ISSN : 0974 - 7532 Volume 6 Issue 12

Trade Science Inc.

Research & Reviews in

BioSciences

Regular Paper

RRBS, 6(12), 2012 [378-384]

Antidiabetic degradation by photocatalysis in aqueous systems on TiO_2 powders

Nacera Yeddou Mezenner*, Amel Hamadi

Laboratory of Chemical Engineering, Faculty of Mechanical and Chemical Engineering University of Sciences and Technology Houari-Boumediene, USTHB, BP 32 El Alia, Bab Ezzouar 16111, Algiers, (ALGERIA)

E-mail : yeddouna@yahoo.fr

ABSTRACT

The photocatalytic oxidation of metformin has been investigated at room temperature in a dynamic photoreactor with system UV/TiO_2 under UVA (=365nm). The effect of various factors, such as photocatalyst dosage, initial substrate concentration, solution pH and co-existing inorganic ions ($H_2PO_4^-$, NO_3^-) and pharmaceutical compound (Paracetamol) on the photocatalytic degradation of metformin was investigated. The experimental results indicate that the optimal pH for metformin elimination is about 8. The optimum catalyst concentration was found equal to 0.5 g/L, under optimal conditions, the extent of photocatalytic degradation was 91% after 135 min. The removal efficiency decreased from 91% to 87.1% and 76.07%, for metformin alone, in the presence of $H_2PO_4^-$ and NO_3^- respectively. The results indicated that the photocatalytic degradation of metformin followed the pseudo-first-order kinetics and the apparent first order rate constant (k_{app}) decreases with the increasing of the initial concentration of metformin.

KEYWORDS

Metformin;
Photodegradation;
Pseudo-first-order;
Inorganic ions.

INTRODUCTION

Most of the active pharmaceuticals ingredients administered to patients are excreted either as metabolites or as the unchanged parent compounds[1]. Pharmaceutical compounds have recently been detected in sewage effluents, surface and groundwater[2,3]. The persistence of their residues in surface waters is of great concern in particular because of their potential impact on ecosystem and public health[4]. Antidiabetics are also released in the environment through urban wastewater treatment plant's discharges[5]. Metformin originally sold as glucophage is an oral antidiabetic drug in the biguanide class. It is the first-line drug of choice for the treatment of diabetes mellitus type II[6]. In humans, metformin is not metabolized and its elimination only occurs via the kidneys[7]. Over the last decades, a great deal of interest has been focused on the photodegradation of Pharmaceutical compounds present in water and wastewaters with application of TiO_2 as photocatalyst. Reaction mechanisms of photocatalytic processes have been discussed extensively in the literature[8].

In polluted waters, organic matter and inorganic ions mixture are prevalent. However, little attention has been paid to systematically examine the effect of the presence of second reactant on photodegradation in contrast to the effect of various operating parameters. In

this context, the objectives of this work were to preliminarily investigate the photocatalytic degradation of metformin, and to examine the potential interference of inorganic anions (NO_3^- and $H_2PO_4^-$) and pharmaceutical substance (Paracetamol) on photodegradation of metformin. To the best of our knowledge, this is the first study that includes a systematic examination of the various parameters that affect the photo-oxidation process of metformin in a dynamic photoreactor. In the last few years, a large number of publications have appeared about the photocatalytic reactor configurations. Examples of these reactors include cylindrical photoreactor[9], helical photorector[10,11], spinning disc reactor[12] and labyrinth flow photoreactor[13]. In our study, the photoreactor is in spiral form and all of catalyst can be illuminated.

MATERIALS AND METHODS

Chemicals

Metformin (Figure 1) and Paracetamol are obtained from SAIDAL complex (Algiers). The photocatlyst isTiO_2 (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca. 55 m^2/ g) is supplied by Degussa. De-ionized water is used throughout this study.

All other chemicals used in our experiments are of analytical grade.

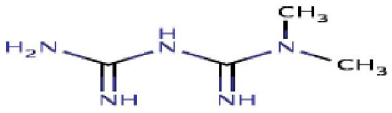

Figure 1 : Molecular structure of metformin.

Procedure and analysis

Photocatalytic degradation of metformin is performed in a closed circulation system at room temperature (25°C) (Figure 2). The photoreactor has a spiral form and is made from Duran glass. The inner diameter and the apparent length are 6.4 and 400 mm respectively. The irradiated volume of the reactor is 200 mL and total volume of 2500 mL of pharmaceutical solution was recirculated using a peristaltic pump. Illumination is achieved by a high-pressure mercury lamp (Philips PK 15 W, 365 nm) placed on the bottom (3 cm) of the photoreactor. The solution was stirred before irradiation and also during irradiation. Samples of 3 mL are collected at regular times and filtered through 0.45 µm millipores discs to remove TiO_2 powder prior to analysis. The concentration is monitored by measuring the absorbance at λ_{max}=233 nm, using a Perkin-Elmer UV-VIS Spectrophotometer. The indicated absorbance is proportional to the Beer-Lambert law in the range of studied metformin concentrations.

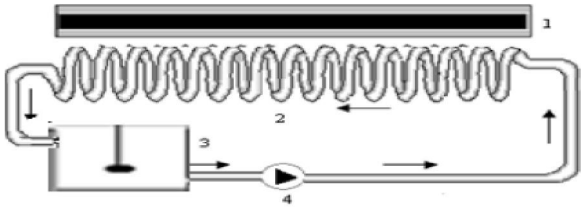

Figure 2 : Experimental system 1: UV lamp; 2: photoréactor; 3: liquid reservoir; 4: pump.

RESULTS AND DISCUSSION

TiO_2 has received a great deal of attention due to its chemical stability, non-toxicity, and low cost[14]. There are many reported studies using TiO_2 as photocatalyst in photocatalytic degradation of pharmaceutical. pollutants. however, photocatalytic degradation is strongly influenced by various parameters In this context, the influence of some experimental parameters as initial concentration of metformin (5-35 mg/L), catalyst-loading (0.2-0.5 g/L), pH (5.4-8), inorganic anions such as NO_3^- and H_2PO4^- and pharmaceutical compound (Paracetamol) is investigated. In accordance with the reported articles[15,16], the kinetic of the photocatalytic degradation rate of most organic compounds is described by pseudo-first order kinetics according to the following equation:

$$\mathbf{Ln\left(\frac{C}{C_0}\right) = -ka_{pp}t} \qquad \mathbf{(1)}$$

Where k_{app} (min^{-1}) is the apparent rate constant of the photocatalytic degradation.

Half- lives $t_{1/2}$ are calculated using Eq. (1) by replacing C with $C_0/2$

$$\mathbf{t_{\frac{1}{2}} = \frac{Ln2}{K_{app}} = \frac{0.6931}{K_{app}}} \qquad \mathbf{(2)}$$

Linear plots of Ln (C/C_0) *versus* time are obtained. For our experimental conditions, data are in good agreement with a pseudo-first order reaction. The results are

Regular Paper

listed in TABLES 1 and 2.

Effect of TiO_2 concentration

The catalyst dosage as an important parameter has been extensively studied in many photocatalytic reactions suggesting that the optimal TiO_2 varies from 0.1 to 5g/L[8]. Hence, the effect of TiO_2 dosage on the photodegradation of metformin was investigated by employing different concentrations of TiO_2 varying from 0.2 to 0.5 g/L and at 5mg/L initial substrate concentration (Figure 3).

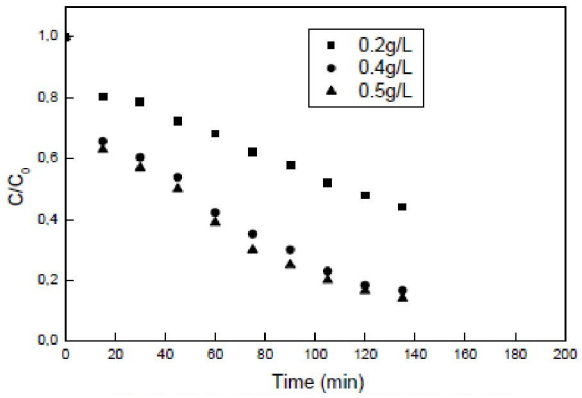

Figure 3 : Photocatalytic degradation of metformin at different TIO2 concentrations (C0 = 5mg/L; pH =8).

TABLE 1 : Photodegradation of metformin in single system

	k_{app} (min^{-1})	r_0 (mg/ L. min)	$t_{1/2}$ (min)	Removal (%)
C_0 (mg/L)				
5	1.44×10^{-2}	7.21×10^{-2}	48.06	91
8	1.14×10^{-2}	$9{,}11 \times 10^{-2}$	60.85	83.7
15	0.76×10^{-2}	$11{,}43 \times 10^{-2}$	90.96	71.63
20	0.64×10^{-2}	12.88×10^{-2}	107.62	66.77
35	0.50×10^{-2}	17.60×10^{-2}	137.8	53.8
TiO_2(g/L)				
0.2	0.63×10^{-2}	$3{,}15 \times 10^{-2}$	110.06	66.77
0.4	1.34×10^{-2}	$6{,}12 \times 10^{-2}$	56.58	87.09
0.5	1.44×10^{-2}	7.21×10^{-2}	48.06	91.00
pH				
5.4	0.82×10^{-2}	$4{,}12 \times 10^{-2}$	84.01	75.5
6.7	1.23×10^{-2}	$6{,}13 \times 10^{-2}$	56.48	88
8.0	1.44×10^{-2}	7.21×10^{-2}	48.06	91

In the absence of TiO_2, no significant decrease in the concentration of metformin is observed (<10%) under UV. Thus, degradation of this antidiabetic is exclusively due to photocatalytic processes via the formation of hydroxyl radicals generated at the surface of the semi conductor 2 (Daneshvar et al. 2003)

As expected, the apparent rate constant (k_{app}) is found to increase with the increasing concentration of TiO_2 (Figure 4). This enhancement is due to the increase of the number of active sites with the semi conductor[17].

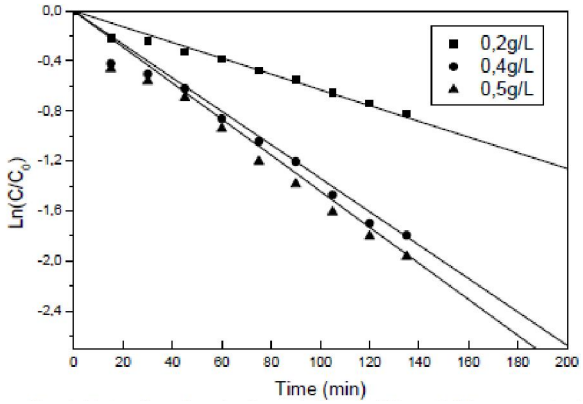

Figure 4 : Rate of metformin degradation at different TIO2 concentrations (C0 = 5mg/L; pH =8).

The dosage of TiO_2 reaches an optimum value (0.5g/L), after which there is no marked increase in the reaction efficiency (TABLE 1).

Effect of metformin concentration

Experiments are carried out varying the initial substrate concentration in the range 5-35mg/L at 0.5 g/L catalyst loading and pH solution of 8. The results are shown in Figure 5 and 6. Evidently, the amounts of metformin degraded increase with increasing initial concentration; however, an increase in the concentration of metformin from 5 to 35mg/L decreases the photodegradation rate constant from 1.44 10^{-2} to $0.5x10^{-2}$ min^{-1} (TABLE 1). Therefore, a decrease in the intensity of light reaching the TiO_2 surface will cause a decrease in the value of k_{app} indeed, at high metformin concentration; the photons are absorbed by the substrate molecules in aqueous solution rather than the semiconductor particles. These results indicate that the photocatalytic degradation process is quite promising at lower substrate concentrations.

The limited number of surface sites on TiO_2 particles may control photodegradation. For example, 91 and 53.8% of metformin are photodegraded within 180 min, when metformin initial concentration increases from 5 to 35mg/L respectively. As the photoreactivity of metformin is low in this case, the result is a decreased efficiency of metformin degradation. Similar results have

been reported concerning the photocatalytic oxidation of others pollutants[18].

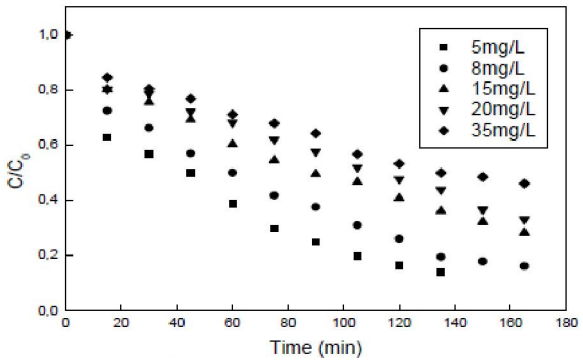

Figure 5 : Photocatalytic degradation of metformin in the TiO2 suspension with different initial concentrations (TiO2 loading =0.5g/L , pH =8).

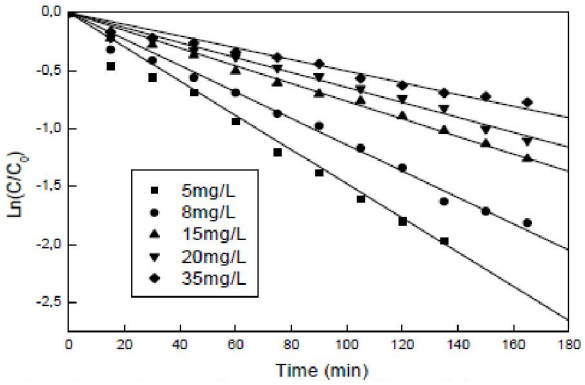

Figure 6 : Rate of metformin degradation at different initial concentrations (TiO2=0.5 g/L; pH =8).

pH effect

In the photocatalytic process, pH can influence the degradation rates. It was observed that the rate constant increases slightly with increasing pH up to 8 (Figures 7 and 8). This can be attributed to enhanced formation of ·OH, because at high pH more hydroxide ions available on TiO_2 surface can be easily oxidized and form more ·OH, which consequently increases the efficiency of metformin degradation (Figure 8). The zero point charge (pHzpc) of TiO_2 is 6.25 1 (yang 2008) and so its surface is predominately positively charged below pHzpc (i.e. $TiO2+H^+ \leftrightarrow TiOH_2^+$) and negatively charged above Pzpc (i.e., $TiOH + OH^- \leftrightarrow TiO^- + H_2O$). The pKa value of metformin is about 11.5[19], so metformin is mostly protoned at pH=8 or below. Under an acidic condition (pH 5.4), the protonated metformin is difficult to adsorb onto such small possibilities of contacts with metformin.

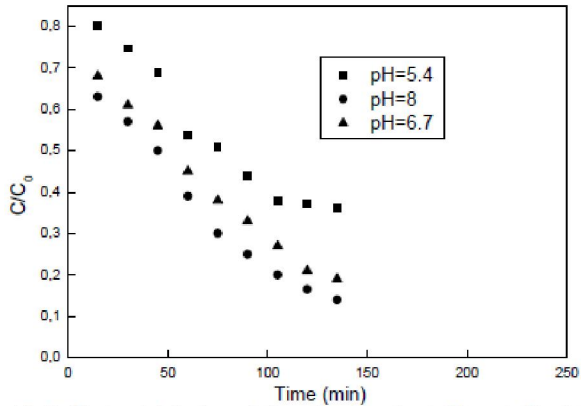

Figure 7 : Photocatalytic degradation of metformin at different pH solutions (C0 = 5mg/L, TIO2 =0.5 g/L).

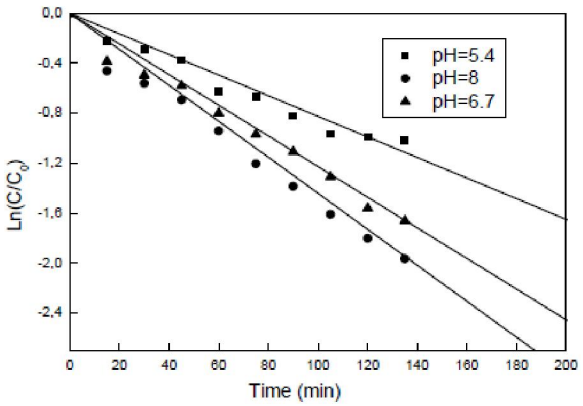

Figure 8 : Rate of metformin degradation at different solutions pH (C0 = 5mg/L; TiO2 =,0.5g/L).

Effect of co- existing inorganic anions

Surface waters, wastewaters contain not only organic contaminants but also considerable amount of inorganic ions. These ions change the ionic strength of medium and thus affect catalytic activity of the photocatalyst. The effect of the presence of dissolved inorganic ions such as NaH_2PO_4, and $NaNO_3$ salts on the photocatalytic degradation rate of metformin was investigated (Figure 9). The same amount (5mg/l) of these salts is used. Figure 10. Shows the effect of anions on the photocatalytic degradation rate of metformin. The parameters k_{app} and initial rate of degradation process are shown in TABLE 2. The removal efficiency decreased from 91 % to 87.1% and 76.07%, for metformin alone, in the presence of $H_2PO_4^-$ and NO_3^- respectively. It is observed that NO_3 exhibited the strongest inhibition effect. These substances may compete for the active sites on the TiO_2 surface then, decrease the degradation rate of the studied molecule. Also, inhibition effects of NO_3^-, $H_2PO_4^-$ can be explained as the

Regular Paper

reaction of hydroxyl radical (OH.) and positive holes (h+) with these anions[20].

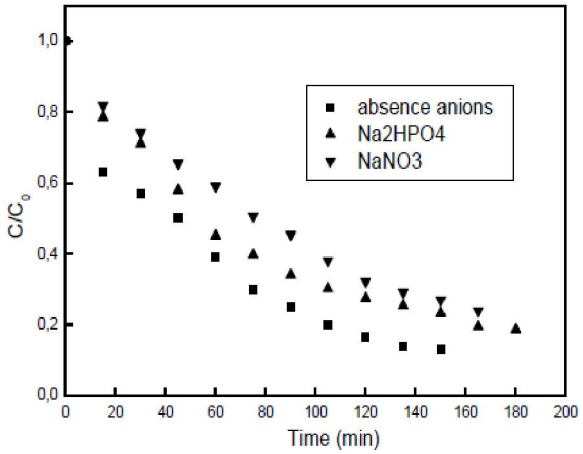

Figure 9 : Effect of anionic ions on the photocatalytic degradation of metformin in the TiO2 suspension (TiO2 loading = 0.5g/L, pH =8).

TABLE 2 : Effect of paracetamol and anionic ions on photocatalytic degradation of metformin (5mg/L) and degradation of paracetamol

	k_{app} (min^{-1})	r_0 (mg/ L min)	$t_{1/2}$ (min)	Removal (%)
Photocatalytic degradation of metformin				
In the presenceof anionic ions (5mg/L)				
NaH_2PO4	1.03×10^{-2}	5.15×10^{-2}	67.22	81.3
$NaNO_3$	0.89×10^{-2}	4.48×10^{-2}	77.35	76.07
In the presence of paracetamol (mg/L)				
Paracetamol (mg/L)				
5	1.28×10^{-2}	6.41×10^{-2}	54.06	87.15
10	1.08×10^{-2}	5.39×10^{-2}	64.23	81.73
In the presence of paracetamol and $NO3^-$ (5mg/L)				
Paracetamol (mg/L)				
5	0.72×10^{-2}	3.61×10^{-2}	95.86	68.5
10	0.53×10^{-2}	2.67×10^{-2}	129.79	60.9
Degradation of paracetamol in binary system (paracetamol/metformin)				
Paracetamol (mg/L)				
5	1.75×10^{-2}	8.77×10^{-2}	39.49	94.49

Effect of co- existing NO_3^- and pharmaceutical compound

The co-existing pharmaceutical compound on the metformin degradation efficiency is investigated, as shown in figure 11, paracetamol was selected as co-existing compound, since it is one of the common analgesic and antipyretic drug used as pain relief and according to Swerdlow[21], paracetamol is excreted from the body during therapeutic use and is detected in sewage treatment plant effluents as well as in surface waters. Different concentrations of paracetamol (5 mg/L and 10 mg/L) are added into metformin solutions (5mg/L) respectively, and the results are reported in TABLE 2. It is observed that the metformin photodegradation is restrained with the addition of paracetamol (Figure 12). Also, according to the results shown in figures 13 and 14, it can be seen that the paracetamol photodegradation occurs faster than metformin photodegradation. As shown in TABLE 2, 94.49% of paracetamol is degraded within 180 min. It is inevitable that paracetamol competed with metformin for the avaible photons. Therefore, with increasing paracetamol concentration, the photons consumed by paracetamol increased, and the photocatalytic degradation efficiency for metformin decreased from 87.15 to 81.73% with an increase in the concentration of paracetamol from 5 to 10 mg/L (TABLE 2). This phenomenon means that hydroxyl free radicals also attacked paracetamol. On the other hand, As NO_3^- has a strong inhibitive effect on the photodegradation of metformin, the effect of paracetamol on the metformin photodegradation was investigated in the presence of this anion (Figures 15 and 16). When NO_3^- (5mg/L) was added into the solution containing paracetamol of 5mg/L and metformin (5mg/L), the photodegradation of metformin decreased from 87.15 to 68.5% after 180 min irradiation. Similar inhibitive effect of NO_3^- is observed in the solution containing paracetamol of 10 mg/L.

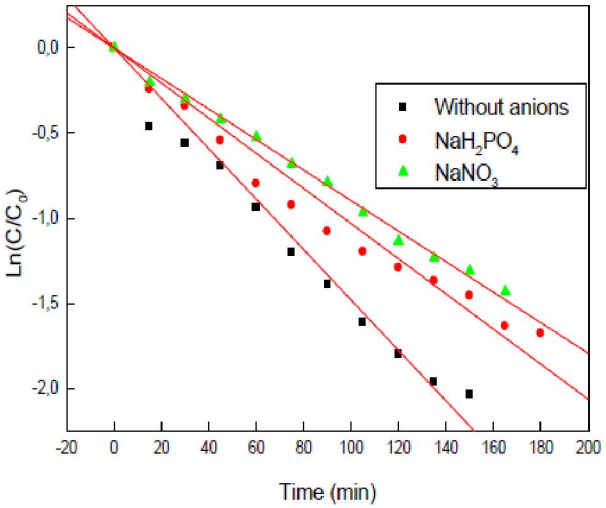

Figure 10 : Effect of anionic ions on the rate of metformin degradation (C0 = 5mg/L; pH =0.5g/L).

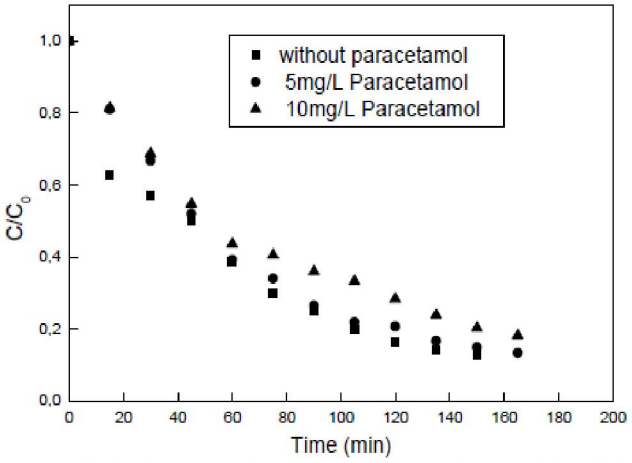

Figure 11 : Effect of paracetamol initial concentration on photocatalytic degradation of metformin (C0=5mg/L, TiO2=0.5g/L, pH=8).

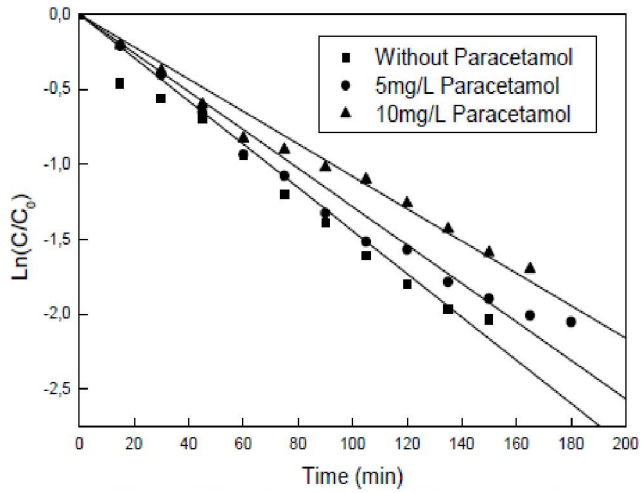

Figure 12 : Effect of paracetamol initial concentration on the rate of metformin degradation at different TIO2 concentrations (C0 = 5mg/L; pH =8, TiO2= 0.5g/L).

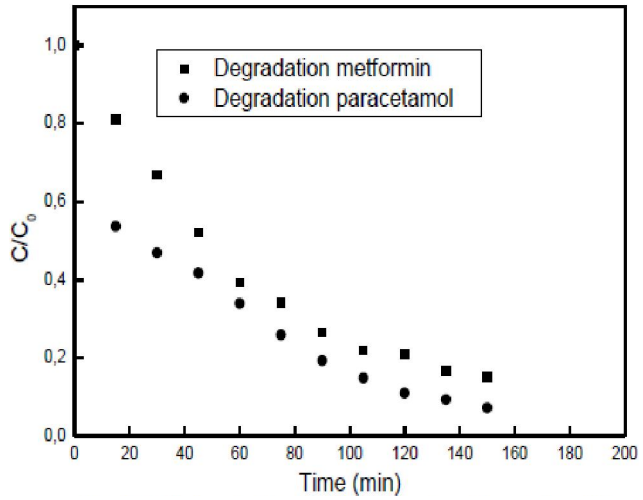

Figure 13 : Photocatalytic degradation of metformin(5mg/L) and paracetamol (5mg/L) (TiO2=0.5g/L, pH= 8).

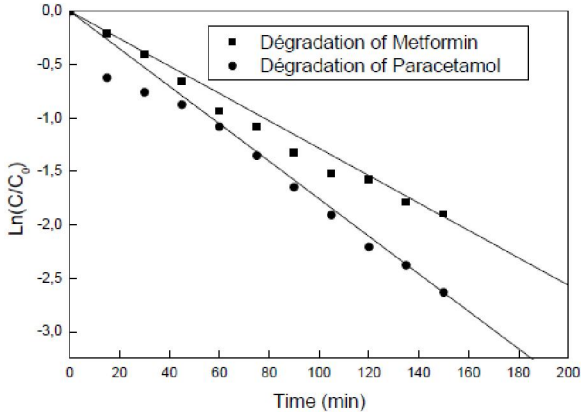

Figure 14 : Photocatalytic degradation of metformin and paracetamol in binary system C0=5mg/l, pH= 8 and TiO2=0.5g/L).

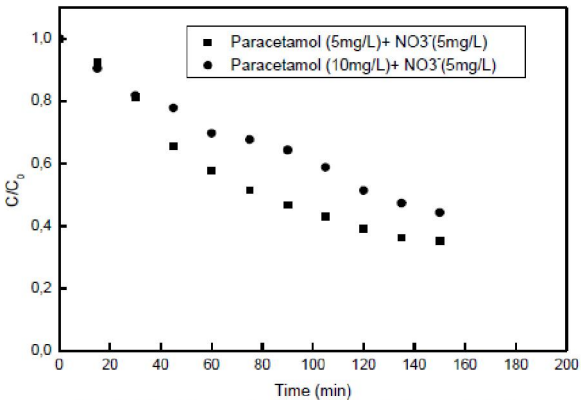

Figure 15 : Effect of paracetamol initial concentration and nitrates on photocatalytic degradation of metformin (C0 = 5mg/L; pH =8, and TiO2=0.5g/L).

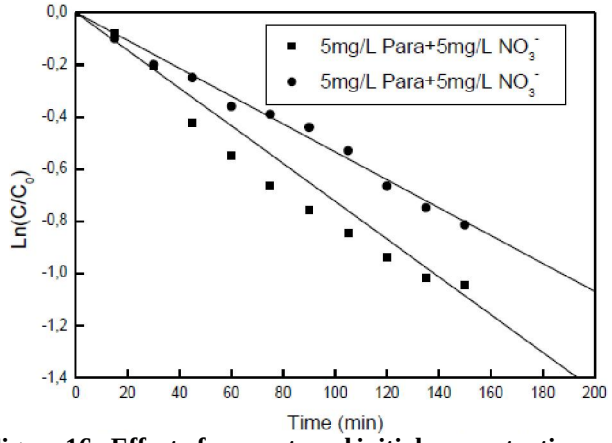

Figure 16 : Effect of paracetamol initial concentration and nitrates on the rate of metformin (C0 = 5mg/L; pH =8, and TiO2=0.5 g/L).

CONCLUSION

The performance of a dynamic photoreactor for the photocatalytic oxidation of metformin depends on

Regular Paper

the operating conditions employed such as the concentration of TiO_2, initial substrate concentration, solution pH, and co-existing anionic ions ($H_2PO_4^-$, NO_3^-) and pharmaceutical compound (Paracetamol). The main conclusions drawn from this study are summarized as follows:

- The rate constants decrease with an increase in the initial concentration of metformin.
- The optimal loading of TiO_2 is found to be 0.5 g/L.
- An optimal pH value was found to be equal to 8.
- The photocatalytic degradation follows the pseudo first kinetic model.
- NO_3^- exhibited the strongest inhibition on photocatalytic degradation of metformin.
- The photocatalytic degradation efficiency for metformin decreased from 87.15 to 81.73% with an increase in the concentration of paracetamol from 5 to 10 mg/L

REFERENCES

[1] H.Yang, L.Guiying, A.Taichen, G.Yanpeng, F.Jiamo; Catal.Today, **153**, 200 **(2010)**.

[2] R.Andreozzi, M.Raffaele, M.R.Nicklas; Chemosphere, **50**, 1319 **(2003)**.

[3] T.E.Doll, F.H.Frimmel; Chemosphere, **52**, 1757 **(2003)**.

[4] G.M.Lalumera, D.Calamari, D.Galli, P.Castiglioni, S.Crosa, R.Fanelli; Chemosphere **54**, 661 **(2004)**.

[5] M.Scheurer, F.Sacher, H.Brauch; Analytical & Bioanalytical Chemistry, **394**, 1585 **(2009)**.

[6] M.L.Reitman, E.E.Schadt; J.Clin.Invest., **117**, 1226 **(2007)**.

[7] P.J.Pentikainen, P.J.Neuvonen, A.Penttila; Eur.J.Clin.Pharmacol., **16**, 195 **(1979)**.

[8] N.Daneshvar, D.Salari, A.R.Khataee; J.Photochem.Photobiol., **157**, 111 **(2003)**.

[9] S.Horikoshi, N.Watanabe, H.Onishi, H.Hidaka, N.Serpone; Appl.Catal.B: Environ., **37**, 117 **(2002)**.

[10] N.A.Laoufi, D.Tassalit, F.Bentahar; Global Nest J., **10**, 404 **(2008)**.

[11] D.Tassalit, A.N.Laoufi, F.Bentahar; Sci.Adv.Mater., **3**, 944 **(2011)**.

[12] H.C.Yatmaz, C.Wallis, C.R.Howarth; Chemosphere, **42**, 397 **(2001)**.

[13] S.Mozia, M.Tomaszewska, W.Morawski; Appl.Catal.B: Environ., **59**, 155 **(2005)**.

[14] L.Yang, L.E.Yu, M.B.Ray; Water Res., **42**, 3480 **(2008)**.

[15] C.Liu, Z.Qiang, F.Tian, T.Zhang; Chemosphere, **76**, 609 **(2009)**.

[16] X.Zhua, J.Jinlong Zhang, F.Chena; Chemosphere, **78**, 1350 **(2010)**.

[17] R.Zouaghi, A.Zertal, B.David, S.Guittonneau; J.Water Sc., **20**, 163 **(2007)**.

[18] T.Velegraki, D.Mantzavinos; Chem.Eng.J., **140**, 15 **(2008)**.

[19] C.Hu, T.Yuchao, L.Lanyu, H.Zhengping, W.Yizhong, T.Hongxioj; Chem.Technol.Biotechnol., **79**, 247 **(2004)**.

[20] N.C.Merbel, G.Wilkens, S.Fowles, B.Oosterhuis, J.H.G.Jonkman; Chromatographia, **47**, 542 **(1998)**.

[21] M.Swerdlow; Pharmacology.Brit.J.Anaesth., **39**, 699 **(1967)**.

[22] J.Org.Chem., **56**, 6998 **(1991)**.