

# Photocatalytic degradation of agricultural *N*-heterocyclic organic pollutants using immobilized nanoparticles of titania

Niyaz Mohammad Mahmoodi<sup>a,\*</sup>, Mokhtar Arami<sup>a,b</sup>,  
Nargess Yousefi Limaee<sup>a</sup>, Kamaladin Gharanjig<sup>a,b</sup>

<sup>a</sup> Colorant Manufacturing and Environmental Science Department, Institute for Colorants, Paint and Coating, Tehran, Iran

<sup>b</sup> Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

Received 2 July 2006; received in revised form 28 October 2006; accepted 31 October 2006

Available online 7 November 2006

## Abstract

Degradation and mineralization of two agricultural organic pollutants (Diazinon and Imidacloprid as *N*-heterocyclic aromatics) in aqueous solution by nanophotocatalysis using immobilized titania nanoparticles were investigated. Insecticides, Diazinon and Imidacloprid, are persistent pollutants in agricultural soil and watercourses. A simple and effective method was developed to immobilization of titania nanoparticles. UV–vis, ion chromatography (IC) and chemical oxygen demand (COD) analyses were employed. The effects of operational parameters such as H<sub>2</sub>O<sub>2</sub> and inorganic anions (NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were investigated. The mineralization of Diazinon and Imidacloprid was evaluated by monitoring of the formed inorganic anions. The selected pollutants are effectively degraded following first order kinetics model. Results show that the nanophotocatalysis using immobilized titania nanoparticle is an effective method for treatment Diazinon and Imidacloprid from contaminated water.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Nanophotocatalysis; Degradation; Immobilized system; Titania nanoparticle; Agricultural organic pollutants

## 1. Introduction

The presence of highly biorecalcitrant organic contaminants such as pesticides in the hydrosphere due to industrial and intensive agricultural activities is of particular concern for the freshwater (surface and groundwater), coastal and marine environments [1]. In general, pesticides applied directly to soils, turf, or plants can be washed into waterways during storm events or through irrigation. As a result, pesticide presence in storm water runoff can directly impact the health of aquatic organisms and present a threat to humans through contamination of drinking water supplies [2]. Pesticides such as Diazinon and Imidacloprid have been associated with toxicity in ambient waters, point source discharges, and agricultural discharges.

Diazinon (*O,O*-diethyl *O*-(2-isopropyl-6-methylpyrimidin-4-yl) thiophosphate) is an organophosphorus insecticide with widespread agricultural and non-agricultural uses. It used in

agricultural and urban applications to control a variety of insects. Diazinon can be quite persistent in aqueous phase, has been shown to take 6 months to degrade to one-half of the original concentration in neutral solutions. Toxic effects of Diazinon are due to the inhibition of acetylcholinesterase [2–9]. The primary environmental concerns associated with its use are bird kills, contamination of surface water, and impacts on aquatic species [3].

Imidacloprid, 1-(6-chloronicotiny)-2-nitroimidazolidine belonging to the class of chloronicotinoids, is an insecticide with high activity against sucking pests, including ricehoppers, aphids, thrips and white flies. Its insecticidal potential, lasting effect in greenhouse and field conditions is well documented. It also finds use against soil insects, termites and some species of biting insects, such as rice water weevil and Colorado beetle [10].

Therefore, in order to minimize the risk of pollution problems from such chemicals, it is advisable to develop new technologies that promote the easy degradation of these biorecalcitrant organic compounds. A promising way to perform the mineralization of these type of substances is the application of advanced

\* Corresponding author. Tel.: +98 21 22956126; fax: +98 21 22947537.  
E-mail address: [nm.mahmoodi@yahoo.com](mailto:nm.mahmoodi@yahoo.com) (N.M. Mahmoodi).

oxidation processes (AOP), that are characterized by the *in situ* production of hydroxyl radicals under mild experimental conditions [1].

Nanophotocatalysis using nanostructuring of materials such as titania nanoparticles constitutes one of the emerging technologies for the degradation of organic pollutants. Several advantages of this process over competing processes are: complete mineralization, no waste-solids disposal problem, and only mild temperature and pressure conditions are necessary [11–13].

In large scale applications, the use of suspended nanoparticle requires the separation and recycling of catalyst from the treated water prior to the discharge, which is a time-consuming and expensive process. In addition, the depth of penetration of UV light is limited because of strong absorptions by both catalyst particles and dissolved pollutants [14]. Above problems can be avoided by immobilization of photocatalyst over suitable supports. Thus, the use of immobilized photocatalysts is gaining importance in the elimination of pollutants from water.

The photocatalytic degradation and mineralization of dyes using immobilized TiO<sub>2</sub> nanoparticle has already been established in our laboratory [15–19]. In the present article, Diazinon and Imidacloprid as persistent insecticide pollutants in agricultural soil and watercourses were used as model compounds for photocatalytic degradation and mineralization. Other researchers carried out the photocatalytic destruction of Diazinon [3,20,21] and Imidacloprid [22–24] previously. The objectives of the present study are (a) immobilization of titania nanoparticles using simple and effective method (b) the feasibility of titania nanoparticle for the photocatalytic degradation and mineralization of Diazinon and Imidacloprid, in bench scale (5L) (c) identification of the main aliphatic carboxylic acids intermediates by IC technique and degradation of these intermediates, and (d) optimization of the operational parameters of the degradation process.

## 2. Experimental

### 2.1. Reagents

The chemical structure of Diazinon (C<sub>12</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>PS, MW: 304 g/mol and Chem Services) and Imidacloprid (C<sub>10</sub>H<sub>11</sub>ClN<sub>4</sub>O<sub>2</sub>, MW: 226.5 g/mol and Bayer AG) are shown in Fig. 1. Titania nanoparticle (Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average primary particle size 30 nm, purity above 97% and with 80:20 anatase to rutile. Other chemicals were purchased from Merck.

### 2.2. Degradation method of insecticides

Photocatalytic degradation processes were performed using a 5 L solution containing specified concentration of pollutants (0.13 mM Diazinon, 0.22 mM Imidacloprid, pH: neutral (5.5) and room temperature). The solutions were first agitated under gentle air in the dark for 30 min to reach equilibrated condition. Samples were withdrawn from sample point at certain time intervals and analyzed for degradation.

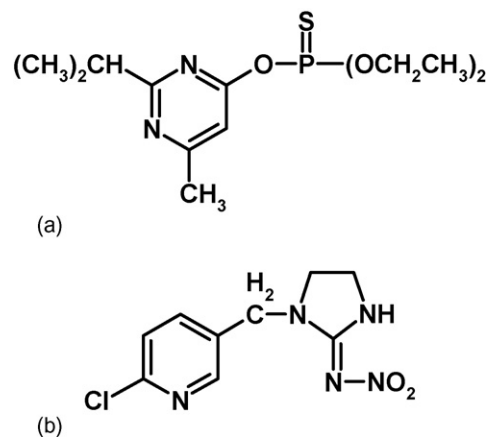


Fig. 1. The chemical structure of Diazinon (a) and Imidacloprid (b).

### 2.3. Immobilization of titanium dioxide nanoparticles and photocatalytic reactor

A simple and effective method was used to immobilization of TiO<sub>2</sub> nanoparticles as follows: inner surfaces of reactor walls were cleaned with acetone and distilled water to remove any organic or inorganic material attached to or adsorbed on the surface and was dried in the air. A pre-measured mass of TiO<sub>2</sub> nanoparticle (16 g) were attached on the inner surfaces of reactor walls using a thin layer of a UV resistant polymer (silicon polymer). Immediately after preparation, the inner surface reactor wall–polymer–TiO<sub>2</sub> system was placed in the laboratory for at least 60 h for complete drying of the polymer [15–19].

Experiments were carried out in a batch mode immersion rectangular immobilized photocatalytic reactor made of Pyrex glass, which is shown in Fig. 2. The radiation source was two UV-C lamps (15 W, Philips). A water pump and air pump were utilized for the transferring and aeration of polluted solution, respectively.

### 2.4. Analyses

Degradation of insecticides were checked and controlled by measuring the absorbance of Diazinon and Imidacloprid solutions at  $\lambda_{\max}$  (287 and 269 nm, respectively) at different time intervals by UV–vis CECIL 2021 spectrophotometer.

The COD tests were carried out according to Close Reflux, Colorimetric method [25] using a DR/2500 Spectrophotometer (Hach, USA) and COD reactor (Hach, USA).

Ion Chromatograph (METROHM 761 Compact IC) was used to determine formate, acetate, oxalate, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions formed during the degradation and mineralization of Diazinon and Imidacloprid using a METROSEP Anion Dual 2, flow 0.8 ml/min, 2 mM NaHCO<sub>3</sub>/1.3 mM Na<sub>2</sub>CO<sub>3</sub> as eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

## 3. Results and discussions

Figs. 3 and 4 show the unconverted fraction ( $C/C_0$ ) of Diazinon and Imidacloprid (respectively) versus irradiation time when

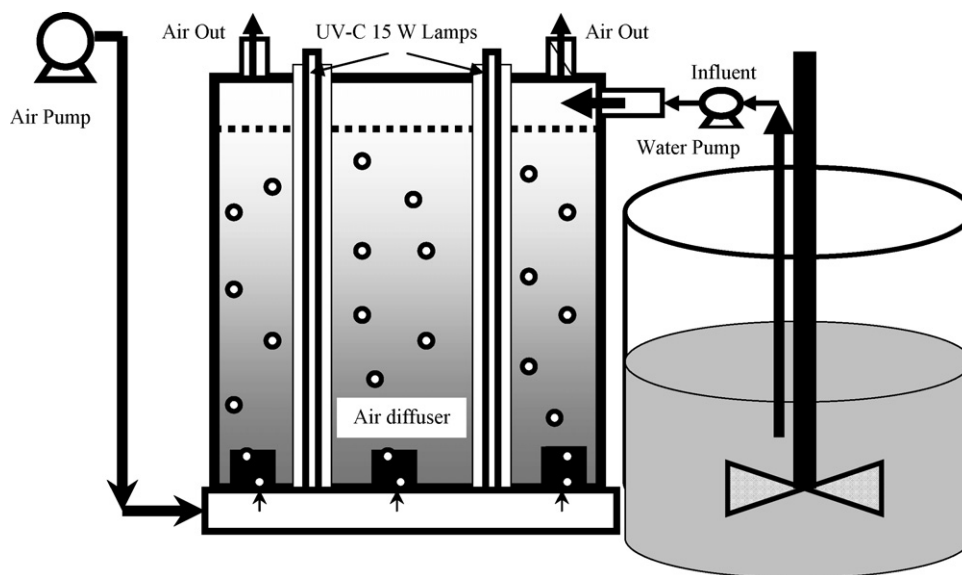


Fig. 2. Scheme of immobilized titania nanoparticles photocatalytic reactor.

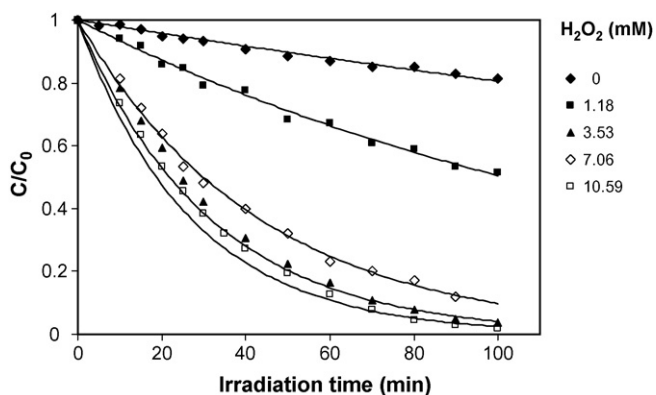


Fig. 3. Photocatalytic degradation of Diazinon with different concentrations of hydrogen peroxide at different time intervals of irradiation (Diazinon: 0.13 mM and pH 5.5).

different  $H_2O_2$  concentrations in the presence of  $TiO_2$  were used. It is shown to be exponential to time at each concentration of  $H_2O_2$ . This means that the first order kinetics relative to pollutants is operative. The correlation coefficient ( $R^2$ ) and

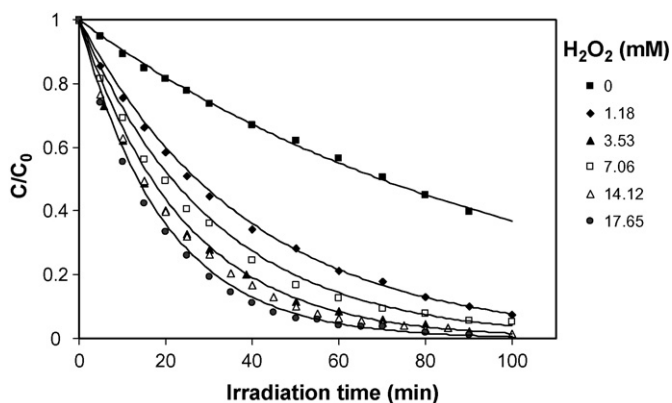
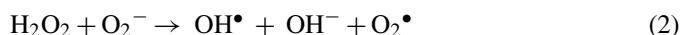


Fig. 4. Photocatalytic degradation of Imidacloprid with different concentrations of hydrogen peroxide at different time intervals of irradiation (Imidacloprid: 0.22 mM and pH 5.5).

degradation rate constants ( $k$ ,  $min^{-1}$ ) of pollutants for the various  $H_2O_2$  concentrations were shown in Table 1. The role of  $H_2O_2$  in the process of photocatalytic degradation is dual. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (Eq. (1)) and it also forms  $OH^\bullet$  radicals via superoxide according Eq. (2)



However, when  $H_2O_2$  concentration is higher than optimal concentration, the degradation rate of selected pollutants slows down. In the presence of excess  $H_2O_2$ , it may act as a hole or  $OH^\bullet$  scavenger or react with  $TiO_2$  to form peroxy compounds, which are detrimental to the photocatalytic action or compete with the organic compound for the adsorption sites on the catalyst surface [15–19].

To consider the influences of the presence of dissolved inorganic anions on the photocatalytic degradation rate of insecticides, we have chosen the  $NaCl$ ,  $NaNO_3$  and  $Na_2SO_4$  salts. The occurrence of dissolved inorganic salts such as  $NaCl$ ,  $NaNO_3$  and  $Na_2SO_4$  is rather common in environmental natural water resources. The same amount (1 mM) of these salts

Table 1  
Parameters ( $k$  and  $R^2$ ) for the effect of different  $H_2O_2$  concentrations on the degradation rate of Diazinon and Imidacloprid

$H_2O_2$ (mM)	Diazinon		Imidacloprid	
	$k$ ( $min^{-1}$ )	$R^2$	$k$ ( $min^{-1}$ )	$R^2$
0	0.0022	0.982	0.0100	0.997
1.18	0.0068	0.992	0.0256	0.993
3.53	0.0318	0.992	0.0414	0.995
7.06	0.0235	0.995	0.0324	0.987
10.59	0.0371	0.984	–	–
14.12	–	–	0.0435	0.992
17.65	–	–	0.0500	0.989

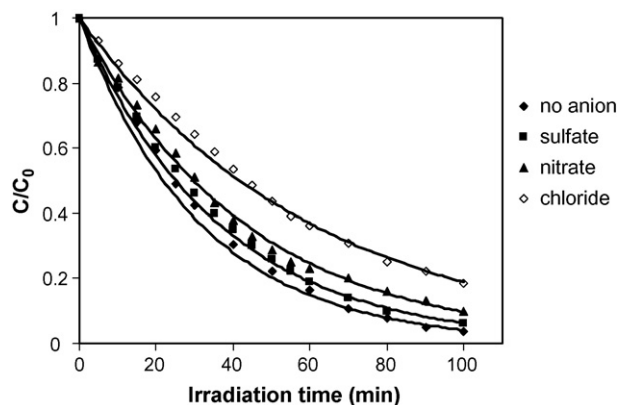


Fig. 5. The effect of anions on the photocatalytic degradation rate constants of Diazinon (Diazinon: 0.13 mM,  $\text{H}_2\text{O}_2$ : 3.53 mM and salt: 1 mM).

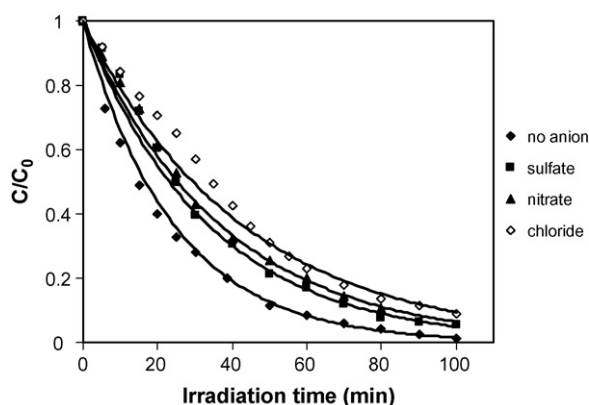


Fig. 6. The effect of anions on the photocatalytic degradation rate constants of Imidacloprid (Imidacloprid: 0.22 mM,  $\text{H}_2\text{O}_2$ : 3.53 mM and salt: 1 mM).

was used. Figs. 5 and 6 show the effects of anions on the photocatalytic degradation rate of Diazinon and Imidacloprid, respectively. The parameters  $k$  (rate constant) and  $R^2$  (correlation coefficient) of degradation process are shown in Table 2. Of the anionic species studied ( $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ ), chloride exhibited the strongest inhibition effect followed by nitrate. The observed detrimental effect on the photocatalytic degradation of selected pollutants obeyed the following order:  $\text{SO}_4^{2-} < \text{NO}_3^- < \text{Cl}^-$ . These substances may compete for the active sites on the  $\text{TiO}_2$  surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of the target molecule. Also, inhibition effects of anions can be explained as the reaction of positive holes ( $\text{h}^+$ ) and hydroxyl radical ( $\text{OH}^\bullet$ ) with anions that behaved as  $\text{h}^+$  and  $\text{OH}^\bullet$  scavengers resulting prolonged contaminant removal. A major drawback resulting

Table 2  
Parameters ( $k$  and  $R^2$ ) for the effect of different anions on the degradation rate of Diazinon and Imidacloprid

Anion	Diazinon		Imidacloprid	
	$k$ ( $\text{min}^{-1}$ )	$R^2$	$k$ ( $\text{min}^{-1}$ )	$R^2$
No anion	0.0318	0.992	0.0414	0.995
Sulfate	0.0277	0.997	0.0301	0.993
Nitrate	0.0234	0.995	0.0274	0.996
Chloride	0.0166	0.995	0.0236	0.987

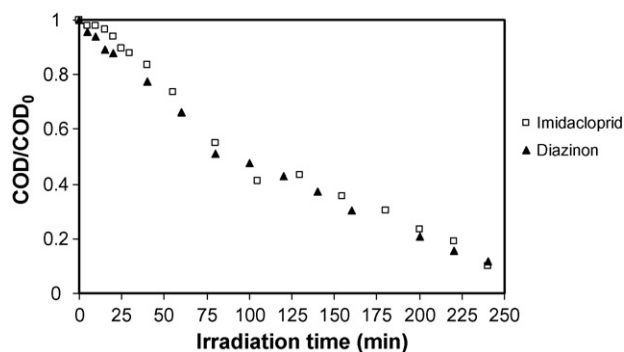


Fig. 7. COD removal of the solution during photocatalytic degradation of Diazinon and Imidacloprid (Diazinon; 0.13 mM, Imidacloprid; 0.22 mM,  $\text{H}_2\text{O}_2$ : 3.53 mM and pH 5.5).

from the high reactivity and non-selectivity of  $\text{OH}^\bullet$  is that it also reacts with non-target compounds present in the background water matrix, i.e. inorganic anions present in water. This results in a higher  $\text{OH}^\bullet$  demand to accomplish the desired degree of degradation, or complete inhibition of advanced oxidation rate and efficiency [12,26].

Degradation of the selected insecticides should be evaluated as an overall degradation process, involving the degradation of both the parental pollutant and its intermediates.

The chemical oxygen demand (COD) gives a measure of degradation of pollutants and generated intermediates during the irradiation [27] and also a measure of the concentration of everything that can be oxidized by the  $\text{Cr}_2\text{O}_7^{2-}$  anion in acid media, and that includes many inorganic species. The rate of COD removal efficiency of pollutants was shown in Fig. 7. This figure shows that after 4 h irradiation, 92% reduction in the COD of the samples was achieved.

Due to the complexity of the reactions occurring in photocatalytic treatments, it is difficult to indicate an exhaustive reaction scheme explaining the formation of all formed intermediates [28]. Further hydroxylation of aromatic intermediates leads to the cleavage of the aromatic ring resulting in the formation of oxygen-containing aliphatic compounds [29]. Formate, acetate and oxalate were detected as important aliphatic carboxylic acids intermediates during the degradation of Diazinon and Imidacloprid (Figs. 8 and 9, respectively).

The formation of carboxylic acids initially increased with the illumination time, and then dropped. Carboxylic acids can react directly with holes generating  $\text{CO}_2$  according to the “*photo-Kolbe*” reaction [30].

Also, the photocatalytic mineralization of organic pollutants implies the appearance of inorganic products, mainly anions, since hetero-atoms are generally converted into anions in which they are at their highest oxidation degree.

The pollutant degradation leads to the conversion of organic carbon into harmless gaseous  $\text{CO}_2$  and that of S, P, N and Cl hetero-atoms into inorganic ions, such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , respectively. Mineralization of Diazinon and Imidacloprid is reported for an irradiation period of 240 min.

Figs. 10 and 11 show that the quantity of  $\text{NO}_3^-$  ions released from Diazinon and Imidacloprid mineralization (0.22

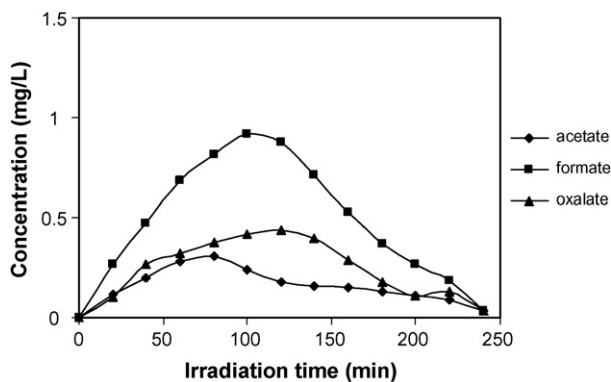


Fig. 8. Formation and disappearance of aliphatic carboxylic acids during the photocatalytic degradation of Diazinon (Diazinon: 0.13 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).

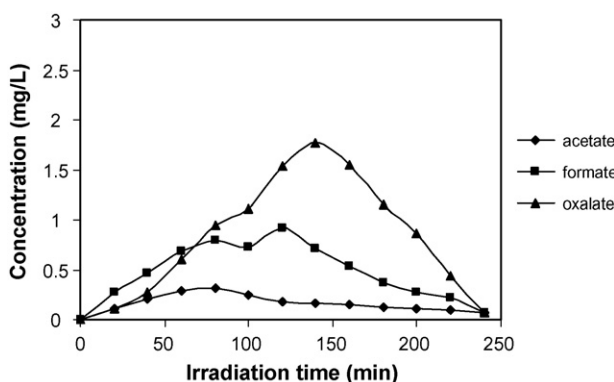


Fig. 9. Formation and disappearance of aliphatic carboxylic acids during the photocatalytic degradation of Imidacloprid (Imidacloprid: 0.22 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).

and 0.80 mM, respectively) is lower than that expected from stoichiometry (0.26 and 0.88 mM, respectively) indicating that N-containing species remain adsorbed in the photocatalyst surface or most probably, that significant quantities of N<sub>2</sub> and/or NH<sub>3</sub> have been produced and transferred to the gas phase. N<sub>2</sub> evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product [12].

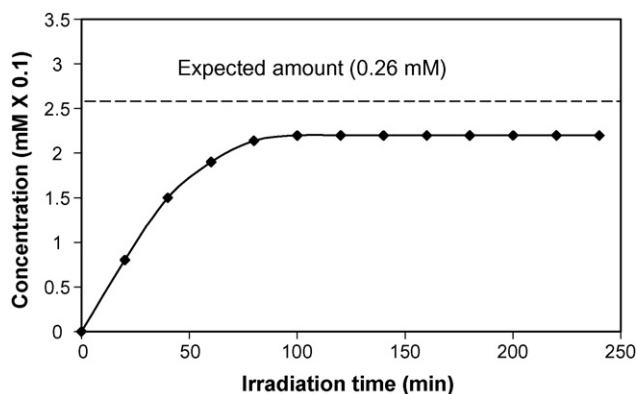


Fig. 10. Evolution of nitrate anion during the photocatalytic mineralization of Diazinon (Diazinon: 0.13 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).

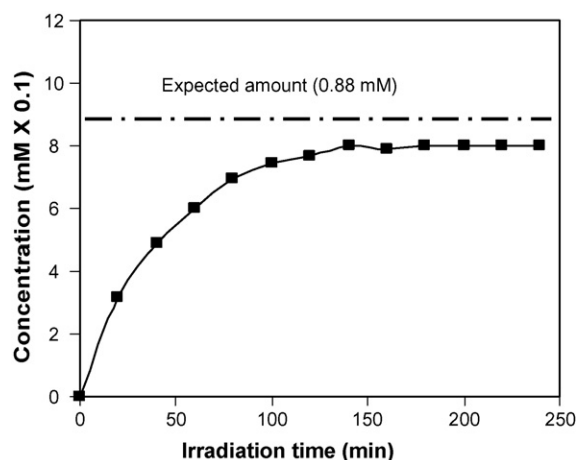


Fig. 11. Evolution of nitrate during the photocatalytic mineralization of Imidacloprid (Imidacloprid: 0.22 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).

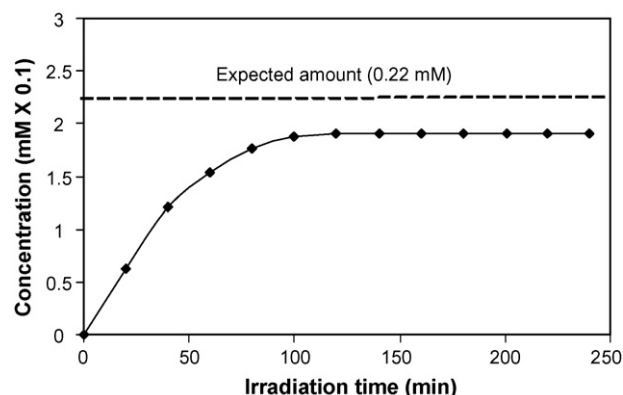


Fig. 12. Evolution of chloride anion during the photocatalytic mineralization of Imidacloprid (Imidacloprid: 0.22 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).

Fig. 12 shows that the quantity of chloride ions released from Imidacloprid mineralization (0.22 mM) is lower than that expected from stoichiometry (0.26 mM) indicating that chloride remains adsorbed in the photocatalyst surface.

The quantity of sulfate ions released from Diazinon mineralization (0.11 mM) is lower than that expected from stoichiometry (0.13 mM) (Fig. 13). This could be first explained

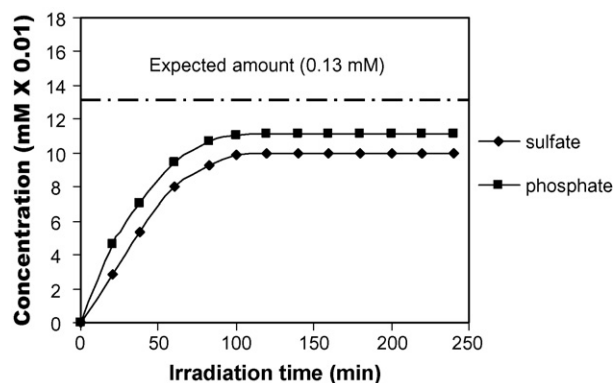


Fig. 13. Evolution of sulfate and phosphate anions during the photocatalytic mineralization of Diazinon (Diazinon: 0.13 mM, H<sub>2</sub>O<sub>2</sub>: 3.53 mM and pH 5.5).



by a loss of sulfur-containing volatile compounds such as H<sub>2</sub>S and/or SO<sub>2</sub>. However, this is not probable since both gases are very soluble in water and known as readily oxidizable into sulfate by photocatalysis. The more probable explanation for the quantity of SO<sub>4</sub><sup>2-</sup> obtained smaller than that expected from stoichiometry is given by the partially irreversible adsorption of some SO<sub>4</sub><sup>2-</sup> ions at the surface of titania as already observed. However, this partial adsorption of SO<sub>4</sub><sup>2-</sup> ions does not inhibit the photocatalytic degradation of pollutants [30].

The quantity of phosphate ions released (0.10 mM) is lower than that expected from stoichiometry (0.13 mM) (Fig. 13). This could be explained by the partially irreversible adsorption of some PO<sub>4</sub><sup>3-</sup> ions at the surface of titania as already observed [31,32].

#### 4. Conclusions

Two insecticides, Diazinon and Imidacloprid, could be successfully degraded and mineralized by nanophotocatalysis in an immobilized titania nanoparticles photocatalytic reactor. The degradation rate for insecticides goes through a maximum when the concentration of the hydrogen peroxide increases from 0 to optimal concentration (3.53 mM) and then it does not appreciable change. Chloride exhibited the strongest inhibition effect on the selected insecticide followed by nitrate. The photocatalytic degradation kinetics follows a first order model. The formation of carboxylic acids intermediates (acetic, formic and oxalic) initially increased with the illumination time, and then dropped due to directly reaction with holes and generation of CO<sub>2</sub> according to the photo-Kolbe reaction. Mineralization of Diazinon and Imidacloprid is identified by production of inorganic anions (nitrate, sulfate, phosphate and chloride). Thin-film coating of photocatalyst may resolve the problem of suspension system of selected insecticides degradation. Nanophotocatalysis by immobilized titanium dioxide nanoparticle in the presence of hydrogen peroxide is able to treatment of selected insecticides from polluted waters without using high pressure of oxygen or heating. Hence, this technique may be a viable one for treatment of large volume of water polluted by insecticides.

#### References

- [1] M.J. Farre, M.I. Franch, S. Malato, J.A. Ayllon, J. Peral, X. Domenech, Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, *Chemosphere* 58 (2005) 1127–1133.
- [2] K.E. Banks, T.D.H. Hunter, D.J. Wachal, Diazinon in surface waters before and after a federally-mandated ban, *Sci. Total Environ.* 350 (2005) 86–93.
- [3] V.N. Kouloumbos, D.F. Tsipi, A.E. Hiskia, D. Nikolic, R.B. van Breemen, Identification of photocatalytic degradation products of Diazinon in TiO<sub>2</sub> aqueous suspensions using GC/MS/MS and LC/MS with quadrupole time-of-flight mass spectrometry, *J. Am. Soc. Mass. Spectrom.* 14 (2003) 803–817.
- [4] I. Dubus, J. Hollis, C. Brown, Pesticides in rainfall in Europe, *Environ. Pollut.* 110 (2000) 331–344.
- [5] S. Garcia, C. Ake, B. Clement, H. Huebner, K. Donnelly, S. Shalat, Initial results of environmental monitoring in the Texas Rio Grande Valley, *Environ. Int.* 26 (2001) 465–474.
- [6] T. Albanis, D. Hela, T. Sakellarides, I. Konstantinou, Monitoring of pesticide residues and their metabolites in surface and underground waters of imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography, *J. Chromatogr. A* 823 (1998) 59–71.
- [7] H. Bailey, L. Deanovic, E. Reyes, T. Kimball, K. Larson, K. Cortright, V. Connor, D. Hinton, Diazinon and chlorpyrifos in urban waterways in Northern California, USA, *Environ. Toxicol. Chem.* 19 (2000) 82–87.
- [8] H. Bailey, R. Kraddoi, J. Elphick, A. Mulhall, P. Hunt, L. Tedmanson, A. Lovell, Whole effluent toxicity of sewage treatment plants in the Hawkesbury-Nepean Watershed, New South Wales, Australia, to *Ceriodaphnia dubis* and *Selenastrum capricornutum*, *Environ. Toxicol. Chem.* 19 (2000) 72–81.
- [9] T. Roberts, D. Hutson, *Metabolic Pathways of Agrochemicals-Part 2: Insecticides and Fungicides*, RSC, UK, 1999, pp. 258–263.
- [10] P.N. Moza, K. Hustert, E. Feicht, A. Ketrup, Photolysis of Imidacloprid in aqueous solution, *Chemosphere* 36 (3) (1998) 497–502.
- [11] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [12] I.K. Konstantinou, T.A. Albanis, TiO<sub>2</sub>-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations, A review, *Appl. Catal. B: Environ.* 49 (2004) 1–14.
- [13] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications—a review, *J. Chem. Technol. Biotechnol.* 77 (2001) 102–116.
- [14] A.K. Ray, A.A.C.M. Beenackers, Novel photocatalytic reactor for water treatment, *AIChE J.* 44 (2) (1998) 477–483.
- [15] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, N. Salman Tabrizi, Decolorization and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO<sub>2</sub> as a photocatalyst, *Chem. Eng. J.* 112 (1–3) (2005) 191–196.
- [16] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, N. Salman Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO<sub>2</sub> photocatalytic reactor, *J. Colloid Interf. Sci.* 295 (1) (2006) 159–164.
- [17] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, Photocatalytic degradation of triazinic ring-containing azo dye (reactive red 198) by using immobilized TiO<sub>2</sub> photoreactor: bench scale study, *J. Hazard. Mater.* B133 (1–3) (2006) 113–118.
- [18] N.M. Mahmoodi, M. Arami, Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium (IV) oxide nanoparticles, *J. Photochem. Photobiol. A: Chem.* 182 (2006) 60–66.
- [19] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee, K. Gharanjig, F. Doulati Ardejani, Decolorization and mineralization of textile dyes at solution bulk by heterogeneous nanophotocatalysis using immobilized nanoparticles of titanium dioxide, *Colloid Surface A: Physicochem. Eng. Aspects* 290 (2006) 125–131.
- [20] V.A. Sakkas, A. Dimou, K. Pitarakis, G. Mantis, T. Albanis, TiO<sub>2</sub> photocatalyzed degradation of Diazinon in an aqueous medium, *Environ. Chem. Lett.* 3 (2) (2005) 57–61.
- [21] D. Mas, T. Hisanaga, P. Pichat, Photocatalytic degradation of the Pesticides Asulam and Diazinon in TiO<sub>2</sub> aqueous suspensions, *Trends Photochem. Photobiol.* 3 (1994) 467–479.
- [22] S. Malato, J. Blanco, J. Cáceres, A.R. Fernández-Alba, A. Agüera, A. Rodríguez, Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO<sub>2</sub> using solar energy, *Catal. Today* 76 (2002) 209–220.
- [23] P. Fernández-Ibáñez, S. Malato, F.J. de las Nieves, Relationship between TiO<sub>2</sub> particle size and reactor diameter in solar photoreactors efficiency, *Catal. Today* 54 (1999) 195–204.
- [24] S. Malato, J. Blanco, A. Vidal, D. Alarcón, M.I. Maldonado, J. Cáceres, W. Gernjak, Applied studies in solar photocatalytic detoxification: an overview, *Solar Energy* 75 (2003) 329–336.
- [25] APHA, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., American Public Health Association, Washington, DC, 1989.
- [26] I. Arsalan-Alaton, A review of the effects of dye-assisting chemicals on advanced oxidation of reactive dyes in wastewater, *Color. Technol.* 119 (2003) 345–353.

- [27] J. Li, C. Chen, J. Zhao, H. Zhu, J. Orthman, Photodegradation of dye pollutants on TiO<sub>2</sub> nanoparticles dispersed in silicate UV-Vis irradiation, *Appl. Catal. B: Environ.* 37 (2002) 331–338.
- [28] I.K. Konstantinou, T.A. Albanis, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Appl. Catal. B: Environ.* 42 (2003) 319–335.
- [29] K. Tanaka, S.M. Robledo, T. Hisanaga, R. Ali, Z. Ramli, W.A. Bakar, Photocatalytic degradation of 3,4-xylol N-methylcarbamate (MPMC) and other carbamate pesticides in aqueous TiO<sub>2</sub> suspensions, *J. Mol. Catal. A: Chem.* 144 (1999) 425–430.
- [30] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B: Environ.* 31 (2001) 145–157.
- [31] B.P. Nelson, R. Candal, R.M. Corn, M.A. Anderson, Control of surface and  $\zeta$  potentials on nanoporous TiO<sub>2</sub> films by potential-determining and specifically adsorbed ions, *Langmuir* 16 (15) (2000) 6094–6101.
- [32] M. Abdullah, G.K.C. Low, R.W. Matthews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, *J. Phys. Chem.* 94 (17) (1990) 6820–6825.