Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1082507

57 (2016) 16670–16677
July

Taylor & Francis
Taylor & Francis Group

TiO_2-photocatalyzed degradation of tetracycline: kinetic study, adsorption isotherms, mineralization and toxicity reduction

S. Bouafıa-Chergui*, H. Zemmourı, M. Chabanı, A. Bensmaılı

Faculté de Génie Mécanique et de Génie des Procédés, Université des Sciences et de la Technologie Houari Boumediene (USTHB), Bab-Ezzouar, 16111 Alger, Algeria, Tel./Fax: +213 24 41 02 00; email: sbouafia@usthb.dz (S. Bouafıa-Chergui)

Received 18 December 2014; Accepted 3 August 2015

ABSTRACT

The photocatalytic degradation of tetracycline has been investigated in aqueous solutions using TiO_2 as photocatalyst. The experiments were carried out to investigate the factors influencing the photocatalytic degradation, such as the previous adsorption in the dark, initial concentration of TC solution, TiO_2 amount, and the system toxicity during TC photodegradation. The experimental results show that adsorption is an important parameter controlling the apparent kinetic constant of the degradation. The photocatalytic degradation rate was favored by a high concentration of solution with respect to Langmuir–Hinshelwood model. The chemical oxygen demand values at the end of the treatment indicated that the percentage mineralization is a function of the initial TC concentration. The acute toxicity increased at the beginning of TC photo-oxidation, and treatment times of around 6 h are generally required for the toxicity to be lower than in the original solution.

Keywords: Photocatalysis; Tetracycline; Adsorption isotherm; Langmuir–Hinshelwood model; COD; Acute toxicity

1. Introduction

Tetracycline (TC) represents a major proportion of the antibiotics currently in use [1,2]. The use of antibiotics and growth hormones in human and veterinary has a significant effect on the quality of surface and groundwater [3]. Among veterinary pharmaceuticals, antibiotics are widely prescribed with a prevalence of the tetracycline family [4]. At present, tetracycline antibiotics rank second in the production and usage of antibiotics worldwide [5]. It has been reported that TCs have been found in soils [6], surface water [7] and [8], and groundwater [8]. Frequent application of tetracycline antibiotics has given a cause for concern about increased antibiotic resistance of micro-organisms in the terrestrial environment and the effect of antibiotics on plant growth [5]. The presence of TC and other antibiotics in natural environments can cause bacteria to acquire and transmit antibiotic-resistant genes, which potentially threatens ecosystem functions and human health [9]. Even, low concentrations of pharmaceuticals released from the environmental matrix into water can pose serious environmental damages. Thus, it is of great importance to develop some efficient and cost-effective treatment technologies to remove such compounds.

The antibiotic residues or contaminated waters cannot be efficiently removed by traditional biological

---

*Corresponding author.

methods [10–14]. On the other hand, advanced oxidation processes (AOPs) have proved to be an appropriate alternative for rapid degradation of recalcitrant and non-biodegradable compounds in water [15–19]. They are based on the *in situ* generation of a powerful non-specific oxidizing agent, the hydroxyl radical ($OH^{\cdot}$) which is able to oxidize a broad range of organic pollutants quickly and non-selectively.

In particular, TiO_2 photocatalysis has been successfully used in the degradation of several kinds of organic compounds. This technique is based upon the use of UV-irradiated semiconductors. When TiO_2 is irradiated with photons whose energy is equal to or greater than its band gap energy ($E_G = 3.2$ eV) i.e. with $\lambda = 390$ nm, electron–hole pairs are created. In aqueous system, holes react with H_2O or OH^- adsorbed on the surface of the semiconductor to produce $OH^{\cdot}$ radicals which are the most oxidizing species in this process. On the other hand, electrons are trapped at surface sites and removed by reactions with adsorbed molecular O_2 to form superoxide anion radical $O_2^{\cdot -}$ (or $HO_2^{\cdot}$ at lower pH) [20].

The objective of the present study was to analyze the effectiveness of heterogeneous photocatalysis degradation of TC. For this purpose, we conducted a kinetic study of the process, the previous adsorption in the dark. We also analyzed the influence of operational variables, including the initial concentration, the catalyst loading, the chemical oxygen demand (COD), and system toxicity during TC photodegradation.

2. Experimental

2.1. Chemicals

All solutions were prepared with distilled water using sulfuric acid or sodium hydroxide (analytical grade) to adjust the pH of the solution. Tetracycline was obtained from Fluka-Sigma-Aldrich (St. Quentin Fallavier, France). A commercially available titanium dioxide was used as a photocatalyst produced by the chemical factory "BIOCHEM ChemoPharma" (Quebec, Canada). This photocatalyst is in an anatase form with BET specific surface area of 4.61 (m^2/g) and 20.2 nm particle diameter [21]. All chemicals were used as received without further purification and purchased from Sigma-Aldrich.

2.2. Procedures

2.2.1. Adsorption isotherm

All batch equilibrium experiments were conducted in the dark over a 30-min period. Measurements were made on suspensions prepared by mixing 100 mL solutions of various initial TC concentrations (5–20 mg/L) at pH free and a fixed amount of TiO_2 (1 g/L). Preliminary experiments performed until 2 h under constant magnetic stirring indicated that equilibrium was reached after 30 min.

2.2.2. Photocatalytic system

Photocatalytic degradation experiments were carried out in an open Pyrex reactor (1,500 mL) with a double-walled cooling water jacket to keep the solution temperature constant (25 ± 1˚C) throughout the experiments (Fig. 1). Irradiations were carried out using a 12 W halogen lamp (Philips). A 1500-mL tetracycline (10 mg/L) and a set amount of TiO_2 were added to the reactor according to experimental design values. Prior to illumination, the suspension was stirred in the dark for 30 min to achieve adsorption equilibrium. Then, the UV light was turned on, signaling the start of photocatalysis. At given time intervals, 5-mL TC solution samples were collected and filtered through 0.45 μm Millipore filters to remove TiO_2 particles for further analysis by spectrophotometer, COD, and toxicity.

Photolysis experiments were performed, in the absence of the TiO_2 catalyst, using the same experimental setup previously described for the photocatalytic system.

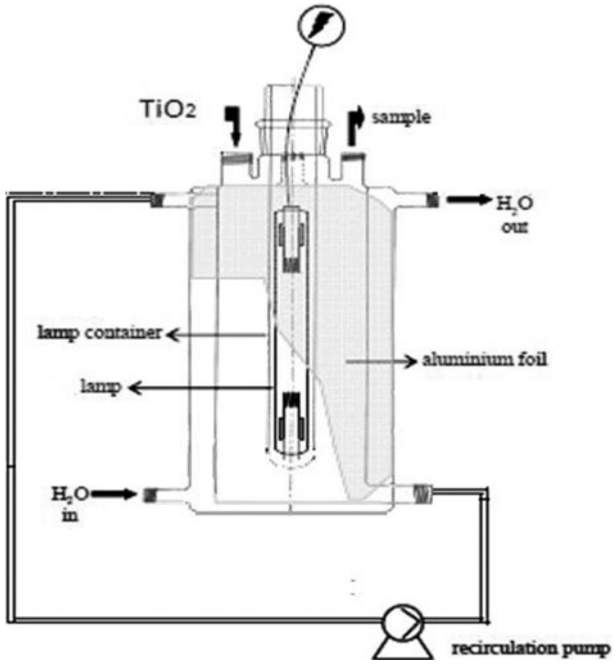

Fig. 1. Schematic diagram of the photocatalytic reactor.

2.2.3. Analysis

TC concentration measurements were made at a maximum absorption wavelength of 350 nm using a UV–vis spectrophotometer (Jenway 6305). The toxicity of TC degradation products was determined by a standardized biotest (DIN/EN/ISO11348-2) of the inhibition of *Vibrio-fischeri* bacteria (NRRL B-11177). Bioluminescence was measured with a LUMISTox equipment, and results were expressed as percentage of luminescence inhibition at 15 min of exposure. COD was determined according to the Standard Methods (APHA, 2005) [22]. All the degradation and toxicity assessment experiments were replicated in triplicate.

3. Results and discussion

3.1. Preliminary study

Adsorption under dark conditions (TiO_2), photolysis (UV), and photocatalysis (UV/TiO_2) was compared for 10 mg/L initial TC concentration (data not shown). The results show that the photolysis experiment did not result in any significant TC photodegradation, after 300 min of irradiation, direct photolysis contributed less than 6% to the degradation process. The adsorption equilibrium was achieved after 20 min of contact, and no further TC adsorption on TiO_2 was observed after 30 min. However, in the presence of TiO_2 with UV radiation, degradation of TC was more significant compared with both adsorption and direct photolysis, demonstrating that TC degradation was carried out at a nearly photocatalytic regime.

3.2. TC adsorption study

Adsorption is important in determining the rate of photocatalytic degradation of organic molecules. The pollutant adsorbed on the surface of the semiconductor particles acts as an electron donor, injecting electrons from the excited state of the semiconductor under UV irradiation to its conduction band [23].

From the values of the initial concentration C_0 and those obtained at the adsorption equilibrium concentration C_e, the specific adsorbed amount of TC was calculated according to the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where V is the volume of the equilibrium solution and m is the mass of TiO_2. The TC adsorption isotherm was then established (Fig. 2), which corresponds to the specific quantity of adsorbed pollutant (in mol/g) as a function of the concentration at equilibrium.

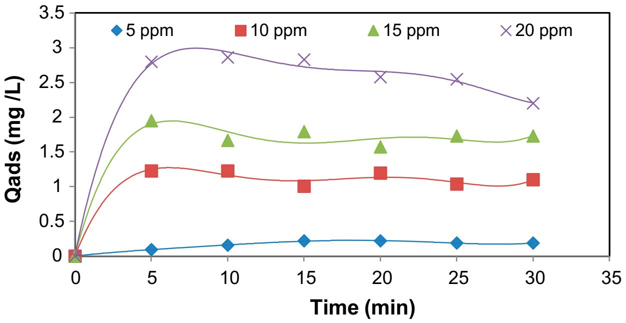

Fig. 2. Adsorption equilibrium of TC on TiO_2. $[TiO_2]$ = 1 g/L, pH free.

Langmuir and Freundlich isotherm models were employed to describe the TC adsorption equilibrium.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites [17,18]. It is given as the following equation:

$$\frac{Q_e}{Q_{max}} = \frac{K_{obs}C_e}{1 + K_{obs}C_e} \tag{2}$$

where Q_e is the adsorbed quantity of TC (mg/g), C_e is the TC concentration (mg/L) at the adsorption equilibrium, K_{obs} is the adsorption constant in the dark (L/mg), and Q_{max} is the maximum adsorbed quantity of TC (mg/g).

The linear transformation of Eq. (2) can be expressed by the following equation:

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}K_{obs}} \cdot \frac{1}{C_e} \tag{3}$$

Indeed, when plotting $1/Q_e$ vs. $1/C_e$ as in Fig. 3, a straight line is obtained and the Langmuir isotherm provides a good fit of the data. The ordinate at the origin is equal to the reciprocal of Q_{max}, whereas K_{obs} can be calculated from the slope ($1/(Q_{max}K_{obs})$). The values Q_{max} and K_{obs} estimated from the plots along with the correlation coefficients are listed in Table 1.

The Freundlich isotherm equation is given as below Eq. (4):

$$Q_e = K_F C_e^{1/n} \tag{4}$$

K_F and n are the constants of adsorption density and adsorption intensity, respectively. Eq. (4) can be linearized as the following equation:

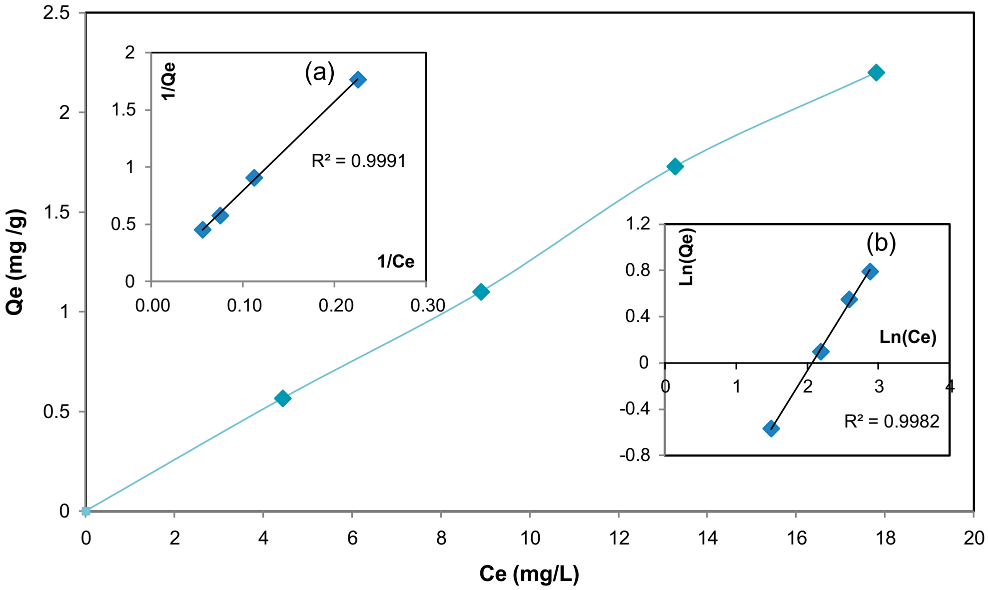

Fig. 3. Adsorption isotherm of TC on the photocatalyst. In the insert: (a) Langmuir model and (b) Freundlich model.

Table 1
Adsorption isotherm parameters of TC on TiO_2 at 25˚C

[TC] = 10 mg/L pH free $[TiO_2]$ = 1 g/L	
Langmuir isotherm constants	Freundlich isotherm constants
Q_{max} = 90.91 mg/g K_{obs} = 0.0014 L/mg R^2 = 0.9991	K_F = 0.1288 L/mg n = 1.0087 R^2 = 0.9982

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

The value of K_F and n can be estimated from the intercept and slope of the linear plot of experimental data of $\ln K_F$ vs. $\ln C_e$. The Freundlich isotherm provides no information on the monolayer adsorption density in comparison with the Langmuir model.

The values of K_F and n from the linearized plots are shown in Table 1 following with the regression correlation coefficients. Langmuir isotherm model was slightly better for describing the adsorption equilibrium than Freundlich model.

3.3. TC photo-degradation kinetics

The kinetics of the photocatalytic degradation of TC at different initial concentrations is plotted in Fig. 4. The quasi-exponential decay observed during irradiation along with the linear plot of $\ln C_{eq}/C_t$ vs. time (Fig. 4, inset) indicates that, in our experimental conditions, TC degradation follows a pseudo-first-order kinetic model. The result illustrates that the removal efficiencies of TC decreased from 99% at 5 mg/L to 85% at 20 mg/L, respectively, TC initial degradation rate (r_0) increased with an increase in the initial concentration, from 0.22 to 0.42 mg/L min.

The photocatalytic reaction rate of most organic compounds is described by pseudo-first-order kinetic model which is rationalized in terms of the Langmuir–Hinshelwood model, modified to accommodate reaction occurring at a solid–liquid interface [24–26].

$$\frac{1}{r_0} = \frac{1}{K_r} + \frac{1}{K_r K_{L-H}} \cdot \frac{1}{C_0} \tag{6}$$

in which r_0 is the TC initial degradation rate, C_0 is the TC initial concentration, K_{L-H} is the equilibrium

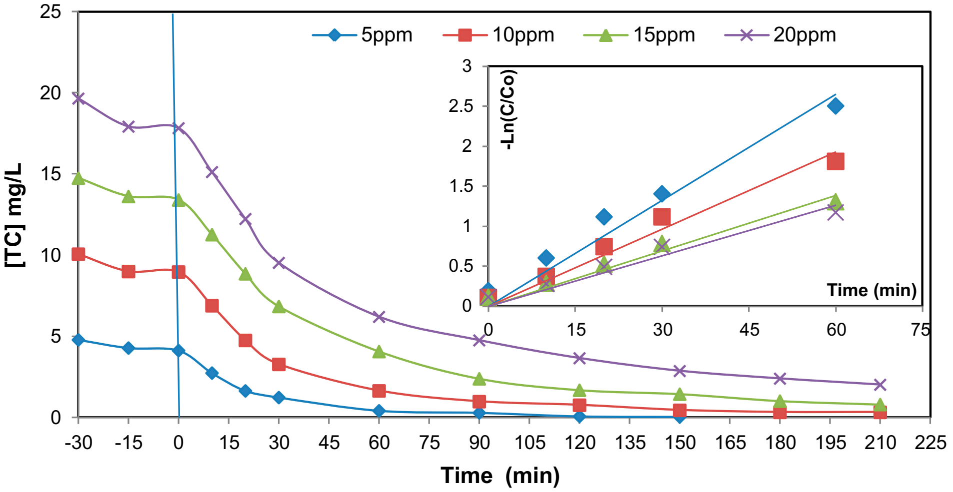

Fig. 4. Kinetics of the photocatalytic degradation of TC at different initial concentrations, inset: the pseudo-first-order kinetic of TC. pH free, $[TiO_2] = 1$ g/L.

constant of TC adsorption on TiO_2 particles, and K_r is the reaction rate of pollutant oxidation which reflects the limiting reaction rate at maximum coverage for the experimental conditions [25].

In Fig. 5 Eq. (6) is plotted at various TC initial concentrations. The linearity obtained shows that the reaction occurs at TiO_2 surface where the pollutant as well as the $OH^{\cdot}$ radicals generated by catalyst UV irradiation are adsorbed. From the intersection of this straight line with the ordinate results $1/K_r$ and the value of the reaction rate is $K_r = 0.6119$ mg/L min. The adsorption equilibrium constant $K_{L-H} = 0.1129$ L/mg was calculated from the slope.

By integrating Eq. (6) and replacing c with $C_0/2$ the half-life time $t^*_{1/2}$ was obtained:

$$t^*_{1/2} = \frac{C_0}{2K_r} + \frac{\ln 2}{kK_{L-H}} \qquad (7)$$

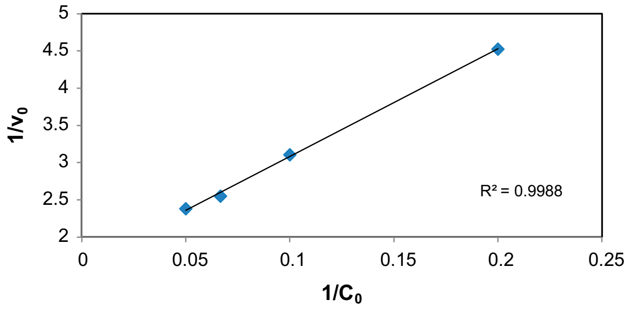

Fig. 5. The linearization of Langmuir–Hinshelwood equation using experimental data.

On the other hand, the half-life time $t_{1/2}$ may be calculated from the value of the pseudo-first-order rate constant $k_{TC,}$ determined from experimental results, as follows:

$$t_{1/2} = \frac{\ln 2}{k_{ap}} \qquad (8)$$

The rate constant k_{ap}, calculated from the slopes of the typical linear plot characteristic to the pseudo-first-order reaction, for various initial pollutant concentrations and half-life time values are presented in Table 2.

Presented data show that $t^*_{1/2}$ and $t_{1/2}$ are approximately identical at low initial TC concentration (5 mg/L). The difference between estimated and observed half-life times becomes larger with an increase in the TC concentration. This behavior is due to the competition between the parent pollutant and its

Table 2
Pseudo-first order rate constant k_{ap}, $t^*_{1/2}$ and $t_{1/2}$ of TC photocatalytic degradation for various initial concentrations

pH free
$[TiO_2] = 1$ g/L

$[TC]_0$	k_{ap} (min^{-1})	$t_{1/2}$ (min)	$t^*_{1/2}$ (min)
5	0.0442	15.68	14.12
10	0.0322	21.53	18.20
15	0.0231	30.01	22.29
20	0.021	33.01	26.38

degradation byproducts for HO$^\bullet$ radical consumption, representing an inhibitory effect [25].

3.3.1. *Effect of TiO_2 concentration*

To observe the effect of TiO_2 concentration, initial TiO_2 concentration was varied in the range of 0.5–2 g/L. Fig. 6 shows the influence of various TiO_2 concentrations on TC initial degradation rate (r_0), calculated for the first 5 min of irradiation. Increasing TiO_2 concentration in the range of 0.5–1.0 g/L increased r_0 due to the increased number of active sites of the catalyst. Further increase in TiO_2 concentration above 2.0 g/L produced lower TC initial degradation rate (r_0). This may be due to the aggregation of TiO_2 under high particle concentration which reduces the interfacial area between the reaction mixture and the photocatalyst, reducing light penetration [27,28]. Based on the results, the optimum TiO_2 concentration for degradation of TC in aqueous solution is 1.0 g/L.

3.4. *TC mineralization and toxicity evaluation*

The COD test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in the terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water [29].

Fig. 7 shows the evolution of COD during the photodegradation of TC. We can see that there are two steps. In the first step, a slight decrease in the COD was obtained, after a period of 210 min; the COD was reduced to about 30% of its initial value. After this time, an important decrease in the COD of the solution was observed; the COD removal rate was reduced reaching 70% of the initial COD value after 330 min of irradiation. Consequently, the complete mineralization of TC required more irradiation time. The result implies that both degradation and mineralization play an important role for the photocatalytic effects under UV irradiation.

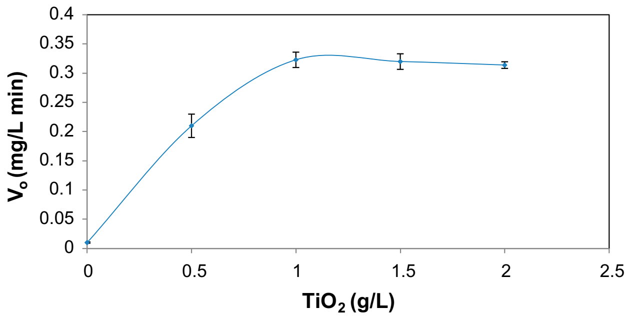

Fig. 6. Concentration of TiO_2 vs. TC initial degradation rate (r_0). pH free $[TC]_0$ = 10 mg/L.

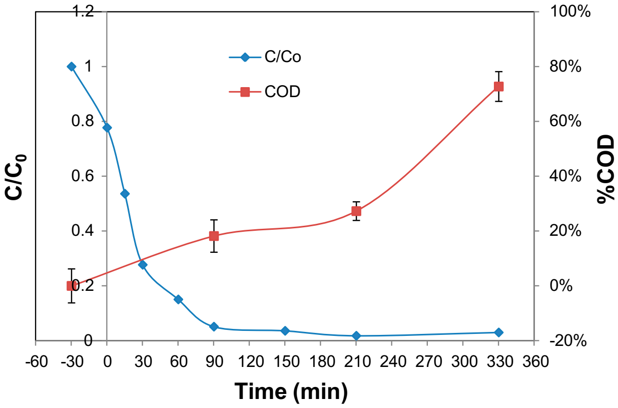

Fig. 7. Evolution of COD during the photodegradation of TC. pH free $[TC]_0$ = 10 mg/L, [TiO2] = 1g/L.

As the COD was not completely removed, one of the most important aspects to be taken into account in the treatment of antibiotics is the toxicity of the byproducts that remains after the photocatalytic treatment. Acute toxicity was evaluated by monitoring changes in the natural emission of the luminescent bacteria *V. fischeri* when challenged with toxic compounds and is expressed as percentage of inhibition of the bacteria luminescence. Toxicity (inhibition %) evolution during the photocatalytic treatment is depicted in Fig. 8. The initial toxicity of TC solution showed an initial inhibition of 60% that is considerably increased at 240 min of irradiation and reaching the value of 84%. It is worth mentioning that the highest toxicity is observed at irradiation times where the majority of the TC was eliminated. Thus, the considerable toxicity increase can be related to the generation of more toxic products

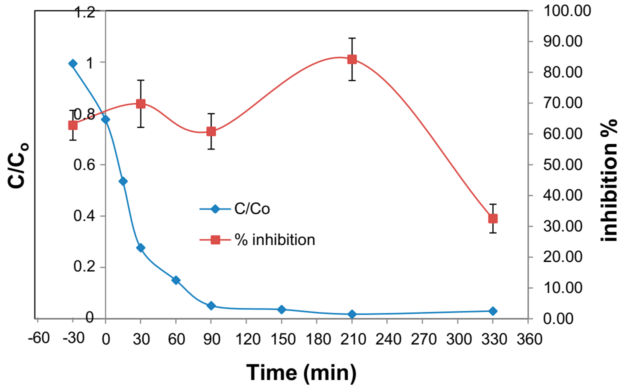

Fig. 8. % Inhibition of the marine luminescence bacteria *Vibrio Fischeri* as a function of photocatalytic treatment ([TC] = 10 mg/L, $[TiO_2]$ = 1 g/L, pH free).

during the photocatalytic treatment. Thereafter, inhibition % decreases reaching the value of 35% after 360 min irradiation, indicating that the formed byproducts are considerably less toxic against *V. fischeri* micro-organisms.

In consequence, TiO_2 photocatalysis is a valuable tool to eliminate the harmful environmental effects of these kinds of substances. It has the added advantage that after short periods of photocatalytic treatment, the oxidation byproducts can be treated by a conventional biological system in an integrated AOP-biological system as proposed for other substances [30].

4. Conclusions

The photocatalytic degradation of TC in the presence of TiO_2 was investigated in detail focusing on the kinetic and mineralization studies. Results of the present study clearly point out that heterogeneous TiO_2 photocatalytic treatment is suitable for the elimination of TC from the aqueous solution. Degradation for TC followed Langmuir–Hinshelwood model. The removal efficiency increased with an increase in the TiO_2 concentrations, but the efficiency decreased over 1.0 g/L of TiO_2 because of UV-screening effect of the catalyst itself. A significant abatement of the overall toxicity was accomplished by transforming the initial substrate into byproducts with lower toxicity, which could then be degraded in a subsequent biological step. The results indicated that TiO_2 photocatalysis allows a rapid and efficient removal of tetracycline.

References

[1] V. Maroga Mboula, V. Héquet, Y. Gru, R. Colin, Y. Andrès, Assessment of the efficiency of photocatalysis on tetracycline biodegradation, J. Hazard. Mater. 209–210 (2012) 355–364.

[2] A.K. Sarmah, M.T. Meyer, A.B.A. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere 65 (2006) 725–759.

[3] P. Chang, J.-S. Jean, W.-T. Jiang, Z. Li, Mechanism of tetracycline sorption on rectorite, Colloids Surf., A 339 (2009) 94–99.

[4] Y. Ait Ouaissa, M. Chabani, A. Amrane, A. Bensmaili, Removal of tetracycline by electrocoagulation: Kinetic and isotherm modeling through adsorption, J. Environ. Chem. Eng. 2–1 (2014) 177–184.

[5] Y. Wan, Y. Bao, Q. Zhou, Simultaneous adsorption and desorption of cadmium and tetracycline on cinnamon soil, Chemosphere 80 (2010) 807–812.

[6] S. O'Connor, D.S. Aga, Analysis of tetracycline antibiotics in soil: Advances in extraction, clean-up, and quantification, TrAC Trends Anal. Chem. 26 (2007) 456–465.

[7] R.S. Valverde, M.D.G. García, M.M. Galera, H.C. Goicoechea, Determination of tetracyclines in surface water by partial least squares using multivariate calibration transfer to correct the effect of solid phase preconcentration in photochemically induced fluorescence signals, Anal. Chim. Acta. 562 (2006) 85–93.

[8] W.-H. Tsai, T.-C. Huang, H.-H. Chen, J.-J. Huang, M.-H. Hsue, H.-Yi. Chuang, Y.-W. Wu, Determination of tetracyclines in surface water and milk by the magnesium hydroxide coprecipitation method, J. Chromatogr. A 1217 (2010) 415–418.

[9] C. Zhao, M. Pelaez, X. Duan, H. Deng, K. O'Shea, D. Fatta-Kassinos, D.D. Dionysiou, Role of pH on photolytic and photocatalytic degradation of antibiotic oxytetracycline in aqueous solution under visible/solar light: Kinetics and mechanism studies, Appl. Catal. B: Environ. 134–135 (2013) 83–92.

[10] C. Reyes, J. Fernández, J. Freer, M.A. Mondaca, C. Zaror, S. Malato, H.D. Mansilla, Degradation and inactivation of tetracycline by TiO_2 photocatalysis, J. Photochem. Photobiol. A: Chem. 184 (2006) 141–146.

[11] F. Ferrag-Siagh, F. Fourcade, I. Soutrel, H. Aït-Amar, H. Djelal, A. Amrane, Tetracycline degradation and mineralization by the coupling of an electro-Fenton pretreatment and a biological, process, J. Chem. Technol. Biotechnol. 88 (2013) 1380–1386.

[12] N. Oturan, J. Wu, H. Zhang, V.K. Sharma, M.A. Oturan, Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials, Appl. Catal. B 140–141 (2013) 92–97.

[13] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641.

[14] I. Yahiaoui, F. Aissani-Benissad, F. Fourcade, A. Amrane, Removal of tetracycline hydrochloride from water based on direct anodic oxidation (Pb/PbO_2 electrode) coupled to activated sludge culture, Chem. Eng. J. 221 (2013) 418–425.

[15] S. Bouafia-Chergui, N. Oturan, H. Khalaf, M.A. Oturan, Parametric study on the effect of the ratio $[H_2O_2]/[Fe^{3+}]$ on the photo-Fenton degradation of Basic Blue 41 cationic azo dye, J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng. 45–5 (2010) 622–629.

[16] A.B. Caracciolo, E. Topp, P. Grenni, Pharmaceuticals in the environment: Biodegradation and effects on natural microbial 4 communities. A review, J. Pharm. Biomed. Anal. 106 (2015) 25–36, doi:10.1016/j.jpba.2014.11.040.

[17] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review, Environ. Int. 40 (2012) 212–229.

[18] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

[19] S. Bouafia-Chergui, N. Oturan, H. Khalaf, M. Oturan, Electrochemical and photochemical oxidation of cationic dyes: A comparative study, Curr. Org. Chem. 16 (2012) 2073–2082.

[20] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Factors influencing the photocatalytic degradation of Rhodamine B by TiO_2-coated non-woven paper, J. Photochem. Photobiol. A: Chem. 195 (2008) 346–351.

[21] N. Chekir, N.A. Laoufi, F. Bentahar, Spiramycin photocatalysis under artificial UV radiation and natural sunlight, Desalin. Water Treat. 52 (2014) 6832–6839.

[22] APHA, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.

[23] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Photocatalytic degradation of patent blue v by supported TiO_2: Kinetics, mineralization, and reaction Pathway, Chem. Eng. Commun. 198 (2011) 1233–1243.

[24] A. Turki, C. Guillard, F. Dappozze, Z. Ksibi, G. Berhault, H. Kochkar, Phenol photocatalytic degradation over anisotropic TiO_2 nanomaterials: Kinetic study, adsorption isothermsand formal mechanisms, Appl. Catal. B: Environ. 163 (2015) 404–414.

[25] I. Nitoi, P. Oancea, I. Cristea, L. Constsntin, G. Nechifor, Kinetics and mechanism of chlorinated aniline degradation by TiO_2 photocatalysis, J. Photochem. Photobiol. A: Chem. 298 (2015) 17–23.

[26] E. Evghenidou, K. Pytianos, I. Poulios, Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalyst, Appl. Catal. B: Environ. 30 (2005) 259–269.

[27] A. Chioma, M. Chaudhuri, Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by, TiO_2 photocatalysis, J. Environ. Manage. 130 (2013) 160–165.

[28] V.K. Gupta, R. Jain, A. Mittal, T.A. Saleh, A. Nayak, Photo-catalytic degradation of toxic dye amaranth on TiO_2/UV in aqueous suspensions. Mater. Sci. Eng., C. 32-C (2012) 12–17.

[29] B. Sarwan, B. Pare, A.D. Acharya, S.B. Jonnalagadda, Mineralization and toxicity reduction of textile dye neutral red in aqueous phase using BiOCl photocatalysis, J. Photochem. Photobiol. B: Biol. 116 (2012) 48–55.

[30] A.L. Giraldo, G.A. Peñuela, R.A. Torres-Palma, N.J. Pino, R.A. Palominos, H.D. Mansilla, Degradation of the antibiotic oxolinic acid by photocatalysis with TiO_2 in suspension, Water Res. 44 (2010) 5158–5167.