Revue des Energies Renouvelables Vol. 20 N°4 (2017) 683 - 691
DOI: https://doi.org/10.54966/jreen.v20i4.660

Degradation of macrolide antibiotic in water by heterogeneous photocatalysis

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(reçu le 18 Décembre 2017 - accepté le 28 Décembre 2017)

Résumé - *Le présent travail porte sur la dégradation photocatalytique d'un antibiotique macrolide nommé tylosine (TYL) dans un réacteur batch en utilisant du dioxyde de titane en poudre (TiO_2) et une irradiation artificielle 'lampe 9W-UV. L'efficacité de la photodégradation a été étudiée en faisant varier certains paramètres clés comme la concentration initiale de TYL (5 - 80 mg/L) et la concentration du catalyseur (0.1 - 4 g/l). Un meilleur rendement réactionnel (environ 99 %) a été obtenu pour les faibles concentrations initiales et 1 g/L en TiO_2 dans de l'eau à pH naturel. L'élimination photocatalytique de TYL suit une cinétique de pseudo-premier ordre et le modèle de Langmuir-Hinshelwood (L-H) approche correctement les données expérimentales avec la réaction chimique considérée comme étape limitante.*

Abstract - *The present work involves the photocatalytic degradation of tylosin macrolide antibiotic (TYL) in a batch reactor using powder titanium dioxide (TiO_2) under artificial '9W-UV lamp'. The photodegradation efficiency has been investigated under the controlled process parameters including initial TYL concentration (5 - 80 mg/L), catalyst loading (0.1 - 4 g/L). The best reaction rate (about 99 %) was obtained for low concentrations and 1 g/L TiO_2 in natural pH water. Under the operating conditions, the TYL photocatalytic removal follows a pseudo-first order kinetic and the Langmuir-Hinshelwood (L-H) model is successfully used to fit the experimental data indicating the dependence of reaction rate with the chemical reaction step.*

Keywords: Tylosin - Antibiotic - Photodegradation - L-H model - Titanium dioxide - kinetic.

INTRODUCTION

Over the past few years, the occurrence and fate of antibiotics in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry [1-4]. Antibiotics in aqueous system might lead to adverse environment effects, including the development of antibiotic resistance to aquatic bacteria, direct toxicity to micro organism and possible risks to human health as allergies through drinking water and/or food-chain [5].

In accordance with some authors, tylosin (TYL) is an antibiotic which represents 13% of the detected drugs. It is ranked in fifth position after trimethoprim (27 %), erythromycin-H_2O (22 %), lincomycin (19 %) and sulfamethoxazole (19 %) [6, 7]. The detection limit of TYL in wastewater is about 0.01 mg/L [6].

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TYL is a fermentation derived macrolide antibiotic, which inhibits protein synthesis of specific bacterial species [8]. It is used as feed additive (5 mg/L) in order to modulate gut microbial flora, thus enhancing the growth rates performances in calves, cattle and poultry.

To prevent the water matrix contamination by this antibiotic and other pharmaceuticals, several removal or degradation processes have been studied [9-13]. Oxidative processes appear to be efficient for the treatment of wastewaters containing pharmaceuticals [14, 15]. The information dealing with the removal of macrolide by Advanced Oxidation Processes, 'AOP' is scarce, especially concerning TYL. A few works have been reported on the removal of TYL antibiotic by heterogeneous photocatalysis, coupled or not to biological treatment process [16-18]. Tassalit *et al.* [17] have studied TYL degradation by photocatalysis in a closed circulation reactor in presence of Degussa P25 titanium dioxide and 24W-UV lamp.

In the present work, the degradation of macrolide TYL was monitored by heterogeneous photocatalysis process with the use of Millennium PC500 titanium dioxide as suspension catalyst in aqueous solution. The process was conducted on a batch reactor system under an immerged artificial UV light lamp with low energy power.

The main operating parameters such as catalyst loading and initial TYL concentration were investigated and optimized.

Moreover, the reaction kinetics were investigated for a better control and understanding of the process. So, application of Langmuir-Hinshelwood kinetic model to the obtained results was checked and the L-H constants were thereby determined.

2. MATERIALS AND METHODS

2.1 Chemicals and reagents

Macrolide antibiotic TYL tartrate was obtained from commercial TYL produced by Sinochem Corporation. Its chemical structure is represented in figure 1.

The photocatalyst was PC500 Titania (TiO_2), supplied by Millennium Inorganic Chemicals. It has crystallite form composed over than 99 % of anatase, with 5-10 nm mean size and about 320 m^2/g specific surface area. Analytical-grade organic solvents were used for ultra high performance liquid chromatography analysis. The water used for the whole of prepared solutions was distilled (resistivity of 2 MΩcm).

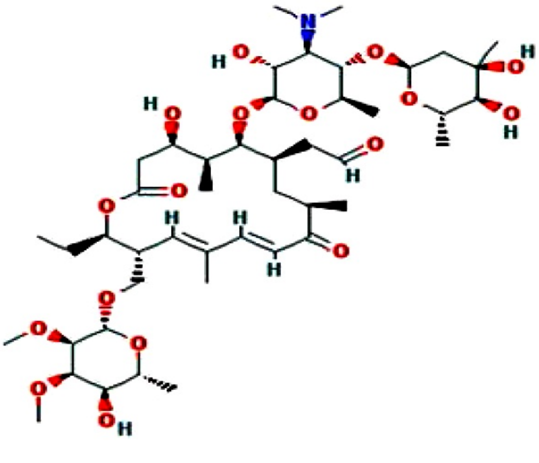

Fig. 1: Chemical structure of Tylosin

2.2 Experimental set-up and procedure

The photocatalytic degradation experiments were carried out using a batch photoreactor. The system is well described in a previous work [20]. The UV light source is a Philips PL-S 9W/10/4P mercury vapor lamp contained. For all of photodegradation tests, the incident light intensity used was equal to 45 Wm-2and was measured by a radiometer (VLX-3W; VilbertLourmat).

Experimental solutions were prepared by dissolving requisite amount of TYL in distilled water and were kept free of adjustment before and during the photocatalysis process. For photocatalysis experiment, TiO_2 was added to the solution and the resulting suspension was circulated again for 30 minutes in the darkness, to ensure that the adsorption equilibrium was reached.

Then, the light was turned on to irradiate the solution. For all the tests, an irradiation was conducted for 300 min. the samples were taken over the illumination time and filtered through 0.45 µm PTFE Millipore syringe filter for analysis. The TYL concentration was monitored by ultra-high performance liquid chromatography, 'HPLC' at $\lambda_{max} = 290$ nm equipped with a photodiode-array detector (Acquity Hclass: Waters). The analysis conditions were detailed in a previous work [20].

The degradation-removal efficiency 'DRE' of TYL was determined as follows:

$$\mathrm{DRE} = \frac{(C_0 - C)}{C_0} \times 100\ \% \qquad (1)$$

where C_0 (mg/L) is the initial antibiotic concentration and C (mg/L) the residual antibiotic concentration at time t (min).

In order to fit all data sets {influence of catalyst loading and initial antibiotic concentration on photodegradation rate}, the removal of TYL was modeled using a first-order equation {Eq. (2)} which is a simplified Langmuir-Hinshelwood model for diluted solutions (<< 1mmol) [21]:

$$C = C_0\, e^{-kap.t} \qquad (2)$$

where k_{ap} (m^{-1}) is the apparent first-order rate constant. It is given by the slope of the graph of $\ln(C_0/C)$ versus t.

3. RESULTS AND DISCUSSION

3.1 Comparison of TiO_2 adsorption, photolysis and photocatalysis

Adsorption under dark conditions (only TiO_2), photolysis (only UV) and photocatalysis (UV/TiO_2) were compared for 20 mg/L initial TYL concentration (figure 2). Approximately 10 % of TYL was removed from the solution within 15 min in the presence of TiO_2 only. The equilibrium during the adsorption reaction was then achieved.

The photolytic and photocatalytic degradation can be achieved by direct reaction with photons produced by UV, and/or by indirect reaction with $^{\bullet}OH$ radicals produced by the reaction between H_2O/OH^- ion and TiO_2. The generation of $^{\bullet}OH$ radical in the photocatalysis of TYL is expected to be greater than in the photolysis. The removal rates of TYL were about 35 % and 80 % after 300 min of UV and UV/TiO_2 irradiation, respectively. It was clearly observed that the photocatalysis is the most efficient treatment process compared to adsorption and photolysis. In fact, it seems that photolysis process is extremely dependent on the chemical structure of the compound. Only the photo-sensitive compounds are easily degraded [22].

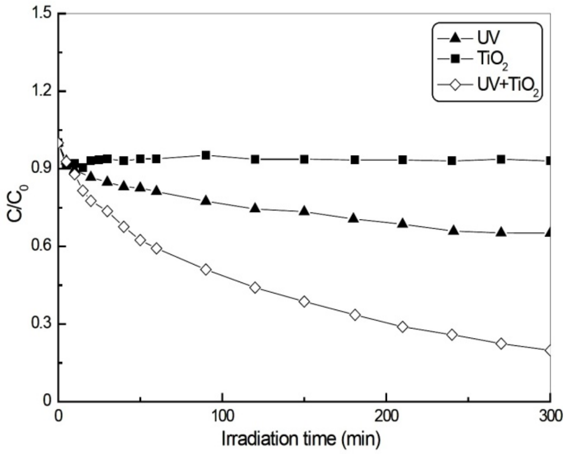

Fig. 2: Comparison of TYL removal efficiency at adsorption (TiO_2), photolysis (UV) and photocatalysis (UV/TiO_2) $\{ TiO_2 = 0.1 g/L ;\ C_0 = 20\ mg/L ;$ initial $pH = 4.5 \}$

3.2 Influence of TiO_2 loading and reaction order determination

The effect of TiO_2 loading was studied in the range 0-4 g/L with TYL concentration equal to 20 mg/L and natural solution pH of 4.6 ± 0.2. Under the selected TiO_2 concentrations, it was found that all decay curves followed pseudo-first order kinetics. The plot of $\ln(C_0/C)$ versus time gives a straight line whose slope is equal to k_{ap}. Only the experimental data obtained during the first 30 min irradiation were involved in calculating the rate constants by using the fitting of pseudo-first-order model (**Table 1**), in order to minimize variations due to competitive effects of the intermediates and pH changes.

The higher amount of catalyst, the better the degradation was, because light absorption increases, giving rise to more free radicals $^{\bullet}OH$. However, from a value of 1.0 g/L, further increase in catalyst loading did not improve substantially TYL degradation rate {a maximum of 99 % is reached, figure 3}. This result can be explained by the fact that a much higher concentration of catalyst nanoparticles will increase light scattering and hence decreases light penetration, which eventually reduces the photodegradation efficiency.

In the other hand, as TiO_2 concentration was increased from 0 to 4 g/L, the rate constant of the antibiotic photodegradation increased too (**Table 1**). Similar tendency has been observed by Kaniou *et al.* [23]. Moreover, the same range of rate constant values has been found in some works as example of antibiotics degradation by heterogeneous photocatalysis [17, 24].

Table 1: Apparent first-order reaction model parameters for the photo degradation of TYL

Process parameter	**Value**	**First-order Reaction Model**	
		k_{ap} (min^{-1})	R^2
Degradation process [a]	Adsorption	0.0050	0.5584
	Photolysis	0.0080	0.8049
	Photocatalysis	0.0130	0.9947
Effect of TiO_2 loading [b]	0.1	0.0130	0.9947
	0.2	0.0129	0.9749

	0.4	0.0163	0.9930
	0.8	0.0161	0.9858
	1.0	0.0223	0.9895
	1.5	0.0207	0.9964
	2.0	0.0289	0.9996
	3.0	0.0253	0.9961
	4.0	0.0301	0.9803
Effect of initial concentration [c]	5	0.0381	0.9721
	10	0.0272	0.9865
	20	0.0223	0.9875
	40	0.0129	0.9472
	80	0.0130	0.9919

[a] Initial TYL concentration =20 m/L; $TiO_2 = 0.1 g/L$, initial pH = 4.5 ± 0.2

[b] Initial TYL concentration =20 m/L; initial pH = 4.6 ± 0.2

[c] $TiO_2 = .1$, initial pH $= 4.6 \pm 0.2 g/L$

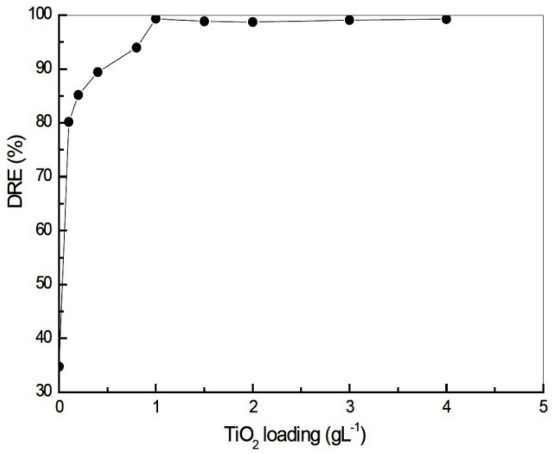

Fig. 3: Degradation removal efficiency of TYL
with different TiO_2 loading ($C_0 = 20 mg/L$, pH = 4.6)

3.3 Effect of initial TYL concentration

The study of the photocatalytic reaction kinetics of TYL based on the initial concentration (from 5 to 80 mg/L) was investigated at constant TiO_2 loading and natural pH (4.8 ± 0.2). The removal rate of TYL was between 73 % and 100 % for the selected concentrations (figure 4).

A maximum degradation was observed for low concentrations (5 - 20 mg/L), indicating that the photocatalytic oxidation is more promising for low organic pollutant concentrations. The degradation rate constant gradually decreases and then reaches a constant value at high concentrations of the compound (**Table 1**).

This result can be explained by adsorption/desorption competition between the antibiotic molecules and intermediates from its degradation, which may be greater for a high concentration in solution. Also, the available reactive species formed on the catalyst surface become insufficient for increased antibiotic concentrations. Consequently, the degradation efficiency of TYL decreases.

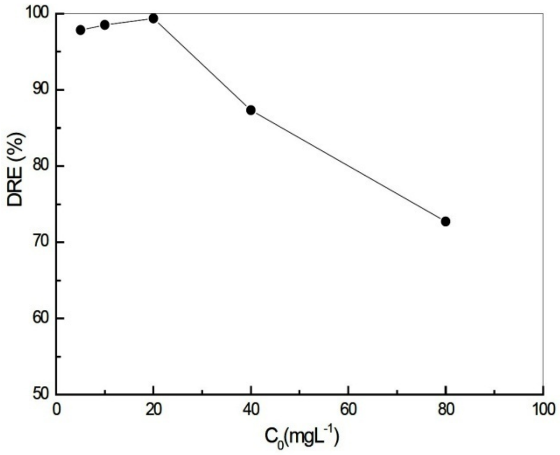

Fig. 4: Degradation removal efficiency of TYL with different initial concentrations ($TiO_2 = 0.1\ g/L$, pH = 4.8)

3.4 Kinetic Langmuir-Hinshelwood model

Although many theoretical model equations have been proposed for describing the kinetics based on mass balance, chemical kinetics and initial/boundary conditions, these equations are not only complicated and impractical while being used, but they also require detailed data such as the characteristics of TiO_2 and reactants.

It was often suggested that the dependence of photocatalytic degradation rate on the concentration of the organic solutes follows the Langmuir-Hinshelwood kinetic model expressed by {Eq. (3)}:

$$r_0 = -\frac{dC_0}{dt} = \frac{K_L . k_{LH} . C_0}{1 + K_L . C_0} \tag{3}$$

where C_0 is the initial concentration, k_{L-H} the reaction kinetic constant or apparent L-H rate (mg/L) and K_L the adsorption/desorption equilibrium conctant (L/mg).

The linearized form of the L-H model is shown in {Eq. (4)}.

$$\frac{1}{r_0} = \frac{1}{k_{L-H} . K_L} \times \frac{1}{C_0} + \frac{1}{k_{L-H}} \tag{4}$$

In order to demonstrate the concordance of our reaction system with the L-H kinetic model, k_{L-H} and K_L values were calculated by linear regression of plotting $1/r_0$ versus $1/C_0$ (figure 5).

The results show that the L–H model can approach correctly the experimental data (regression coefficient of the linear fitting is 0.995). The obtained values of k_{L-H} and K_L were $k_{L-H} = 1.098\ mg/L.min$ and $K_L = 0.018 L/mg$ KL = 0.018Lmg-1.

This means that the kinetic reaction is probably the limitedstep. The degradation of TYL occurred mainly on the surface of TiO_2 by the oxidation reaction, such as photohole and $^{\bullet}OH$ radical.

These constants values are the same order of magnitude thanthose reported in the literature concerning the photocatalytic degradation of antibiotic pollutants [23, 25, 26].

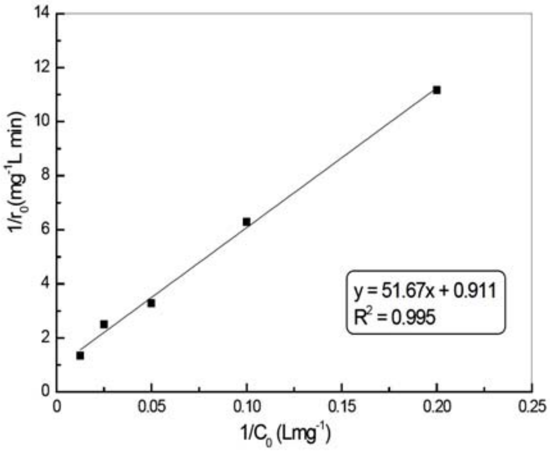

Fig. 5: Application of L-H model on TYL photodegradation process

4. CONCLUSION

In this work, the efficiency of TYL veterinary antibiotic degradationin a low power energy UV/TiO_2 suspension system was investigated under some operating conditions such as the catalyst loading and initial substrate concentration. It was found that the optimal conditions in the photodegradation process could be performed at initial TYL concentration lower than 20 mg/L and TiO_2 loading = 1 g/L.

In all the photocatalytic experiments, the reaction kinetics can be well described by pseudo-first-order reaction model. However, the Langmuir-Hinshelwood model can be applied regardless of the concentration in the studied range.

The obtained results allowed an insight into the behavior of TYL against the elimination process. It clearly appears that the photocatalytic degradation of TYL in the TiO_2 suspension process with low power UV lamp of 9W proves to be an efficient method for quickly lowering the concentration of the antibiotic compound in water.

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