Immobilized titania nanophotocatalysis: Degradation, modeling and toxicity reduction of agricultural pollutants

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ABSTRACT

In this paper, the feasibility and performance of degradation, modeling of degradation, mineralization and toxicity reduction of agricultural organic pollutants (Alachlor and Fenitrothion) have been studied using immobilized titania nanophotocatalysis. Total organic carbon (TOC) and ion chromatography (IC) analyses were employed to obtain the details of the photocatalytic degradation and mineralization of both pesticides. *Daphnia magna* bioassay has been used to test the diminution of toxicity during the treatment process. Computational fluid dynamics (CFD) model was used to solve the mathematical equation describing degradation process. The model predictions were compared to those results obtained from experimental tests for the degradation of both pesticides and close agreement was achieved. Kinetic studies revealed that the degradation rate followed first-order model for both pesticides. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediates where, they were further oxidized slowly to CO_2. Inorganic anions such as nitrate and sulphate were detected as the photocatalytic mineralization of Alachlor and Fenitrothion. The results showed that immobilized titania nanophotocatalysis was an environmentally friendly method of degradation and toxicity reduction of agricultural organic pollutants (Alachlor and Fenitrothion).

1. Introduction

The presence of harmful organic compounds in watercourses and wastewater of several chemical industries such as textile, agricultural sources, etc. is a topic of global concern. Polluted waters with organic contaminant such as pesticides, dyes, etc. create serious problems to various segments of the environment. Organic pollutants in water affect the nature of the water, inhibit light penetration into the streams and reduce the photosynthetic reaction. Some of them are toxic and even at very low concentrations may significantly affect aquatic life. Some others may cause allergy, skin irritation and cancer to humans [1–9].

Daphnia magna is often used for the assessment of acute and chronic toxicity in wastewater [10]. Many European countries conduct their routine, acute as well long-term toxicity tests with *D. magna*, because of its easy growth, maintenance, relatively simple test procedure and reproducibility, as well as high sensitivity towards industrial pollutants and industrial wastewater [11].

Pesticides, one of the most important organic pollutants, have been detected in ground water sources. Alachlor (2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide) was detected in raw, tap, treated, and rain waters at concentrations of 1.0–270 mg/L. Other studies reported its presence in groundwater at concentrations as high as 3000 mg/L. The alachlor molecule essentially consists of an aniline moiety with a carbonyl group having allylic chlorine. It is regulated by the United States Environmental Protection Agency (EPA) with a maximum contaminant level (MCL) of 2 mg/L for drinking water. The desirable and yet non-enforceable maximum contaminant level goal (MCLG) has been set to zero with regard to drinking water standards [12–17].

Fenitrothion (*O,O*-dimethyl *O*-4-nitro-m-tolyl phosphorothioate) is one of the most representative and commonly used organophosphorous compounds [18,19]. Because of its partial solubility in water, it can penetrate to deep soil strata and reach the groundwater. Fenitrothion undergoes photodegradation in natural water and results many toxic metabolites to aquatic organisms. Fenitrothion and its photoproducts are suspected endocrine disruptors [20].

In order to address this significant problem, extensive research is underway to develop advanced methods for the elimination of pesticides from water. Processes based on aqueous phase hydroxyl radical chemistry are powerful oxidation methods to destroy toxic organic compounds present in water. Photocatalysis using titania is one of the advanced oxidation processes that couples low-energy ultraviolet light with semiconductors acting as photocatalysts. Dur-

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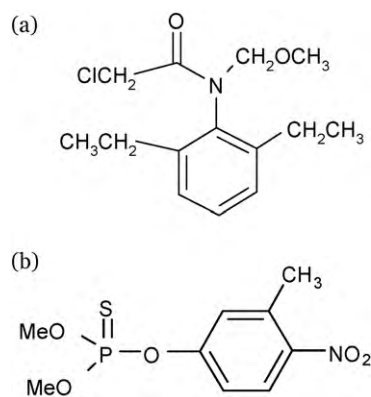(N.M. Mahmoodi).

Fig. 1. Chemical structure of (a) Alachlor and (b) Fenitrothion.

Fig. 2. Comparison of concentrations of Ala. versus time in aqueous phase for different concentrations of hydrogen peroxide and an initial concentration of 0.2 mM predicted by numerical model (solid lines) and determined at laboratory (dots).

ing the photocatalytic reactions, valence band hole (h_{vb}^+) and hydroxyl radical are produced. The h_{vb}^+ is a strong oxidant, which can either oxidize a compound directly, or react with electron donors like water or hydroxide ions to form hydroxyl radicals, which react with pollutants such as pesticides. Hydroxyl radicals react with organic pollutants leading to the total mineralization of most of them. 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 [21–24].

In the present article, Alachlor and Fenitrothion pollutants in agricultural soil and watercourses were used as model compounds for photocatalytic oxidation and mineralization. A review of past research revealed that the photocatalytic degradation of Alachlor [25–35] and Fenitrothion [18,19,36–44] was carried out but no researches had been carried out to CFD modeling the photocatalytic degradation of pesticides in literature. The objective of this paper is degradation, to model the degradation and mineralization of pesticides by nanophotocatalysis using immobilized titania. A multi-purpose CFD package called PHOENICS [45] incorporating the numerical finite volume approach was used to simulate the photocatalytic degradation process. Also, little research has been done to reduce the toxicity using immobilized titania photocatalysis [46]. In this research, the reduction of acute toxicity during the degradation Alachlor and Fenitrothion using titania nanophotocatalysis on *D. magna* was investigated.

2. Materials and methods

Unless stated otherwise all chemicals were purchased from Merck and used as received. The chemical structures of Alachlor (Ala.) ($C_{14}H_{20}ClNO_2$, MW: 269.5 g/mol and Riedel-de Haën Company) and Fenitrothion (Fen.) ($C_9H_{12}NO_5PS$, MW: 277 g/mol and Kanto Chemicals Company) were shown in Fig. 1. Titania nanoparticle (Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average particle size 30 nm, purity above 97% and with 80:20 anatase to rutile.

Experiments were carried out in a batch mode immersion rectangular immobilized TiO_2 nanoparticle photocatalytic reactor made of Pyrex glass. Two UV-C lamps (15 W, Philips) were used as the radiation source.

A simple and effective method was developed for the immobilization of TiO_2 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_2 nanoparticle (16 g) was attached on the inner surfaces of reactor walls using a thin layer of a UV resistant silicone polymer (reaction temperature 25 °C and preparation time 1 h). Immediately after preparation, the inner surface reactor wall–polymer–TiO_2 nanoparticle system was placed in the laboratory for at least 60 h for complete drying of the polymer [1–6].

Photocatalytic oxidation and mineralization processes were performed using a 4 L solution containing specified concentration of pesticide. Solutions were prepared using distilled water to minimize interferences. The initial concentration of pesticide was 0.2 mM. Samples were withdrawn from sample point at certain time intervals and analyzed for degradation and mineralization processes.
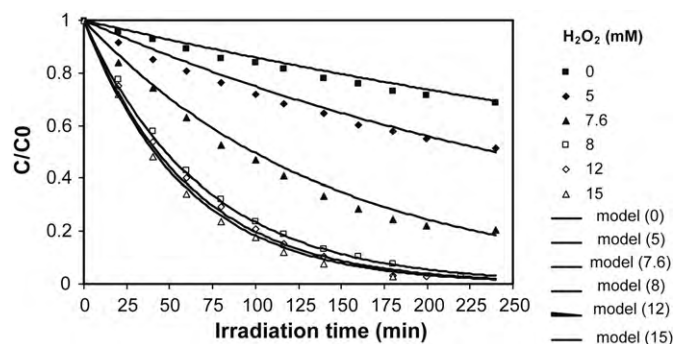
Oxidation of pesticides was checked by measuring the total organic carbon (TOC) removal at different time intervals using a digester and Spectrophotometer DR/2500 (Hach).

Computational fluid dynamics modeling incorporating the finite volume descretization scheme was used to simulate the photocatalytic degradation of both pesticides.

Ion chromatograph (METROHM 761 Compact IC) was used to assay the appearance and quantity of formate, acetate, oxalate, $H_2PO_4^-$, Cl^-, SO_4^{2-} and NO_3^- ions formed during the degradation and mineralization of both pesticides using a MET-ROSEP anion dual 2, flow 0.8 mL/min, 2 mM NaHCO$_3$/1.3 mM Na$_2$CO$_3$ as eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

Acute toxicity of agricultural pollutants was determined using *D. magna* neonates as the test species in accordance with standard methods [47]. In the first step of toxicity analyses, the samples were prepared for the test procedure. The remaining hydrogen peroxide after photocatalytic degradation was removed with an excess of sodium sulphite and any remaining sulphite was removed by bubbling O_2 [48]. The pH of the raw and treated samples was adjusted to the required value. The test animals were grown with a 16 h light/8 h dark light cycle using 1000-lx fluorescent lamps. Toxicity tests were carried out using ten young daphnids in 50 mL test beakers at pH 8.0, providing a minimum of 6 mg/L dissolved oxygen and a constant temperature of 20 °C. The LC_{50} values (lethal concentration causing 50% death) of the agricultural pollutant samples were calculated by interpolation of the log (percent agricultural pollutant dilution) versus percent death, that were established using the experimental data obtained form the acute toxicity tests [49].

3. Results and discussions

3.1. Degradation

Figs. 2 and 3 (dots) show the pesticide removal as a function of the illumination time (for Ala. and Fen., respectively) at different H_2O_2 concentrations. It is shown to be exponential to time at each concentration of H_2O_2. This means that the first-order kinetics relative to pesticide is operative. The correlation coefficient (R^2) and degradation rate constants (k, min^{-1}) of pesticide for the var-
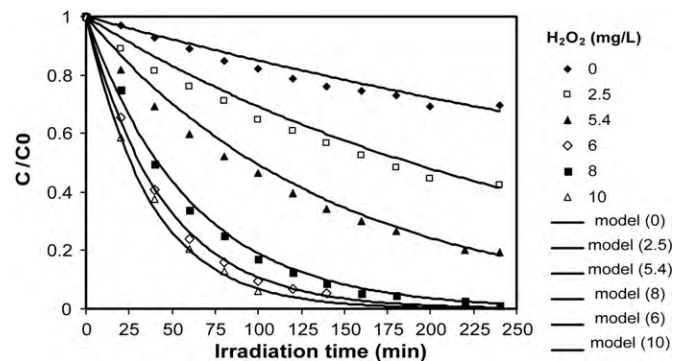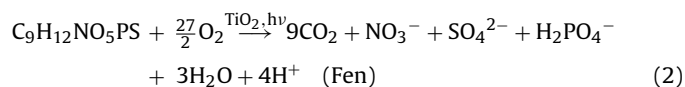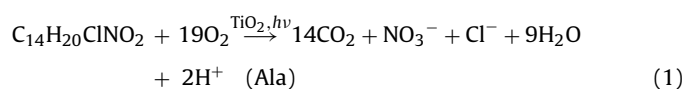

Fig. 3. Comparison of concentrations of Fen. versus time in aqueous phase for different concentrations of hydrogen peroxide and an initial concentration of 0.2 mM predicted by numerical model (solid lines) and determined at laboratory (dots).

Table 1
First-order kinetics rate constants for photocatalytic oxidation of pesticides.

H_2O_2 (mM)	Alachlor		H_2O_2 (mM)	Fenitrothion	
	k (1/min)	R^2		k (1/min)	R^2
0	0.0017	0.97	0	0.0015	0.97
5	0.0030	0.98	2.5	0.004	0.98
7.6	0.0074	0.98	5.4	0.0074	0.99
8	0.0145	0.99	6	0.0222	0.99
12	0.0150	0.99	8	0.0190	0.99
15	0.0152	0.99	10	0.0230	0.99

Table 2
Model input data used for the simulation of photocatalytic oxidation of pesticides.

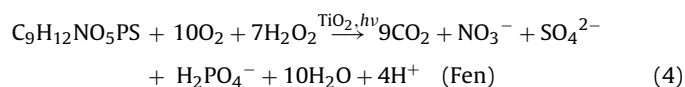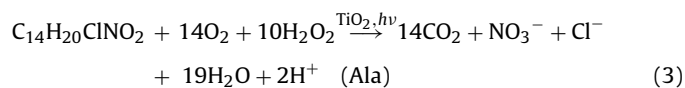| Input parameter	value
Initial pesticide concentration (mM)	0.2
Kinetic rate constant (1/min)	Table 1
Molecular diffusion (m²/s)	1×10^{-9}
Number of iterations	1000
Number of time steps	12
PHOENICS-term for density (g/cm³)	1.0
Differencing scheme	Hybrid

ious H_2O_2 concentrations were shown in Table 1. Apparently, as H_2O_2 concentration increases from 0 to optimal concentration (8 and 6 mM for Ala. and Fen., respectively), the oxidation rate is greatly enhanced because more hydroxyl radicals are formed at higher hydrogen peroxide concentrations in solution. However, when H_2O_2 concentration is larger than optimal concentration, the degradation rate slows down. This can be explained by the scavenging effect when using a higher H_2O_2 concentration on the further generation of hydroxyl radicals in aqueous solution [1–6].

The overall stoichiometry for photocatalytic oxidation and mineralization of pesticides without H_2O_2 can be written as

$$C_{14}H_{20}ClNO_2 + 19O_2 \xrightarrow{TiO_2, h\nu} 14CO_2 + NO_3^- + Cl^- + 9H_2O + 2H^+ \quad \text{(Ala)} \tag{1}$$

$$C_9H_{12}NO_5PS + \tfrac{27}{2}O_2 \xrightarrow{TiO_2, h\nu} 9CO_2 + NO_3^- + SO_4^{2-} + H_2PO_4^- + 3H_2O + 4H^+ \quad \text{(Fen)} \tag{2}$$
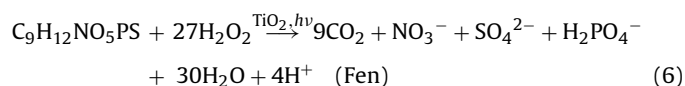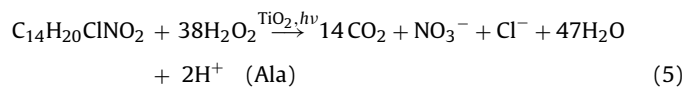
After 4 h of irradiation time, 22 and 23% of Ala. and Fen. were degraded (Fig. 3).

Also, the overall stoichiometry for photocatalytic oxidation and mineralization of pesticides in the presence of H_2O_2 can be written as

$$C_{14}H_{20}ClNO_2 + 14O_2 + 10H_2O_2 \xrightarrow{TiO_2, h\nu} 14CO_2 + NO_3^- + Cl^- + 19H_2O + 2H^+ \quad \text{(Ala)} \tag{3}$$

$$C_9H_{12}NO_5PS + 10O_2 + 7H_2O_2 \xrightarrow{TiO_2, h\nu} 9CO_2 + NO_3^- + SO_4^{2-} + H_2PO_4^- + 10H_2O + 4H^+ \quad \text{(Fen)} \tag{4}$$

On the basis of this equation, 10 and 7 mol of H_2O_2 are theoretically needed to completely degrade 1 mol of Ala. and Fen., respectively. In our case, the optimal $[H_2O_2]/[$pesticide$]$ molar ratio equals 40 and 30 mol for Ala. and Fen., respectively. It should be pointed out that it has been assumed in Eqs. (3) and (4) that oxygen can play a dominant role in the destruction rate of pesticides. If we assume that H_2O_2 can be used as the dominant oxidant, the required H_2O_2 will be 38 and 27 mol for 1 mol of Ala. and Fen., respectively, according to the following chemical reaction:

$$C_{14}H_{20}ClNO_2 + 38H_2O_2 \xrightarrow{TiO_2, h\nu} 14CO_2 + NO_3^- + Cl^- + 47H_2O + 2H^+ \quad \text{(Ala)} \tag{5}$$

$$C_9H_{12}NO_5PS + 27H_2O_2 \xrightarrow{TiO_2, h\nu} 9CO_2 + NO_3^- + SO_4^{2-} + H_2PO_4^- + 30H_2O + 4H^+ \quad \text{(Fen)} \tag{6}$$

Therefore, our optimal $[H_2O_2]/[$pesticide$]$ molar ratio of 40 and 30 for Ala. and Fen., respectively, is only higher than the theoretical value.

3.2. Modeling of oxidation process

In this paper, a computational fluid dynamics model incorporating the finite volume descretization scheme is presented to simulate the photocatalytic oxidation of both pesticides using photocatalysis process.

The partial differential equation describing the photocatalytic oxidation process is given at Eq. (7). This equation was numerically solved using PHOENICS package and incorporating finite volume integration scheme in order to simulate the degradation from aqueous solution. It was assumed that the photocatalytic oxidation process is the only mechanism for pesticide removal in a batch system.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC \tag{7}$$

where C = pesticide concentration in aqueous system (mM); k = first-order rate constant (1/s); t = time (s); x = Cartesian coordinates (m) and D = diffusion coefficient (m²/s).

The equation describing photocatalytic degradation of pesticides in solution phase was solved using the PHOENICS CFD package. PHOENICS is a general-purpose CFD package that can be used for simulation of fluid flow, heat transfer, and mass transfer processes. In the case of a single-phase problem, the partial differential equation solved by PHOENICS has the following general form [45]:

$$\frac{\partial}{\partial t}(\rho\psi) + \frac{\partial}{\partial x_j}\left(\rho u_j\psi - \Gamma_\psi\frac{\partial\psi}{\partial x_j}\right) = S_\psi \tag{8}$$

where ψ = any of the dependent variable; t = time; ρ = PHOENICS-term for density; u_j = velocity component in the x_j direction; Γ_ψ = diffusive exchange coefficient for ψ and S_ψ = source rate of ψ.

The general source term S_ψ can include all terms other than diffusion, convection and transient terms in the equation.

Since the model equation may contain terms which are not included in the PHOENICS general equation, they are implemented in PHOENICS by introducing the appropriate setting for each term in the Q1 file and applying extra FORTRAN coding in the GROUND subroutine.

In order to model the photocatalytic degradation of pesticides from the solution phase, a one-dimensional simulation was performed using PHOENICS package. The model input data are given in Table 2.

A one-dimensional finite volume model with a reactor length of 380 mm was divided into 50 equal size control volumes. The x-direction of Cartesian coordinate was used to simulate horizontal batch system in which photocatalytic degradation process takes place. The number of time steps used was 12. Total iteration of 1000 was assigned to the simulation. The model was then run for a simulation time of 60 min. A molecular diffusion coefficient of 1×10^{-9} m²/s was assigned for both pesticides dissolved in solution system. All model input data were set through the Q1 file of PHOENICS package.
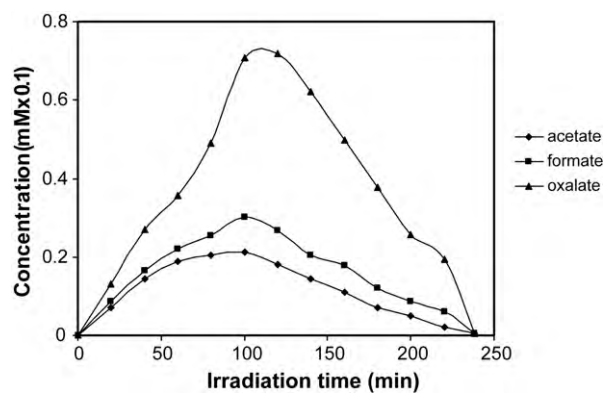
Fig. 4. Changes of formate and oxalate concentrations during photocatalytic oxidation Alachlor (Ala.: 0.2 mM, H_2O_2: 8 mM).

Figs. 2 and 3 compare experimental data and model predictions for the relative concentrations of Ala. and Fen., as a function of irradiation time, respectively. The agreement between the predicted results and measured data are somewhat close. These figures were plotted for different H_2O_2 concentrations.

3.3. Mineralization

During the photocatalytic oxidation and mineralization of pesticide, various organic intermediates were produced. Consequently, destruction of the pesticide should be evaluated as an overall degradation process, involving the degradation of both the parent pesticide and its intermediates. Further hydroxylation of aromatic intermediates leads to the cleavage of the aromatic ring resulting in the formation of oxygen-containing aliphatic compounds [50–57].

Carboxylic acids (formate, acetate and oxalate) were detected as important aliphatic carboxylic acid intermediates. Figs. 4 and 5 showed the formation and disappearance of carboxylic acids with the irradiation time during the degradation of Ala. and Fen., respectively. After 240 min of irradiation, Carboxylic acids disappeared, indicating the mineralization of pesticide into CO_2 [54].

The mineralization of Alachlor and Fenitrothion leads to the conversion of organic carbon into harmless gaseous CO_2 and that of N, S, P and Cl heteroatoms into inorganic ions, such as NO_3^-, SO_4^{2-}, $H_2PO_4^-$ and Cl^-, respectively.

Fig. 6 shows the mineralization of Alachlor after 240 min of irradiation time. The quantity of NO_3^- ions released (0.173 mM) is lower than that expected from stoichiometry (0.2 mM from Eq. (5)). This could be explained that *N*-containing species remain adsorbed in the photocatalyst surface or most probably, that significant quantities of N_2 and/or NH_3 have been produced and
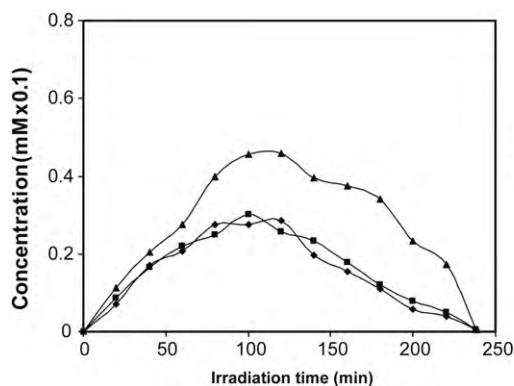

Fig. 5. Formation and disappearance of aliphatic carboxylic acids in the solution during the photocatalytic oxidation of Fenitrothion (Fen.: 0.2 mM, H_2O_2: 6 mM).
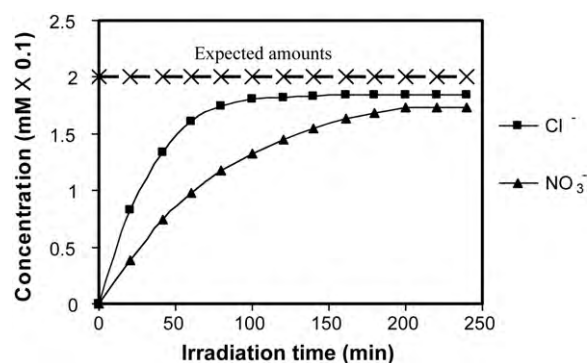

Fig. 6. Evolution of NO_3^- and Cl^- during the photocatalytic oxidation of Alachlor (Ala.: 0.2 mM, H_2O_2: 8 mM).

transferred to the gas phase. N_2 evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product [22]. The quantity of chloride ions released (0.180 mM) is lower than that expected from stoichiometry (0.2 mM from Eq. (5)) indicating that chloride remains adsorbed in the photocatalyst surface.

Fig. 7 shows the mineralization of Fenitrothion after 240 min of irradiation time. The quantity of sulphate ions released (0.18 mM) is lower than that expected from stoichiometry (0.2 mM from Eq. (6)). This could be first explained by a loss of sulphur-containing volatile compounds such as H_2S and/or SO_2. However, this is not probable since both gases are very soluble in water and known as readily oxidizable into sulphate by photocatalysis. The more probable explanation for the quantity of SO_4^{2-} obtained smaller than that expected from stoichiometry is given by the partially irreversible adsorption of some SO_4^{2-} ions at the surface of titania as already observed. However, this partial adsorption of SO_4^{2-} ions does not inhibit the photocatalytic degradation of pollutants [22,54].

The quantity of $H_2PO_4^-$ ions released (0.15 mM) is lower than that expected from stoichiometry (0.2 mM from Eq. (6)) indicating that $H_2PO_4^-$ remains adsorbed in the photocatalyst surface. Also, the quantity of NO_3^- ions released (0.17 mM) is lower than that expected from stoichiometry (0.2 mM from Eq. (6)).

3.4. Toxicity reduction

In the last part of the experimental study, changes in toxicity of the agricultural pollutants (Alachlor and Fenitrothion) during the degradation process with optimized degradation condition using immobilized titania nanophotocatalysis was examined. Table 3 presents toxicity test results in terms of LC_{50} values (in % v/v) and compares them with dearomatization (UV_{280} removal) efficiencies obtained under the same degradation conditions. Table 3
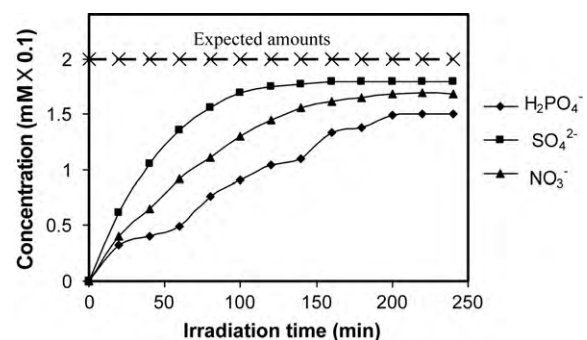

Fig. 7. Evolution of SO_4^{2-}, NO_3^- and $H_2PO_4^-$ ions during the photocatalytic oxidation of Fenitrothion (Fen.: 0.2 mM, H_2O_2: 6 mM).

Table 3
Acute toxicity test results (LC$_{50}$ values) compared with UV$_{280}$ removal results obtained for the degradation of Alachlor and Fenitrothion with immobilized titania nanophotocatalysis (Ala.: 0.2 mM, H$_2$O$_2$: 8 mM and Fen.: 0.2 mM, H$_2$O$_2$: 6 mM).

Reaction time (min)	Alachlor		Fenitrothion	
	LC$_{50}$ (% v/v)	UV$_{280}$ removal (%)	LC$_{50}$ (% v/v)	UV$_{280}$ removal (%)
30	17	20	15	18
60	30	45	27	35
90	57	63	52	60
120	75	80	70	78
180	100	100	100	100

shows that both detoxification as well as dearomatization efficiencies were high. This observation showed a relationship between the trends in toxicity and the UV$_{280}$ removal parameter, and that the prerequisite of complete detoxification was a significant reduction (almost complete removal) in aromaticity. Consequently, UV$_{280}$ that was closely linked with the disappearance of toxicity can be regarded as the control parameter for the treatment of the tested compound [49]. The obtained data are in good agreement with the previous reported results [49].

4. Conclusion

This paper presents the photocatalytic degradation, modeling, mineralization and toxicity reduction of agricultural organic pollutants (Alachlor and Fenitrothion) using immobilized titania nanophotocatalysis. Computational fluid dynamics model using a multi-purpose commercial package was studied to simulate photocatalytic oxidation of pesticides (Alachlor and Fenitrothion). Carboxylic acids (formate, acetate and oxalate) were detected as important aliphatic carboxylic acid intermediates. After 240 min of irradiation, carboxylic acids disappeared, indicating the mineralization of pesticide into CO$_2$. The results of the model and the experimental method incorporating nanophotocatalysis using immobilized titania nanoparticles can help to design an appropriate environmental management strategy to minimise the adverse impacts caused by industrial wastes. *D. magna* bioassay showed the residual acute toxicity was reduced during the photocatalytic degradation of Alachlor and Fenitrothion. The results showed that immobilized titania nanophotocatalysis was an environmentally friendly method of degradation and toxicity reduction of agricultural organic pollutants.

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