# Photocatalytic Deterioration of Tylosin in an Aqueous Suspension Using UV/TiO$_2$

D. Tassalit[1, 2, *], A. N. Laoufi[1], and F. Bentahar[1]

[1] *Laboratory of Transfer Phenomena, Faculty of Mechanical Engineering and Processes Engineering University of Sciences and Technology Houari Boumedien, Bab Ezzouar, 16111 Algiers, Algeria*
[2] *Solar Equipment Development Unit, UDES, Route Nationale n° 11, BP386, Bou Ismaïl, 42400, Tipaza, Algeria.*

This study was conducted to investigate the efficiency of a photocatalysis oxidation system for pharmaceutical pollutants treatment. Oxidative degradation of tylosin by hydroxyl radicals (OH$^.$) was studied in aqueous medium using suspended forms of TiO$_2$ (Degussa P-25) under UVA (365 nm) irradiation light. The results showed that the degradation of tylosin was affected by many factors. The optimum rate of photodegradation was obtained with a flow rate and a catalyst coating equal to 3.78 mL/s and 0.05 g/L respectively. And the rate of photodegradation was found to increase when the tylosin concentration decreases from 30 to 5 mg/L. In addition, it was shown that the tylosin degradation followed the first-order kinetics and the reaction rate was well fitted with Langmuir–Hinshelwood model. The removal ratio of tylosin was 97% in less than 60 minutes. Thus, the UV/TiO$_2$ photocatalysis process is very efficient and can be suggested for the degradation of tylosin in aqueous solution.

**Keywords:** Advanced Oxidation Techniques, Photocatalysis, TiO$_2$, UV, Tylosin.

## 1. INTRODUCTION

The consumption of pharmaceutical derivatives is in constant increase. We count about 4000 active molecules used to relieve various affections.[1] A big part of these active compounds is excreted and meet in the worn-out waters. Unfortunately, most are not biodegradable and are not eliminated completely by waters purification systems using biologic way.[2–3] Other processes of purification as the ozonolysis or the chlorination drive to the formation of deterioration products whose toxicity is identified well or little known but that meets also in the waters of rivers.[4] The photocatalysis is a technique that already gave its proofs on the deterioration of organic molecules in water.[5–6]

Antibiotics are probably the most successful family of drugs so far developed for improving human health. Besides this fundamental application, antibiotics have also been used for preventing and treating animals and plants infections as well as for promoting growth in animal farming.[7–10] All these applications made antibiotics to be released in large amounts in natural ecosystems.

The residues of these drugs and their metabolites may be accumulated in soil and will disturb the balance of the soil ecosystem. One potential adverse effect is to have harmful impact on some non-target organisms utilizing the excrement.[11, 12] Only in the recent years more attention has been paid to the discharge, presence and potential adverse effects of veterinary drugs in the environment.[13, 14]

There are many reported studies using TiO$_2$ as catalyst in photocatalytic degradation of pharmaceutical pollutants. Perez-Estrada et al studied the decomposition of diclofenac by solar driven photo-Fenton and TiO$_2$ photocatalysis at a pilot plant scale.[15] The TiO$_2$ photocatalytic treatment of lower diclofenac initial concentrations (0.76–9.24 mg·L$^{-1}$) was investigated by Calza et al., using a photocatalyst loading range of 0.1–0.9 g·L$^{-1}$. A complete elimination of diclofenac was achieved after 1 h of irradiation.[16] Photooxidation of paracetamol was conducted in an annular cylindrical reactor In the presence of TiO$_2$ by Liming Yang et al., more than 95% of 2.0 mM paracetamol was degraded within 80 min.[17]

Several studies have demonstrated that ultraviolet (UV) is able to decompose pharmaceuticals by direct photolysis or indirect photolysis through an advanced oxidation process (AOP). Indeed, ketoprofen, diclofenac, ceftiofur, sulfamethoxazole, sulfamonomethoxine, and antipyrine are easily degraded by UV treatment.[18, 19]
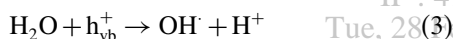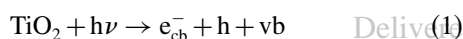
Tylosin, a fermentation-derived macrolide antibiotic, was tested by Jerold et al. to determine its aerobic degradation rate. The results indicate that tylosin residues degrade rapidly in animal excreta.[20] Biodegradation and

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*Author to whom correspondence should be addressed.

biosorption of tetracycline and tylosin were conducted by A. Arane. Tetracycline presented good adsorbability while tylosin remained mostly present in the soluble phase. The Langmuir maximum adsorption capacity was found to be 72 and 7.7 mg g$^{-1}$ for tetracycline and tylosin respectively.[2] Ching and al were estimating the concentrations of tylosin in liquid animal waste to 496 mg/day-animal.[21] The detection limit of tylosin in waste water is 0.01 mg/L.[22]

The photocatalysis consists to radiating a semiconductor, generally, titanium dioxide (TiO$_2$), with the help of an ultraviolet radiance (UV) product naturally via the solar light or artificially with using an UV lamp.[23]

The initial step in the TiO$_2$ mediated photocatalysis reaction is proposed to involve the generation of (e$^-$, h$^+$) pair leading to the formation of hydroxyl radical and super oxide radical anion,[24] (Eqs. (1–3)):

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h + vb \qquad (1)$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\cdot-} \qquad (2)$$

$$H_2O + h_{vb}^+ \rightarrow OH^{\cdot} + H^+ \qquad (3)$$

It has been suggested that the hydroxyl radicals (OH$^{\cdot}$) and superoxide radical anions (O$_2^{\cdot-}$) are the primary oxidizing species in the photocatalytic oxidation processes.[25] These oxidative reactions would result in the degradation of the organic pollutants and the efficiency of the degradation will depend upon the oxygen presence in solution, which determines the efficiency with which the conduction band electrons are scavenged and the (e$^-$h$^+$) recombination is prevented.

The present study was undertaken to evaluate the optimum operating conditions for degradation of tylosin in aqueous solution and the kinetics of degradation by UV/TiO$_2$ photocatalysis.

## 2. EXPERIMENTAL DETAILS

### 2.1. Chemical and Reagents

Tylosin was obtained from commercial tylosin produced by Sinochem Corporation. The semiconductor employed as photocatalyst (Dugussa P25) was obtained from Merck, with a BET surface area of 50 m$^2$/g and an average particle size of 2 $\mu$m. This kind of particle is small enough to be transported by water suspension through or stirring. Solutions were prepared by dissolving requisite quantity of tylosin in distilled water before each Experiment. The pH of the solutions was not adjusted (free pH solution) and the catalyst was introduced in solution of tylosin.

### 2.2. Experimental Installation

Photocatalytic decomposition of tylosin was carried out in a closed circulation system (Fig. 1) by using a helical glass
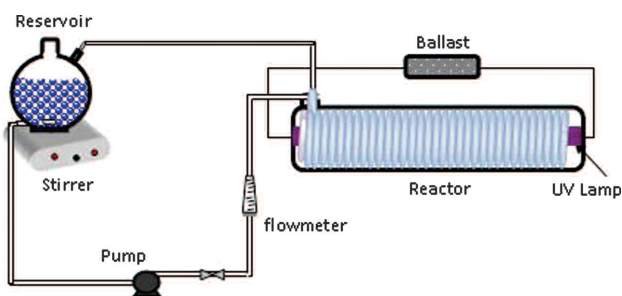


**Fig. 1.** Experimental setup.

reactor with double streamer (double helical glass pipe) of 2 m length and volume of 0.8 L. Reservoir of 2 Litres was used, in which the tylosin solution was introduced. Oxide particles in different amounts were constantly dispersed by a magnetic stirrer. The samples were irradiated from the center of the reactor. A Phillips ATLD 24 W lamp ($\lambda$ max = 365 nm), was used as the UV light source. The suspension was recycled at different flow rates by means of a peristaltic pump.

### 2.3. Experimental Procedure

In order to investigate the effect of various parameters on the photocatalytic degradation such as: Flow rate effect, TiO$_2$ suspension concentration and tylosin concentration, different solutions of tylosin were prepared under different conditions. The solution was stirred before irradiation and also during irradiation. Samples (2 mL) were taken each 5 min periods, from the reservoir by a plastic syringe and then filtered in Millipore disk of 0.45 $\mu$m. The tylosin concentration was determined by measuring the absorption at $\lambda$ = 290 nm, on a UV–vis spectroscopy (U.V-Visible Lambda 25, commercialised by Perkin Elmer Company). A correlation curve between tylosin concentration and the absorption was pre-established.

The photocatalytic processes were carried out in the presence of TiO$_2$ and were supposed pseudo first-order reactions:[26]

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

Where $r$ is the reaction rate and $k$ is the reaction rate constant. For this reason and in order to estimate the kinetics of degradation processes in the presence of TiO$_2$, the following relationship was improved:

$$\ln \frac{C}{C_0} = -kt \qquad (2)$$

## 3. RESULTS AND DISCUSSION

In general, a sensitized photocatalytic oxidation process is one in which a semiconductor upon photon absorption of a suitable energy can act as a photocatalytic substrate by
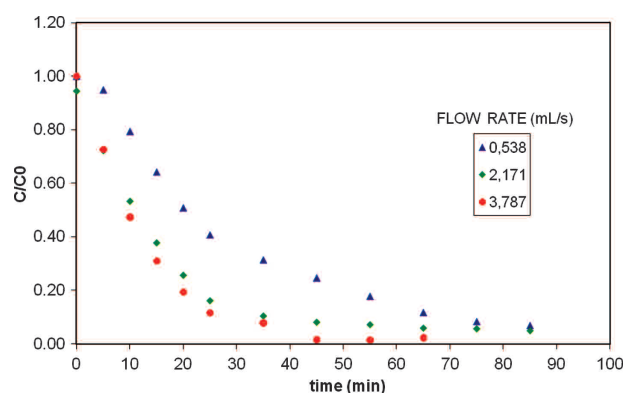
**Fig. 2.** Temporal evolution of the reduced concentration of tylosin for different flow rates, $C_{\text{tylosin}} = 10$ mg/L, $C_{\text{TiO}_2} = 0.2$ g/L.

producing highly reactive radicals that can oxidize organic compounds.

The heterogeneous photocatalysis using UV/TiO$_2$ gave interesting results in treatment of water polluted by tylosin.[27] It is however greatly influenced by a certain number of factors. In the precise case of this survey, to get the most favourable activity, that will permit an optimal deterioration of tylosin, it was thus, necessary to study the influence of the flow, catalyst concentration and initial pollutant concentration.

### 3.1. Effect of the Flow Rate

The survey of the influence of recirculation flow showed that the kinetic rate constants, the times of half reaction and initial rates increase with the increase of the recirculation flow rate (Fig. 2, Table I). Also, the deterioration rate of tylosin depends on the flow rate, it decreases with the reduction of this parameter. The best tylosin conversion rate (97%) has been gotten with a flow rate of 3.787 mL/s.

### 3.2. Influence of the Catalyst (TiO$_2$) Concentration

The concentration of catalyst is a major parameter, which affect the photocatalytic oxidation rate. It's important to find out the optimum loading for efficient removal of tylosin. The effect of catalyst concentration (TiO$_2$) on tylosin photo-oxidation was investigated from 0.05 g/L to 1 g/L at free pH of solution.

Figures 3 and 4 shows that the effect of catalyst concentration (TiO$_2$) is significant. The rates of tylosin

**Table I.** Values of kinetic constants, times of half reaction and initial rates of tylosin deterioration for different flow rates.

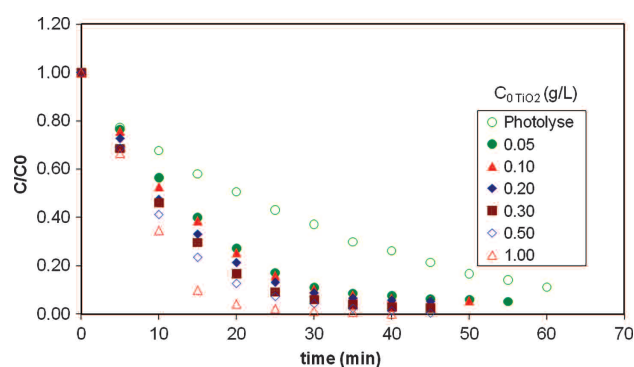| Flow rate (mL/s) | $K$ (min$^{-1}$) | $r_0$ (mg/L·min) | $t_{1/2}$ (min) | $R^2$ |
|---|---|---|---|---|
| 0.538 | 0.0319 | 0.319 | 2.73 | 0.999 |
| 2.171 | 0.0629 | 0.629 | 11.02 | 0.998 |
| 3.787 | 0.0820 | 0.820 | 8.45 | 0.996 |



**Fig. 3.** Temporal evolution of the reduced concentration of tylosin for different concentration of catalysis, $C_{\text{tylosin}} = 10$ mg/L, $Q = 3.787$ mL/s.

deterioration in the presence of TiO$_2$ with different concentrations are very important. At high concentrations of catalyst (0.5 and 1 g/L) the degradation rate of the pollutant can reach the value of 100%. The increase of TiO$_2$ doses during the photocatalytic process generates the augmentation of tylosin exhaustion rate so that an important quantity of active phase (TiO$_2$) can trap more hydroxyl radicals and consequently enhances the elimination of the pollutant.[28] Let's note that a great deal of catalyst inhibits the penetration of U.V light and provoke the catalyst deposition on the reactor streamers.

According to Table II, tylosin degradation follows the pseudo-first order kinetic model. The rate constant increase with the TiO$_2$ concentration and approaches a limit value at 1 g/L of catalyst. In order to avoid the deposition of the catalyst in the reactor and also for economic reasons we have considered in this study the value of 0.05 g/L as an optimal concentration of TiO$_2$.

### 3.3. Influence of Tylosin Initial Concentration

The photocatalytic oxidization of tylosin has been valued in maintaining a flow rate of 3.787 mL/s and differents initial concentrations of pollutant: 5; 10; 20 and 30 mg/L. The obtained results (Fig. 5) show that the deterioration of
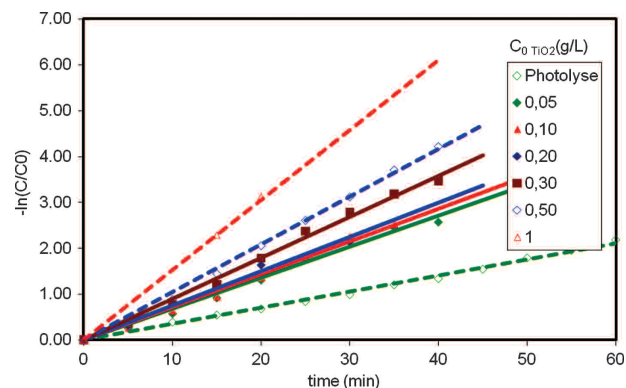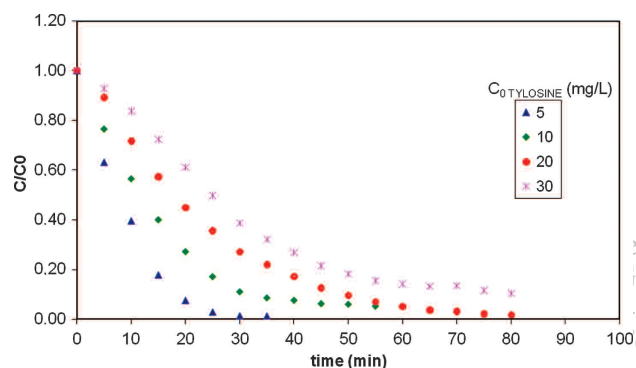


**Fig. 4.** Temporal evolution of $\ln(C/C_0)$, $C_{\text{tylosin}} = 10$ mg/L, $Q = 3.787$ mL/s.

**Table II.** Kinetic constants values, times of half reaction and initial rates of tylosin deterioration for different concentrations of TiO$_2$.

| $C_{TiO_2}$ (g/L) | $K$ (min$^{-1}$) | $r_0$ (mg/L·min) | $t_{1/2}$ (min) | $R^2$ |
|---|---|---|---|---|
| 0.00 | 0.0352 | 0.352 | 19.69 | 0.999 |
| 0.05 | 0.0677 | 0.677 | 10.24 | 0.999 |
| 0.10 | 0.0717 | 0.717 | 9.67 | 0.998 |
| 0.20 | 0.0748 | 0.748 | 9.27 | 0.998 |
| 0.30 | 0.0894 | 0.894 | 7.75 | 0.998 |
| 0.50 | 0.1041 | 1.041 | 6.66 | 0.999 |
| 1.00 | 0.1526 | 1.526 | 4.54 | 0.995 |



**Fig. 5.** Temporal Evolution of reduced concentration of tylosin for different initial concentrations, $Q = 3.787$ mL/s, $C_{TiO_2} = 0.05$ g/L.

**Table III.** kinetic constants Values, times of half reaction and initial rates of deterioration of tylosin for the different initial tylosin concentration.

| $C_{0tylosin}$ | $K$ (min$^{-1}$) | $r_0$ (mg/L·min) | $t_{1/2}$ (min) | $R^2$ |
|---|---|---|---|---|
| 5 | 0.1346 | 0.673 | 5.15 | 0.987 |
| 10 | 0.0667 | 0.667 | 10.39 | 0.998 |
| 20 | 0.0486 | 0.972 | 14.26 | 0.994 |
| 30 | 0.0324 | 0.972 | 21.39 | 0.992 |

tylosin is very fast that its concentration decreases quickly. The rate constant is reversely dependent on the initial concentration of tylosin in the solution: it is the highest for the lowest concentration and decreases with increasing concentration. As mentioned before, the degradation is faster for lower Tylosin initial concentration. The values given in Table III showed that in the case of 5 mg/L of pollutant, the half-life time is four times less than that obtained for 30 mg/L. Other authors have reported similar behavior in the degradation of pentoxifyllin.[29] In all studied cases the deterioration of tylosin was found governed by the pseudo first order kinetics model and the removal rate is superior to 97% for the different initial concentrations of pollutant.

## 4. CONCLUSION

The degradation of tylosin in waste water was investigated by heterogonous photocatalytic processes, in the presence of TiO$_2$ (catalyst) and UV artificial radiation. The treatment was affected by many factors such as flow of solution, pollutant concentration and catalyst concentration. The best results were obtained at a low flow rate of 3.787 mL/s. A catalyst concentration of 0.05 g/L was sufficient to have a total degradation of tylosin in less than 60 minutes. Tylosin removal increased faster when lowering its initial concentration. However, the decomposition yield was the greatest for high initial concentrations. The rate constant varied between 0.1346 min$^{-1}$ for 5 mg/L and 0.0324 min$^{-1}$ for 30 mg/L of tylosin. The reaction kinetics followed the first-order model and was rationalized by a Langmuir-Hinshelwood mechanism. Based on these results, this study confirms that this photocatalytic process might be of interest as a treatment method for wastewater containing tylosin or others recalcitrant pharmaceutical compounds.

## References and Notes

1. S. C. Monteiro, B. Alistair, and A. Boxall, *J. Environmental Contamination and Toxicology* 202, 53 (**2010**).
2. N. Prado, J. Ochoa, and A. Amrane, *J. Process Biochemistry* 44, 1302 (**2009**).
3. P. Saravanan, K. Pakshirajan, and P. Saha, *J. Hydro-Environment Research* 3, 45 (**2009**).
4. C. Wang, Y. Ao, P. Wang, J. Hou, and J. Qian, *J. Applied Surface Science* 25, 227 (**2010**).
5. A. Khan, M. M. Haque, N. A. Mir, M. Muneer, and C. Boxall, *J. Desalination* 261, 169 (**2010**).
6. B. B. Wang, M. H. Cao, Z. J. Tan, L. L. Wang, S. H. Yuan, and J. Chen, *J. Hazardous Materials* 18, 187 (**2010**).
7. M. cManus, P. S. Stockwell, V. O. Sundin, and G. W. Jones, *Rev. Phytopathol.* 40, 443 (**2002**).
8. F. C. Cabello, *Environ Microbiol.* 8, 1137 (**2006**).
9. J. Radjenovic, M. Petrovic, and D. Barcel, *J. Water Res.* 43, 831 (**2009**).
10. C. Zhaoa, H. Denga, Y. Lia, and Z. Liub, *J. Hazardous Materials* 176, 884 (**2010**).
11. H. Y. Yoshimur, S. Endoh, and K. Harada, *Ecol. Indic.* 5, 181 (**2005**).
12. P. K. Jjemba, *Ecotoxicol Environ.* 63, 113 (**2006**).
13. J. Jensen, X. P. Diao, and A. D. Hansen, *J. Environ Pollut.* 148, 514 (**2007**).
14. C. Jin, Q. Chen, R. Sun, Q. Zhou, and J. Liu, *J. Ecotoxicology* 18, 878 (**2009**).
15. P. Estrada, L. A. Maldonado, M. I. Gernjak, W. Aguera, A. Fernandez-Alba, A. R. Ballesteros, and M. M. Malato, *J. Catal Today* 10, 219 (**2005**).
16. P. Calza, V. A. Sakkas, C. Medana, C. Baiocchi, A. Dimou, E. Pelizzetti, and T. Albanis, *J. Appl. Catal. B* 67, 197 (**2006**).
17. L. Yanga, E. Liya Yua, and B. Madhumita Rayb, *J. Water Research* 42, 3480 (**2008**).
18. I. Kim, N. Yamashita, and H. Tanaka, *Hazardous Materials* 166, 1134 (**2009**).
19. M. V. N. Mouamfon, W. Li, S. Lu, Z. N. QiuChen, and K. Lin, *Environnemental Technology* 31, 489 (**2010**).

20. J. S. Teeter and D. Meyerhoff, *Chromatography B* 766, 57 (**2001**).

21. L. T. Angenent, M. Mau, U. Georgec, J. A. Zahn, and L. Raskin, *Water Research* 42, 2377 (**2008**).

22. C. H. Huang, J. E. Renew, K. Pinkston, and D. L. Sedlak, *Water Environment Federation, Atlanta* (**2001**).

23. S. Ahmed, M. G. Rasul, W. N. Martens, R. Brown, and M. A. Hashib, *Desalination Journal* 261, 3 (**2010**).

24. M. Gratzel, Energy Resources through Photochemistry and Catalysis, Academic Press, New York, NY (**1983**).

25. R. W. Mathews, *J. Chem. Soc. Faraday Trans.* 80, 457 (**1984**).

26. D. Dong, P. Li, X. Li, Q. Hao, Y. Zhang, C. Jiaa, and Peng Li, *Hazardous Materials* 174, 859 (**2010**).

27. M. N. Abellan, B. Bayarri, J. Gimenez, and J. Costa, *Appl. Catal. B: Environ.* 74, 233 (**2007**).

28. A. N. Laoufi, D. Tassalit, and F. Bentahar, *Global NEST Journal* 10, 404 (**2008**).

29. M. Magureanu, D. Piroi, N. B. Mandache, and V. David, *Water Research* 44, 3445 (**2010**).

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