Boffin Access

Open Access Journal | Volume: 1.4

Journal of Water Technology and Treatment Methods

ISSN 2517-7427

A Comparative Heterogeneous Photocatalytic Removal Study on Amoxicillin and Clarithyromicin Antibiotics in Aqueous Solutions

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Abstract

Since most of antibiotics have been demonstrated to be low degradable in biological treatment systems, advanced oxidation processes have gained an essential attraction to oxidize them through OH radicals formation. This study attempts to optimize the removal of 10 mg/L of two antibiotics, namely amoxicillin and clarithromycin heterogenous photocatalytic oxidation process at varying catalyst doses and pH conditions. The process efficiency was evaluated in terms of degradation (UV absorbance) and mineralization (Total organic carbon, TOC) efficiencies. A different rate of mineralization and degradation was observed for each antibiotic. pH and TiO_2/antibiotic ratio were observed to be important factors for process optimization.

Keywords

Antibiotics, Amoxicillin, Clarithromycin, Degradation, Mineralization, Photocatalysis, TiO_2

Introduction

Antibiotics are highly consumed for human and veterinary treatment and a portion (1-10%) is remained unchanged to reach urban wastewater treatment plants (UWWTP). However they are not biodegraded effectively in UWWTPs and reach surface waters in the effluents, thus they can pose severe risk to the aquatic environment [1,2]. Antibiotics have also potential to promote development of antibiotics resistant (AR) bacteria and AR genes causing non-easily mediated diseases [3,4]. Thus, removal of antibiotics in the UWWTP effluents urged to improve treatment technologies such as advanced oxidation processes (AOPs) [5-7]. Photocatalysis (PC), being more tolerant to variations at pH conditions has been demonstrated to degrade effectively most of the antibiotics while most of the physicochemical processes require a specific pH range [8-14].

In this study, comparative heterogenous photocatalytic removal of two antibiotics (10 mg/L) were tested in a lab-scale reactor in a light flux adjustable illumination media by varying dose of TiO_2 and pH as pH dependent charge interactions are assumed to be a determining factor on photocatalytic efficiency. PC process efficiency was evaluated in terms of degradation (UV absorbance) and mineralization (TOC) in parallel toecotoxicityto Daphnia magna(immobility percentages for 24-48 hours) to monitor if any adverse effect could occur by transformation by products during irradiation.

Materials and Methods

Chemicals and solutions

Amoxicillin (AMX) and Clarithromycin (CLRT) were provided from a pharmaceutical company at ingredients purity and used as obtained. Chemical structure and UV spectra of antibiotics are shown in Figure 1. Titanium dioxide (TiO_2) (CAS# 546-68-9)*was purchased by Sigma-Aldrich* with a specificsurface area varying between 35 and 65 m^2/g (BET) and a mean particle size of 21 nm.

Nuve ND12 distilled water system was used for the preparation ofstock antibiotic solution. A 10 mg/L solution of each antibiotic was prepared daily from the stock solution (50 mg/). Initial antibiotic concentration was set to 10 mg/L to enable:

i. Assessment of PC process efficiency within a measurable time scale at the experimental conditions concerned,
ii. The accurate determination of organic carbon and UV and
iii. Enrich existing literature that take into account (or not) the eco-toxicity aspects for the heterogenous PC removal of pharmaceuticals with in analogous conditions be it initial antibiotic and photocatalyst concentration [6-8].

Experimental

TiO_2 nanoparticles were subjected to adsorption experiments under dark conditions with (5 min) and without prior ultrasound irradiation (40000 Hz). A 300 mL rectangular

Article Information

DOI:	10.31021/jwt.20181116
Article Type:	Research Article
Journal Type:	Open Access
Volume:	1 **Issue:** 4
Manuscript ID:	JWT-1-116
Publisher:	Boffin Access Limited
Received Date:	May 03, 2018
Accepted Date:	June 08, 2018
Published Date:	June 15, 2018

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Citation: Özkal CB, Meriç S. A Comparative Heterogeneous Photocatalytic Removal Study on Amoxicillin and Clarithyromicin Antibiotics in Aqueous Solutions. J Water Technol Treat Methods. 2018 Jun;1(4):116

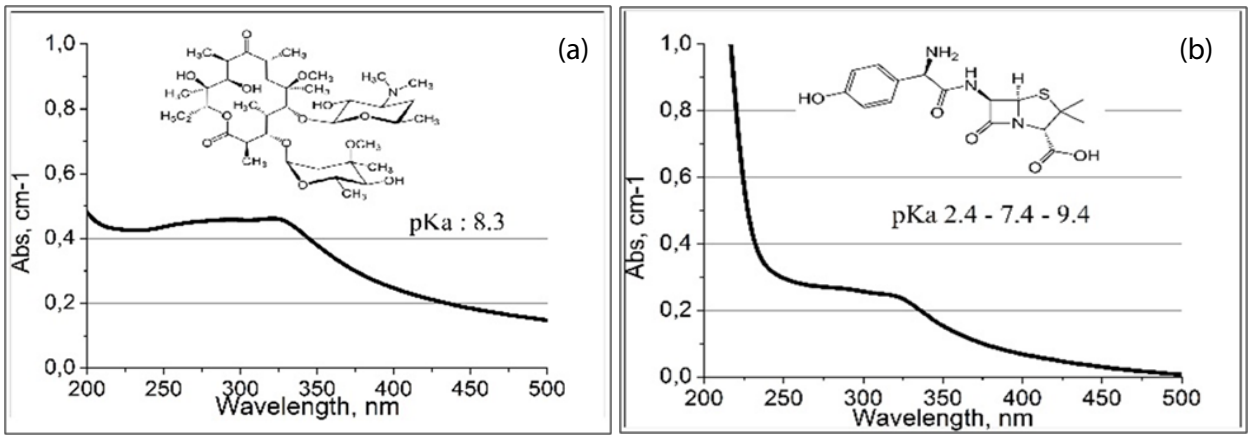

Figure 1 : Chemical structure, pKa values and UV Spectrum of a)CLRT, and b) AMX antibiotics.

Pyrex reactor was filled with 10 mg/L antibiotic solutions and magnetically stirred during the treatment. TiO_2 was added into solutions just after pH adjustments and reaction vessel was placed in the photoreactor. UV-A lamps were kept turned-off for 15 minutes before each experiments to ensure their smoot funtion. All PC experiments were performed under an incident photon flux of 36,6 w/m^2 measured by Universal photometer. The schematic representation of the reactor configuration is described elsewhere [11]. Three doses of TiO_2, (0.5-1-2 g/L) and four pH values were investigated considering pKa values of the studied antibiotics and zero point charge of TiO_2 (6.2), in order to provide comparable conditions with the litearature [9-11]. pH was measured at the end of each treatment cycle,.. Photocatalytic experiments were carried out by time intervals and the treated solutions were filtered through cut-of filters (Cellulaseacetate-Millex MF Millipore) to remove remainig TiO_2 particles before being used or stored for further analysis.

Daphnia magna

Acute toxicity of aqueous raw and treated samples of antibiotics was assessed on new born (<24 h) freshwater crustacean, Daphnia magna according to ISO6341 method [15]. Experiments were performed as four replicates and 5 daphnids were tested in each replicate for 24 and 48 hours of exposure times. Immobilization percentage determined by dividing total immobilized organisms to total number of tested organisms in four replicate.

Analysis

TOC was monitored to optimize mineralization using TC-TOC-TN analyzer equipped with an ASI-V autosampler (Shimadzu, TOC-L CPN) while absorbance was scanned using UV-vis spectrophotometer (Shimadzu UV Lamda 1800). pH (MRC Multiparameter) was also monitored in parallel with a multiparameter pH meter both in raw and treated solutions.

Results and discussion

Dark adsorption

The effect of pH on adsorption mechanism between photocatalyst and antibiotic is evaluated with experiments carried out at dark conditions and it was found negligible and the time required for the system to reach equilibrium found to be 30 min in accordance with the literature findings. Pre-ultra-sonication of nanoparticles that is known to promote nanoparticles to get smaller size and form, did not improve adsorption (data not shown) under studied conditions in accordance with the literature [16].

Photolysis

Photolysis was unable to considerably attack the molecules of AMX thus it did not mineralize them in the given period of irradiation time (120 min). This can be explained by the fact that the absorption of UV radiation from the range of UV radiation that enters the reactor, by the AMX molecule is negligible. Xu et al. [17] reported that direct photolysis in a solar simulator accounted for 6–21 % of AMX loss in simulated natural waters for significantly higher exposure times (40 h) that is far higher than irration time of this study.

Photocatalytic degradation

The UV_{254} parameter is taken as an indicator of ongoing parent compound degradation. However, the formation of organic intermediates detectable at the same wavelength of the characteristic absorbance peaks of the antibiotics studied may interfere with the target antibiotics absorbance measurement. For instance, UV absorbance between 230-275 nmwavelengths are indicative of by-products [10], formation as reported elsewhere.As can be seen in Figures 2 and 3 (a-b), UV absorbance peaks disappeared after a certain period of oxidation, based on increasing photocatalyst concentration. The effect of hydrolysis is reported to be neglected between pH 5-8 conditions for AMX which is in its most stable form at the conditions of concern [18]. For all antibiotics at pH 11, the variation in UV254 may be attributed to the high alkalinity of the solution resulting with antibiotics hydrolysis. Strong basic environment causes a large production of OH- ions which, together with the action of the photocatalytic TiO2 (hydroxyl radical, hole and superoxide ion) surface mechanism, splits the process into two distinct phases: production of by-products (within the first 30-60 minutes) and subsequent mineralization (as indicator of mineralization). However, it has been reported in the literature that such behaviour is not very functional and no significant degradation was expected due UV irradiation [19] (Figures 2 and 3).

The effect of pH on photocatalytic degradation/mineralization of antibiotics is better to be evaluated in a way that consider properties of antibiotics and photocatalyst of concern at different initial pH conditions as different pKa values of antibiotics are reported to be responsible for creating varying levels of surface interaction with the TiO_2 nanoparticles in the solution [20]while surface charge status for the antibiotics and TiO_2 by order at their optimum conditions can be described as; (+/+), (-/-) and (-/-) respectively.Several authors have already reported the influence of pH on TiO_2-mediated photocatalytic degradation of AMX and found minimal influence in the near-neutral pH range.In this study, four pH values were investigated considering the surface charge change of TiO_2 that could affect the adsorption capacity thus the photocatalytic removal of CLRT and AMX antibiotics.

For dilute aqueous solutions, as is the case of pharmaceuticals which are detected at very low concentrations in waters, a pseudo-first-order (PFO) kinetic equation has been applied (equation 1).

$$-\frac{dC}{dt} = kC \qquad (1)$$

On the other hand, taking into account that the analysis of kinetics of liquid phase photocatalyzed reactions has been recently a point of

discussion [21] a second-order (SO) kinetic reaction was also made [equations 2-3]:

$$r = kC^2 \quad (2)$$

$$\frac{1}{C} = kt + \frac{1}{C_0} \quad (3)$$

As seen in Table 1, reaction kinetics of CLRT at pH 8 and 11 conditions and on the basis of UV_{254} nm absorbance are analogous by means of both reaction rates (PFO and SO) and highest R^2 values were observed. However, PFO-SO models fitted the data of AMX at high pH values at high regression rates, specifically at pH 11. When TiO_2 dose increased SO model better fitted during oxidation of both CLRT and AMX than PFO model (Table 2). There was no notable fit of models to the TOC removal of AMX while increasing TiO_2 dose that evidenced a strong interference of by-products formed during oxidation of the antibiotics near UV_{254} band although Pereira et al. claimed that solar photocatalytic removal AMX obeyed PFO model in their study (Table 2).

TOC removal with residual toxicity were taken as indicator parameters to define optimum treatment conditions for the antibiotics studied. The final optimized process efficiencies differed between antibiotics (Figures 4 and 5). This is attributed to the interaction of oxidation intermediates and parent compounds with photo-catalyst at the given pH conditions. It should be noted that a simultaneous degradation of intermediates (for which type and quantity are to be antibiotic-specific and process duration dependent), in parallel

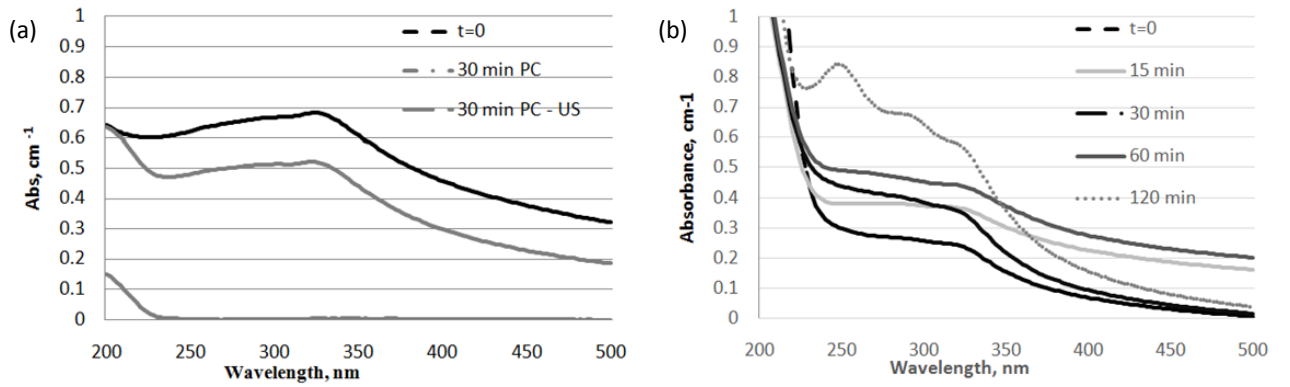

Figure 2: UV Absorbance spectra of photocatalltic treated CLRT (10 mg L^{-1}) at pH:5, UV-A energy of 36.6 w/m^2 and initial TiO_2 concentrations of a) 0.5g/L^{-1} b) 2g/L^{-1}.

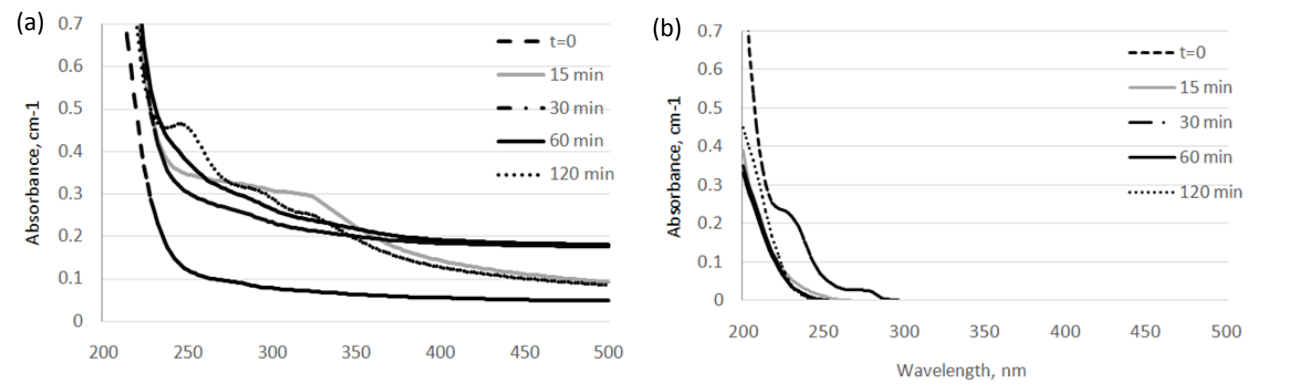

Figure 3: UV Absorbance spectra of photocatalytic treated AMX (10 mg/L) at pH:8, UV-A energy of 36.6 w/m^2 and initial TiO_2 concentrations of a) 0.5 g/L and b) 2 g/L.

		PFO			SO	
Antibiotic	**pH**	**k**	**$t_{1/2\ (min)}$**	**R^2**	**k**	**R^2**
CLRT	3	-0.0009	770	0.78	0.0009	0.79
	5	-0.0023	302	0.35	0.0029	0.36
	8	-0.0026	267	0.36	0.0034	0.38
	11	-0.0041	169	0.86	0.0057	0.91
AMX	3	-0.0021	330	0.30	0.0032	0.62
	5	-0.0007	990	0.18	0.0007	0.18
	8	-0.0057	122	0.35	0.0034	0.33
	11	-0.0049	142	0.69	0.0033	0.59

Table 1: Pseudo first order (PFO) and Second order (SO) kinetics of photocatalytic antibiotics degradation based on UV_{254} variation at varying pH values, initial antibiotic concentration: 10 mg/L, 0.5 g/L TiO_2 dose and UV-A energy: 36.6 w/m^2

Antibiotic	TiO_2 dose g/L	PFO			SO	
		k	$t_{1/2\ (min)}$	R^2	k	R^2
CLRT, pH=5	0.5	-0.0023	302	0.35	0.0029	0.36
	1	-0.0005	1386	0.15	-0.0005	0.15
	2	-0.0079	88	0.98	0.013	0.98
AMX, pH=8	0.5	-0.0057	122	0.35	0.0034	0.33
	1	-0.0013	533	0.69	0.0013	0.64
	2	-0.0060	116	0.95	0.0083	0.96

Table 2: Pseudo first order (PFO) and Second order (SO) kinetics of photocatalytic antibiotics degradation based on UV_{254} variation at varying TiO_2 doses, [C]antibiotic: 10 mg/L, UV-A energy: 36.6 w/m²

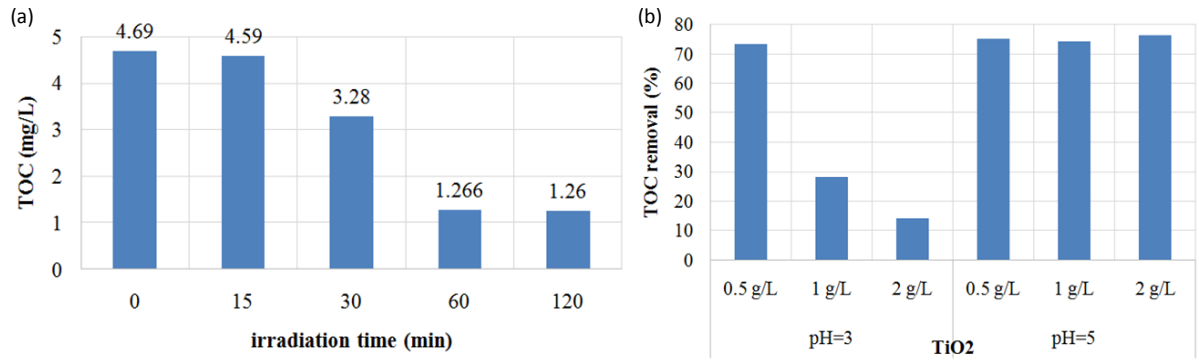

Figure 4: (a) TOC removal efficiencies of CLRT at 36.6 w/m² UV-A energy level and varying TiO_2 doses after 120 min irradiation, (b) at 0.5 g/l TiO_2 loading and initial pH=5 versus time

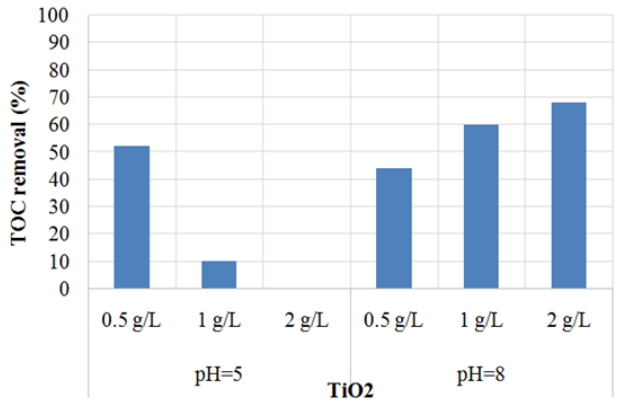

Figure 5: TOC removal efficiencies of AMX at 36,6 w/m² UV-A energy level and varying TiO_2 doses and pH values after 120 min oxidation time.

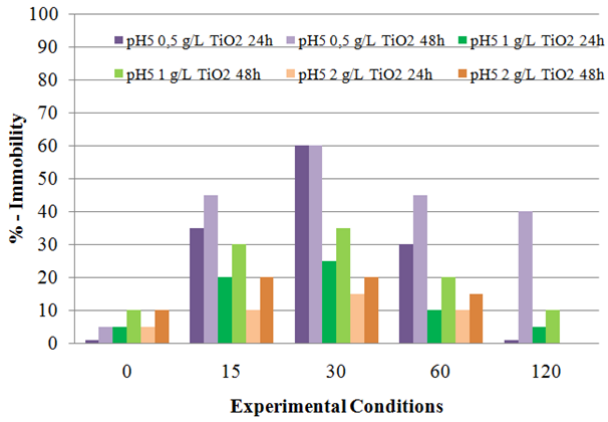

Figure 6: Toxicity evolution in photocatalytic treated CLRT samples at pH=5, 36,6 w/m² UV-A energy level and varying TiO_2 doses (0.5, 1 and 2 g/L).

to target antibiotic might have occurred and necessitate concurrent analysis of degradation pathway for the antibiotics of concern.

Degradation of antibiotics parent compound is continuous along the process duration (120 min) with the rate order exhibit decreasing behaviour that may potentially be arising from occupied surface sites of nanoparticles TiO_2 by degradation by-products formed during oxidation.Intermediates formed during first 15 min oxidation may have potentially increased toxicity to 100%. Considering CLRT, increased initial TiO_2 concentration did not lead to any advances in the TOC removal rates (Figure 4), but improved the toxicity removal (from 40% to 0% after 120 min of process time) (Figure 6). This indicates a 0.5 g/L photocatalyst concentration to be adequate for efficient degradation of the parent compound but not effectual for simultaneous degradation of the degradation by-products formed.

Photocatalytic degradation for both AMX and its by-products followed a more simultaneous trend in both TiO_2 concentrations (Figure 5), as it is seen from the advances in TOC removal rates not being correlated with increasing TiO_2 concentration conditions but could be due to the energy level as reported by that solar photolysis and photocatalysis werecompared in a compound parabolic collectors pilot scale photoreactor. They reported that a 3.1 kJUV/L energy was sufficient to fully degrade 20 mg/L AMX and remove 61 % of initial DOC content in the presence of 0.5 g/L TiO_2 photocatalyst and sunlight at pH 7.5. A large percentage of the remaining DOC was in the form of low molecular weight carboxylic acids.

All together, optimum pH was defined to be 5 for CLRT and 8 for AMX antibiotics by means of TOC removal (Figures 4 and 5) and toxicity reduction potentials (Figures 6 and 7) in this study.

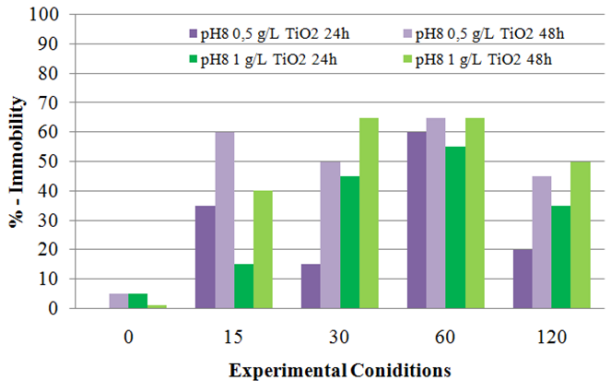

Figure 7: Toxicity evolution in photocatalytic treated AMX samples at pH=8, 36,6 w/m² UV-A energy level and two TiO_2 doses (0.5, 1 and 2 g/L).

Conclusions

In this study photocatalysis process was optimized for the removal of two antibiotics using the same treatment conditions. The outlines of this study are the following:

- Varying TiO_2 dose/antibiotic concentration ratio enhanced photocatalysis efficiency for the investigated antibiotics.
- Optimum pH was defined to be 8 for AMX and 5 for CLRT at 0.5 g/L TiO_2 dose.
- Degradation of antibiotics was confirmed by ecotoxicity results at optimum process conditions.
- Ecotoxicity test results evidenced to monitor ecotoxicty is essential for deciding optimum process conditions to secure environmentally safe process effluent.

Acknowledgements

This study was funded by NKUBAP. 00.17.AR.13.13. project. We would like to thank undergraduate students Ünal Elbasan and Eda Büyükkayalı for their technical assistance in the laboratory study.

References

1. Baumann M, Weiss K, Maletzki D, Schüssler W, Schudoma D, et al. Aquatic toxicity of the macrolide antibiotic clarithromycin and its metabolites, Chemosphere. 2015 Feb;120:192-198.
2. Singh V, Pandey B, Suthar S. Phytotoxicity of amoxicillin to the duckweed Spirodela polyrhiza: Growth, oxidative stress, biochemical traits and antibiotic degradation, Chemosphere. 2018 Jun; 201: 492-502.
3. Michael I, Rizzo L, McArdell CS, Manaia CM, Merlin C, et al. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review, Water Res. 2013 Mar;47:957-995.
4. Sharma VK, Johnson N, Cizmas L, McDonald TJ, Kim H. A review of the influence of treatment strategies on antibiotic resistant bacteria and antibiotic resistance genes, Chemosphere. 2016 May;150:702-714.
5. Homem V, Santos L. Degradation and removal methods of antibiotics from aqueous matrices – A review, J. Environ. Manage. 2011 Oct; 92: 2304-2347.
6. Karaolia P, Michael I, García-Fernández I, Agüera A, Malato S, et al. Reduction of clarithromycin and sulfamethoxazole-resistant Enterococcus by pilot-scale solar-driven Fenton oxidation, Sci. Total Environ. 2014 Jan;468:19-27.
7. Lofrano G, Libralato G, Casaburi A, Siciliano A, Iannece P, et al. Municipal wastewater spiramycin removal by conventional treatments and heterogeneous photocatalysis, Sci. Total Environ. 2018 May;624:461-469.
8. Rizzo L, Meric S, Kassinos D, Guida M, Russo F, Belgiorno F. Degradation of diclofenac by TiO2 photocatalysis: UV absorbance kinetics and process evaluation through a set of toxicity bioassays, Water Res. 2009 Mar;43:979-988.
9. Elmolla ES, Chaudhuri M. Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO2 and UV/H2O2/TiO_2 photocatalysis, Desalination. 2010 Mar;252:46-52.
10. Dimitrakopoulou D, Rethemiotaki I, Frontistis Z, Xekoukoulotakis NP, Venieri D, Mantzavinos D. Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO_2 photocatalysis, J. Environ. Manage. 2012 May;98:168-174.
11. Ozkal CB, Koruyucu A, Meric S. Heterogeneous photocatalytic degradation, mineralization and detoxification of ampicillin under varying pH and incident photon flux conditions, Desalin. Water Treat. 2016 Aug; 3994: 1-7.
12. Serna-Galvis EA, Silva-Agredo J, Giraldo AL, Flórez OA, Torres-Palma RA. Comparison of route, mechanism and extent of treatment for the degradation of a β-lactam antibiotic by TiO_2 photocatalysis, sonochemistry, electrochemistry and the photo-Fenton system, Chem. Eng. J. 2016 Jan; 284: 953-962.
13. Borges VJP, Boaventura RAR. 5 Assessment of Solar Driven TiO_2-Assisted Photocatalysis Efficiency on Amoxicillin Degradation, Sol. Photocatalytic Degrad. Antibiot. Chem. Ecotoxicological Biodegrad. Assess. 2014 Jan;5: 93-108.
14. Kanakaraju D, Kockler J, Motti CA, Glass BD, Oelgemöller M. Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin, Appl. Catal. B Environ. 2015 May;166–167:45-55.
15. INTERNATIONAL STANDARD ISO inhibition of the mobility of Daphnia, 2012.
16. Elmolla ES, Chaudhuri M. Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process, J. Hazard. Mater. 2009 Dec; 172: 1476-1481.
17. Xu H, Cooper WJ, Jung J, Song W. Photosensitized degradation of amoxicillin in natural organic matter isolate solutions, Water Res. 2011 Jan; 45: 632-638.
18. Hirte K, Seiwert B, Schüürmann G, Reemtsma T. New hydrolysis products of the beta-lactam antibiotic amoxicillin, their pH-dependent formation and search in municipal wastewater, Water Res. 2016 Jan; 88: 880-888.
19. Klauson D, Babkina J, Stepanova K, Krichevskaya M, Preis S. Aqueous photocatalytic oxidation of amoxicillin, Catal. Today. 2010;151:39-45.
20. Dogan S, Kidak RA Plug flow reactor model for UV-based oxidation of amoxicillin, Desalin. Water Treat. 2015 Mar; 3994: 1-14.
21. Murzin DY. On Langmuir kinetics and zero order reactions, Catal. Commun. 2008 May; 9: 1815-1816.