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Photocatalytic Degradation of Selected Organophosphorus Pesticides Using Titanium Dioxide and UV Light

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Additional information is available at the end of the chapter

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Abstract

The photocatalytic degradation of five selected organophosphorus pesticides (OPPs), azinphos methyl, azinphos ethyl, disulfoton, dimethoate, and fenthion, has been investigated using TiO_2 (photocatalyst) and UV irradiation. The addition of H_2O_2 (oxidant agent) into the illuminated aquatic suspensions was also surveyed. The degradation kinetics was studied under different experimental conditions such as pesticides' and catalyst's concentration. Experiments were performed in a Pyrex UV laboratory-constructed photoreactor equipped with 4×18 W low-pressure Hg lamps emitting at 365 nm (maximum intensity 14.5 mW cm^{-2} at distance 15 cm). The concentration of pesticides was determined by GC-NPD means. The extent of pesticide mineralization was assessed through TOC measurements. The results demonstrated that photolysis of target organophosphates in the absence of catalyst or oxidant is a slow process resulting in incomplete mineralization. Contradictory, studied pollutants were effectively degraded in the presence of TiO_2 ; evolution of inorganic heteroatoms (SO_4^{2-} , PO_4^{3-} , NO_2^- , NO_3^- , and NH_4^+) as final products provided evidence that pesticide deterioration occurred. The photolysis efficiencies decreased in the order: disulfoton > azinphos ethyl > azinphos methyl > fenthion > dimethoate. Furthermore, a synergistic effect was observed with the addition of H_2O_2 in the pesticide- TiO_2 suspensions. In all cases examined, reduction process appeared to follow pseudo first-order kinetics (Langmuir-Hinshelwood model). In conclusion, both catalytic systems investigated (UV- TiO_2 and UV- TiO_2 - H_2O_2) have good potential for small-scale applications.

Keywords: advanced oxidation processes, organophosphorus pesticides, water treatment, heterogeneous photocatalysis, TiO_2 , mineralization

1. Introduction

Several human activities may result in the presence of numerous and various types of emerging chemical contaminants and toxicants in water or wastewater. Pesticide is one of the most common groups of chemical pollutants found in wastewater effluents due to their widespread use in agriculture in order to maintain crop quality and quantity [1, 2]. Their widespread use for the prevention, control, or elimination of pests has led to public health concerns in recent years. According to an extended published literature, pesticides are usually detected in trace concentrations (ng L^{-1} or $\mu\text{g L}^{-1}$) and consequently are considered as micropollutants, which among other characteristics are specific water and wastewater constituents that cannot be removed by primary or secondary conventional treatment. As a result, the adaptation and application of advanced oxidation processes (AOPs) are necessary to decompose these persistent compounds from contaminated environmental matrices [3].

AOP is a class of oxidation techniques and procedures that are based on the in situ generation of highly reactive and oxidizing radical species (mainly powerful hydroxyl radicals ($\cdot\text{OH}$)), which interact with the molecules of the organic pollutants and lead to their progressive degradation. AOPs can be classified as photochemical or non-photochemical processes that furthermore can be categorized either as homogeneous or heterogeneous. More specifically, heterogeneous AOPs require the addition of a solid semiconductor (such as metal oxides and sulfurs of Ti, Al, Zn, V, Cr, Mn, etc., or organometallic catalysts) to produce a colloidal suspension that is stable under radiation and is required to stimulate a photochemical reduction reaction in the solid/liquid interface (occurrence of accelerated photoreaction). In particular, illumination of the catalyst with radiation of the proper wavelength ($\geq E_g$, bandgap energy) generates electron and hole pairs (e^- and h^+ , respectively, acting as energy carriers) that can recombine or dissociate (both reactions take place in competition); when dissociation occurs, conduction band electrons and valence band holes are produced, which are able to migrate to the particle surface and interact with adsorbed electron acceptors (oxygen) and oxidize electron donors ($\cdot\text{OH}$ and H_2O) yielding in hydroxyl radicals. Compared with the homogeneous AOPs, the heterogeneous AOPs have the advantage of the easier separation from the product (meaning the treated effluents) [4, 5].

The use of heterogeneous photocatalysis has been shown as an ideal methodology for the decontamination and restoration of water contaminated with persistent organic pollutants (POPs) in developing countries [6–8]. Nowadays, among the most promising and successful applications of heterogeneous photocatalysis applied for the removal of various toxicants from water, photocatalysis over titanium dioxide (TiO_2) is included, since it has been demonstrated as one of the most frequently used methodologies employed for the treatment of chlorinated phosphate esters and carbamic, thiocarbamic, and triazine pesticides [4–6, 9–11].

The focus of the present chapter is to provide the results of the photocatalytic degradation study conducted with five selected organophosphorus pesticides (OPPs) (azinphos methyl, azinphos ethyl, disulfoton, dimethoate, and fenthion) by heterogeneous photochemical process using UV light and TiO_2 . The process of UV- TiO_2 system was applied to the photooxidation of all selected OPPs, while the UV- TiO_2 - H_2O_2 system was applied only to degradation of dimethoate and fenthion as they proved to be more resistant in the previous set of photolysis

experiments. More specifically, the objectives of this work were (i) to evaluate and compare the kinetics of pesticide disappearance, (ii) to examine the influence of oxidant reagent (H_2O_2) added into the photocatalytic system of selected OPPs, and (iii) to investigate the potential of the catalytic systems studied to be applied in a small scale for the removal of OPPs, as, for instance, by research laboratories for purifying the wastewater they produce.

Disappearance of the investigated organophosphates contained in spiked water samples (that were irradiated) was detected by a gas chromatographic (GC) system equipped with a nitrogen-phosphorus detector (GC-NPD means). Degradation kinetics and obtained kinetic parameters, expressed as rate constant and half-life values, are presented. Moreover, mineralization of parent compounds during the batch photocatalytic experiments was assessed by quality and quantity determination of formed and released inorganic end products (evolution of heteroatoms at their highest oxidized states, such as SO_4^{2-} , NO_3^- , and PO_4^{3-}) along with TOC analyzer measurements. Based on the acquired results, the applicability of the UV- TiO_2 method that was employed in the present survey is discussed and compared with other successful applications and treatments reported in the literature.

2. Materials and methods

2.1. Test chemicals, reagents, and standards

High-purity analytical standards (>97.7%) of the five selected organophosphorus pesticides (azinphos methyl, azinphos ethyl, dimethoate, disulfoton, and fenthion) were purchased from Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) and used without further purification. Their chemical structures and data for selected physicochemical properties of studied OPPs, taken from Ref. [12], are shown in **Table 1**. Titanium dioxide (TiO_2) catalyst was Degussa P-25 (Frankfurt, Germany). Hydrogen peroxide (30% solution H_2O_2) was obtained from Merck & Co (Darmstadt, Germany). Pesticide-grade and HPLC-grade solvents (acetone, hexane, methanol, and dichloromethane) were supplied from Labscan Ltd. (Dublin, Ireland). Organic-free water used for all aquatic solutions was of specific resistance greater than $18.2 \text{ M}\Omega \text{ cm}$ (25°C) and was produced by a Milli-Q/Milli-RO water purification system (Millipore, USA). Individual pesticide stock solutions were prepared by gravimetric weighting of high-purity standards (to concentrations of approximately 1000 mg L^{-1}) in methanol (HPLC-grade) and were stored at -10°C in the dark. Working standard solutions of individual compounds were prepared by appropriate dilutions of the stock solutions. Other chemical reagents used (HCl , NaOH , Na_2SO_4 , and $\text{C}_8\text{H}_4\text{K}_2\text{O}_4$) were of analytical grade and procured from Merck (Merck, Germany).

2.2. Irradiation procedure

For the performance of photolysis experiments, a self-constructed illumination system was used which has been described in detail in the previous published survey of our laboratory [6]. In brief, the apparatus was a stainless steel illuminated box (chamber) irradiated by a set of UV low-pressure lamps (Hg-lamps manufactured in Philips TL-D, $4 \times 18 \text{ W}$, $\lambda_{\text{uv}} = 365 \text{ nm}$) that dominantly emitted radiation with maximum light intensity

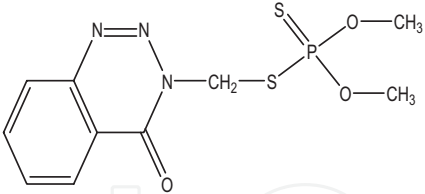
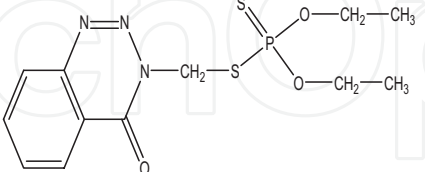
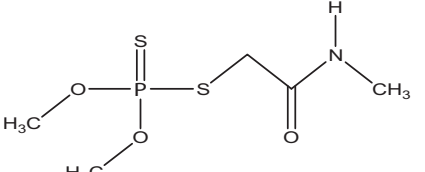
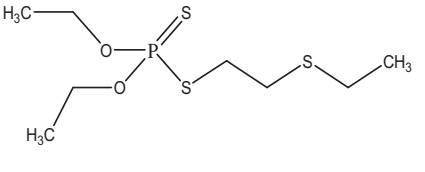
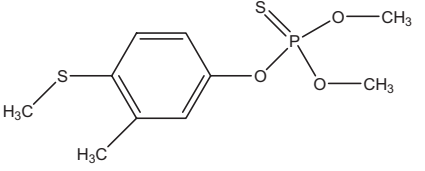
Compound [IUPAC name]	Chemical structure	Physicochemical properties
Azinphos methyl [O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] dithiophosphate]		Melting point, 73°C; boiling point, >200°C at 0.01 mmHg; vapor pressure, <0.18 mPa (at 20°C); water solubility, 28 mg L ⁻¹ (at 20°C); log K _{ow} , 2.96; and M _r , 317.3
Azinphos ethyl [O,O-diethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] dithiophosphate]		Melting point, 50°C; boiling point, 147°C (at 1.3 Pa); vapor pressure, <0.32 mPa (at 20°C); water solubility, 4–5 mg L ⁻¹ (at 20°C); log K _{ow} , 3.18; and M _r , 345.4
Dimethoate [O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate]		Melting point, 49°C; boiling point, 117°C (at 0.1 mmHg); vapor pressure, 0.29 mPa (at 20°C); water solubility, 23 g L ⁻¹ (at 20°C and pH = 5); log K _{ow} , 0.704; and M _r , 229.28
Disulfoton [O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate]		Melting point, <-25°C; boiling point, 128°C (at 1 mmHg); vapor pressure, 24 mPa (at 20°C); water solubility, 25 mg L ⁻¹ (at 20°C and pH = 7); log K _{ow} , 3.95; and M _r , 274.4
Fenthion [O,O-dimethyl O-4-methylthio- <i>m</i> -tolyl phosphorothioate]		Melting point, 7°C; boiling point, 90°C (at 1 Pa); vapor pressure, 0.74 mPa (at 20°C); water solubility, 55 mg L ⁻¹ (at 20°C and pH = 7); log K _{ow} , 4.84; and M _r , 278.33

Table 1. Chemical names, chemical formulas, and physicochemical properties of selected pesticides.

of 14.5 mW cm⁻² at 15 cm distance. Pyrex glass bottles with a capacity of 250 mL were employed as photoreactors, containing the pesticide solutions and placed in the center of the photolysis construction. Substrates were dissolved in distilled water at ppm (mg L⁻¹) levels, under their solubility levels by spiking the appropriate volume of a stock solution in methanol, so as to have a methanol content <0.05% [13]. Fortified aqueous solutions containing each tested insecticide individually (optimum pesticide's final concentration, 10 mg L⁻¹, unless otherwise stated), in the presence and absence of the photocatalyst, were prepared by dissolving the appropriate quantities of each one of the substances in water. When TiO₂ was used (optimum TiO₂ concentration, 100 mg L⁻¹, unless otherwise stated), the mixtures were magnetically stirred to obtain homogenization and a good dispersion of the catalyst and equilibrated in the dark for 30 min prior to illumination. Samples of 250 mL of the above-fortified solutions (in the absence of the photocatalyst) or suspensions (in the presence of the photocatalyst) were added to Pyrex bottles covered air tightly

with caps and photolyzed. Finally, in the case that H_2O_2 was applied as an oxidant in the photolysis system, a certain volume of the stock solution of H_2O_2 was added into the mixtures to yield the desired concentration (optimum H_2O_2 concentration, 5 mM, unless otherwise stated). Immediately, after adding hydrogen peroxide, the UV lamps were turned on, and irradiation started. The irradiated samples were magnetically stirred throughout the experiment. Photolysis was carried out at a constant ambient temperature of $30 \pm 2^\circ\text{C}$ in the photolysis apparatus. Prior to the photolysis tests, the pH value of the samples was not adjusted unless otherwise stated. In such cases, the adjustment was accomplished by dropwise addition of 0.1 N HCl or 0.1 N NaOH solutions.

2.3. Analysis of the photolyzed solutions

At specific time intervals, samples were removed from the photoreactor, and 5 mL aliquots of the photolyzed aqueous matrices were withdrawn for further analysis. In order to remove TiO_2 , samples were centrifuged at 8000 rpm for 15 min. OPP concentrations were determined after liquid-liquid extraction of the filtrated aqueous phases twice with 5 mL hexane or dichloromethane by vortex (1 min). Elimination of humidity in two combined extracts was accomplished by the addition of anhydrous Na_2SO_4 , whereas 1 μL of the organic extract was used for further analysis. Qualitative and quantitative determination of extracted pesticides' residues was performed on a Hewlett-Packard gas chromatographic (GC) system, model HP-5890, Series II, (Hewlett Packard, USA) equipped with a nitrogen-phosphorus detector (NPD). The chromatographic method and conditions applied are discussed in detail by Vagi et al. [14]. The validation of the method was carried out by the analysis of fortified water samples containing each target analyte at three different spiking levels in the range of 0.5–2 mg L^{-1} and prepared in triplicate individual solutions [15]. Percentage recoveries for the five selected insecticides were above $95.2 \pm 2.4\%$, LOD values were 0.0050 $\mu\text{g L}^{-1}$ for dimethoate and 0.0025 $\mu\text{g L}^{-1}$ for the other four selected organophosphates (azinphos methyl, azinphos ethyl, disulfoton, and fenthion), and LOQ for dimethoate was 0.0165 $\mu\text{g L}^{-1}$, while for the rest four OPPs 0.0083 $\mu\text{g L}^{-1}$ [14].

2.4. Evaluation of the extent of mineralization

Total organic carbon (TOC) measurements were performed with a Teledyne Instruments Tekmar TOC Combustion Analyzer (model Apollo 9000, Ohio, USA) calibrated with standard solutions of potassium phthalate [6]. Additionally, the release of inorganic anions containing the heteroatoms of the organophosphorus pesticides was monitored, such as phosphate (PO_4^{3-}), nitrate (NO_3^-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) ions, as a function of irradiation time was performed spectrophotometrically by using UV/Vis spectrophotometer (Varian, model Cary 50, Australia) and by following the appropriate method of the American Standard Test Method (ASTM). Specifically, nitrate ion determination was performed according to the ASTM 4500- NO_3^- -E cadmium reduction method and ammonium ions according to ASTM 4500- NH_3 -F phenate method, whereas **sulfate** and phosphate ions according to ASTM 4500- SO_4^{2-} -E turbidimetric and ASTM 4500- P^- -E ascorbic acid methods, respectively [16].

3. Results

3.1. Preliminary studies: control experiments

Two control experiments were performed under the same experimental conditions that were employed for photolysis experiments which are mentioned in detail in Section 2.2. More specifically, in order to estimate the thermal (dark) reactions between the solute and TiO_2 , a first set of experiments were carried out over the same periods as those used in the photolysis experiments, but in the dark (bottles were covered with aluminum foil for the protection against light interference). The second set of experiments involved the irradiation of the pesticide aquatic solutions without the presence of catalyst to account any direct photolysis of the studied substances.

3.1.1. Adsorption in the dark

As presented in a dotted line of **Figure 1** (curve A), the addition of the catalyst without UV radiation had a negligible effect on initial concentration of target analyte azinphos methyl (10 mg L^{-1}). The same trend was followed for the other four tested compounds (data not shown), and these observations suggest that within 48 h, which was the total duration of the experiments conducted for all of the examined substances, no obvious degradation in dark reaction occurred. Therefore, it can be concluded that negligible adsorbance of the compounds on the catalyst's surface took place and that hydrolytic processes during the experimental course can be neglected. Similar results have been previously published by several other authors [17, 18]. For example, Evgenidou and her co-workers reported that the addition of two metal oxide catalysts, TiO_2 and ZnO , without UV radiation had a negligible effect on dimethoate's photooxidation rate [17].

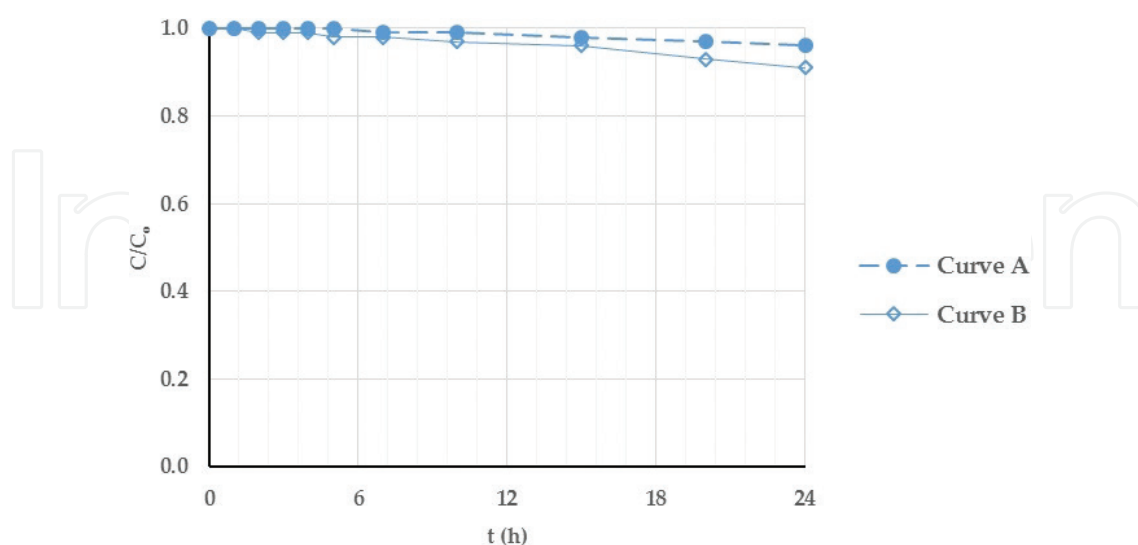


Figure 1. Disappearance of target pesticide azinphos-methyl (10 mg L^{-1}) in control as function of time. (Curve A) In the presence of the catalyst TiO_2 (100 mg L^{-1}) and in the absence of light (in the dark); (Curve B) in the absence of the catalyst TiO_2 and in the presence of light ($\lambda_{\text{UV}} = 365 \text{ nm}$).

3.1.2. Direct photolysis: photodegradation in the absence of TiO_2

The photolytic decomposition of the tested pesticides in the presence of UV light and in the absence of the catalyst TiO_2 was investigated. Experimental results for the case of azinphos methyl are illustrated in **Figure 1** (curve B). Direct photolysis of 10 mg L^{-1} of studied OPPs under illumination of 365 nm did not decrease significantly pesticides' original concentrations. Obviously, under these experimental conditions and at the end of irradiation, the observed disappearance of the OPP compounds occurred at very slow rates. According to the acquired results (not shown for azinphos ethyl, dimethoate, disulfoton, and fenthion), reduction in pesticides' initial concentration varied from 6.03 (for azinphos ethyl) to 10.68% (for dimethoate), depending on the physicochemical properties of the studied OPP individually. Moreover, these results are in agreement with TOC changes of initial TOC during direct photolysis tests conducted in the current study (presented in Section 3.4.1.).

These results are conforming to other published data according to which direct photolysis is not expected to be an important process in water for several organophosphates, because their molecules do not absorb UV light at wavelengths greater than 290 nm, despite the fact that the most important wavelengths for the photolytic degradation of the majority of the organic pesticides are 280 and 320 nm [17, 19]. It should also be mentioned that the photocatalytic deterioration of numerous cases of organophosphates in the absence of several catalysts has been studied from researchers, such as fenitrothion [20], dimethoate [17], ethyl parathion, methyl parathion, ethyl bromophos, methyl bromophos, and dichlofenthion [13]. In all these data available in the literature, photolytic process was slower compared to photocatalytic decomposition of these substances.

3.2. Photocatalytic degradation of OPPs in UV- TiO_2 system

Figure 2 depicts the photodecomposition of the compounds studied in the presence of the semiconducting catalyst under UV illumination. It is clear that all investigated organophosphorus insecticides were sufficiently degraded in aqueous titanium dioxide (TiO_2) suspensions (100 mg L^{-1}) under illumination of UV light with wavelength of 365 nm.

It is well established in the bibliography that the rates of the photocatalytic reaction depend on several experimental parameters among which included initial concentration of illuminated solute reactant, radiant flux, wavelength, type and mass of catalyst, type of photoreactor, pH, and temperature. As a consequence, only the comparison between data measured for a given set of experimental conditions is meaningful and valuable.

Obtained experimental results demonstrated that under the employed set of conditions the decomposition efficiencies of OPPs in UV- TiO_2 system depended on the nature and the structure of tested compounds and decreased in the order: disulfoton > azinphos ethyl > azinphos methyl > fenthion > dimethoate. Semiconductor TiO_2 working as a catalyst with UV light to generate highly reactive oxidizing agents caused the total decomposition (100%) of disulfoton after 12 h of illumination, whereas complete disappearance of azinphos ethyl and azinphos methyl was achieved after 24 h of light exposure.

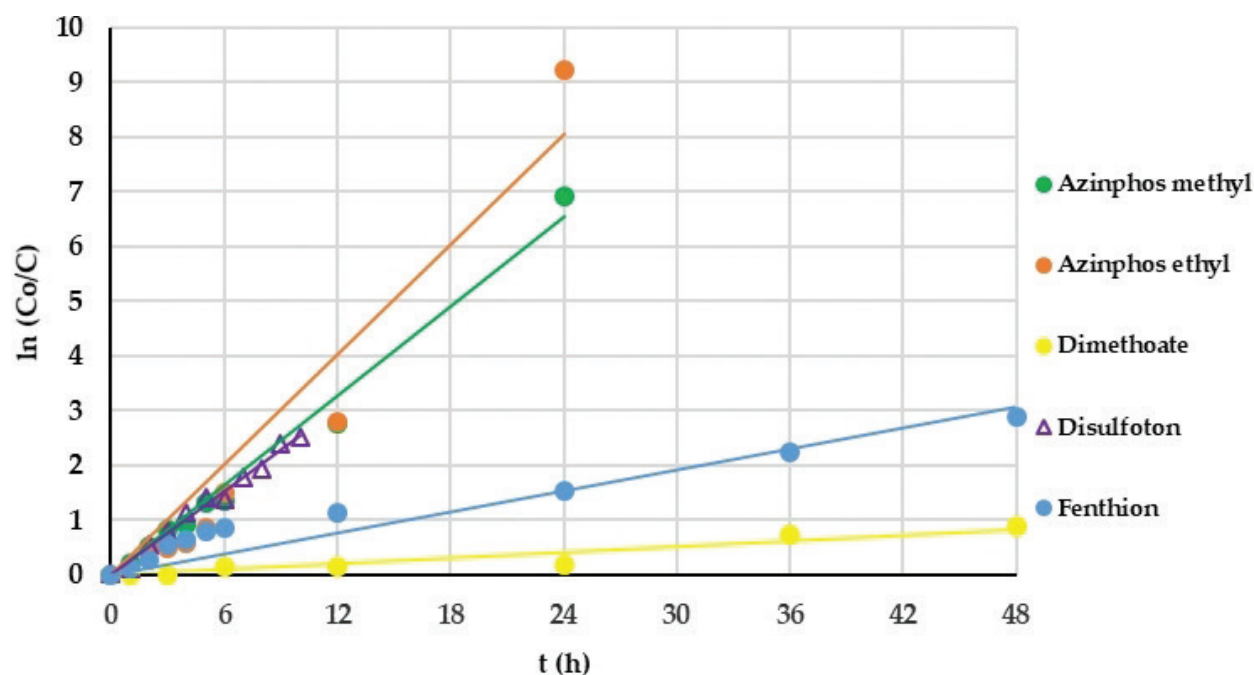


Figure 2. Photodegradation rates of studied OPPs in aqueous suspensions of the catalyst TiO_2 under UV light (pesticide's concentration, 10 mg L^{-1} ; catalyst's concentration, 100 mg L^{-1} ; pH_0 , 6.06; λ_{UV} 365 nm, in the presence of methanol).

On the contrary, fenthion and dimethoate proved to be very resistant to photocatalytic reduction, and even after 48 h of light exposure, 95 and 60% of their original concentration decomposed, respectively. That is the main reason that those two substances were selected for the study of photodegradation in the UV- TiO_2 - H_2O_2 oxidation systems.

In general, the comparison of obtained results with other experimental data previously reported for other organic pesticide micropollutants shows that degradation rates estimated in the present survey are lower. This phenomenon can be ascribed to differences in the laboratory conditions used by other researchers. For instance, Echavia and co-workers [21] reported a complete (100%) decomposition of dimethoate within 60 min of irradiation, using TiO_2 immobilized on silica gel and UV light emitting mostly at 365 nm with light intensity of 1.4 mW cm^{-2} . Evgenidou and co-workers reported 65% reduction of dimethoate after 10 min of irradiation, using UV light with $\lambda > 290 \text{ nm}$ in the presence of TiO_2 100 mg L^{-1} [17].

3.2.1. Effect of the catalyst's concentration on photocatalytic degradation rate

The reaction rate of heterogeneous photodegradation as a function of the catalyst's concentration is very important and has been investigated in several other cases reported in the literature [5, 10, 22, 23]. Hence, the purpose of these experiments was to determine the optimum TiO_2 concentrations for subsequent experiments and to investigate how the TiO_2 concentration affected the photocatalytic decomposition pathway of selected toxicants. Therefore, photolytic procedures employing different concentrations of TiO_2 ranging from

0 to 500 mg L⁻¹ were conducted, whereas the initial concentration of the pesticide tested was maintained the same, 10 mg L⁻¹. The reaction rate (r) of the photocatalytic reactions was expressed as the change (decrease) in concentration of photolyzed pesticide reactants divided by the time interval during which this change was observed. Values of r were calculated by Eq. 1:

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

where r is the reaction rate of photolysis (in mg L⁻¹ h⁻¹), C is the level of concentration of the degraded reactant (in mg L⁻¹), and t is the illumination time (in h). The initial reaction rates as a function of TiO₂ concentration for all cases investigated are depicted in **Figure 3**.

Obviously, as shown in **Figure 3**, the initial rate of photocatalytic degradation of all studied analytes decreased when TiO₂ concentration was increased from 0 to 10 mg L⁻¹ and then increased as the TiO₂ concentration was increased to 100 mg L⁻¹, where it seemed to level off. These trends and observations correspond with those of other researchers who have reported that this may be due to different contributions of distinct homogenous and heterogeneous photochemical reactions at different TiO₂ concentrations [17, 24–26]. More specifically, in the absence of TiO₂, only the homogeneous photochemical reduction was

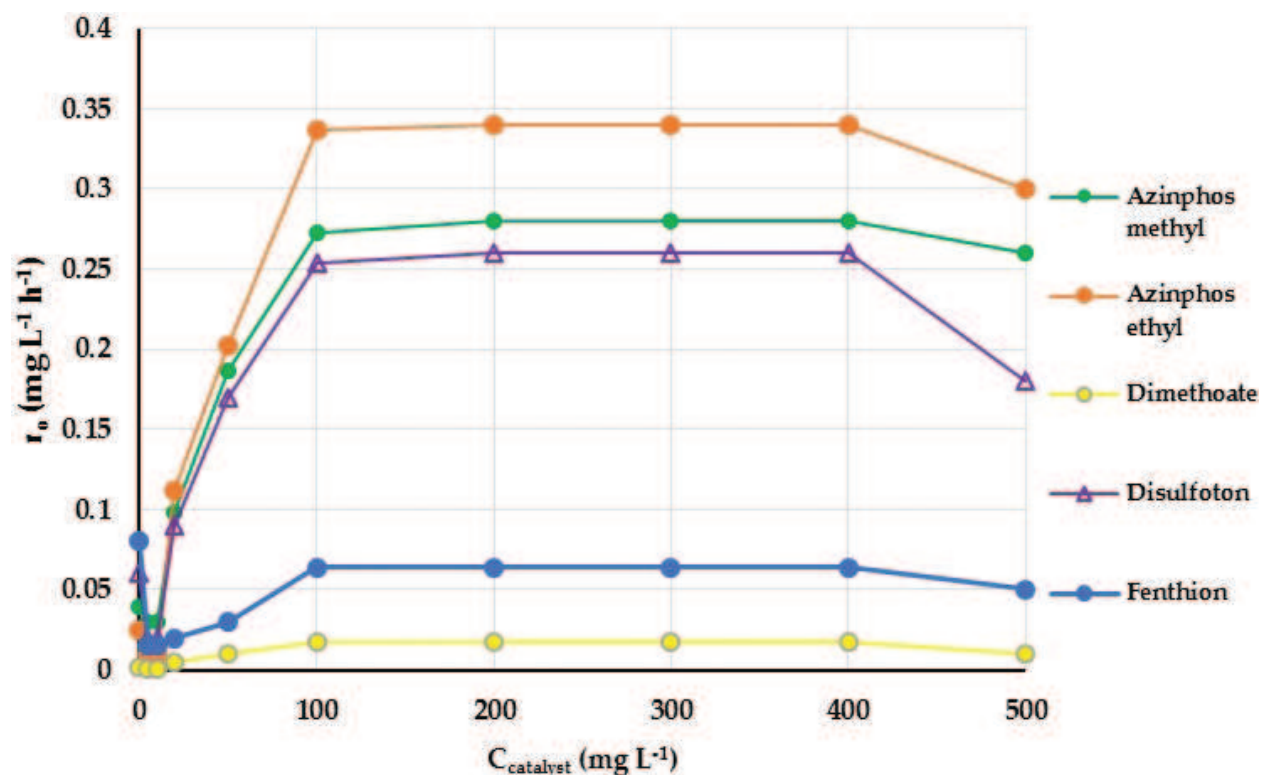


Figure 3. Effect of TiO₂ concentration on initial rate of photocatalytic degradation of studied OPPs (pesticide's concentration, 10 mg L⁻¹; catalyst's concentration, 0–500 mg L⁻¹; pH₀, 6.06; λ_{UV}, 365 nm, in the presence of methanol).

possible. The downward trend in initial rates of pesticide's photocatalytic decomposition that is shown in **Figure 3**, when only a small amount of TiO_2 ($<10 \text{ mg L}^{-1}$) was present, can be explained by the fact that the photocatalyst acted mainly to absorb and/or scatter UV light, thus inhibiting the homogenous reaction but not yet causing a significant heterogeneous reaction of photodegradation. However, at higher TiO_2 concentrations ($>10 \text{ mg L}^{-1}$), an increase in the rate of the process was observed as the heterogeneous reaction increased in importance. Actually, from the obtained data, it became obvious that in this range of concentrations the reaction rate is directly proportional to the mass of the photocatalyst. This can be explained on the basis that with the increase in catalyst dosage, the total active surface area increases; hence, availability of more active sites on catalyst surface increases as well. However, above a certain value, the reaction rate leveled off and became independent of the TiO_2 concentration.

The eventual leveling off of the initial rates of photocatalytic deterioration (**Figure 3**) could be explained by the fact that suspended particles of TiO_2 were present at a high-enough concentration to block UV light passage to the interior parts of the reactor, increased the light scattering, and made the homogeneous reaction insignificant. Moreover, other phenomena such as particle-particle interactions (agglomeration) that may occur at high TiO_2 concentration ($>100 \text{ mg L}^{-1}$) could result in a loss of surface area available for light harvesting and thus lead in a decrease of the photoreaction rates [17, 24]. Chen and Chou reported that further increase in TiO_2 catalyst amount beyond 200 mg L^{-1} may result in the deactivation of activated molecules due to collision with the ground-state molecules [25] as shown in the chemical reaction (Eq. (2)):



where TiO_2^\bullet is the active species of the catalyst that is adsorbed on its surface, whereas $\text{TiO}_2^\#$ is the deactivated form of the catalyst [24].

The photocatalytic degradation of other organic pollutants has also exhibited the same dependency on catalyst dose [17, 24]. According to previous studies, the concentration of optimum catalyst was found to be dependent on the initial solute concentration of the photocatalyzed compound [17, 26].

In the present study, as it can be concluded from data illustrated in **Figure 3**, under the applied experimental conditions, the optimum value of catalyst's concentration TiO_2 P-25 on photocatalytic decomposition of investigated insecticides is 100 mg L^{-1} , and consequently, this amount was selected to work throughout the study. This result is in agreement with other studies [17].

3.2.2. Effect of the pesticides' initial concentration on photocatalytic degradation rate

In order to investigate the dependence of the photolysis rate (r_p) on the pesticide reactants' initial concentration (C_o), a set of photodegradation experiments was carried out by varying the initial concentration of the solute from 5 to 60 mg L^{-1} (a concentration range that

facilitated the procedure of LLE method), whereas the catalyst loading was maintained constant (100 mg L^{-1}). Throughout the performed tests, it was assumed that, in the first stages of irradiation ($\leq 20\%$ reduction), no variations took place resulting from other parameters such as competitive effects of intermediates, pH changes, etc. [6, 17]. The effect of the insecticides' initial concentration (C_o) of each individual pesticide reactant on the initial reaction rate (r_o) was independently obtained and illustrated in **Figure 4** (the inset of **Figure 4** is the linear transform of $1/r_o$ versus $1/C_o$ values).

From the depicted experimental data acquired in current investigation and are shown in **Figure 4**, it is obvious that the degradation rate increased with the increase of the concentration of all of the studied compounds until it reached a saturation value (10 mg L^{-1}). At higher concentrations above that value ($>10 \text{ mg L}^{-1}$), the initial rate started to become constant and independent of target solutes' concentration.

3.2.3. Photodegradation kinetics

According to several laboratory studies that have conducted, the use of Langmuir-Hinshelwood kinetics model and first-order rate equations provided reasonable simulations to the observed photocatalysis process of various organic pollutants over illuminated TiO_2 [5, 6, 13, 17]. Langmuir-Hinshelwood model is described by the following relationship:

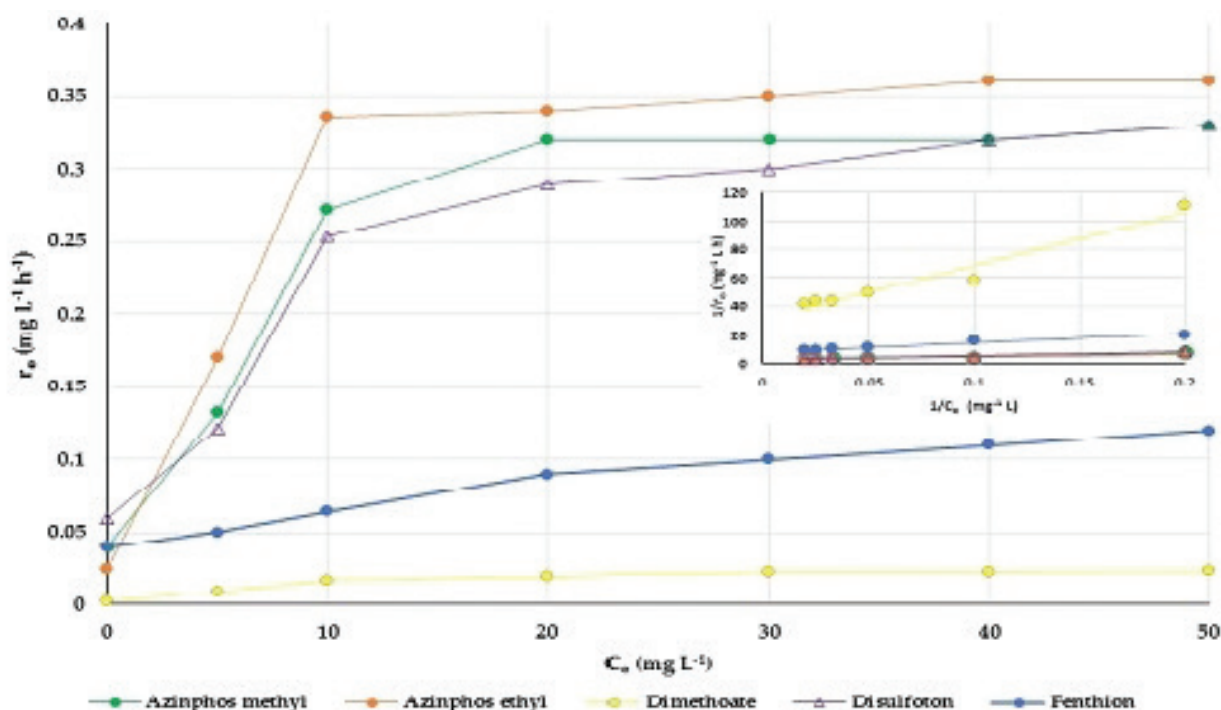


Figure 4. Effect of initial concentration of selected OPPs on photocatalytic degradation rate (pesticide's concentration, 5–60 mg L^{-1} ; catalyst's concentration, 100 mg L^{-1} ; pH_o 6.06, λ_{UV} 365 nm, in the presence of methanol).

$$r = -\frac{dC}{dt} = \frac{k_r K C}{1 + K C} \quad (3)$$

where r is the rate of reaction (in $\text{mg L}^{-1} \text{h}^{-1}$), C is the concentration at any time t during degradation (in mg L^{-1}), t is the irradiation time (in h), k_r is the limiting rate constant of reaction at maximum coverage under the employed experimental conditions (in $\text{mg L}^{-1} \text{h}^{-1}$), and finally, K is the equilibrium constant for adsorption of the substrate onto catalyst TiO_2 particles (in $\text{mg}^{-1} \text{L}$) [6]. The linear transformation of Eq. 3 is Eq. (4), which is used in the bibliography for demonstrating the linearity of data when plotted as the inverse rate versus inverse concentration (as in the inset of **Figure 4**, previously presented):

$$\left(\frac{1}{r}\right) = \left(\frac{1}{k_r}\right) + \left(\frac{1}{k_r K}\right) \left(\frac{1}{C}\right) \quad (4)$$

Integration of Eq. (3) yields Eq. (5):

$$\ln\left(\frac{C_o}{C}\right) + K(C_o - C) = k_r K t \quad (5)$$

When the initial concentration of the pesticide C_o is very small (in millimolar solution as in the case), Eq. (5) is transformed into Eqs. (6) and (7):

$$\ln\left(\frac{C_o}{C}\right) = k_r K t = K_{obs} t \quad (6)$$

$$C_t = C_o e^{-K_{obs} t} \quad (7)$$

where C_t represents the concentration at time t , C_o represents the initial concentration, and K_{obs} is the rate constant. In all cases, reduction process followed an apparent first-order rate reaction, and the calculations were performed using Eq. (7). The kinetic parameters calculated by Eqs. (4) and (7) are shown in **Table 2**. In this point, it must be mentioned that these constants reflect to the experimental conditions which have been used and are only useful for comparison between reactants that have been oxidized using the same catalyst and illumination source.

3.3. Photocatalytic degradation of OPPs in UV- TiO_2 - H_2O_2 system

The addition of an oxidant into a semiconductor suspension has been proven to enhance the photodegradation of a variety of organic pollutants among which pesticides are included [8, 17, 27, 28]. In current study, the addition of hydrogen peroxide (H_2O_2) was evaluated only for the cases of dimethoate and fenthion as these compounds proved to be more resistant in the previous set of photocatalytic experiments. The initial concentration (5 mM) of H_2O_2 was chosen according to the results obtained in previously conducted experiments

employing different initial concentrations of the oxidant (not shown). This level of concentration of H_2O_2 is in accordance with relative published studies [17].

Blank experiments with the oxidant without the catalyst or UV light (not shown) proved a negligible reduction of OPPs studied. Experiments with UV light and the oxidant, without the catalyst, were performed too, are presented by the dotted lines of **Figure 5**, and showed that H_2O_2 is able to cause photooxidation of the pesticides tested. **Figure 5** illustrates the photocatalytic decomposition of fenthion and dimethoate in the UV- TiO_2 - H_2O_2 system.

A significant enhancement on degradation efficiency was observed when 5 mM of H_2O_2 was added into the system. The kinetic parameters shown in **Table 3** demonstrated 18.20- and

Pesticides	R^2	k_r	K	k_{obs}	$t_{1/2}$
		($\text{mg L}^{-1} \text{ h}^{-1}$)		(h^{-1})	(h)
Azinphos methyl	0.9076	0.4569	1.4398	0.2293	3.02
Azinphos ethyl	0.8663	0.4574	1.3242	0.2378	2.91
Dimethoate	0.9612	0.0321	0.1402	0.0184	37.67
Disulfoton	0.9254	0.4553	1.6594	0.2587	2.68
Fenthion	0.9704	0.1289	0.4632	0.0535	12.96

Table 2. Photocatalytic kinetic parameters of selected pesticides in UV- TiO_2 (100 mg L^{-1}) system, in the presence of methanol, using a radiant UV energy of 14.5 mW cm^{-2} .

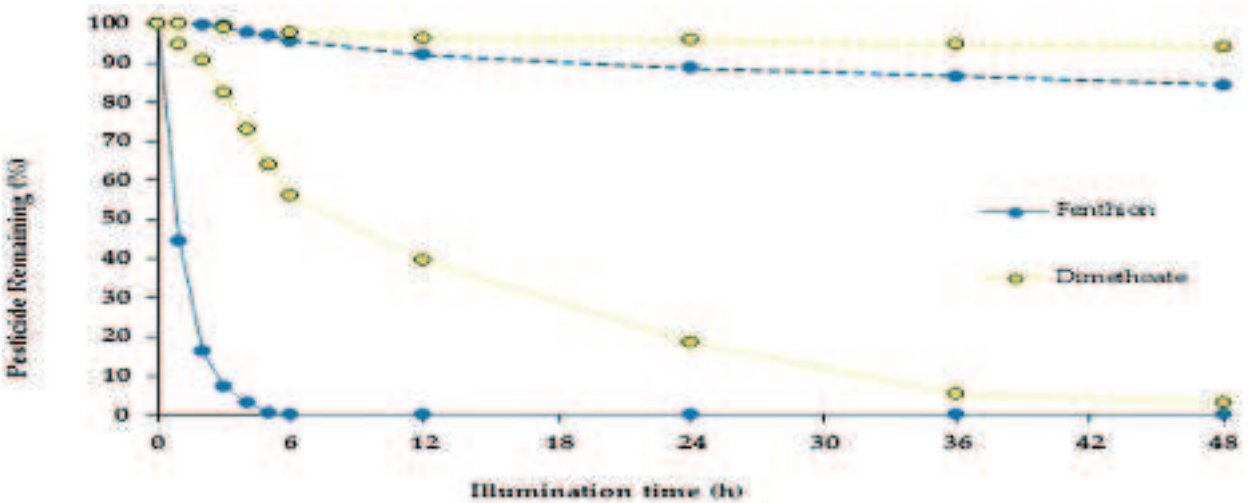


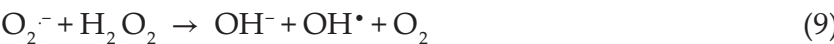
Figure 5. Effect of the addition of hydrogen peroxide on the photocatalytic degradation of dimethoate and fenthion (pesticide's concentration, 10 mg L^{-1} ; catalyst's concentration, 100 mg L^{-1} ; oxidant's concentration, 5 mM ; pH_0 , 6.06; λ_{UV} 365 nm, in the presence of methanol).

Pesticide	R^2	$k_{obs} \text{ (h}^{-1}\text{)}$	$t_{1/2} \text{ (h)}$
Dimethoate	0.9907	0.0744	9.32
Fenthion	0.9838	0.9739	0.71

Table 3. Photocatalytic kinetic parameters of selected pesticides in UV-TiO₂ (100 mg L⁻¹)-H₂O₂ (5 mM) system, in the presence of methanol, using a radiant UV energy of 14.5 mW cm⁻².

4.04-fold increase in rate constants, k_{obs} , compared to the results obtained in UV-TiO₂ systems for fenthion and dimethoate, respectively.

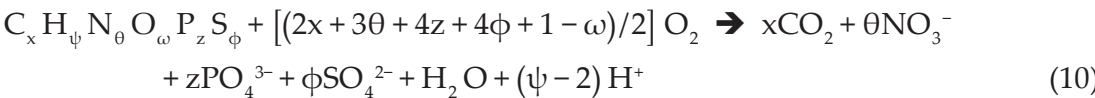
The magnitude of enhancement is in agreement with other studies concerning phosphorus-containing pesticides [27, 28]. This observation is explained by the fact that H₂O₂ can act as an alternative electron acceptor to oxygen (Eq. (8)) that is a thermodynamically more favorable reaction than oxygen reduction [29]. This should consequently promote the charge separation and accelerate the heterogeneous photocatalysis [30]. At the same time, hydroxyl radicals able to oxidize organic pollutants, such as pesticides, are generated by either the reduction of H₂O₂ at the conductance band [29] or the acceptance of an electron from superoxide again (chain reactions) (Eq. (9)) [31]. As a consequence, and regardless which conductance band reaction overrules, additional •OH oxidizing species may be produced resulting in the increase of the oxidizing power of the system [30]:



Experimental data obtained proved that the addition of H₂O₂ in the aqueous suspensions of 100 mg L⁻¹ TiO₂/10 mg L⁻¹ OPPs was more effective on the photocatalytic oxidation of fenthion (100% decomposition in 5 h) rather than in the case of dimethoate (95% decomposition in 36 h). The $t_{1/2}$ in the presence of both TiO₂ and H₂O₂ was 0.71 h (42.6 min) for fenthion and 9.32 h for dimethoate.

3.4. Mineralization studies

The general stoichiometric reaction proposed for the photocatalytic oxidation of the studied pesticides that leads to the conversion of all of their carbon atoms to gaseous CO₂ and the heteroatoms into inorganic anions at their highest oxidation states which remain in the solution is described by the following reaction (Eq. (10)). Consequently, in order to assess the extent of mineralization during photocatalysis of selected organic pollutants, TOC measurements were carried out along with determination of released inorganic anions containing the heteroatoms of the selected organics (**Figure 6**):



3.4.1. TOC content

As shown in **Figure 6**, in the presence of TiO_2 and under UV irradiation, the TOC concentration of the insecticides exhibited a constant decrease with time, reaching TOC reduction that ranged between 58 and 100% (total mineralization) after the end of illumination time. In addition, it can be seen that the rates of TOC reduction during irradiation of solutions of azinphos methyl, azinphos ethyl, and disulfoton were higher compared to those of dimethoate and fenthion, suggesting that former ones exhibit greater susceptibility to photocatalysis than the

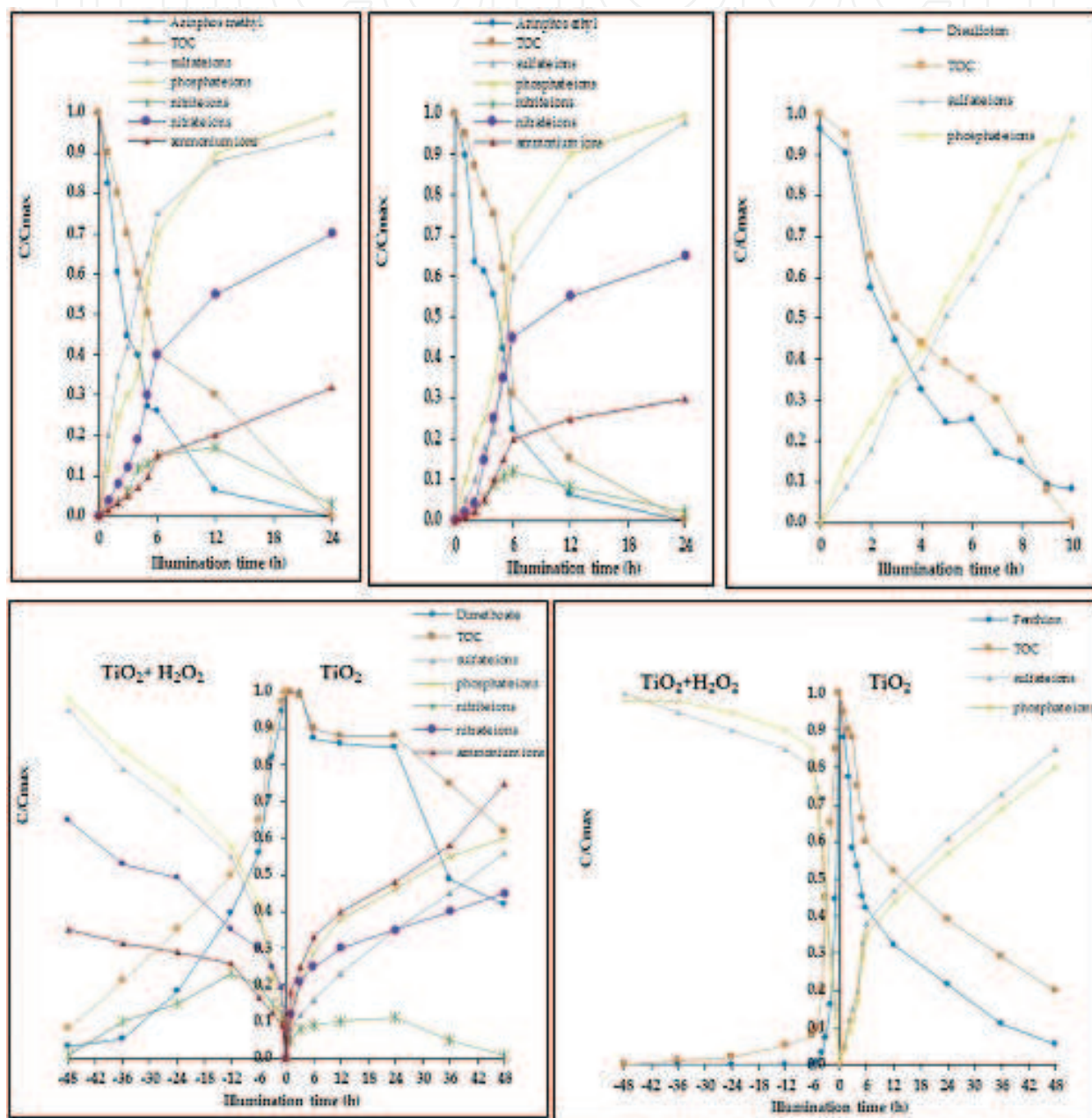


Figure 6. Pesticide and TOC reduction and evolution of sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+) ions originating from photocatalytic degradation of selected pesticides as a function of irradiation time (pesticide's concentration level, 10 mg L^{-1} ; TiO_2 , 100 mg L^{-1} ; H_2O_2 , 5 mM ; λ_{UV} 365 nm , in the presence of methanol).

latter. Furthermore, these results are confirming the kinetic data acquired in the current study from the application of Langmuir-Hinshelwood model. The addition of H_2O_2 in the irradiated photocatalytic media of dimethoate and fenthion not only enhanced the removal of TOC in both cases but also resulted in almost total decomposition of target pesticide pollutants.

In general, the trend in TOC reduction was similar to that observed in pesticide disappearance. However, when the obtained k_{obs} values of these two studied processes were compared, the reduction in TOC content of irradiated solutions was found to be a slower phenomenon than the photodecomposition of the parent pesticides. This observation can be explained by the fact that the photocatalytic decomposition of the parent compounds occurred through the formation of various organic intermediates and not instantaneously. Moreover, taking into consideration the complex nature of photocatalysis and the wide variety of stable and unstable photoproducts that can be formed, rate of TOC reduction depended on the individual tested organophosphate. The same behavior has been observed in numerous irradiated pesticide solutions reported in the available literature; for instance, the formation and evolution of several carboxylic acids (such as formic, acetic, glycolic, and cyanuric acids) as transient intermediates of photocatalytic reaction, which could eventually undergo complete mineralization as irradiation progresses, have been published [4, 5, 9, 21]. Formation of oxon derivatives (such as paraoxon ethyl, pirimiphos-oxon, fenthion-oxon), corresponding phenols (e.g., nitrophenol), various and different trialkyl and dialkyl phosphorothioate or phosphate esters, and quinonidal compounds has also been observed and detected as major intermediate photoproducts that subsequently underwent mineralization [5]. On the contrary, in the absence of UV light (dark condition, not presented in TOC reduction data), no significant percent reduction in TOC of studied compounds occurred, suggesting negligible adsorbance of the pesticides on TiO_2 surface.

3.4.2. Mineral inorganic ions

Evolution of the heteroatoms at their highest oxidation states such as SO_2^{4-} , NO_3^- , and PO_4^{3-} provides evidence that pesticide degradation occurred primarily through photocatalytic oxidation reactions [21]. Therefore, in order to further confirm the extent of photocatalytic reduction and better understand the reaction mechanisms involved, the formation of inorganic anions containing the heteroatoms of the selected organophosphorus compounds was surveyed. More specifically in the present study, the formation of sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrite (NO_2^-), nitrate (NO_3^-), and ammonium (NH_4^+) ions, originating from photocatalytic degradation of selected toxicants under UV irradiation, was investigated.

As illustrated in **Figure 6**, photocatalytic treatment of target pesticides resulted in the destruction of the parent molecules as evidenced by the evolution of monitored inorganic anions. Decomposition of all five tested organophosphates released SO_2^{4-} and PO_4^{3-} , while that of the three nitrogen-containing molecules, azinphos methyl, azinphos ethyl, and dimethoate (chemical formulas in **Table 1**), liberated NO_2^- , NO_3^- , and NH_4^+ ions as well. These findings are consistent with published works involving mineralization studies of other organophosphorus pesticides during heterogeneous photolysis over TiO_2 suspensions. It is well documented that the pesticides containing sulfur atoms are mineralized into sulfate ions [5, 17, 20, 21]. Overall, the monitoring of SO_2^{4-} ions showed that a rapid increase in their concentration was observed achieving finally (in the final stages of irradiation treatment) their expected amounts according to the stoichiometry proposed in the reaction (10). Formation of sulfate ions took place by the rupture of the sulfur

group from the P=S and P–S bonds, which occurred firstly in the case of phosphorothioates, leading to the formation of oxon intermediate derivatives as reported in previous studies [5, 13].

Acquired results are in accordance with several experimental results, which have shown that photodecomposition of several organophosphorus substances in the presence of TiO₂ suspensions produces phosphate ions [5, 17, 20]. Release of phosphate ions occurred by the cleavage of the phosphorus atom from the P=S, P–S, and P–O bonds caused by the continuous oxidation attack of the •OH radicals. However, according to other reported studies, non-detection of PO₄³⁻ ions in the irradiated solutions of phosphorus-containing pesticides, such as acephate and dimethoate, is possible due to incomplete mineralization of the pesticides as well as competitive adsorption of PO₄³⁻ on the photoactivated reaction sites of the catalyst TiO₂, a strong phenomenon in the pH range used, that partially inhibits the reaction rate of deterioration (20–70% reduction at levels of greater than 10⁻³ mol dm⁻³) [5, 21].

The formation of nitrite, nitrate, and ammonium ions was also monitored for the three selected nitrogen-containing molecules, since these compounds could give rise to these ions [5, 32], based on relative literature, even N₂ gas can be generated mainly from the photodegradation of the -N = N- double bond moieties contained in aliphatic or heterocyclic nitrogen-containing compounds, such as azinphos methyl and azinphos ethyl. Obviously, the release of NO₂⁻ that was observed in the first stage of irradiation can be ascribed to the fact that these ions are formed as an intermediate of NO₃⁻, which was demonstrated by the disappearance of NO₂⁻ and concomitant formation of NO₃⁻ after longer irradiation periods. Generally, it has been found that nitrate anions, probably formed through oxidation pathways, have little effect on the kinetics of reaction [5], whereas ammonium ions are relatively stable cations released from reduction processes [5]. The molar ratio of NO₃⁻ and NH₄⁺ concentration (NO₃⁻/NH₄⁺) depends mainly on the nature of the N-containing organic compounds and the initial oxidation state of nitrogen and some experimental conditions, including the irradiation time, the pH of the solution, and the substance concentration [5, 32]. Under the employed experimental conditions, higher nitrate-to-ammonium concentration ratio was produced for the cases of azinphos methyl and azinphos ethyl that contained ring nitrogen converted mainly into NO₃⁻ ([NO₃⁻] > [NH₄⁺]) than for dimethoate in which the contained amino group was predominantly mineralized into NH₄⁺ species ([NO₃⁻] < [NH₄⁺]).

Mineralization studies of dimethoate and fenthion during photocatalysis were also conducted in the presence of oxidant (H₂O₂) (**Figure 6**). Based on the kinetics of formation and disappearance of mineral ions, it is obvious that the addition of the oxidant enhanced the transformation of both parent compounds and was able to achieve higher mineralization. This is in agreement with previous studies supporting that the final products of organophosphorus pesticides photooxidation are eventually carbon dioxide and inorganic ions containing the heteroatoms [18].

4. Conclusions

Based on the results of the current study concerning the photocatalytic decomposition of five selected organophosphorus insecticides contained individually in aqueous solutions and by using the heterogeneous systems of UV-TiO₂ and UV-TiO₂-H₂O₂, it appeared that TiO₂ is a semiconductor with high catalytic activity; photodegradation of all studied compounds proceeded at higher reaction rates in its presence than in its absence (direct photolysis). Total decomposition

in UV-TiO₂ system was accomplished for the three cases of azinphos ethyl, azinphos methyl, and disulfoton after illumination time that depended on the tested organophosphate, whereas longer irradiation time for the cases of dimethoate and fenthion is probably needed. With the addition of H₂O₂ into illuminated TiO₂ suspensions, a synergistic effect was observed, which led to an enhancement of the photolytic process, achieving total disappearance of dimethoate and fenthion. Finally, the experimental data revealed that both catalytic systems investigated have good potential for small-scale applications, such as the wastewater purification systems of research laboratories or agrochemical manufacturer, formulators, and producer companies. The advantages of the proposed photocatalytic systems among others include simplicity in design because they give the opportunity to employ UV lamps easily found in the market and semiconductor powder (TiO₂) of low cost as catalyst.

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