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Photocatalytic Degradation of Acetaminophen

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ABSTRACT: The photocatalytic degradation of a common analgesic (acetaminophen) with titanium dioxide irradiated with low energy ultraviolet light (365 nm) was studied in order to determine the effect of several parameters such as catalyst's weight, photochemical effect, and initial concentration. The results indicate that acetaminophen is degraded in the order of 4% by the photochemical effect. The presence of titanium dioxide in optimal amounts increases the rate of reaction and the overall conversion. The kinetic study demonstrated that photocatalytic degradation of acetaminophen follows a pseudo first order reaction rate which could be represented by a model similar to Langmuir-Hinshelwood equation. Accordingly, the results confirmed that the degradation of acetaminophen proceeds even while other intermediate organic products (IOP) are being formed; some of these organic products were identified by High Performance Liquid Chromatography (HPLC). These products (OIP) remain in the solution for a while before being degraded to CO_2. Furthermore, the experimental results indicate that the mineralization of acetaminophen can be described by an overall kinetic rate equation obtained from the experimental values of total organic carbon (TOC).

Key words: Acetaminophen,Titanium dioxide,Total organic carbon

INTRODUCTION

The demand for drinking water has increased in the last years. Unfortunately, availability of quality groundwater resources is getting scarcer. Soil erosion resulting from irrational use of land does not allow the recharge of aquifers. The disposition of agricultural, industrial and domestic residues has polluted the water bodies; this has caused the depletion of drinking water sources. Industrial and agricultural activities have generated a significant number of pollutants which threat both surface and groundwater.

Many polluting substances are highly toxic and difficult to be naturally degraded. Disinfectants and pesticides should have a special consideration since their residues are particularly dangerous for human health and the environment (Moctezuma *et al,* 2003). Therefore, their use, disposal, and treatment are regulated by the different environmental legislations in order to avoid related pollution. Nowadays, medical prescription includes a wide range of therapeutic agents, such as analgesics, antibiotics, anticonceptives, antidepressants, anti-coagulants (Kolpin *et al.,* 2002). The use and disposal of these substances are not regulated by any current environmental legislation, as it is considered that medicines have a low level of toxicity. Furthermore, wastewater contains a small amount of these substances and its concentration rarely exceeds 10 μg/L (Ternes, 1998; Daughton, 2004). For the aforementioned, it is considered that wastewater treatment plants can easily eliminate the active ingredients of medicines. However, most pharmaceutical compounds are dangerous and even lethal for bacteria that degrade organic matter (Wang *et al.,* 2008). Traditional water treatment processes cannot completely eliminate drugs residues and their metabolites. These residues must be eliminated by an oxidation process to avoid the contamination of the land and waters. Diverse studies have revealed the presence of ibuprofen, acetaminophen, aspirin, and carbamazepine in different water bodies (Jones *et al.,* 2002; Huber *et al.*, 2003; Löeffler *et al.,* 2005). Although the concentration of organic compounds was within the limits, the results showed that there is a continuous inflow of these substances. Therefore their concentration cannot be lowered by natural degradation.

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Advanced oxidation processes (AOPs) including heterogeneous photocatalysis have proved to be one of the most effective methods for water treatment (He, 2008). These processes are based on the generation of hydroxyl radicals (•OH) which oxidize a broad range of organic pollutants that could present in water and wastewater (Han *et al.*, 2004; Qamar *et al.,* 2006). A photocatalytic process using semiconductor particles is an emerging technique for the treatment of toxic pollutants (Alfano *et al.,* 2000; Fujishima *et al.,* 2000). Titanium dioxide (TiO_2) is one the most popular and efficient phototocatalysts.

Since there are only a few studies of the photocatalytic degradation of pharmaceutical organic compounds, we have focused on the degradation of acetaminophen to obtain important information about the effect of some operations parameter on the photocatalytic process.

MATERIALS & METHODS

Acetaminophen (98%) was purchased from Aldrich. Titanium dioxide (Degussa P25, 80% anatase and 20% rutile, specific surface area 55 m^2/g) was donated by Degussa Corporation. The mobile phase for HPLC was prepared with a mixture of citric acid and EDTA in water solution (60%) and methanol (40%) (Mallinckrodt C.A). Potassium biphtalate and sodium bicarbonate (Nakalai Tesque) were used as standards for total organic carbon (TOC) analysis. All the reaction mixtures were filtered through a 0.22 µm GV cellulose acetate membrane (Millipore Corp. Bedford, MA) prior to analysis.

Photocatalytic degradation experiments were carried out in a reactor system as described in Moctezuma *et al.* (2003). This system was adapted with a Pyrex glass tube reactor (250 mL) irradiated with four long-wave UV-Vis lamps (λ_{max} = 365 nm, Cole-Parmer E-09815-55). For each set of experiments, 250 mL of an acetaminophen solution were placed inside the glass reactor and mixed with 2 g/L of TiO_2. This slurry was agitated with a magnetic stirrer. Oxygen supply was constant, with a flow of 100 mL/min. Samples were taken at different times to monitor progress of the reaction by different analytical techniques. Acetaminophen was quantified by HPLC with a Waters Chromatographer, model 600 E, equipped with a UV-486 detector. To separate the intermediate organic products, a Nova-Pack Phenil column (60 Å, 4 µm, 150 x 3.9 mm) was used. The mobile phase solution was delivered at a rate of 1 mL/min and the wavelength of detection was set at 242 nm. TOC in each sample was measured with a Shimadzu carbon analyzer model 5000 A. Some of the reaction mixtures were monitored by UV-vis spectroscopy in a Shimadzu UV-2401 PC.

RESULTS & DISCUSSION

Preliminary experiments were carried out to study the photocatalytic degradation de acetaminophen in aqueous solution with 2 g/L of TiO_2, UV light and oxygen flow of 100 mL/min. The composition changes in the reaction mixture were monitored by HPLC and TOC, as shown in Fig. 1. Experimental HPLC results reveal that acetaminophen is quickly oxidized into other organic compounds. TOC results show that the intermediate organic species remain in the solution for several minutes and eventually mineralize into CO_2 and H_2O. The comparing between HPLC and TOC curves shows that the organic intermediate products degrade at a slower rate than acetaminophen.

In order to evaluate the formation and eventual degradation of intermediate compounds formed during the process of photocatalytic degradation reaction

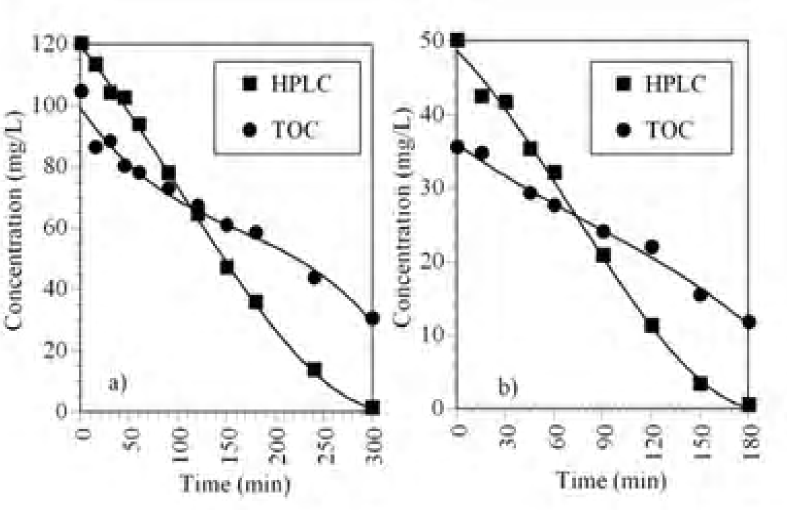

Figure 1. Photocatalytic degradation of acetaminophen in presence of TiO_2, (a) 50 mg/L and (b) 120 mg/L (V = 250 mL, O_2 flow = 100 mL/min, catalysts weight = 2g/L, λ_{max} = 365 nm)

samples were analyzed by UV-vis spectroscopy as shown in Fig. 2. Acetaminophen has a maximum absorption band of 242 nm which matches the C=C bonds of the aromatic ring. This band represents the transition from a fundamental state to a more active one, with the same distribution of electrons but with a slight difference in the vibrational energy. After a certain time of irradiation it was observed that the maximum absorption band decreases as a result of chemical degradation of the aromatic ring of the acetaminophen molecule.

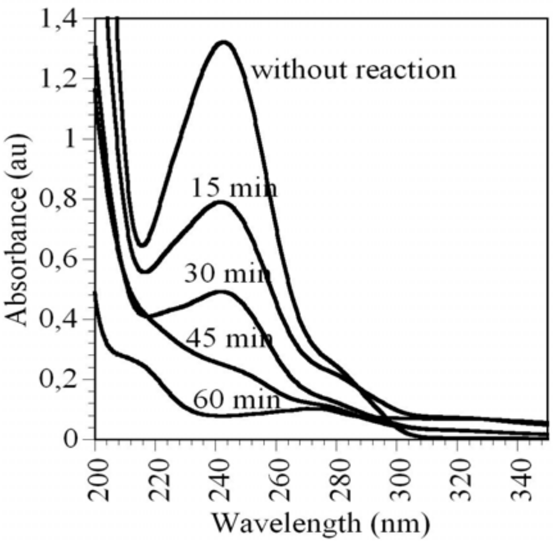

Fig. 2. Photocatalytic degradation of acetaminophen in presence of TiO_2. Samples for UV analysis were taken at different reaction times ($V = 250$ mL, $C_o = 20$ mg/L, O_2 flow = 100 mL/min, catalysts weight = 2g/L, $\lambda_{max} = 365$ nm)

The photocatalytic degradation of organic compounds can follow different pathways depending on the reaction conditions (Leyva et al., 2008), in which a series of organic products are generated and consumed. Intending to elucidate the majority of the intermediate products resulting from the degradation of acetaminophen, a series of experiments at different concentrations of acetaminophen were carried out using HPLC for the analysis.

The photocatalytic degradation of acetaminophen was monitored by HPLC along with appropriate detectors to assess the formation and eventual degradation of some organic intermediates as shown in Fig. 3. Hydroquinone (HQ) and benzoquinone (BQ) were detected in the reaction mixture. These organic compounds were detected during the photochemical and electrochemical oxidation of acetaminophen (Andreozzi *et al.*, 2003; Brillas *et al.*, 2005). Both organic compounds were fully identified and quantified by the co-injection of standards technique during the HPLC analysis. In this research, the maximum concentration of intermediate organic products was detected at 90 minutes into the reaction during the photocatalytic degradation of acetaminophen; the early presence of these compounds is expected as they comprise the basic structure of acetaminophen. The main intermediates HQ and BQ could be degraded by the hydroxyl radical to form hidroxilation products. Based on the experimental results, it was concluded that HQ was generated by the attack of the •OH replacing the acetamide as it was oxidized to oxamic acid through hydroxylation (Yang *et al.*, 2009).

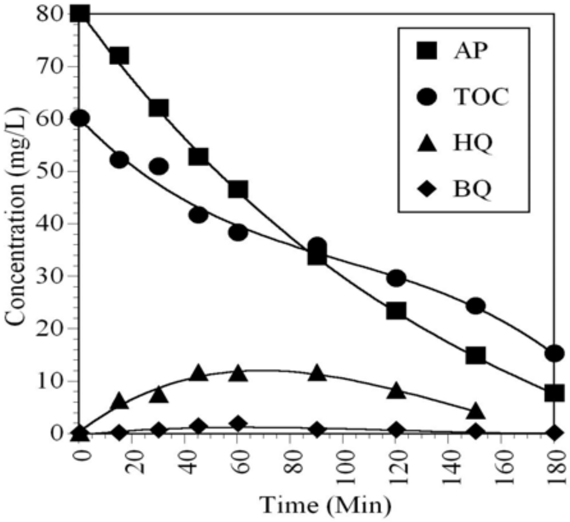

Fig. 3. Formation and disappearance of intermediate organic products during the photocatalytic degradation of acetaminophen in presence of TiO_2. (AP= acetaminophen, TOC=Total organic carbon, HQ= hydroquinone, BQ=benzoquinone, $V = 250$ mL, $C_o = 80$ mg/L, O_2 flow = 100 mL/min, catalysts weight = 2g/L, $\lambda_{max} = 365$ nm)

An aqueous solution of acetaminophen of 40 mg/L, both in presence and absence of TiO_2, was irradiated with four 15 W UV lamps. The role of photocatalytic degradation and the purely photochemical effect on the decomposition of acetaminophen were studied. Figure 4 shows that the photochemical degradation process is accelerated when using the catalyst with a 97% conversion of the initial concentration at 300 minutes; a control experiment showed that degradation of acetaminophen was less than 10% in the absence of catalysts. In both cases, oxygen remained constant with a flow of 100 mL/min for the entire reaction.

The influence of the catalyst's weight on the photocatalytic degradation of acetaminophen was studied. Different TiO_2 weights–ranging from 0.5 to 3 g/L were used. Fig. 5 shows that an increase in the

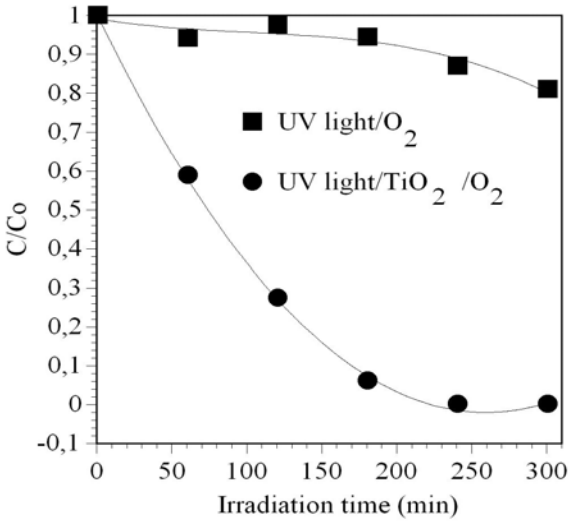

Fig. 4. Effect of the presence of the catalyst in the acetaminophen conversion rate (V = 250 mL, O_2 flow = 100 mL/min, λ_{max} = 365 nm, C_o = 40 mg/L)

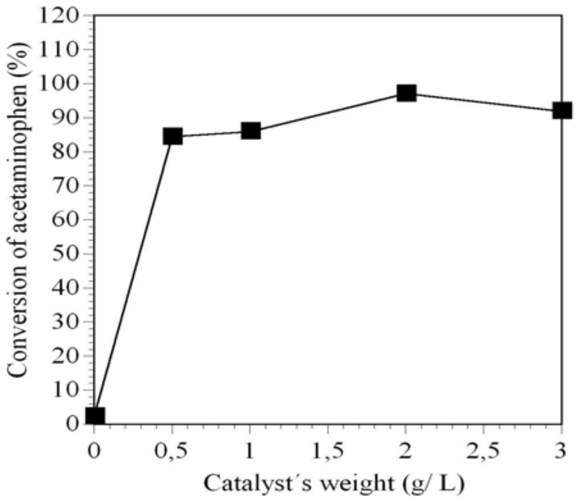

Fig. 5. Effect of the catalyst's weight in the acetaminophen conversion rate (V = 250 mL, C_o = 40 mg/L, O_2 flow = 100 mL/min)

concentration of TiO_2 is reflected in the conversion rate to a limit of 2 g/L. The right amount of catalysts is very important in a photocatalytic reaction (Dalrymple *et al.*, 2007). If a small amount of TiO_2 is used for the photocatalytic experiments, there will not be enough generation of ·OH radicals on the active sites for degradate and mineralize the organic pollutant. On the other hand, if the amount of TiO_2 is larger than needed, the excess of solid particles does not allow the light to penetrate the solution and activate the surface of the catalyst, thus reducing the generation of active sites and the reaction rate.

The photocatalytic degradation of acetaminophen was studied in a range of concentrations from 20–200 mg/L. Fig. 6 shows the concentration profiles of acetaminophen obtained by HPLC. These results reveal that the photocatalytic degradation of acetaminophen follows a pseudo first order rate low regarding the acetaminophen concentration. When the acetaminophen concentration is small, the degradation is faster and the total conversion takes place in less time. On the contrary, when the concentration is high, the degradation requires more time and the kinetic reaction adjusts to a zero-order reaction rate equation. The Langmuir-Hinshelwood equation has been widely used to model the photocatalytic degradation (Kabra *et al.*, 2004; Moctezuma *et al.*, 2006; Dalrymple *et al.*, 2007; Leyva *et al.,* 2008). The general reaction rate equation is represented as follows:

$$-r_0 = -\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C + \sum K_i C_i} \qquad (1)$$

Where:

$-r_0$ = the oxidation rate of the reactant; C = the concentration of the reactant (mg/L), K_1 = the reaction rate (min^{-1}), K_2 = the adsorption coefficient of the reactant onto the TiO_2 particles $(mg/L)^{-1}$

and $\sum K_i C_i$ = absorption term for all organic intermediate products. If we consider t = 0, C = C_0 and the term for the intermediate organic products $\sum K_i C_i = 0$, the equation reduces to the expression:

$$-r_0 = -\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C} \qquad (2)$$

This equation was used to represent the kinetic behavior of the photocatalytic degradation of acetaminophen. The optimization of the values of the kinetics constants $K_1 = 0.093\ min^{-1}$ and $K_2 = 0.065\ (mg/L)^{-1}$, was obtained by the method of non-linear least squares regression, using the Levenberg-Marquardt algorithm.

Fig. 7 shows the prediction of the behavior of the Langmuir-Hinshelwood equation with the experimental data and the calculated values of K_1 and K_2. It is observed that when the concentration of acetaminophen increases to 100 mg/L, the reaction rate value diminishes. This behavior is predictable when there are high concentrations of organic compounds as the reaction system does not produce enough ·OH radicals to mineralize them completely. In order to increase the degradation efficiency, López *et al.* (2003) and Coleman *et al.* (2007) have recommended to use a

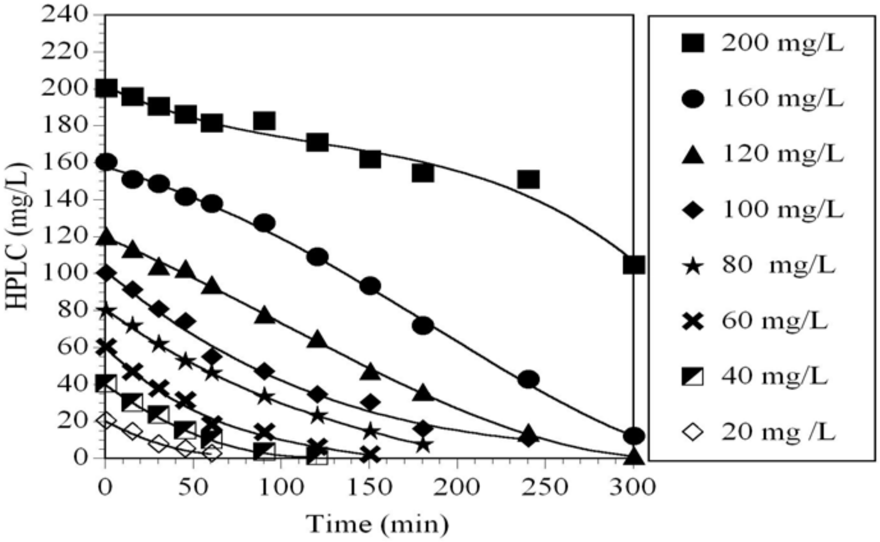

Fig. 6. Photocatalytic degradation of acetaminophen in the presence of TiO_2 ($V = 250$ mL, O_2 flow = 100 mL/min, catalyst's weight= 2g/L, λ_{max}=365 nm)

different advanced oxidation treatments combining the use of O_3, H_2O_2, UV and TiO_2 to favor the formation of ·OH radicals.

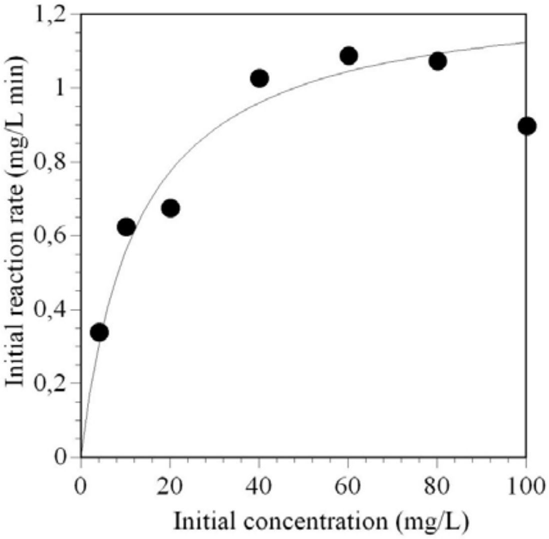

Fig. 7. Initial reaction rate as a function of the initial concentration for the photocatalytic degradation of acetaminophen using TiO_2 as catalyst ($V = 250$ mL, O_2 flow = 100 mL/min, catalyst's weight = 2g/L, λ_{max} = 365 nm)

The oxidation of an organic compound is a complex reaction; in many cases, it goes through complicated routes, leading to the formation of different intermediate compounds before being reduced to CO_2. The results of the analysis of TOC that are shown in Figure 8, and indicate that mineralization reactions are very slow. These information confirmed that acetaminophen is transformed to other organic intermediates products before being mineralized to CO_2. The behavior of acetaminophen mineralization can be predicted by the mathematical method suggested by Zhang and Chuang (1999).

The rate constants $K_1 = 0.05375$ min^{-1} and $K_2 = 0.1824$ min^{-1} were obtained using the experimental data of Figure 8 and applying a non-linear least squares regression that uses the Levenberg-Marquardt algoritm. The results of the prediction model are shown in Fig. 9.

The overall oxidation reaction can be represented by the following equation:

$$AP + O_2 \xrightarrow{K_1} OIP \xrightarrow{K_2} CO_2 + H_2O \qquad (3)$$

Where AP = concentration of acetaminophen, OIP = organic intermediates products, K_1 and K_2 = are the kinetic constants. It is assumed that the reaction in which occurs the oxidation of the organic compounds has two stages.

Complete oxidation

$$AP + O_2 \xrightarrow{K_1} CO_2 + H_2O \qquad (4)$$

Partial oxidation

$$AP + O_2 \xrightarrow{K_2} OIP \qquad (5)$$

Then, equations describing the reaction rate of an organic compound in liquid phase in a batch reactor can be expressed as follows:

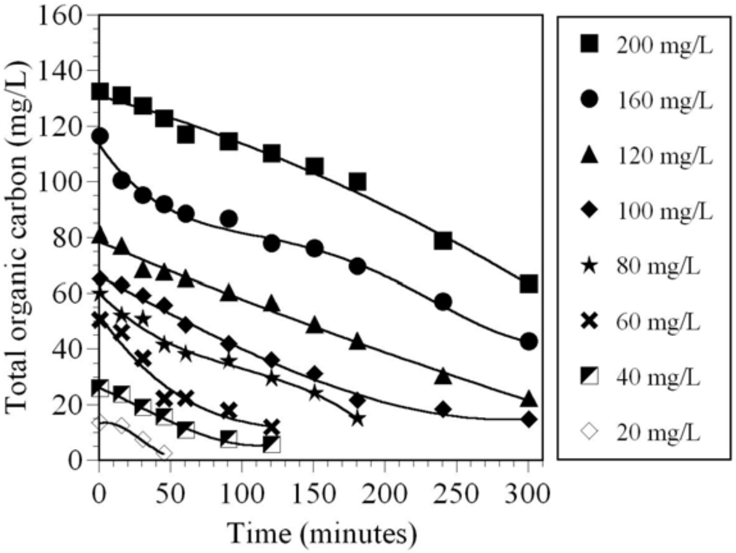

Fig. 8. Photocatalytic degradation of acetaminophen, concentration profiles of Total Organic Carbon (TOC) (V = 250 mL, O_2 flow = 100 mL/min, catalyst's weight = 2g/L, λ_{max} = 365 nm)

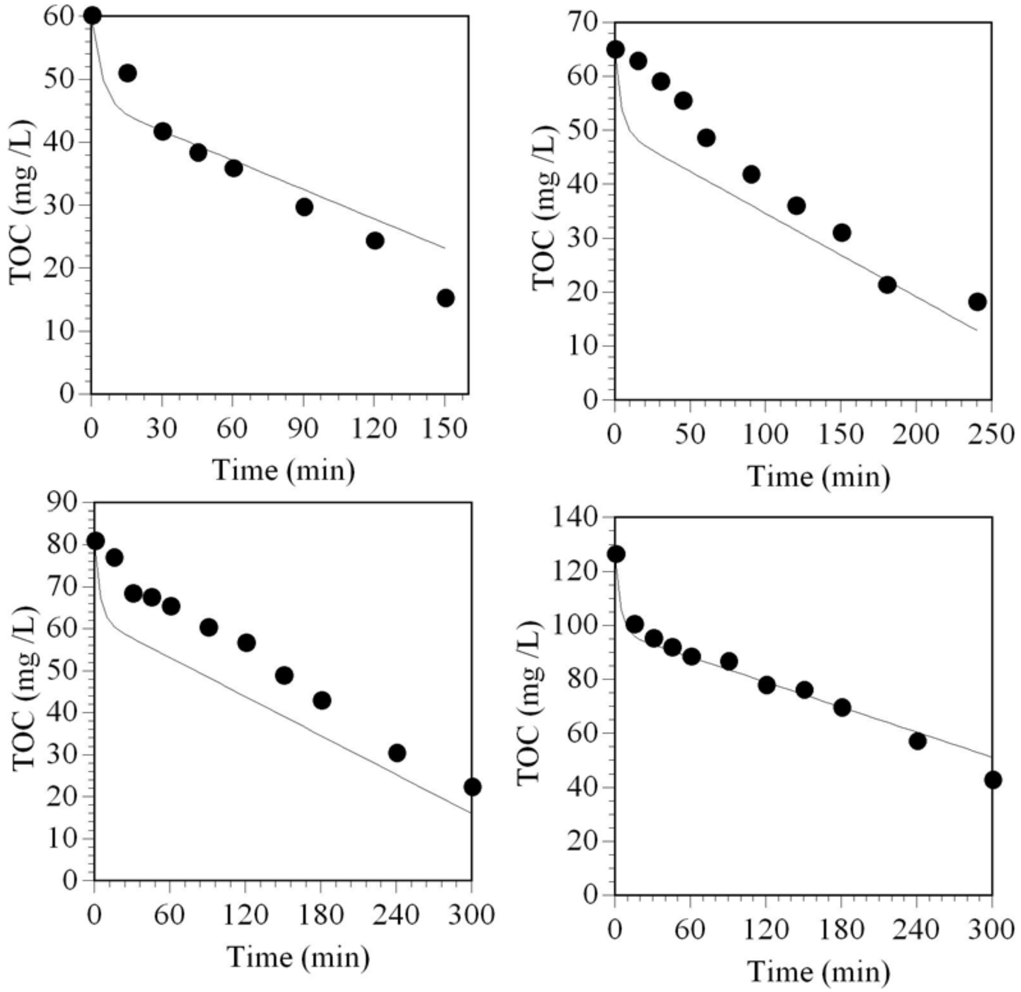

Fig. 9. Prediction of the behavior of TOC as a function of time. (V = 250 mL, O_2 flow = 100 mL/min, catalyst's weight = 2g/L, λ_{max} = 365 nm)

$$-r_{AP} = \frac{-dAP}{dt} = K_1[AP][O_2] + K_2[AP][O_2] \qquad (6)$$

For IOP, it can be obtained:

$$\frac{dOIP}{dt} = K_2[AP][O_2] \qquad (7)$$

$$\ln\left(\frac{[AP_0]}{[AP]}\right) = (K_1 + K_2)t \qquad (8)$$

$$OIP = \frac{[AP]_0 K_2}{K_1 + K_2}\left\{1 - \exp[-(K_1 + K_2)t]\right\} \qquad (9)$$

Results were combined assuming [AP] + [OIP] = [COT], $[AP]_0 = [COT]_0$

$$AP + OIP = COT = \left\{ \begin{array}{l} \frac{K_2}{K_1 + K_2} + \frac{K_1}{K_1 + K_2} \\ \exp[-(K_1 + K_2)t \end{array} \right\} COT_0 \qquad (10)$$

CONCLUSION

The photocatalytic degradation of acetaminophen solutions with TiO_2 catalyst illuminated with UV-light was studied. The results indicated that acetaminophen is not mineralized by UV-light in the absence of catalyst. Nevertheless, acetaminophen can be slowly degraded by direct photolysis in the presence of dissolved oxygen and catalyst. The presence of TiO_2 increases the reaction rate and the overall conversion. The optimum amount of catalyst was 2 g/L. Several reaction intermediates such as hydroquinone and benzoquinone were detected in the reaction mixtures and HPLC analysis. The degradation process follows a pseudo first order degradation behavior, which was represented by the Langmuir-Hinshelwood equation and the mineralization process can be model by the Zhang and Chuang (1999) method.

REFERENCES

Alfano, O. M., Bahnemann, D., Cassano, A. E., Dilert, R. and Goslich, R. (2000). Photocatalysis in water environments using artificial and solar light. Catal. Today, **58 (2)**, 199-230.

Andreozzi, R., Caprio, V., Marotta, R. and Vogna, D. (2003). Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system. Water Res., **37 (5)**, 993-1004.

Brillas, E., Sires, I., Arias, C., Cabot, P. L., Centellas, F., Rodríguez ,R. M. and Garrido, J. A. (2005). Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode. Chemosphere, **58 (4)**, 399-406.

Coleman, H. M., Vimonses, V., Leslie, G. and Amal, R. (2007). Removal of contaminants of concern in water using advanced oxidation techniques. Water Sci. Technol., **55 (12)**, 301-306.

Dalrymple, O., Yeh, D. and Trotz, M. (2007). Removing pharmaceuticals and endocrine disrupting compounds from wastewater by photocatalysis. J. Chem. Technol. Biot., **82 (2)**, pp. 121-134.

Daughton, C. G. (2004). Non-regulated water contaminants: emerging research. Environ. Impact Asses., **24 (7-8)**, 711-732.

Fujishima, A., Rao, T. N. and Tryk, D. A. (2000). Titanium dioxide photocatalysis. J. Photoch. Photobio. C, **1 (1)**,1-21.

Han, W. Y., Zhu, W. P., Zhang, P. Y., Zhang, Y. and Li, L. S. (2004). Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light. Catal. Today, **90 (3-4)**, 319-324.

He, H. Y. (2008). Photo-catalytic Degradation of Methyl Orange in Water on CuS-Cu_2S powders. Int. J. Environ. Res., **2 (1)**, 23-26.

Huber, M. M., Canonica, S., Park, G. Y. and Gunten, U. V. (2003). Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environ. Sci. Technol., **37 (5)**, 1016-1024.

Jones, O. A. H., Voulvoulis, N. and Lester, J. N. (2002). Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. Water Res., **36 (20)**, 5013-5022.

Kabra, K., Chaudhary, R. and Sawhney, R. L. (2004). Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review. Ind. Eng. Chem. Res., **43 (24)**, 7683-7696.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B. and Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. Streams, 1999-2000: a national reconnaissance. Environ. Sci. Technol., **36 (6)**, 1202-1211.

Leyva, E., Montalvo, C., Moctezuma, E. and Leyva, S. (2008). Photocatalytic degradation of pyridine in water solution using ZnO as an alternative catalyst to TiO_2. J. Ceram. Process. Res., **9 (5)**, 455-462.

Löeffler, D., Römbke, J., Meller, M. and Ternes, T. (2005). Environmental fate of pharmaceuticals in water/sediment systems. Environ. Sci.Technol., **39 (14)**, 5209-5218.

López, A., Bozzi, A., Mascolo, G. and Kiwi, J. (2003). Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution. J. Photoch. Photobio. A, **156 (1-3)**, 121-126.

Moctezuma, E., Zamarripa, H. and Leyva, E. (2003). Degradación fotocatalítica de soluciones de alta concentración de Paraquat. Rev. Int. Contam. Ambien., **19 (3)**, 117-125.

Moctezuma, E., González, R., Zamarripa, H., Palestino, G. and Oros, S. (2006). Kinetic studies of the photocatalytic degradation of the herbicide Paraquat. J. Environ. Eng. Manage., **16 (5)**, 343-349.

Qamar, M., Munner, M. and Bahnemann, D. (2006). Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueos suspensions of titanium dioxide. J. Environ. Manage., **80 (2)**, 99-106.

Ternes, T. A, (1998). Occurrence of drugs in German sewage treatment plants and rivers. Water Res., **32 (11)**, 3245-3260.

Wang, S., Holzem, R. M. and Gunsch, C. K. (2008). Effects of pharmaceutically active compounds on a mixed microbial community originating from a municipal wasterwater treatment plant. Environ. Sci. Technol., **42 (4)**, 1091-1095.

Yang, L., Yu, L., and Ray, M. (2009). Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms. Environ. Sci. Technol., **43 (2)**, 460-465.

Zhang, Q. and Chuang, K. T. (1999). Lumped kinetic model for catalytic wet oxidation organic compounds in industrial wastewater. AICHE J., **45 (1)**, 145-150.