 (2011) 250-254.
16. I. Michael, E. Hapeshi, C. Michael, D. Fatta-Kassinou, *Water Res.* 44 (2010) 5450-5462.
17. A. Kaur, G. Gupta, Alex O. Ibadon, D. B. Salunke, A.S.K. Sinha, S. K. Kansal, *J. Envir. Chem. Eng.* 00 (2017) 00-00, <https://doi.org/10.1016/j.jece.2017.05.032>.
18. M. El-Kemary, H. El-Shamy, I. El-Mehasseb, *J. Lumin.* 130 (2010) 2327-2331.
19. S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, *J. Envir. Manage.* 92 (2011) 311-330.
20. V. Augugliaro, M. Litter, L. Palmisano, J. Soria, *J. Photochem. Photobiol. C* 7 (2006) 127-144.

(2017) ; <http://www.jmaterenvironsci.com>