Removal of a Persistent Pharmaceutical Micropollutant by UV/TiO2 Process Using an Immobilized Titanium Dioxide Catalyst: Parametric Study

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Antibiotics are considered as emerging environmental microcontaminants because of their potential adverse effects on ecosystems and human health. The photocatalysis process, in presence of TiO_2 particles, is one of the most promising techniques for the removal of antibiotics.

In the present work, photodegradation of tylosin, a veterinary antibiotic, has been released in a photoreactor containing a catalyst (TiO_2 P25 from Degussa) deposited on a glass substrate. The study of tylosin photodegradation was conducted in the presence of a black light UV radiation of 18 watts. Different parameters were investigated and optimized on the removal of tylosin.

The results showed that this process with the use of optimized operating parameters can lead to total degradation of tylosin. Thus, photodegradation is favored for low pollutant concentration and a high rate of the reaction mixture recirculation.

The antibiotic was completely removed after 7 hours of illumination; the best degradation was obtained at pH 3. More than 98% of tylosin has been oxidized after an irradiation time of 7 hours at the optimum position of UV light. The photolysis of tylosin has reached an abatement not exceeding 30 %.

In addition, the study of the effect of the volume of the reaction mixture showed that a change in the rate of degradation was obtained for differences in volumes of 100 mL, below this value, no change were observed. The kinetic study showed the high activity and efficiency of titanium dioxide Degussa P25 and the degradation of 98 % of tylosin after 7 hours of UV irradiation at the optimal position of 5.5 cm from the catalyst surface. The kinetics was described by the Langmuir-Hinshelwood kinetic model.

1. Introduction

Heterogeneous photocatalysis in presence of a semiconducting photocatalyst (Mills and Le Hunte, 1998; Andreozzi, 1999) has recently emerged as an advanced oxidation process for environmental decontamination method suitable for the treatment of water, aqueous wastes and wastewater (Hoffmann et al., 1995; Hoon and Jae-Hong, 2009) containing inorganic or organic pollutants present at low concentration levels. It is very promising for solving the environmental problems in the most economic way. The feasibility of this technology on a commercial scale has also been demonstrated by the implementation of numerous small-scale applications, including treatment of air and water streams, photodecomposition of toxic compounds, and purification of drinking water (Matthews,1990; Bergamini et al., 2009).Photocatalysis by titanium dioxide has become a very active field of research (Fox and Dulay,1993) in particular, for the decomposition of a variety of organic contaminants present in water and aqueous wastes. Titanium dioxide Degussa P25 has proven to be the most promising semiconductor photocatalyst for widespread environmental applications because it is nontoxic, inert chemically, stable, inexpensive, highly resistant to photocorrosion and shows high reactivity under ultraviolet (UV) light, (Tsai and Cheng, 1997). Photocatalytic oxidation is an advanced oxidation process (AOP) utilizing a semiconducting photocatalyst such as titanium dioxide (TiO_2) and appropriate light sources such as

ultraviolet (UV) irradiation ($\lambda \leq 380$ nm) to generate charge carriers e_{cb}^- and h_{vb}^+ (Bahnemann et al., 2007). These charge carriers react with species that are adsorbed on their surface to generate a highly reactive hydroxyl radical ˙OH, which was recognized to be the most powerful oxidant (Yamazaki and Matsunaga, 2001; Guoliang et al., 2009). These charge carriers react with species that are adsorbed on the semiconductor surface to generate a highly reactive hydroxyl radical. In the past few years, some efforts have been put in increasing the TiO_2 surface area by dispersing nano-particles of TiO_2 on high surface area materials. Many supports have been used including silica gels, active carbon, zeolites and clays (Yu-Hsiang et al., 2001). Some of these studies have also included an effort to increase the adsorption of organic substrates on the catalyst surface for improving the efficiency of catalytic activity. Among the various pollutants found in groundwater and rivers, pharmaceuticals are rejected by water from hospitals, domestic waste and antibiotics given to farm animals. One of the best known antibiotics is tylosin represented in Figure 1, it is a macrolide administered to livestock and poultry.
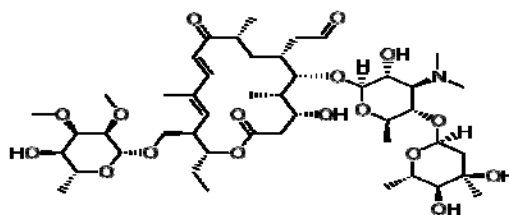

Figure 1: Molecular Structure of tylosin

2. Kinetic studies

The Langmuir-Hinshelwood (L-H) kinetic model was initially developed to provide quantitative descriptions for the gas-solid reactions (Satterfield, 1970); nevertheless, it was recently used to describe solid-liquid reactions (Ollis, 1985). In this model, the rate of the reaction (r) is proportional to the fraction of surface covered by the substrate (θ).

$$r = -dC / dt = k_r \theta \tag{1}$$

Under steady-state conditions, the equilibrium coverage, considering Langmuir's equation, is given as:

$$\theta = KC /(1 + KC) \tag{2}$$

So:

$$r = -dC / dt = k_r \theta = k_r KC /(1 + KC) \tag{3}$$

Equation (3) can be simplified to a first-order reaction rate equation:

$$r = -dC / dt = k_r K \; C = k_{app} \; C \tag{4}$$

Where k_{app}, is the apparent reaction rate constant of a pseudo-first order reaction, in which case one has:

$$ln(C_0 / C) = k_{app}t \tag{5}$$

The value of K is obtained empirically through a kinetic study in the presence of light, and is better than that obtained in the darkness (Pedro et al., 2006), starting from Langmuir's isotherm. By plotting $ln(C_0 / C)$ versus t, the apparent rate constant k_{app} can be determined from the slope of the straight line obtained.

3. Material and methods

3.1 Reagents

The catalyst used in the experiments was TiO_2 Degussa P25, mainly anatase (80 % anatase and 20 % rutile), with a specific surface area of 50 $m^2 g^{-1}$ and a particle size of 30 nm, it is the best catalyst for tylosin abatement, (Tassalit et al., 2011; Alatrache et al., 2010).

Tylosin, with the molecular formula ($C_{46}H_{77}NO_{17}$), is used as tylosin tartrate. All the chemicals used in the experiments were of laboratory reagent grade and used as received without further purification. The solutions were prepared with distilled water. The pH solution is adjusted by H_2SO_4 (1N) or NaOH (1N).

3.2 Photoreactor and light source

The installation, used in this study and represented in Figure 1, functioned in a closed circuit. It was composed of a photochemical reactor which in itself included a glass vat in which a catalytic plaque of ordinary glass was placed. This plaque was covered with several layers of TiO2 P25. The reactor is linked to a reservoir of a 250 mL capacity. The circulation of the solution to be treated is assured by a peristaltic pump. The light source is a Phillips TLD 18 Watt/08 UV lamp which emits mainly at a wavelength of 365 nm; it is mounted on a support platform positioned in a manner to be parallel to the reactor and thus the catalyst.
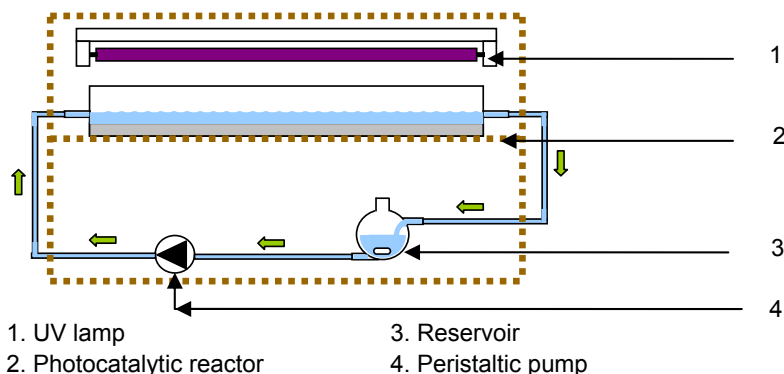

1. UV lamp   3. Reservoir
2. Photocatalytic reactor   4. Peristaltic pump

Figure 2: Reactor setup in fixed bed

3.3 Photodegradation procedures- Analysis

In the present study, the photocatalytic degradation of tylosin has been investigated; the efficiency of photocatalytic oxidation using TiO_2 towards this antibiotic was examined.

The solution of tylosin was prepared with distilled water at different concentrations. The solution was subjected to magnetic stirring for an hour. A volume of 250 mL of this solution were extracted and added to the reservoir. The solution was circulated in a closed circuit and the UV lamp was switched on at the same time. The samples were taken at different time intervals and were immediately analyzed under a double ray UV/Vis spectrophotometer (Perkin Elmer Lambda 25 UV/VIS), the concentrations of residual tylosin was followed by measuring the absorbance at its maximum absorption, worth knowing 290.29 nm and then put back into the reservoir. The pH of the solution was measured at each instance. All experiments were performed by continuously bubbling air through the liquid phase in order to cover the catalyst surface with oxygen and keep it constant during the oxidation process.

4. Results and discussion

4.1 Adsorption, photolysis and photocatalysis

To compare and evaluate the efficiency of the different processes in the elimination of the pollutant, we have subjected tylosin to different processes: adsorption, photolysis and photocatalysis.
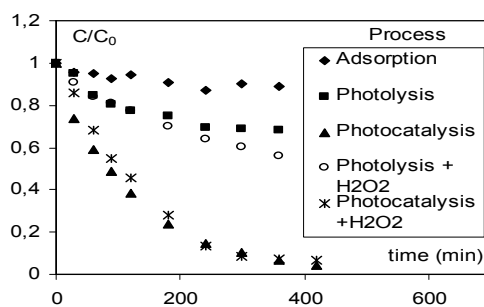

Figure 3: Temporal evolution of tylosin elimination for different processes

According to Figure 3, we noted that the photocatalytic process in absence or presence of hydrogen peroxide was the most efficient treatment as it allowed for a 96 % elimination of tylosin after 7 h of ultraviolet radiation. Nevertheless, the ($H_2O_2/TiO_2/UV$) process allowed the elimination of an equivalent quantity of tylosin, where the abatement reached 93 %.

The efficiency of the photocatalytic process may be explained by the molar absorption coefficient of tylosin which is low in the range of radiation used during the photolysis. Tylosin degradation is exclusively due to the photoactivation of TiO_2. The antibiotic adsorption, which is a physical phenomenon, was less important than photolysis, 12% of tylosin was eliminated, and the amount of tylosin removed during photolysis was less than 30 %.

4.2 Effect of the distance between the plane catalytic sheet and the UV light source, the flowrate and the volume of solution.

Considering Figures 4, 5 and 6; for the different parameters studied, the optimal abatement of tylosin during photocatalysis was obtained at optimal values.
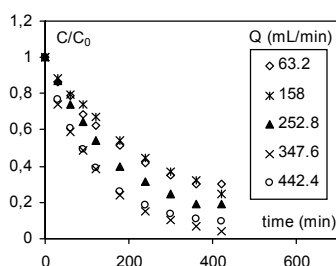

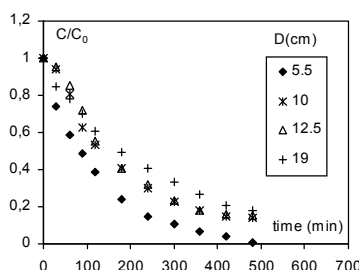Figure 4: Effect of flowrate on tylosin elimination.
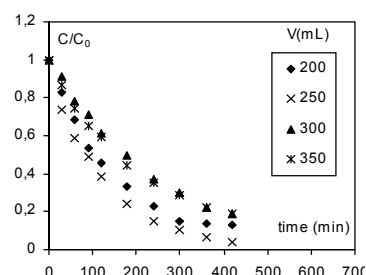
Figure 5: Effect of position on tylosin oxidation.

Figure 6: Effect of volume on tylosin photodegradation.

According to Figure 4, the photocatalytic activity of TiO_2 and the reduction of tylosin concentration with reaction time was more effectiveness with a high flowrate, for lower values than 347.6 mL/min, which is an optimal flowrate, recirculation was not enough, and for values greater than 347.6 mL/min residence time in the reactor was inadequate. For the optimal flowrate, production of hydroxyl radical species ($HO^{\bullet}$), responsible for the photodegradation of organic compounds, increased; which caused the efficiency of the photochemical process, (Guittonneau et al., 1988). The abatement of tylosin reached 96 % after 7 hours exposure to UV light. Figure 5, representing temporal evolution of tylosin oxidation for different distances between the lamp emitting UV radiation and the surface of the plaque supporting the catalyst, demonstrated that better oxidation of the antibiotic was obtained with a distance of 5.5 cm where the abatement reached 96 %. However, when the distance increased, the abatement was always higher than 80%.Considering Figure 6, we noted that the quantity of tylosin eliminated decreased with the increase of the volume of the reactional mixture. It is interesting to note that for the same photon flux density and the same initial concentration of pollutant, when the volume increased, the effect of UV rays which decomposed tylosin decreased because the tylosin molecules are brought to browse more long way to reach the surface of the catalyst due to the dilution phenomenon, Matouq et al. (2008) have obtained the same results when they studied the degradation of diazinon using a high frequency of ultrasound wave.

4.3 Effect of initial concentration of tylosin on the photodegradation process

To obtain the optimal initial tylosin concentration, the investigation was carried out in the range of 4.4 10^{-3} mM to 109.2 10^{-3} mM at natural. Figure 7 showed that, for the selected range of antibiotic concentration, the initial concentration of the pollutant did not have a big influence on its elimination. In weak concentrations, from 4.4 10^{-3} mM to 32.7 10^{-3} mM, the abatement of tylosin, after an exposure time to radiations of 7 h, was between 90 and 96 %. When the concentration of tylosin was raised, the efficiency of the TiO2/UV process decreased to 63%. This phenomenon could be explained by the fact that in strong concentrations of tylosin, a part of the photons released by light radiation was intercepted in the tylosin molecules before reaching the surface of the catalyst, hence the absorption of photons by the catalyst decreased, and consequently the degradation was restricted, which was confirmed by several authors (Laoufi et al., 2008; Mangalampalli et al., 2008; Qamar et al., 2006).

The application of the Langmuir-Hinshelwood model for the degradation of tylosin was confirmed by the straight line obtained from the representation of the inverse of the apparent constant depending on the initial substrate concentration as shown in Figure 8. The values of the kinetic constant, the pseudo-first

order constant and the equilibrium constant of adsorption were calculated and were respectively equals to $4.44 \ 10^{-4}$ mol/L.min, $6.53 \ 10^{-3}$ min^{-1} and 14.69 L/mol.
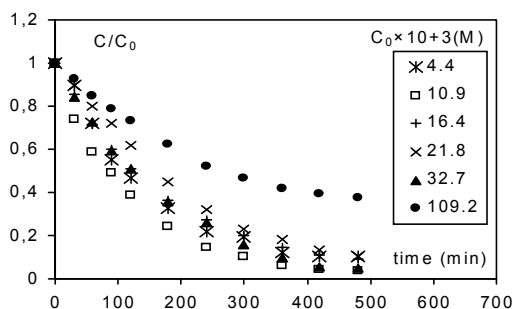

Figure 7: Temporal evolution of tylosin elimination for different initial concentrations
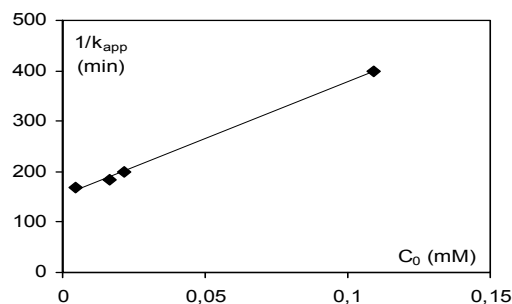

Figure 8: Application of Langmuir-Hinshelwood model

4.4. Effect of pH on tylosin photodegradation

It is important to study the effect of pH on the degradation of organic components. To identify its influence on the efficiency on the photodegradation of tylosine some experiments were conducted using solutions of 10 mg/L of tylosin solution. The pH of the solution was adjusted adding H_2SO_4 or NaOH. We mean by an adjusted pH (A), the pH of a solution to which the addition of acid or the base is made throughout the photocatalytic process, a non adjusted pH (NA) is that regulated just before the switching of the UV lamp, without any addition during the photocatalytic process.
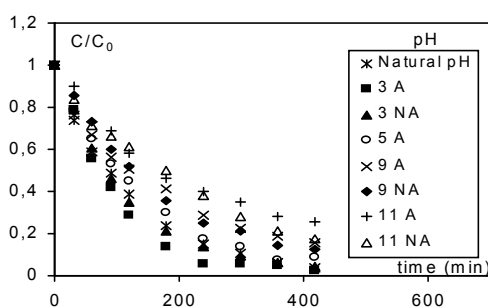

Figure 9: Temporal evolution of tylosin elimination for different pH.
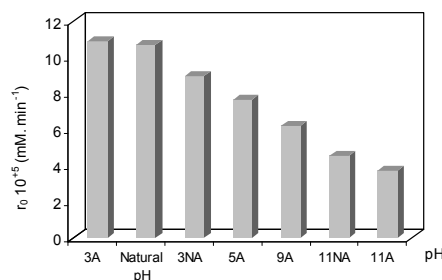

Figure 10: Initial degradation rate of tylosin at different pH levels after 7 h of photodegradation.

Figure (9) showed that regardless solution pH, tylosin has been degraded. The abatement increased from basic pH to acidic pH, this level increased from 74.4 % to 97.6 % when the medium became acid. The degradation was obtained for an adjusted pH equal to 3. It is noted that the movement of pH from level 3 to 11 adjusted caused a variation in the level of conversion of tylosin of 20%. Yang et al, (2008) studied the photocatalysis of paracetamol, results showed that the abatement increased between pH 3.5 and 9.5 but decreased when pH levels increased between 9.5 and 11. Multiple conflicting studies have been published on the effect of pH on the photodegradation of organic compounds (Hoffmann et al., 1995) and many studies have shown that the variations of the degradation rate were rather insignificant on a large variant of pH (Gaya and Abdullah, 2008; Emeline et al., 2000).

5. Conclusion

Degradation of tylosin has been successfully conducted by a photocatalytic process using an immobilized TiO_2 catalyst. It is a promising technique; its advantage is that it does not require separation or filtration prior to analysis compared to a slurry reactor. The effect of different parameters on the photocatalytic activity was studied. The kinetics obey satisfactorily the Langmuir-Hinshelwood model from which kinetic constants were determined.

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