

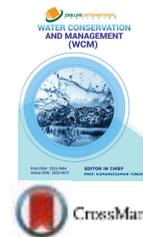


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# PHOTOCATALYTIC DEGRADATION OF FENITROTHION IN WATER WITH TiO<sub>2</sub> UNDER SOLAR IRRADIATION

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### ARTICLE DETAILS

### ABSTRACT

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Fenitrothion is widely used as herbicide with strong estrogenic activity, and it can lead to abnormalities of the thyroid gland and can give mutations. Hence, their degradation treatment is necessary for the environment. The photocatalytic remediation under sunlight irradiation is very effective for the degradation of fenitrothion. Fenitrothion is completely degraded during 10 min under the optimized conditions. The influence of various conditions, such as irradiation time, sunlight intensity, pH, temperature, TiO<sub>2</sub> loading amount and initial substrate concentration, is investigated on the degradation of fenitrothion. The photocatalytic degradation mechanisms are speculated, from the experimental results with molecular orbital (MO) simulation for frontier electron density. The primary photocatalytic degradation reaction keeps a pseudo first order kinetic law. The activation energy ( $E_a$ ) and half-life ( $t_{1/2}$ ) are 20.6 kJ/mol and 1.4 min, respectively. The fenitrothion wastewater photocatalytic treatment may become a good technique under solar irradiation.

#### KEYWORDS

Fenitrothion, sunlight irradiation, titanium dioxide, wastewater treatment, remediation.

### 1. INTRODUCTION

The large use of pesticides in agriculture tends to an increase in both productivity and environmental contamination. Fenitrothion (Figure 1; IUPAC name: O,O-Dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate; molecular weight: 277.24 g/mol) is widely employed as the organophosphorus pesticide. Widespread use and disposal of fenitrothion result in the release of residue into aquatic systems, thus inducing an environmental problem. Owing to the partial solubility of fenitrothion in water ( $7 \times 10^{-5}$  mol/dm<sup>3</sup>), it can penetrate to deep soil strata and move to the groundwater [1]. Fenitrothion undergoes

photodegradation in natural water and shows many toxic metabolites to aquatic organisms. Fenitrothion and its photoproducts are recognized as endocrine disruptors [2,3]. The toxicity dosage of fenitrothion to LC50 in carp (48 h) is 4.1 mg/L [4]. Therefore, developing advanced water treatment technologies to effectively remove fenitrothion residues is urgently demanded in both scientific and industrial communities. Several techniques have been reported for the removal of fenitrothion from wastewater such as photolysis, photocatalysis and photo-Fenton processes [5-10]. However, the photocatalytic systems present large advantages for the removal of pollutants including complete oxidation, no formation of polycyclised products, utilization of natural sunlight, availability of cheap catalysts [11].

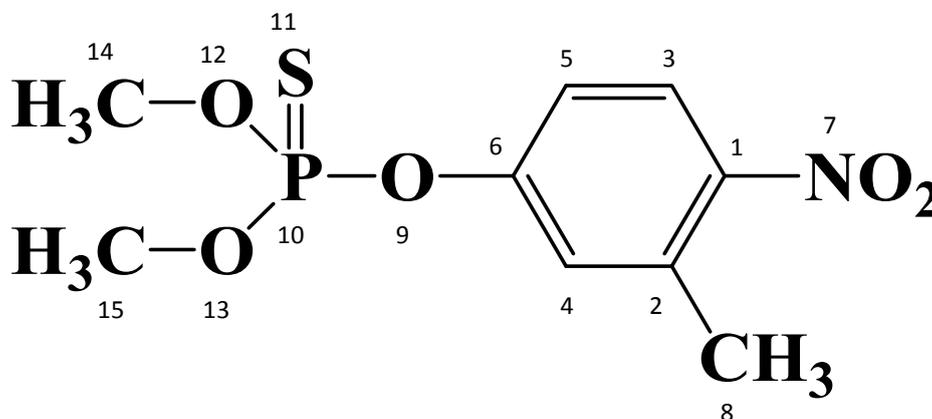


Figure 1: Molecular structure of fenitrothion.

Titanium dioxide (TiO<sub>2</sub>) is one of the most functional materials, due to its stability under harsh conditions, commercial availability and high photoactivity. Much attention has been focused in the past three decades

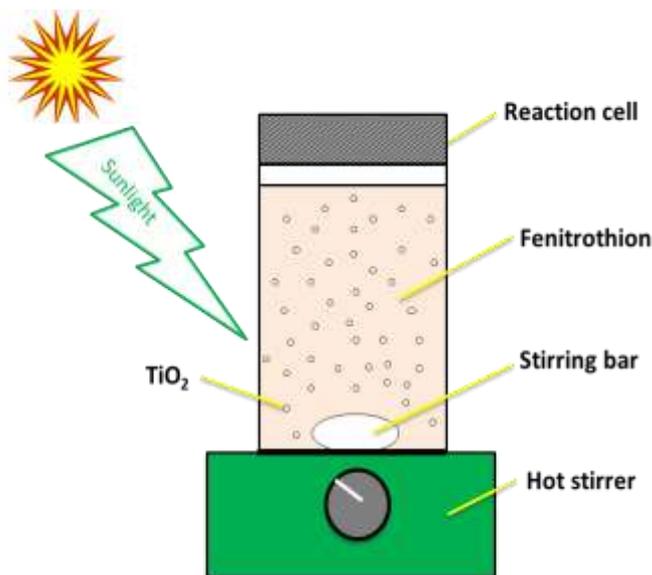
on the photocatalytic degradation of organic pollutants with TiO<sub>2</sub> in aqueous suspension solution under UV irradiation [12]. UV sources such as low-pressure mercury vapor lamps represent an environmental hazard

due to the high toxicity of mercury, have relatively short life spans and are intensive energy. These defects make the processing cost intensive and environmentally problem. On the other hand, solar photocatalytic water treatment with irradiated semiconductors has been proposed as an effective and attractive technique for degradation. In this process, the  $\text{TiO}_2$  is excited with UV light of wavelengths less than 380 nm to form valance band holes ( $h\nu_{VB}^+$ ) and conduction band electrons ( $e_{CB}^-$ ) which are capable of initiating the photocatalytic oxidation and reduction reactions, respectively. The photocatalytic remediation of environmental pollution on bare  $\text{TiO}_2$  in water under sunlight irradiation by using the UV range, that is, a small fraction of solar light, is possible, although it takes long time for the photocatalytic treatment.

The destruction of fenitrothion in water by  $\text{TiO}_2$ -photocatalytic processes under sunlight has been rarely studied for an effective technique for the removal of recalcitrant contaminants. Therefore, in the present study, we have investigated the photocatalytic degradation of fenitrothion in aqueous solution with  $\text{TiO}_2$  under sunlight irradiation. The mineralization of fenitrothion is monitored by total organic carbon (TOC) content.

## 2. MATERIALS AND METHODS

Fenitrothion in the present work is obtained from Wako Pure Chemical Industries, Ltd. (HPLC grade > 98%, pesticide residue analysis). Aqueous fenitrothion solutions are prepared with ultrapure water, which is produced by an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) showing in a resistivity >18 M $\Omega$  cm. A 30 mL aqueous solution containing 10 mg/L fenitrothion is put into a Pyrex reaction vessel (50 mL capacity).  $\text{TiO}_2$  powder is purchased from Degussa Co., Germany and its physical data are as follows: particle size ~21 nm, surface area 50 m<sup>2</sup>/g, band gap 3.2 eV, purity 99.9% and with 80: 20 anatase to rutile [13]. The catalyst powder (30 mg) is added to the solution to produce a concentration of 1 g/L. The pH of the solution is 6.0. The temperature is kept constant at 10 to 60 °C. The photocatalytic degradation process is displayed in Figure 2. The fenitrothion solutions containing  $\text{TiO}_2$  are irradiated under sunlight illumination. In this case, the short ultraviolet region ( $\lambda < 300$  nm) is filtered out by the vessel wall. The intensity of light is measured by a UV radio meter with a sensor of 320 to 410 nm wavelengths (UVR-400, Luchi Co., Osaka, Japan). The variations of sunlight intensity are less than 3% during 5 min. After the illumination, the fenitrothion concentration in the aqueous solution is measured using a high-performance liquid chromatograph equipped with a UV optical detector (GC-7410, GL Science Inc.) and a separation column ODS-2 (GL Science Inc.). The elution is monitored at 254 nm. The eluent used is a mixed solvent of acetonitrile and water (65/35, v/v). The flow rate of the mobile phase is 1.0 mL/min.



**Figure 2:** Photocatalytic degradation reactor for fenitrothion

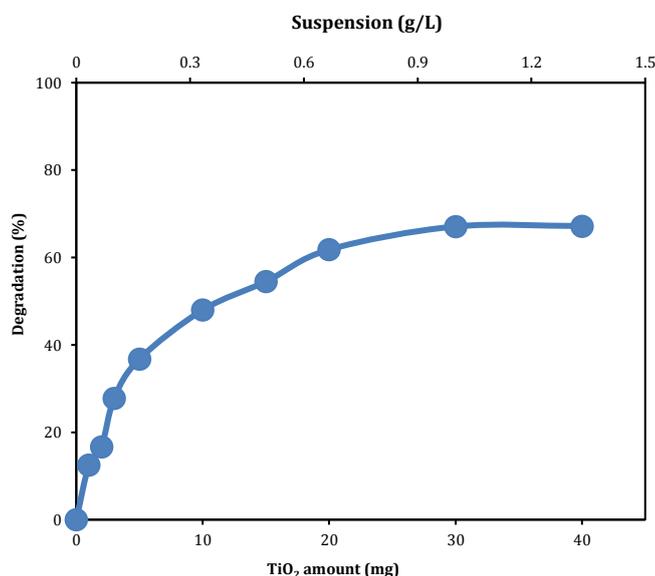
The mineralization of fenitrothion is monitored by checking the total organic carbon (TOC). The TOC is determined with a Shimadzu TOC analyzer (TOC-V<sub>E</sub>) based on  $\text{CO}_2$  quantification by non-dispersive infrared analysis after high-temperature catalytic combustion. Ten  $\mu\text{L}$  of the sample is injected into the TOC analyzer.

Molecular orbital calculations are performed at the single determinant (Hartree-Fock) level for optimization of the minimum energy obtained at the AM1 level. All semi-empirical calculations are performed in MOPAC Version 6.01 with a CAChe package (Fujitsu Co. Ltd.). An initial position for a possible  $\cdot\text{OH}$  radical attack is estimated from calculations of frontier electron densities of the fenitrothion structure. The element with large frontier electron density tends to be attacked by  $\cdot\text{OH}$  radical. The mode by which fenitrothion might adsorb onto the  $\text{TiO}_2$  surface is estimated from calculated partial charges of fenitrothion [14].

## 3. RESULTS AND DISCUSSION

### 3.1 Influence of $\text{TiO}_2$ dosages

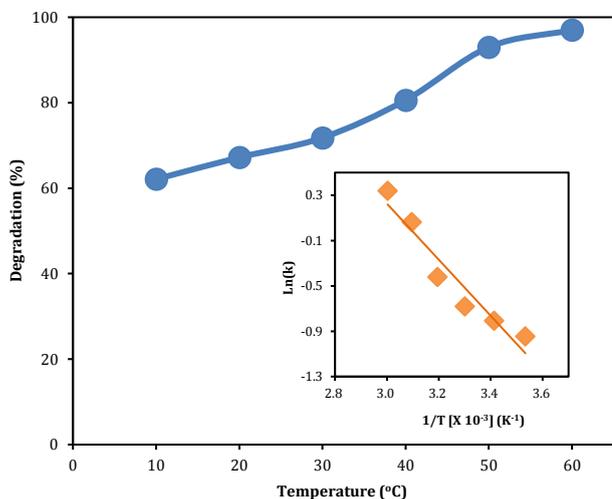
The catalyst concentration is one of the main parameters for the photodegradation system. So as to avoid the use of excess catalyst, it is necessary to optimize the loading amount for efficient photodegradation of fenitrothion. Several researchers have studied the reaction efficiencies as a function of catalyst loading amount [15,16]. The influence of amount of  $\text{TiO}_2$  on the photocatalytic treatment has been evaluated. The results are shown in Figure 3. The efficiency increases with increasing the amounts up to 30 mg, and then the efficiency remains constant. The increase in the efficiency appears to be owing to the increase in the total surface area, namely the number of active sites available for the reaction. However, when  $\text{TiO}_2$  is overdosed, the active site number may become almost constant due to the loss in surface area occasioned by agglomeration (particle-particle interactions) at high solid concentration, the increased light scattering and the decreased light penetration [17]. Hence, 30 mg (1 g/L) of  $\text{TiO}_2$  is used as the optimal amounts for the next works.



**Figure 3:** Influence of  $\text{TiO}_2$  amount on the solar photocatalytic degradation of fenitrothion in water. Fenitrothion: 10 mg/L; illumination time: 2.5 min; light intensity: 1.6 mW/cm<sup>2</sup>; temperature: 20 °C; pH: 6

### 3.2 Influence of temperature

The influence of temperature on the degradation of fenitrothion in water with  $\text{TiO}_2$  is checked in the range of 10–60 °C. The results are shown in Figure 4. The degradation efficiency gradually increases as the temperature increases. In the imazaquin photodegradation of aqueous  $\text{TiO}_2$  suspension, the influence of temperature is evaluated in the range 20–40 °C, and the efficiencies increase with increasing temperature [18]. From the plotting of the natural logarithm of the rate constant as a function of reciprocal absolute temperature, a linear behavior is obtained (insert figure in Figure 4). The activation energy ( $E_a$ ) of fenitrothion is estimated to be 20.6 kJ/mol. It is described in the  $\text{TiO}_2$  photocatalytic degradation of amitrole and naphthalene that the activation energy ( $E_a$ ) are 6.7 and 22 kJ/mol, respectively [19,20]. Because the photoactivation process is irrelevant to thermal activation, the estimated activation energy may be only apparent. Consequently, all next illuminations are carried out at 20 °C owing to the operating cost.

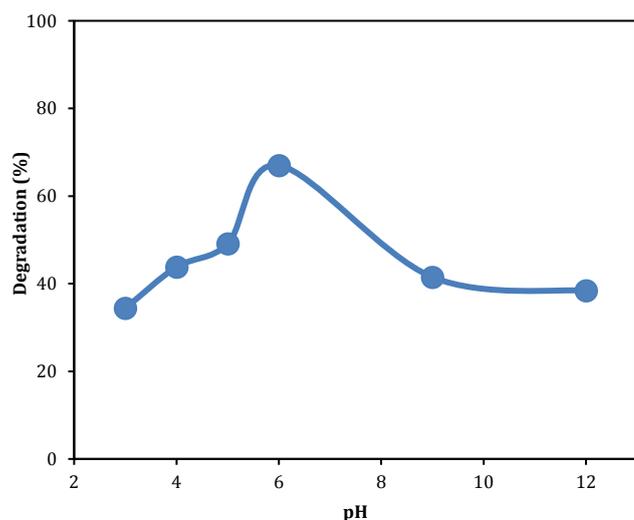


**Figure 4:** Influence of temperature on the solar photocatalytic degradation of fenitrothion in water with TiO<sub>2</sub>. Inset figure: plot of Ln(k) versus 1/T. Fenitrothion: 10 mg/L; TiO<sub>2</sub>: 30 mg; light intensity: 1.6 mW/cm<sup>2</sup>; illumination time: 2.5 min; pH: 6

**3.3 Effect of initial pH**

The role of initial pH on the degradation efficiency of fenitrothion is studied (Figure 5). The maximum degradation efficiency is observed at pH 6. Then, the degradation efficiency gradually decreases as the pH increases. The zero-point charge (zpc) pH<sub>zpc</sub> of TiO<sub>2</sub> is approximately 6 [21]. TiO<sub>2</sub> surface is positively charged in acidic (pH < 6), whereas it is negatively charged under alkaline (pH > 6). Generally, the pH changes can have a non-insignificant result not only on the mode of adsorption of the fenitrothion on TiO<sub>2</sub> surface, but also on the selectivity of the photo reaction occurring on the surface, because redox reactions are very sensitive to changes in the surface potential [22].

The adsorption of fenitrothion on the surface is estimated from the simulation of molecular partial charges (Table 1). The most negative partial charge atom in the fenitrothion structure is the sulphur atom (11S) and the most positive partial charge atom is phosphorus atom (10P). Therefore, we deduce that in alkaline the positively charged phosphorus 10P atom is easily adsorbed on the TiO<sub>2</sub> surface through electrostatic interaction, and in acidic condition the negatively charged sulphur 11S atom. Since the fenitrothion cannot be dissociated and is neutral around pH 6, the maximum efficiency may be obtained in this pH. Therefore, pH 6 is chosen for the optimal conditions, because of the unnecessary of chemical treatment including neutralization process.



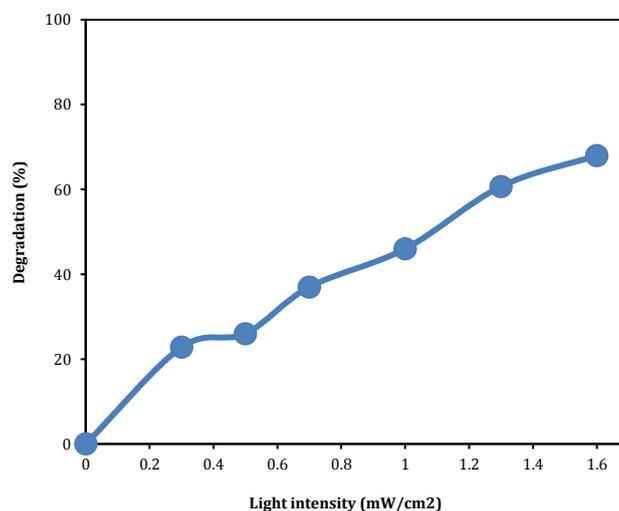
**Figure 5:** Influence of initial pH on the solar photocatalytic degradation of fenitrothion in water with TiO<sub>2</sub>. Fenitrothion: 10 mg/L; TiO<sub>2</sub>: 30 mg; illumination time: 2.5 min; light intensity: 1.6 mW/cm<sup>2</sup>; temperature: 25 °C

**Table 1:** Calculations of partial charge (PC) and frontier electron density (FED) for fenitrothion

Atom	PC	FED
1C	-0.147	0.183
2C	0.079	0.150
3C	-0.030	0.093
4C	-0.267	0.117
5C	-0.146	0.213
6C	0.181	0.093
7N	0.600	0.022
7O-1	-0.412	0.024
7O-2	-0.396	0.024
8C	-0.220	0.022
9O	-0.673	0.093
10P	2.694	0.494
11S	-1.351	0.243
12O	-0.727	0.058
13O	-0.703	0.060
14C	-0.051	0.008
15C	-0.055	0.006

**3.4 Influence of light intensity**

The influence of light intensity on the solar photodegradation of fenitrothion in water with TiO<sub>2</sub> is studied (Figure 6). The experiments are carried out with various light intensities on sunny and cloudy days. The efficiency increases with an increase in the light intensity. Because the catalyst is suspended in a stirred solution, the light intensity will affect the degree of absorption of light by the catalyst surface. Hence, the results from the photocatalytic degradation of fenitrothion in TiO<sub>2</sub> suspension are reasonable.



**Figure 6:** Influence of light intensity on the solar photocatalytic degradation of fenitrothion in water with TiO<sub>2</sub>. Fenitrothion: 10 mg/L; TiO<sub>2</sub>: 30 mg; illumination time: 2.5 min; temperature: 20 °C; pH: 6

**3.5 Influence of illumination time**

The Influence of illumination time on the photocatalytic degradation of fenitrothion with TiO<sub>2</sub> is investigated. The results are shown in Figure 7. The photocatalytic degradation process proceeds rapidly until 2.5 min. At 10 min, fenitrothion in the solution is almost disappeared. The heterogeneous photodegradation of fenitrothion follows apparently pseudo-first-order kinetics at low initial substrate concentration, and the expression is given by the equation:

$$r = -\frac{dc}{dt} = -kC \tag{1}$$

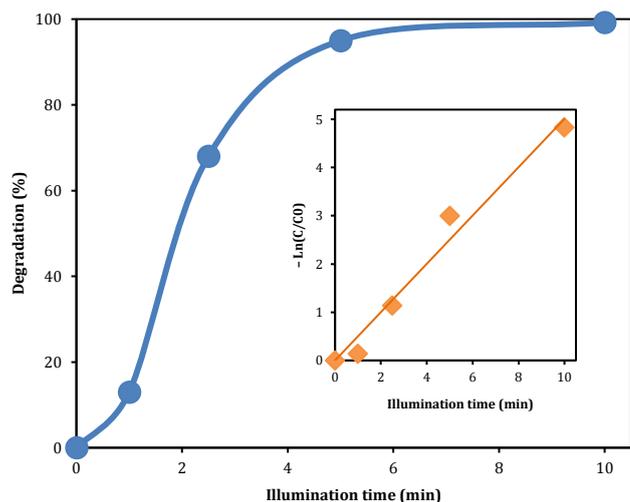
where k is the pseudo-first-order rate constant. Integration of the above equation with the limit of C = C<sub>0</sub> at t = 0 with C being the equilibrium concentration of the bulk solution produces the following equation:

$$\ln \frac{C}{C_0} = -kt \tag{2}$$

where C<sub>0</sub> is the equilibrium concentration of fenitrothion, and C is the concentration at time t.

The primary degradation reaction is estimated to have a pseudo-first-order kinetic law, according to Eq. (2). So as to confirm the speculation, Ln(C/C<sub>0</sub>) is plotted versus a function of illumination time. A linear relation between Ln(C/C<sub>0</sub>) and irradiation time has been observed for the

degradation (insert figure in Figure 7). The values of rate constants have been obtained from the slope and shown in Table 2.



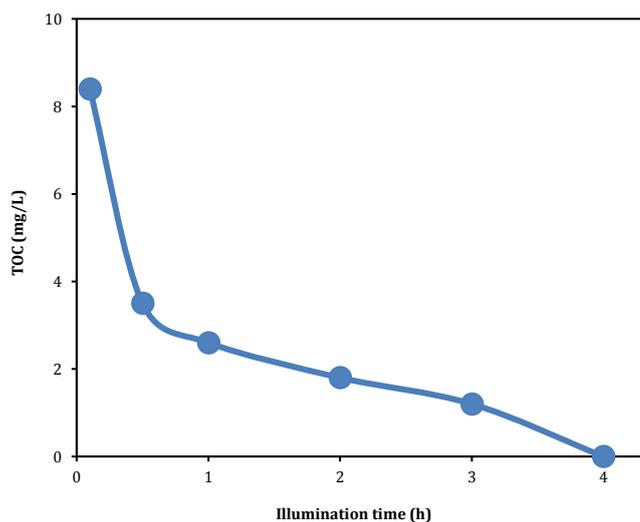
**Figure 7:** Influence of illumination time on the solar photocatalytic degradation of fenitrothion in water using  $\text{TiO}_2$ . Inset figure: Plot of  $-\ln(C/C_0)$  versus illumination time for the photodegradation of fenitrothion. Fenitrothion: 10 mg/L;  $\text{TiO}_2$ : 30 mg; illumination time: 0–10 min; light intensity: 1.6  $\text{mW}/\text{cm}^2$ ; temperature: 20 °C; pH: 6

**Table 2:** Photocatalytic degradation kinetic parameters

Fenitrothion $C_0$ (mg/L)	Rate constant $k$ ( $\text{min}^{-1}$ )	Correlation coefficient, $R^2$	Half-life $t_{1/2}$ (min)
10	0.501	0.98	1.38

### 3.6 TOC analysis

The mineralization is a very important parameter because wastewater mineralization is the main goal of the treatment. The mineralization of fenitrothion is monitored by measuring the total organic carbon (TOC). As shown in Figure 8, TOC of fenitrothion rapidly decreases with increasing the reaction time, and complete mineralization occurs within 4 h. Therefore, the mineralization of fenitrothion can be possible under sunlight illumination.

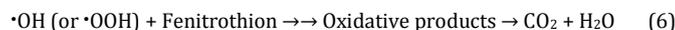
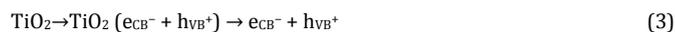


**Figure 8:** TOC removal in the fenitrothion solution under sunlight. Fenitrothion: 10 mg/L;  $\text{TiO}_2$ : 30 mg; total illumination time: 4 h; light intensity: 1.6  $\text{mW}/\text{cm}^2$ ; temperature: 20 °C; pH: 6

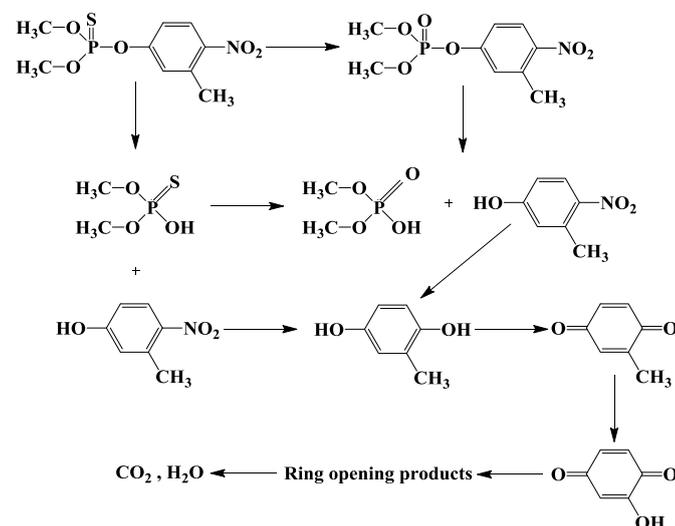
### 3.7 Proposed photodegradation pathway of fenitrothion

In photocatalytic degradation with  $\text{TiO}_2$ , photons having energies greater than the band-gap energy can result in the excitation of valence band electrons, which leads to the promotion of electron from valence band to conduction band, producing negative electron in the conduction band and [2] Derbalah, A.S.H., Wakatsuki, H., Yamazaki, T., Sakugawa, H. 2004. Photodegradation kinetics of fenitrothion in various aqueous media and

positive hole in the valence band, as shown in Eq. (3) [23]. The charges carriers,  $h\nu_{VB}^+$  can be scavenged by oxidizing species ( $\text{H}_2\text{O}$  and  $\text{OH}^-$ ) and  $e_{CB}^-$  can be trapped by reducing specie ( $\text{O}_2$ ) in the solution. These reactions lead mainly to the formation of hydroperoxyl radicals ( $\text{HOO}^\bullet$ ), superoxide radical anions ( $^\bullet\text{O}_2^-$ ) and hydroxyl radicals ( $^\bullet\text{OH}$ ) on  $\text{TiO}_2$ , which are able to degrade fenitrothion (Eqs. 4–6).



From the MOPAC simulation (Table 1), phosphorus (10P) has the largest frontier electron density, with the next ones being sulphur atom (11S). Hence, these elements would become one of most likely sites of attack by  $^\bullet\text{OH}$ . The attack of the hydroxyl radical to the P=S bond occurs firstly in the case of phosphorothioates [24,25]. The continuous attacking of  $^\bullet\text{OH}$  followed by the breaking of the P–O bond results in the formation of the corresponding phenol, and different dialkyl (or trialkyl) phosphorothioate or phosphate esters are formed [26]. The aliphatic carboxylic intermediates (formic, acetic and oxalic acids) are detected during the fenitrothion degradation [27]. Furthermore, p-nitrophenol is confirmed as main intermediates. The final degradation products for fenitrothion are  $\text{CO}_2$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  [9,27]. From the MOPAC simulation (Table 1) and the literature data [8,9,27], the potential degradation mechanism for fenitrothion is estimated in Figure 9.



**Figure 9:** Proposed solar photodegradation pathway of fenitrothion with  $\text{TiO}_2$

## 4. CONCLUSIONS

The photocatalytic degradation conditions of fenitrothion in water using  $\text{TiO}_2$  under sunlight irradiation are optimized. The primary photocatalytic decomposition reaction shows a pseudo-first-order kinetic law. The activation energy ( $E_a$ ) and half-life ( $t_{1/2}$ ) are 20.6 kJ/mol and 1.4 min, respectively. The photocatalytic degradation technique under solar irradiation may be available in nonexclusive areas.

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