High efficient degradation of Cefixime using UV/TiO₂ photocatalytic process: A comparison between photocatalytic and photolytic

Shima Sahraeian [1]   Vali Alipour [1]   Omid Rahmanian [1]

[1] Department of Environmental Health, Faculty of Health, Hormozgan University of Medical Sciences, Bandar Abbas, Iran.

Original Article

Abstract

Correspondence:
Omid Rahmanian, PhD.
Faculty of Health, Hormozgan
University of Medical Sciences.
Bandar Abbas, Iran
Tel:+98 76 33338583
Email:
om.rahmanian@gmail.com

Introduction: The existence of pharmaceuticals in aquatic ecosystem, their persistence and possible effects on living organisms and inefficient systems in removal of these compounds from water and wastewater are a growing concern. In this research, the UV/TiO₂ photocatalytic degradation of Cefixime was investigated so as to identify if this method was efficient for removal of Cefixime or not.

Methods: The experimental parameters like as primary concentration of Cefixime, catalyst dosage, solution pH and time were assessed and optimized. The photocatalytic analysis was based on residual Cefixime identification by HPLC. The chromatographic conditions were comprised of a reversed-phase C18 column with mobile phase consisting of 45:55 v/v mixture of Acetonitrile: water.

Results: The optimum removal efficiency for Cefixime was obtained after 60 min (90.98%) when 1 mg/L TiO₂ was used at pH=3. The increase of catalyst concentration from 1 to 70 mg/L led to a decrease in degradation efficiency.

Conclusion: According to results, UV/TiO₂ process could be a promising technique for the removal of Cefixime with good efficiency in a relatively short reaction time

Key words: Cefixime, Removal, HPLC, Photocatalytic

Introduction:

Medications are considered as micro-contaminants if they enter the environment from different sources, like as effluents of pharmaceutical factories and waste disposal (1). Among various drug combinations, special attention has been paid to antibiotics. Antibiotics can have adverse effects on aquatic and terrestrial environments because they can accumulate in the environment and maintain their stability. These adverse effects are evident even in very low concentrations (ng/L to mg/L) (2). The fate of pharmaceutical compounds according to their chemical and physical properties is predictable. Biodegradable antibiotics may mineralize to H₂O and CO₂ or may analysis to hydrophilic compounds which can pass over the wastewater systems and come into water sources, but non-biodegradable antibiotics can't break down easily, thus they remain in sedimentation sludge and come to the environment without any changes (3). Cefixime (Figure 1), is an orally absorbed third generation cephalosporin antibiotic with molecular weight of 453.4 g/mol that was permitted by the U.S. Food and Drug Administration in 1997 for the

therapy of minor to moderate bacterial infections (4, 5). It acts by intrusive in the synthesis of bacterial cell wall. It binds to specific penicillin binding proteins positioned inside the bacterial cell wall make happen the inhibition of the third and last step of bacterial cell wall synthesis (6).
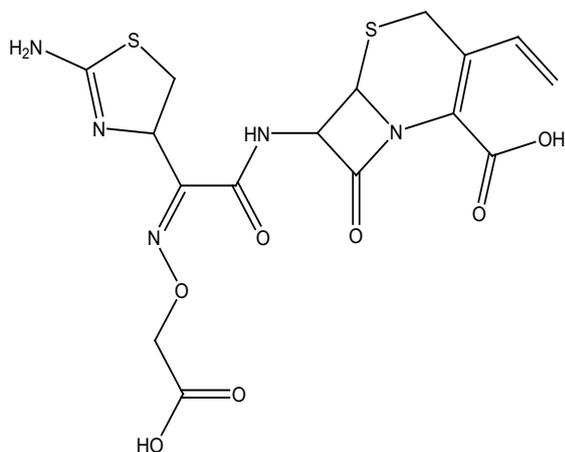

Figure 1. Cefixime structure

Different chemical and physical techniques such as membrane systems (7,8), biodegradation (9-13), chemical oxidation (14,15), adsorption (16-18) and ion-exchange (19) can be used to remove antibiotic from wastewater. Heterogeneous advanced oxidation processes (AOPs) treatment by means of semiconductors as photo-catalysts has been a capable process amongst advanced oxidation technologies (20). The benefit of AOPs is that they shortage mass transfer limitations and operate at ambient conditions. Three fundamental elements require in UV/catalyst processes: 1) a semiconductor whit photosensitive surface (such as titanium dioxide due to its high stability, commercially existing, non-toxic, good performance and low cost), 2) a source of photon energy and 3) suitable position of the valence band potential. Semiconductors are characterized by valence and conduction bands that are separated by a band gap (2,21). When aqueous TiO_2 suspension is irradiated by a source of photon of energy equal or greater than the band gap of the semiconductor (E_g= 3.2 eV), electrons in the valence band excite to the conduction band and subsequently positive holes (h^+) and electrons (e^-) are generated and photo-catalytic oxidation happen (eqn.1).

$$TiO_2 + h\nu\ (UV) \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)\quad (1)$$

Oxygen in the water can react with photo generated electron and reduce to superoxide radical anion ($O_2^{\bullet-}$). The antibiotic may also reduce by the electrons. Hydroxyl radicals are highly reactive species which are the oxidation result of hydroxide anions and water by photo generated holes (22-25).

The goal of this paper is to assess the efficacy of advanced oxidation processes by UV-TiO_2 as a photo-catalytic system for efficient elimination of Cefixime antibiotic from aqueous solution and finally make a comparison among this system, TiO_2 in darkness, TiO_2 in sun-light and alone UV to elucidate the photo-catalytic efficiency. However, there is no reported study, based upon the best our knowledge, on Cefixime degradation by TiO_2 photo-catalysis in aqueous phase. The influence of operating parameters such as catalyst dose, irradiation time, pH and Cefixime concentration are investigated for field scale requests. Langmuir–Hinshelwood (L–H) model is used to attain kinetic parameters for the photo-catalytic degradation.

Methods:

Cefixime trihydrate was obtained from Farabi Company (Iran). Acetonitrile and Water both HPLC grade were purchased From Merk. Titanium (IV) oxide for analysis was purchased from merck (EMSURE®). Deionized water with an electrical conductivity of 0.05 μS/cm (Millipore S.A.S 67120 Molsheim) was used for the preparation of aqueous solutions. Sodium hydroxide and hydrochloric acid solution 0.1 M were apply to adjust the pH of the solutions. All chemicals were used without more purification.

The reactor used for photo-catalytic reactions is illustrated in Figure 2. A water bath was considered to maintain the temperature of the solution (30±1°C). Reactions were carried out using a medium-pressure UVC lamp (125 W, λ_{max}=247.3 nm) as the irradiation source and kept in a quartz glass. Experimental solutions at different concentrations of Cefixime were prepared and transferred to a beaker within the reactor, under magnetic stirring.

The concentration of Cefixime was determined by HPLC (Shimadzu, Japan) that is consist of

single pupm, 20 AD UFLC and UV-VIS detector which detect the analyte at 225 nm. Analysis was done on C18 column (250 mm× 4.6 mm) with 5 μm particle size and Injection Volume of 20 μl. LabSolution software was used to achieve Chromatogram. The mobile phase was made of 45 ml Acetonitrile and 55 ml water and an isocratic flow rate of 1 ml/min was used (26).
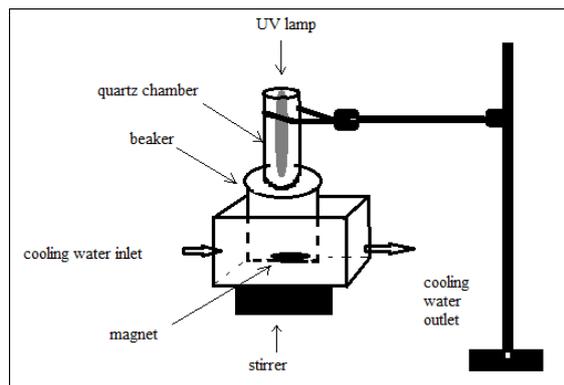

Figure 2. Photo-catalytic reactor scheme.

Cefixime stock solution (500mg/L) was prepared in deionized water and kept at 4°C, protected from light. Influence of each parameter was studied as a one at a time (A parameter was varied and the other parameters was kept constant). The Cefixime working solutions were prepared by diluting stock solution using deionized water for the different concentration of Cefixime (0.5-20 mg/L). Volume of the working solution was 50 mL. Then a certain dosage of TiO_2 (1-70 mg/L) was added to the prepared solution. Different pHs were adjusted by adding hydrochloric acid or sodium hydroxide and measured by the pH meter (Amtast AMT12, USA). Eventually the solution was transferred into the beaker and was magnetically stirred so as to ensure thorough mixing during the reaction. Cooling water was recirculated through the beaker to make a constant temperature (30±1°C). After that, TiO_2 was removed from the solution by a 0.45 μm membrane filter. Then the aqueous solution with the remaining Cefixime was quantified by HPLC analysis and the removal efficiency of Cefixime destroyed by the photo-catalytic process was calculated by the eqn. (2):

$$\%R = (C_0-C)/C_0 \quad (2)$$

Where, %R is percent removal, C_0 and C refer to Cefixime concentration at initial and after degradation process, respectively. A typical HPLC chromatogram of Cefixime is shown in Figure 3. All experiments were repeated in duplicate.
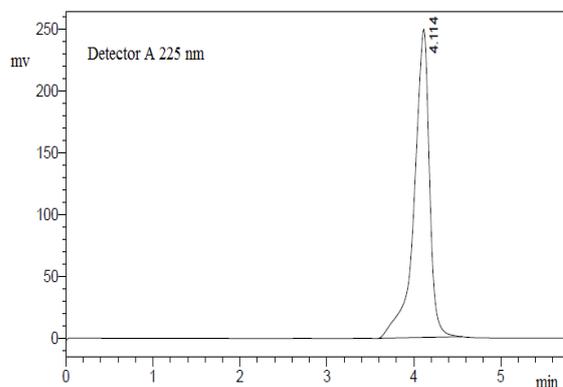

Figure 3. A typical HPLC chromatogram of Cefixime (Injection Volume=20 μl, wave length=225 nm, mobile phase= Acetonitrile: water with 45 to 55 ratio, C18 column (250 mm× 4.6 mm) with 5 μm particle size)

Results:

The effect of different parameters on photo-catalytic degradation of Cefixime is shown in Figures 4-7. The removal efficiency of Cefixime is a function of pH. The effects of initial pH levels ranging from 3 to 11 on fixed concentration of Cefixime (20 mg/L) and catalyst loading (30 mg/L) are presented in Figure 4.
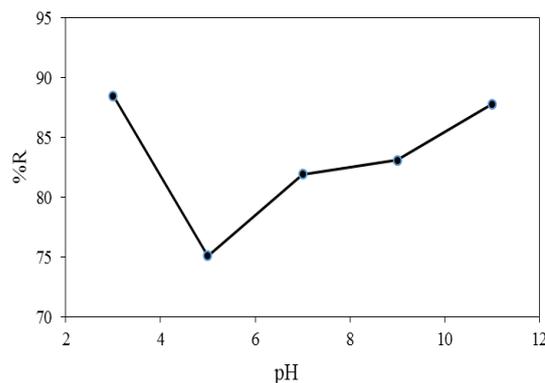

Figure 4. Effect of catalyst dosage on the photo-catalytic degradation of Cefixime (pH=3, Cefixime=20 mg/L, time= 20 min).
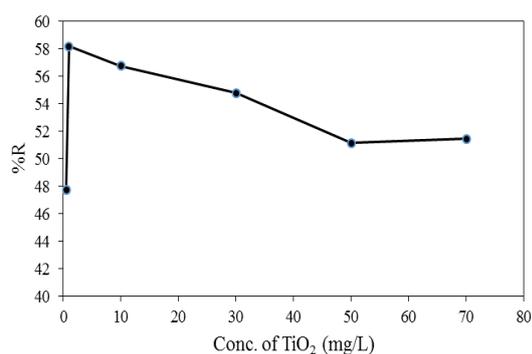
Figure 5. Effect of Cefixime concentration on the photo-degradation efficiency (TiO₂= 1 mg/L, pH=3 and irradiating time=20 min).

As can be seen, in pH=3 maximum degradation efficiency (88.5%) was occurred. When pH was increased to 5 a drop in efficiency removal was happened. When the pH increased from 7 to 11, the degradation rate raised up slightly.

The influence of catalyst dosage on the photo-degradation of Cefixime was investigated in the range of 0.5 to 70mg/L meanwhile the other reaction conditions were kept the same. As detailed in Figure 5, when 1mg/L TiO₂ was used the maximum degradation was achieved. By increasing the TiO₂ up to the 70mg/L, a little decrease was occurred.
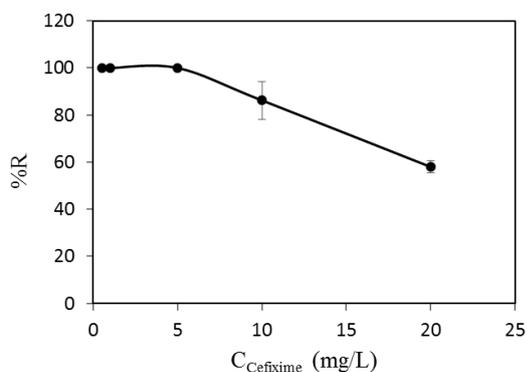

Figure 6. Effect of irradiation time on the photo-degradation efficiency (pH=3, TiO₂=30 mg/L, Cefixime=20 mg/L).

Base on Figure 6, Cefixime removal decreased from 100% to 58% by increasing the initial concentration from 5 to 20 mg/L.
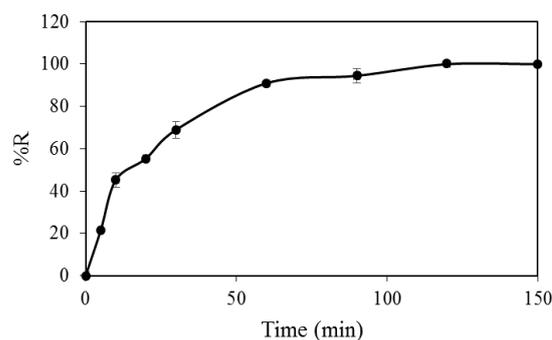

Figure 7. Effect of irradiation time on the photo-degradation efficiency (pH=3, TiO₂=30 mg/L, Cefixime = 20 mg/L).

In this study, times of 0-150 min was considered to evaluate the effete of time on the degradation procedure. According to the results in Figure 7, as time went on the removal rate was increased.

Conclusion:

Influence of pH

The pH has multiple roles on the efficiency of Cefixime photo-degradation process. pH effects can be evaluated by electrostatic interactions between TiO₂ charged particles and the contaminants. The pH of solution has a significant role in determining the degree of dissociation of pollutant and subsequently the amount of absorption in the ionized form. This point is related to pKa value of the pollutant which is considered 2.5 for Cefixime (27). Acid-alkaline properties of TiO₂ surface can have significant effects on its photo-catalytic function (28) as shown in eqn. 3 and 4:

$$TiOH + H^+ \leftrightarrow TiOH_2^+ \qquad (3)$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \qquad (4)$$
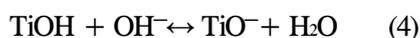
TiO₂ point of zero charge is around 6.5 (29). Therefore, TiO₂ has a positive charged surface in acidic conditions (pH<6.5) and has opposite charge in alkaline conditions (pH>6.5). As can be seen in Figure 4, maximum degradation efficiency was observed in pH=3 (88.5%). Because Cefixime is almost negatively charged at this pH while TiO₂ is positively charged. So antibiotic can be absorbed on the catalyst surface. Photo generated holes are considered as the main oxidation agent at low pHs

because of their high oxidation potential. As the eqns. 5-6 show, they can produce hydroxyl radicals from water molecules and destroy Cefixime by oxidation reactions (30,31):

$$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + HO^\bullet + H^- \quad (5)$$

Organic Pollutants + h_{VB}^+ → oxidation products   (6)
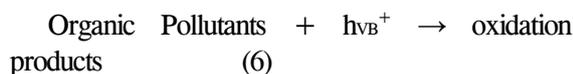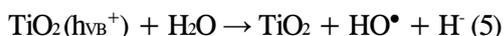
According to the eqns. 7-10, electrons formed in conduction band at low pH may also play an important role by converting oxygen into hydrogen peroxide or ruin Cefixime by reduction reactions (32):

$$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (7)$$
$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (8)$$
$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (9)$$
$$\text{Organic Pollutants} + e_{CB}^- \rightarrow \text{reduction products} \quad (10)$$
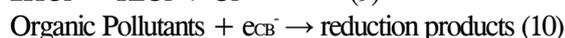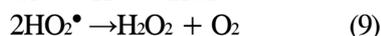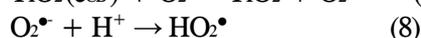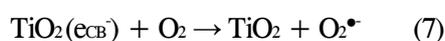
In alkaline solution the negatively charged surface of titanium dioxide prevents adsorption of hydroxide anions and anionic Cefixime on the surface of TiO_2 thus, the degradation efficiency reduces. Since the hydroxide anions are more available at very high pHs like as 11, hydroxyl radicals are generated easily (eqns. 11-12) (31):
$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (11)$$
Organic Pollutants + $OH^\bullet$ → degradation products   (12)
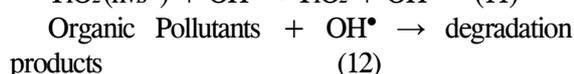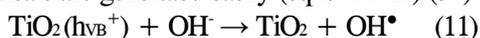
According to the above discussion, it is expected that in the range of pH values 3-11 the removal efficiency is less than pH $\leq$ 3 and pH $\geq$ 11.

Effect of TiO₂ dosage

Catalyst concentration depends on factors such as particle geometry, photochemical reactor operating conditions and specifications of the lamp such as the wavelength and intensity. It is necessary to optimize the amount of catalyst to prevent the use of excessive amounts and also ensure that all photons received by the catalyst surface (24,33).

The catalyst concentration of 1mg/L was used as optimum dose, because the higher dosages of the catalyst led to decrease the photo-degradation efficiency. Two reasons can be expressed for this fact: 1) with increasing concentrations of TiO₂,

aggregation may occur and the number of active sites reduce, 2) increasing the concentration of catalyst, increase the turbidity of the solution and prevents the penetration of UV rays. Therefore, the photo-catalytic degradation process is weakened (23,28,34).

Effect of Cefixime concentration

The results showed that increase in the Cefixime concentration lead to decrease in photo-degradation efficiency, which was like as majority of the previous studies report (35,36). It is assumed that for a solution with high concentration of pollutant, a fraction of light might be absorbed by the contaminant molecules instead of catalyst. As a result, •OH and $O_2^{\bullet-}$ generation reduces and lowers the efficiency of the photo-catalytic process. Moreover, the availability of the generated active species on the surface of catalysts is inadequate for increased contaminant concentrations. The formation of organic intermediates during photo-catalytic process may occupy the active sites on the surface of catalyst and results in a reduction in the photo-catalytic degradation of the pollutant (24,36,37).

Effect of Irradiation Time

Contact time is one of the factors that should be considered properly in photo-catalytic processes to ensure maximum efficiency. According to the results obtained in this study, over time, reaction efficiency is increased.

As Figure 7 shows, the trend of Cefixime degradation is faster at early 60 minutes and after that the removal efficiency becomes slower. Perhaps in the first times Cefixime is oxidized rapidly by the generated radicals. With the passage of time and creation of intermediates, the radicals are consumed (38).

Kinetic study

First-order kinetics equation can usually be used for different contaminants to measure the photo-catalytic reaction rate by considering the effect of intermediates and radiation (31):

$$Ln (C_0/C_t) = kt \quad (13)$$

Where C_0 and C represents the Cefixime concentration at initial and after specific time, respectively. A plot of ln (C_0/C) versus irradiation time gives a straight line whose slope is k. the regression analysis gave a correlation coefficient (R^2) of 0.9756 for UV/TiO₂, which display the good validity of the supposed first order kinetics (39).

Comparison with other works

In order to assess the degradation of Cefixime, different conditions by UV/TiO₂, UV, TiO₂ suspension alone under darkness and under sun light were studied and the results and kinetic data were shown in Figures 8-9 and Table 1.
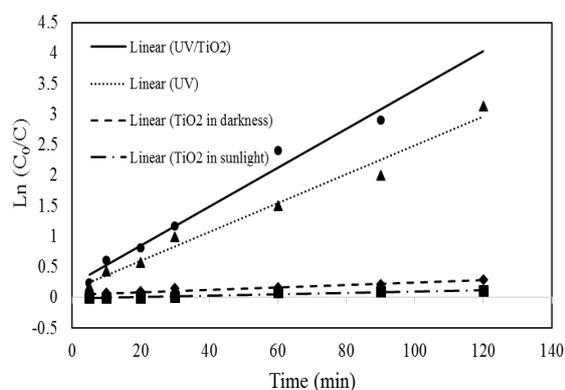

Figure 8. First-order kinetic model for the photo-catalytic degradation of Cefixime (TiO₂= 1 mg/L, pH=3, Cefixime=20 mg/L).
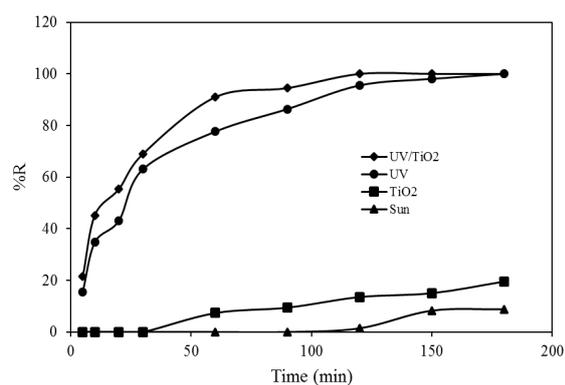

Figure 9. Degradation of Cefixime by UV/ TiO₂, UV, TiO₂ under darkness and TiO₂ under sun (TiO₂=1 mg/L, pH=3, Cefixime=20 mg/L).

Table 1. Pseudo-first order kinetic parameters for degradation of Cefixime (catalyst dose=1mg/L, Cefixime concentration =20 mg/L and pH=3).

Method	R2	1/kobs (min)	Kobs (1/min)
UV/TiO₂	0.975	31.35	0.0319
UV	0.985	39.84	0.0251
TiO₂	0.971	714.28	0.0014
Sun light/TiO₂	0.784	1666.67	0.0006

All experiments followed pseudo-first-order rate law. Rate constants (k_{obs}) was calculated for each of them and the trend of UV/TiO₂ > UV > TiO₂ under darkness > TiO₂ under sun light was presented. According to above literature and Cefixime degradation results obtained in present study, it might be said that this drug can be efficiently degraded by photocatalysis. Also, Table 2 shows report's findings about the UV/catalyst process to remove antibiotics. As can be seen in this Table, a good degradation efficiency at reasonable time was achieved.

In this paper photo-catalytic degradation of Cefixime antibiotic by TiO₂ was studied. Parameters that have significant roles in antibiotic degradation process such as dosage of catalyst, pH, concentration of Cefixime and time, were evaluated and optimized. Complete degradation was achieved when 50 ml aqueous solution containing 20mg/L Cefixime and 1 mg/L TiO₂ at pH=3 irradiated in 90 min. In order to comparison and evaluate the degradation process, the experiment was repeated for UV, TiO₂ under darkness and TiO₂ under sun light. The pseudo-first-order rate constants (k_{obs}) corresponded to trend of UV/TiO₂ > UV > TiO₂ > sun light.

The results showed that UV/TiO₂ system has most success to reduce Cefixime from aqueous solution so that after 60 and 90 min the degradation efficiency was 90.98%, 94.51%, respectively. However, the amount of catalyst dose in this study was as low as 1mg/L. The degradation efficiency by TiO₂ in darkness and sun light weren't significant after 210 min and was obtained 24.95% and 10.25% respectively. The results indicate that TiO₂ photo-catalysis is a rapid and efficient technique for removal of Cefixime and could be a promise technique for removal of pollutant from wastewaters.

Table 2. Summary of studies on the antibiotic degradation processes by UV/catalyst

Antibiotic	Conc.	Operating conditions	Analytical methods	Results and comments	Ref.
Cefixime	5 μg/L	pH=5, 0.25 g/L of photocatalyst dosage, 300 min, $NiO_{13.3\%}$- NCP photocatalysis	UV-Vis.	-more than 80% degradation of Cefixime solution in 300 min using 0.25 g/L	(37)
Cefixime	10.11 mg/L	0.41 g/L of ZnO/α-Fe_2O_3 catalyst, 127 min, 8 W/m²	UV-Vis.	-about 99.1% of the drug was degraded	(40)
Amoxicilin	104 mg/L	UV light (6 W) at 365 nm	HPLC-DAD,	-No significant degradation occurred by 300 min of UV irradiation.	
Ampicilin	105 mg/L	0.5-2.0 g/L TiO_2	COD,	-At pH=5 and 1.0 g/L TiO2, 50% degradation was achieved for all compounds (81% DOC removal),	(41)
Cloxacilin	103 mg/L	pH=3-11	BOD5, TOC, DOC		
Lincomycin	10-50 mg/L	MP UV (125 W) pH=6.0 TiO_2 1 g/L 100%anatase	HPLC-UV, TOC, Absorbance 200-500 nm	-After 5 h, 20% of lincomycin was photolytic degraded. In the presence of TiO2 more than 98% of drug was oxidized within about 2 h.	(42)
Metronidazole	40 mg/L 80 mg/L 120 mg/L	Medium pressure UV lamp (125 W) 0.5-3 g/L P-25 TiO_2 pH=3,7,11	HPLC, Electrical energy Pre order (E_EO)	-99.48% of Metronidazole was removed after 120 min at neutral pH and 0.5 g/L catalyst	(38)
Tetracycline	27 mg/L	MP UV (125 W) pH=5.0 TiO_2 1 g/L 100%anatase	HPLC-UV, TOC,	-After 90 min, 91.4% of Tetracycline degraded.	(43)
Cefixime	5 mg/L	60 min, 1 mg/L of catalyst	HPLC-UV	-more than 90% of the drug was degraded	This work

Ethical issues:

There were no ethical issues for this article.

Competing interests:

We affirm that this article is the original work of the authors and have no conflict of interest to declare.

Acknowledgments:

References:

1. Dimitrakopoulou D, Rethemiotaki I, Frontistis Z, Xekoukoulotakis NP, Venieri D, Mantzavinos D. Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO2 photocatalysis. Journal of environmental management. 2012;98:168-174.

2. Homem V, Santos L. Degradation and removal methods of antibiotics from aqueous matrices–a review. Journal of Environmental Management. 2011;92(10):2304-2347.

3. Pulicharla R, Brar S, Drogui P, Verma M, Surampalli R. Removal Processes of Antibiotics in Waters and Wastewaters: Crucial Link to Physical-Chemical Properties and Degradation. Journal of Hazardous, Toxic, and Radioactive Waste. 2015;19(4):04015008.

4. Fouda A, Abdallah A, Yousef M. Corrosion Inhibition and Adsorption Properties of Cefixime on Carbon Steel in Acidic Medium. Chemical Science Review and Letters. 2014; 3(11S):130-143.

5. Tank M, Thumar K, Tanna R. Method development and validation for simultaneous estimation of cefixime trihydrate and dicloxacillin sodium in combined dosage form by high performance thin layer chromatography. Inventi. 2012;2012(3):183-186.

6. Deekonda P, Reddy MS. Method development and validation for the quantitative estimation of cefixime and ofloxacin in Pharmaceutical preparation by RP-HPLC. Der Pharma Chemica. 2014;6(2):31-37.

7. Radjenović J, Petrović M, Ventura F, Barceló D. Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. Water Research. 2008;42(14):3601-3610.

8. Prasertkulsak S, Chiemchaisri C, Chiemchaisri W, Itonaga T, Yamamoto K. Removals of pharmaceutical compounds from hospital wastewater in membrane bioreactor operated under short hydraulic retention time. Chemosphere. 2016;150:624-631.

9. Adams C, Wang Y, Loftin K, Meyer M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. Journal of Environmental Engineering. 2002;128(3):253-260.

10. Buchicchio A, Bianco G, Sofo A, Masi S, Caniani D. Biodegradation of carbamazepine and clarithromycin by Trichoderma harzianum and Pleurotus ostreatus investigated by liquid chromatography–high-resolution tandem mass spectrometry (FTICR MS-IRMPD). Science of the Total Environment. 2016;557-558:733-739.

11. Martínez-Alcalá I, Guillén-Navarro JM, Fernández-López C. Pharmaceutical biological degradation, sorption and mass balance determination in a conventional activated-sludge wastewater treatment plant from Murcia, Spain. Chemical Engineering Journal. 2017;316:332-340.

12. Onesios KM, Jim TY, Bouwer EJ. Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review. Biodegradation. 2009;20(4):441-466.

13. Prado N, Ochoa J, Amrane A. Biodegradation and biosorption of tetracycline and tylosin antibiotics in activated sludge system. Process Biochemistry. 2009; 44(11):1302-6.

14. Guinea E, Brillas E, Centellas F, Cañizares P, Rodrigo MA, Sáez C. Oxidation of enrofloxacin with conductive-diamond electrochemical oxidation, ozonation and Fenton oxidation. A comparison. Water Research. 2009;43(8):2131-2138.

15. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environment International. 2009;35(2):402-417.

16. Yu F, Ma J, Bi D. Enhanced adsorptive removal of selected pharmaceutical antibiotics from aqueous solution by activated graphene. Environmental Science and Pollution Research. 2015;22(6):4715-4724.

17. Yu F, Ma J, Han S. Adsorption of tetracycline from aqueous solutions onto multi-walled carbon nanotubes with different oxygen contents. Scientific Reports. 2014;4:5326.

18. Chen W-R, Huang C-H. Adsorption and transformation of tetracycline antibiotics with aluminum oxide. Chemosphere. 2010; 79(8):779-785.

19. Zhuang Y, Yu F, Ma J. Enhanced Adsorption and Removal of Ciprofloxacin on Regenerable Long TiO_2 Nanotube/Graphene Oxide Hydrogel Adsorbents. Journal of Nanomaterials. 2015;2015:1-8.

20. Shirzadi A, Nezamzadeh-Ejhieh A. Enhanced photocatalytic activity of supported CuO–ZnO semiconductors towards the photodegradation of mefenamic acid aqueous solution as a semi real sample. Journal of Molecular Catalysis A: Chemical. 2016;411:222-229.

21. Bansal P, Verma A, Aggarwal K, Singh A, Gupta S. Investigations on the degradation of an antibiotic Cephalexin using suspended and supported TiO_2: Mineralization and durability studies. The Canadian Journal of Chemical Engineering. 2016;94(7):1269-1276.

22. Autin O, Hart J, Jarvis P, MacAdam J, Parsons SA, Jefferson B. Comparison of UV/H_2O_2 and UV/TiO_2 for the degradation of metaldehyde: kinetics and the impact of background organics. Water Research. 2012; 46(17):5655-5662.

23. Chen D, Ray AK. Photodegradation kinetics of 4-nitrophenol in TiO_2 suspension. Water Research. 1998;32(11):3223-3234.

24. Konstantinou IK, Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review. Applied Catalysis B: Environmental. 2004;49(1):1-14.

25. Yan Y, Liao Q-N, Ji F, Wang W, Yuan S, Hu Z-H. Decomposition of 3, 5-dinitrobenzamide in aqueous solution during UV/H_2O_2 and UV/TiO_2 oxidation processes. Environmental Science and Pollution Research. 2017;24(6):5360-5369.

26. Trivedi KJ, Chokshi PV, Patel NS. Development and validation of rp-hplc method for analysis of cefixime trihydrate and sulbactam sodium in their combination tablet dosage form. Int J Chem Tech Res. 2012; 4(4):1628-1632.

27. Srinivas D, Suman M, Preethi N, Sivaneswari S, Mounika B, Naveen B, et al. Formulation and In-vitro characterization of Floating Micro-carriers of Cefixime. Int Journal of Advances in Pharmacy, Biology and Chemistry. 2014;3(3).

28. Peres M, Maniero M, Guimarães J. Photocatalytic degradation of ofloxacin and evaluation of the residual antimicrobial activity. Photochemical & Photobiological Sciences. 2015;14(3):556-562.

29. Friedmann D, Mendive C, Bahnemann D. TiO_2 for water treatment: parameters affecting the kinetics and mechanisms of photocatalysis. Applied Catalysis B: Environmental. 2010; 99(3):398-406.

30. Andreozzi R, Caprio V, Insola A, Marotta R. Advanced oxidation processes (AOP) for water purification and recovery. Catalysis Today. 1999;53(1):51-59.

31. Bayarri B, Gimenez J, Curco D, Esplugas S. Photocatalytic degradation of 2, 4-dichlorophenol by TiO_2/UV: kinetics, actinometries and models. Catalysis Today. 2005;101(3):227-236.

32. Ismail L, Rifai A, Ferronato C, Fine L, Jaber F, Chovelon J-M. Towards a better understanding of the reactive species involved in the photocatalytic degradation of sulfaclozine. Applied Catalysis B: Environmental. 2016;185:88-99.

33. Herrmann J-M. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catalysis Today. 1999;53(1):115-129.

34. Gurkan YY, Turkten N, Hatipoglu A, Cinar Z. Photocatalytic degradation of cefazolin over N-doped TiO_2 under UV and sunlight irradiation: prediction of the reaction paths via conceptual DFT. Chemical Engineering Journal. 2012;184:113-124.

35. Zhang X, Wu F, Wu X, Chen P, Deng N. Photodegradation of acetaminophen in TiO_2 suspended solution. Journal of Hazardous Materials. 2008;157(2):300-307.

36. Shokri M, Isapour G, Shamsvand S, Kavousi B. Photocatalytic Degradation of Ceftriaxone in Aqueous Solutions by Immobilized TiO_2 and ZnO Nanoparticles: Investigating Operational Parameters. 2016;7(8):2843-2851.

37. Pourtaheri A, Nezamzadeh-Ejhieh A. Photocatalytic properties of incorporated NiO onto clinoptilolite nano-particles in the photodegradation process of aqueous solution of cefixime pharmaceutical capsule. Chemical Engineering Research and Design. 2015; 104:835-843.

38. Farzadkia M, Rahmani K, Gholami M, Esrafili A, Rahmani A, Rahmani H. Investigation of photocatalytic degradation of clindamycin antibiotic by using nano-ZnO catalysts. Korean Journal of Chemical Engineering. 2014;31(11):2014-2019.

39. Vasconcelos TG, Henriques DM, König A, Martins AF, Kümmerer K. Photo-degradation of the antimicrobial ciprofloxacin at high pH: identification and biodegradability assessment of the primary by-products. Chemosphere. 2009;76(4):487-493.

40. Shooshtari NM, Ghazi MM. An investigation of the photocatalytic activity of nano α-Fe_2O_3/ZnO on the photodegradation of cefixime trihydrate. Chemical Engineering Journal. 2017;315:527-536.

41. Elmolla ES, Chaudhuri M. Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO_2 and UV/H_2O_2/TiO_2 photocatalysis. Desalination. 2010;252(1):46-52.

42. Addamo M, Augugliaro V, Di Paola A, Garcia-Lopez E, Loddo V, Marci G, et al. Removal of drugs in aqueous systems by photoassisted degradation. Journal of Applied Electrochemistry. 2005;35(7-8):765-774.

43. Safari G, Hoseini M, Kamali H, Moradirad R, Mahvi A. Photocatalytic Degradation of Tetracycline Antibiotic from Aqueous Solutions Using UV/TiO_2 and UV/H_2O_2/TiO_2. Journal of Health. 2014;5(3):203-2013.