EFFECT OF OXIDANTS IN THE PHOTOCATALYTIC DEGRADATION OF DEET UNDER SIMULATED SOLAR IRRADIATION IN AQUEOUS TiO$_2$ SUSPENSIONS

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ABSTRACT

Recently, considerable efforts have been devoted to overcome a major limitation in semiconductor photocatalysis, the recombination of photogenerated e$^-$-h$^+$ pairs which leads to reduced quantum yields. Considering the impacts of various parameters on the photocatalytic degradation efficiency, our attention has been mainly focused on the improvement of the TiO$_2$ mediated photocatalysis for the degradation of a representative emerging micro-pollutant, DEET (N,N-dimethyl-*m*-toluamide), a widespread insect repellent. The efficiency of TiO$_2$ photocatalysis to degrade DEET was investigated in the presence of hydrogen peroxide and persulfate ions as oxidants-sacrificial electron acceptors under simulated solar irradiation (SSL). The degradation rates were found to be strongly influenced by the addition of oxidants. Higher degradation rates were observed in the presence of oxidants with the following order: S$_2$O$_8$$^{2-}$ > H$_2$O$_2$. The effect of solution pH in the range of 3–10 was investigated and the photodegradation rate was found to increase along with decreasing pH. Scavenging experiments indicated that that sulfate radicals were predominant species at acidic pH while HO$^{\bullet}$ radicals were principally responsible for DEET degradation in alkaline media using SSL/TiO$_2$/S$_2$O$_8$$^{2-}$, the most efficient process.

Keywords: DEET degradation, TiO$_2$ photocatalysis, Scavengers, Oxidants, Electron acceptors, Mineralization

1. Introduction

The photocatalytic process using TiO$_2$ as photocatalyst has been employed extensively for the degradation of a vast array of organic compounds due to its high efficiency to generate hydroxyl radicals. As broadly documented, the photocatalytic process involves the generation of electron/hole pairs by the photo-excitation of the TiO$_2$ particles with light energy greater than the band gap energy. The photogenerated holes can either directly oxidize the adsorbed organic molecule or react with the surface-bound OH$^-$ and/or the adsorbed water molecules to produce the highly reactive oxidant, hydroxyl radical (HO$^{\bullet}$) (Konstantinou and Albanis, 2004; Hazime *et al.*, 2014).

In spite of the fact that nowadays heterogeneous photocatalysis appears as one of the most promising advanced oxidation processes, the undesired electron-hole recombination which dominates in the absence of electron acceptor or donor would markedly reduce its efficiency. When recombination occurs, the excited electron reverts to the valence band without reacting with adsorbed species dissipating the energy as light or heat (Malato *et al.*, 2009). In the majority of the photocatalytic systems, oxygen acts efficiently as an electron trap, preventing the recombination of photogenerated

electrons and holes. To improve the efficiency of TiO_2 photocatalysis various strategies have been adopted. Among them, the addition of inorganic oxidants such as $S_2O_8^{2-}$, IO_4^-, BrO_3^- and H_2O_2 has demonstrated promising results (Konstantinou and Albanis, 2004; Ahmed *et al.*, 2010).

The addition of oxidants has resulted in higher degradation rates for a variety of organics pollutants such as methamidophos (Wei *et al.*, 2009) tebuthiuron, propachlor, chlortoluron, thiram (Bahnemann *et al.*, 2007), dimethoate (Chen *et al.*, 2007), 4-flurophenol (Selvam *et al.*, 2007), phenol (Chiou *et al.*, 2008), glyphosate (Chen and Liu, 2007), prometryn (Evgenidou *et al.*, 2007) and dyes of different chemical groups including azo dyes (Konstantinou and Albanis, 2004) among others.

These oxidants improve the performance of the photocatalytic process by 1) reducing the probability of recombination of the photogenerated electrons and holes, 2) increasing the hydroxyl radical concentration and 3) forming other reactive radicals and oxidizing species able to contribute to the degradation efficiency (Ahmed *et al.*, 2010). Following our previous studies (Antonopoulou and Konstantinou, 2013; Antonopoulou *et al.*, 2013) on the systematic kinetic and mechanistic study of DEET (N,N-dimethyl-*m*-toluamide) photocatalytic degradation, the present study focuses on the effect of various oxidants in the photocatalytic degradation of DEET as well as to probe the role of the reactive species in the reaction mechanism using different electron acceptors. DEET is widely used as an effective insect repellent, which has been recognized as an important emerging environmental contaminant (Antonopoulou *et al.*, 2013).

In addition to previous studies concerning the photocatalytic degradation of DEET (Antonopoulou and Konstantinou, 2013; Antonopoulou *et al.*, 2013), the novelty of this work is associated with the study of (i) the effects of various oxidants and different concentration levels in the photocatalytic degradation efficiency; (ii) the effect of pH; (iii) the contribution of different radicals on the photocatalytic degradation in the pH range studied; (iv) the mineralization of DEET under the optimum conditions.

2.   Experimental

2.1 Materials and reagents

DEET was residue analysis grade, purchased from Sigma-Aldrich. Commercial titania nanoparticles of P25 from Degussa, a known mixture of 80% anatase and 20% rutile with an average particle size of 30 nm, non-porous with a reactive surface area of $50\pm10\ m^2\,g^{-1}$, was used as received for all degradation experiments. HPLC-grade solvents (acetonitrile, methanol, isopropanol, *tert*-butanol) and H_2O_2 solution 30% were supplied from Merck. $K_2S_2O_8$ was purchased by Sigma Aldrich. HA 0.45 µm filters were supplied by Millipore (Bedford, USA) and used throughout the work for removing the TiO_2 particles of the solution samples.

2.2 Irradiation procedure

All the photolytic and photocatalytic experiments were carried out in a Suntest XLS+ apparatus from Atlas (Germany) equipped with a xenon lamp (2.2 kW) and special glass filters restricting the transmission of wavelengths below 290 nm. Chamber and black panel temperature were regulated by a pressurized air cooling circuit and monitored using thermocouples supplied by the manufacturer. The temperature of the samples did not exceed 25 °C using a tap water cooling circuit for the UV reactor. For the irradiation experiments, a 250 mL Pyrex glass UV-reactor containing 250 mL of DEET aqueous solutions (10 mg l^{-1}) at different pH, was used. The pH of solutions was adjusted by H_2SO_4 or NaOH aqueous solutions. In the photocatalytic experiments, the solution was mixed with a relevant low concentration of TiO_2 (100 mg l^{-1}) and was magnetically stirred before and during the illumination. The suspension was kept in the dark for 30 minutes prior to illumination in order to achieve the adsorption equilibrium of substrate onto TiO_2. An average irradiation intensity of 600 W m^{-2} was maintained throughout the experiments. Aliquots were collected and filtered through a 0.45 µm filter at specific time intervals for further analysis.

2.3. Analytical measurements

2.3.1 Kinetic Study

The quantitative determination of DEET was performed by a Dionex P680 HPLC equipped with a Dionex PDA-100 Photodiode Array Detector and a Discovery C_{18} (250 mm length × 4.6 mm ID: 5 µm particle size) column from Supelco (Bellefonte, PA, USA). The elution was performed isocratically using as mobile phase a mixture of LC-grade water H_2O (50%) at pH 3 (adjusted with formic acid) and acetonitrile (50%) with a flow rate of 1 ml min^{-1}. The detection was realized at 210 nm, corresponding to the maximal wavelength of absorption for DEET. The total run time of the HPLC analysis was 10 min. Under these conditions, DEET retention time was 7.817 min and the quantification limit (LOQ) was 0.83 mg l^{-1}.

2.3.2 Mineralization study

Total organic carbon (TOC) was measured using a Shimadzu V-csh Analyzer equipped with a NDIR detector. 10 mL of filtered irradiated samples were directly injected. The instrument calibration was performed using potassium acid phthalate standard solutions for total carbon (TC) calibration, while for inorganic carbon (IC) hydrogen carbonate and carbonate solutions were prepared. Nitrates concentration was determined by a Dionex ICS-1500 Ion Chromatography system equipped with ASRS Ultra II suppressor and an IonPac AS9-HC. The elution was isocratic with aqueous sodium carbonate (9 mM) solution, at a flow rate of 1ml min^{-1}. Ammonium concentrations were measured by the colometric method based on indophenol blue formation (Solorzano, 1969) using an UV-Vis spectrophotometer (Hitachi, U-2000).

3. Results and discussion

3.1. Preliminary experiments

A series of control experiments under dark conditions (i.e., in the absence of light) in the presence of oxidants showed a negligible degradation of the substrate under the conditions tested (data not shown). Moreover, experiments with simulated solar light (SSL) and the oxidants, without the photocatalyst, were performed. At natural pH, the photolytic degradation rates of DEET followed the order SSL/$S_2O_8^{2-}$ > SSL /H_2O_2 (Fig. 1).
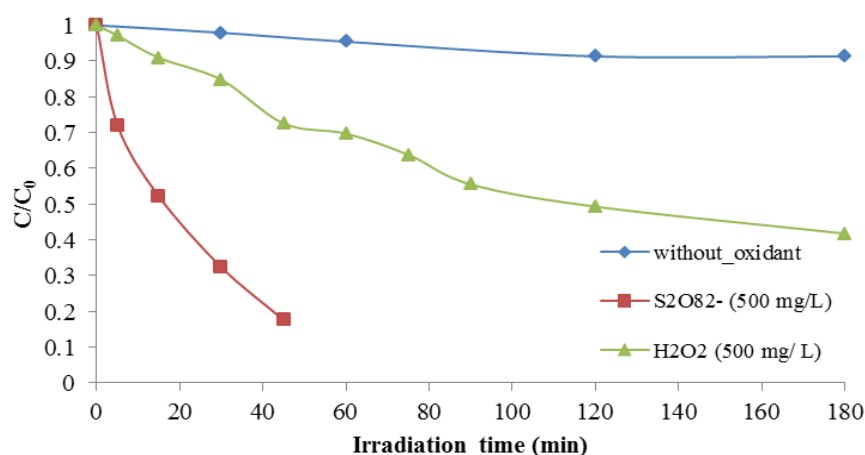

Figure1. Photolytic degradation of DEET (10 mg l^{-1}) in the presence of oxidants (500 mg l^{-1})

Among the tested oxidants, $S_2O_8^{2-}$ were able to cause enhanced photooxidation of DEET (about 80% degradation within 45 min), due to their own ability to absorb light and act as sensitizers through the production of hydroxyl and sulfate radicals, under the applied experimental conditions. Sulphate radicals are strong and relatively selective oxidants with an oxidation potential of 2.6 eV and can react

with organic molecules by three different mechanisms: (i) hydrogen abstraction, (ii) addition on double bond and (iii) electron transfer (Hazime *et al.*, 2014). On the other hand, the oxidation rate was much lower in the presence of H_2O_2 and 60% removal was achieved in about 180 min. The observed trends in the SSL/oxidant systems can be adequately explained by the oxidants UV-Vis absorption spectra (Yu *et al.*, 2010; Selvam *et al.*, 2007) since increased UV light-absorption promotes the formation of reactive radical species (Yu *et al.*, 2010). Among the tested oxidants, $K_2S_2O_8$ has the higher UV light absorption followed by H_2O_2. SSL/$S_2O_8^{2-}$ process exhibited the highest performance. Similar beneficial effect of $S_2O_8^{2-}$ ions was also found on the photolytic degradation of other organic pollutants such as C.I. Reactive Black 5 and fluorophenol (Yu *et al.*, 2010; Selvam *et al.*, 2007).

3.2. Effect of $S_2O_8^{2-}$

In order to examine the role of $S_2O_8^{2-}$, experiments of the photocatalytic degradation of DEET employing different initial concentrations of the oxidant in the range of 100 to 1000 mg l^{-1} were conducted and the results are depicted in Figure 2a. It is evident that the degradation increases with increasing $S_2O_8^{2-}$ concentration up to a certain level which corresponds to the optimum concentration under the experimental conditions studied. The enhancement can be attributed to the ability of persulfate to act as an electron acceptor preventing the charge recombination but also to the production of very strong oxidants $HO^\bullet$ and sulphate radicals according to the Eq. 1-3 (Liu *et al.*, 2009a; Chen *et al.*, 2007). Due to its high potential (2.6 eV) sulphate radicals are powerful oxidants (Hazime *et al.*, 2014) able to participate in DEET degradation.
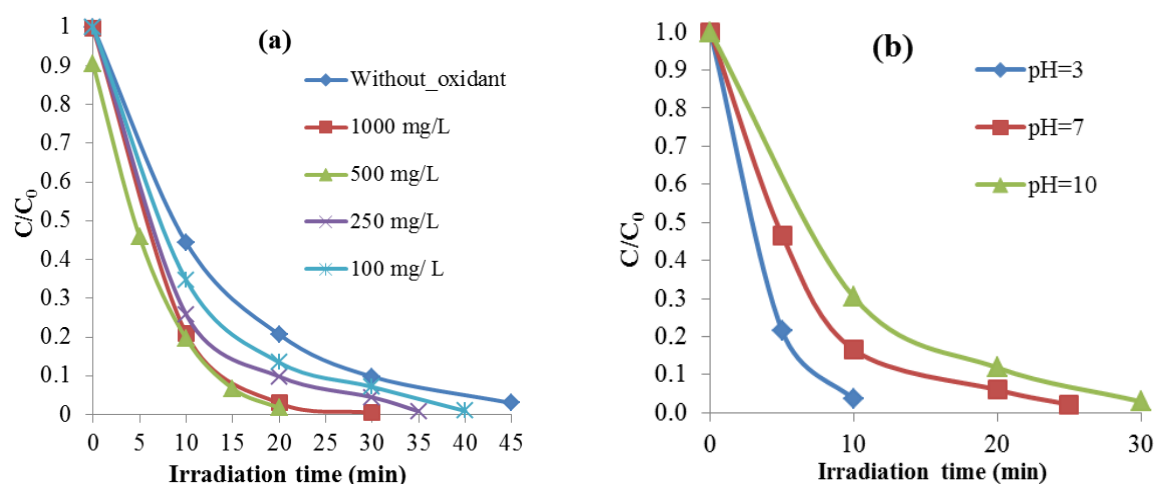
$$S_2O_8^{2-} \quad + \quad e_{CB^-} \quad \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{1}$$

$$SO_4^{\bullet-} \quad + \quad e_{CB^-} \quad \rightarrow \quad SO_4^{2-} \tag{2}$$

$$SO_4^{\bullet-} \quad + \quad H_2O \quad \rightarrow SO_4^{2-} \quad + \quad HO^\bullet + H^+ \tag{3}$$

Figure 2. Photocatalytic degradation of DEET (10 mg l^{-1}) a) under various concentrations of $S_2O_8^{2-}$, b) under different pH value in the presence of 500 mg l^{-1} $S_2O_8^{2-}$

Although the concentration of SO_4^{2-} increases with oxidant loading, above the optimum value the generated ions can be adsorbed onto TiO_2 particles leading to the modification of their surfaces and subsequently decrease its catalytic activity. Another reason may be the generation of SO_4^{2-} excess in high $S_2O_8^{2-}$ concentrations which may adsorb on the surface of the catalyst and exert a competitive action for the oxidative species according to the Eq. 4 and 5. Results of prior studies on photocatalytic degradation of other model organic compounds under different experimental conditions have been consistent with the results obtained in the present study (Yu *et al.*, 2010; Liu *et al.*, 2009a; Chen and Liu, 2007).

$$SO_4^{2-} + h^+ \rightarrow SO_4^{\cdot-} \tag{4}$$

$$SO_4^{2-} + HO^{\bullet} \rightarrow SO_4^{\cdot-} + OH^- \tag{5}$$

The influence of the pH on the DEET degradation rate in the presence of $S_2O_8^{2-}$ was determined in a range between pH 3 and 10 (Figure 2b). Under optimum oxidant concentration, pseudo-first order kinetics was recorded for the degradation of DEET in the pH range studied. Table 1 lists the values of apparent rate constants (k_{app}) and the correlation coefficients of DEET. Among the studied values, pH 3 was found the more favorable for DEET degradation. This can be attributed to the surface charge properties of the photocatalyst. Since, the point of zero charge of the TiO_2 (Degussa P25) has been reported to be 6.25, the TiO_2 surface is negatively charged at pH > 6.25, whereas is positively charged in acidic conditions (pH < 6.25). At acidic pH, both $S_2O_8^{2-}$ and $HS_2O_8^-$ are formed according to the following reaction (Hazime et $al.$, 2013).

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^{2-} \tag{6}$$

Both species are strongly adsorbed on the surface of TiO_2 under acidic conditions because of the electrostatic attraction of the negative charge of ions and the positive charge associated with the TiO_2 surface. As a result both $S_2O_8^{2-}$ and $HS_2O_8^-$ can react efficiently with the photogenerated electrons leading to the formation of the reactive $SO_4^{\bullet-}$ species as well as preventing the recombination of e^--h^+. On the other hand, under alkaline conditions the electrostatic repulsion between the anions and the negative charge of TiO_2 reduces the adsorption and thus, inhibit the scavenging of the electrons. Such pH effects have been observed for imalazil pesticide during its photocatalytic degradation under UV irradiation in the presence of persulfate (Hazime et $al.$, 2013).

Table 1. Rate constants and correlation coefficients (R^2) of DEET in the presence of $S_2O_8^{2-}$ (500 mg l^{-1}) and H_2O_2 (100 mg l^{-1}) in different pH values

pH values	$S_2O_8^{2-}$		H_2O_2	
	k (min^{-1})	R^2	k (min^{-1})	R^2
3	0.335	0.9977	0.113	0.9741
7	0.148	0.9872	0.090	0.9966
10	0.115	0.9947	0.084	0.9948

3.3. Effect of H_2O_2

H_2O_2 is also used frequently as an oxidizing agent in order to improve the photocatalysis rates. Figure 3a shows the effect of H_2O_2 addition on the removal efficiency of DEET that increased with H_2O_2 concentrations ranging from 50 to 100 mg l^{-1}. The following possible reasons can be invoked to explain this positive effect. Firstly, direct photolysis of H_2O_2 by UV light ≤ 300 nm can generate $HO^{\bullet}$ radicals, which are likely to be the dominant rate-improving mechanism in this process (Eq. 7). Another reason may be the capability of H_2O_2 to suppress the electron hole pair recombination reacting with the electrons to generate $HO^{\bullet}$ and OH^- as shown in Eq. (8) (Konstantinou and Albanis, 2004, Liu et $al.$, 2009b).

$$H_2O_2 + hv + 2HO^{\bullet} \tag{7}$$

$$H_2O_2 + e_{CB}^- + HO^{\bullet} + OH^- \tag{8}$$

However, the effect of H_2O_2 on DEET degradation is not as important as in the presence of the $S_2O_8^{2-}$ .This can be related with the wavelength of the employed light source which affect significantly the H_2O_2 performance as oxidizing agent in photocatalytic degradation of organic pollutants (Sun et $al.$, 2006). Moreover, $S_2O_8^{2-}$ was found to be the most efficient oxidant due to the generation of highly reactive intermediate radicals such as $SO_4^{\bullet-}$ as well as to its ability to act as a more efficient electron acceptor. Similar to our results, $S_2O_8^{2-}$ was demonstrated to be more effective than H_2O_2 for the degradation of various organic contaminats such as methamidophos (Wei et $al.$, 2009), 4-flurophenol (Selvam et $al.$, 2007) and trichlorfon (Liu et $al.$, 2009b). On the other hand, H_2O_2 concentration over 100 mg l^{-1} decreases the photodegradation efficiency gradually. At high concentration levels H_2O_2 can also

become a scavenger of valence band holes and $HO^{\bullet}$ (Ahmed *et al.*, 2010; Chen *et al.*, 2007). As both $h_{VB}{}^{+}$ and $HO^{\bullet}$ are strong oxidants and the main species on the photocatalytic degradation of DEET (Antonopoulou *et al.*, 2013) the oxidation will be inhibited when H_2O_2 dosage gets too high. In addition, with the increase in H_2O_2 concentration, fewer photons reach the photocatalyst surface (UV screening effect), resulting in slower production of oxidative species (Konstantinou and Albanis, 2004; Liu *et al.*, 2009a).

In contrast to other oxidant tested, H_2O_2 addition is more detrimental at high concentrations and consequently causes a significant reduction to the reaction rate. This is in agreement with other studies which support that the degradation rate of organic compounds increases with increasing H_2O_2 concentration up to a certain level, above which degradation efficiency decreases as H_2O_2 scavenges $HO^{\bullet}$ (Yu *et al.*, 2010; Ahmed *et al.*, 2010; Liu *et al.*, 2009a; Liu *et al.*, 2009b) resulting in hydroperoxyl radicals with reduced oxidation potential (Eq. 9, 10).

$$H_2O_2 \;+\; HO^{\bullet} \;\rightarrow\; H_2O \;+\; HO_2{}^{\bullet} \tag{9}$$

$$HO_2{}^{\bullet} \;+\; HO^{\bullet} \;\rightarrow\; H_2O \;+\; O_2 \tag{10}$$

In order to find the optimal pH of reaction mixture for the photodegradation of DEET, a series of experiments was conducted at different pH values from 3.0 to 10.0. The results are illustrated in Fig. 3b, while the rate constants and correlation coefficients (R^2) of DEET in the presence of H_2O_2 (100 mg l^{-1}) in different pH values are presented in Table 1.
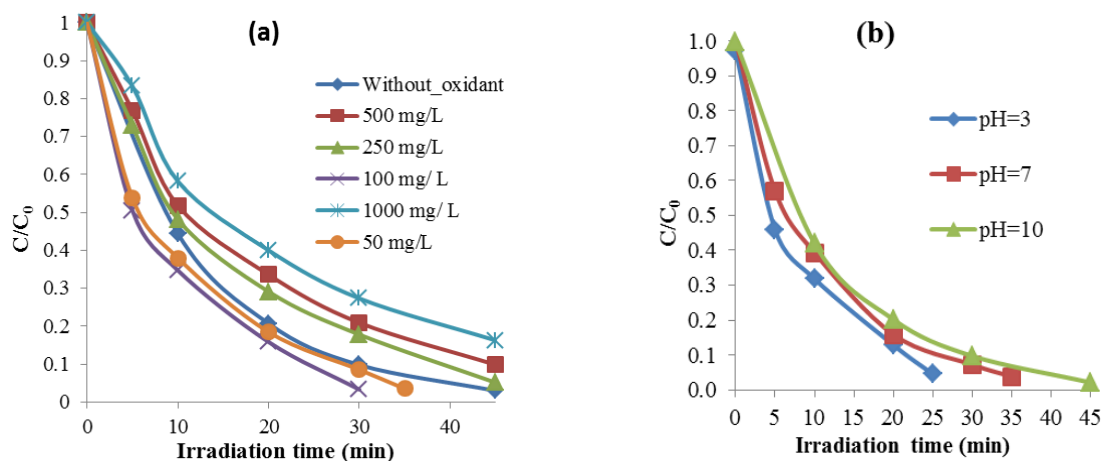

Figure 3. Photocatalytic degradation of DEET a) under various concentrations of H_2O_2, b) under different pH value in the presence of 100 mg l^{-1} H_2O_2

A partial inhibitory effect on the efficiency in DEET degradation was observed when increasing the pH from acid to alkaline area. Low degradation efficiency at high pH values may be attributed to the fact that H_2O_2 becomes unstable and self-decomposition occurs. The self-decomposition is strongly dependent on pH and in alkaline medium H_2O_2 decomposes to water and oxygen rather than hydroxyl radical (Selvam *et al.*, 2007).

3.4. Contribution of $SO_4{}^{\bullet-}$ and $HO^{\bullet}$ on the degradation of DEET using the system $SSL/TiO_2/S_2O_8{}^{2-}$

Obviously, $S_2O_8{}^{2-}$ are the most effective oxidant for the photodegradation of DEET and the contribution of two different radicals, $HO^{\bullet}$ and $SO_4{}^{\bullet-}$, in the photocatalytic process, was demonstrated. Two different alcohols, isopropanol (i-PrOH) and *tert*-butanol were used, to assess the role of each radical in the degradation mechanism in different pH values. Isopropanol a well-established hydroxyl radical quencher due to its high-rate constant reaction with the radical (1.9×10^9 M^{-1} s^{-1}) was used to discriminate the direct oxidation of DEET by hydroxyl radicals. On the other hand, *tert*-butanol has been used as both $HO^{\bullet}$ and sulphate radical scavenger with rate constants of k = 6×10^8 $M^{-1}s^{-1}$ and k= 8×10^5 $M^{-1}s^{-1}$,

respectively (Hazimeet $al.$, 2014). The degradation kinetics of DEET in the presence of scavengers followed also apparent first-order degradation curve. Table 2 lists the kinetic constants and the inhibitory effect on DEET degradation at different pH values. A difference in the inhibitory effect was observed according to the pH studied. At acid medium (pH = 3), the addition of $tert$-butanol in the solution, provokes only 10.14% inhibition of DEET degradation. On the contrary, when $tert$-butanol was added to the DEET solution at pH 7 and 10, the inhibition percentage was 43.2% and 52.2%, respectively. This suggests that sulfate radicals play a significant role on DEET oxidation, at acidic pH and as the pH values increases the participation of hydroxyl radicals becomes more and more significant. The above statements were verified once more by the inhibitory effects obtained in the presence of isopropanol. Strong inhibition of the process by the addition of isopropanol in pH 10 clearly pointed out the participation of $HO^\bullet$ radicals in alkaline solution. On the other hand, a negligible inhibition at about 6.0% was observed when photocatalysis was performed in acid environment, verifying the limited contribution of $HO^\bullet$ radicals. The scavenging experiments revealed that (i) at acidic pH, $S_2O_8^{2-}$ is well adsorbed on the TiO_2 surface and that $SO_4^{\bullet-}$ radicals are the dominant species (ii) at neutral pH both sulfate and hydroxyl radicals contribute to the degradation of the pollutant and (iii) at alkaline pH the transformation proceeds through the $HO^\bullet$ radicals attack. Our findings are in accordance with the results of the comprehensive studies of Hazime et $al.$ dealing with the photocatalytic degradation of imazalil in the presence of $S_2O_8^{2-}$ (Hazime et $al.$, 2013; Hazime et $al.$, 2014). Confirmation about the role of the reactive species in the reaction mechanism comes also from a study focused on the identification of predominant radical species formed in thermally activated persulfate under different pH conditions. Liang and Su (2009), investigated the inter-conversion from sulfate radical to hydroxyl radical and concluded that at pH < 7: $SO_4^{\bullet-}$ is the predominant radical, at pH = 9: $HO^\bullet$ and $SO_4^{\bullet-}$ are both present and at pH > 9: $HO^\bullet$ is the predominant radical.

Table 2. Rate constants and percent inhibition of rate constant, (% Δk) of DEET in the presence of isopropanol and tert-butanol ([DEET]) = 100 mg l^{-1}, ([$S_2O_8^{2-}$]= 500 mg l^{-1}, [alcohol]= 2.5 g l^{-1}]

	Without scavenger	i-PrOH		*tert*-butanol	
Experiments	k (min^{-1})	k (min^{-1})	% Δk	k (min^{-1})	% Δk
pH 3	0.335	0.315	5.97	0.301	10.1
pH 7	0.148	0.089	39.8	0.084	43.2
pH 10	0.115	0.044	61.7	0.055	52.2

3.5. Mineralization study

In order to study the extent of mineralization of DEET during photocatalysis under the different experimental conditions, TOC measurements were carried out along with the determination of the formation of nitrogen ions. Moreover, the evolution of TOC was also investigated during photolysis under SSL in the presence of the studied oxidants (data not shown). The photolytic decrease of TOC appears to be quite effective only in the presence of $S_2O_8^{2-}$, achieving 80% mineralization after 180 min of irradiation. The level of mineralization during photolysis in the presence of H_2O_2 was almost negligible and never higher than 20% was recorded even after prolonged irradiation time. However, high mineralization percentages greater than 70% were accomplished over a short period of time in the presence of both oxidants under photocatalytic regime. Among the oxidants tested, $S_2O_8^{2-}$ showed better mineralization rates as compared to H_2O_2 and almost complete mineralization at about 85% is achieved within 60 min (Figure 4a). Although the addition of H_2O_2 enhances the removal of TOC, it is unable to achieve high mineralization percentages. The decrease of TOC appears to be effective only at the early stages of irradiation and since then it starts to level off after 120 min of treatment achieving a 72% reduction (Figure 4b). Release of nitrate and ammonium ions in the presence of $S_2O_8^{2-}$ was also a fast process, reaching the stoichiometric amount in less than 90 min. On the contrary, the release of nitrogen ions in the presence of H_2O_2 is also partial, reaching almost the 50% of expected amount. According to previous studies nitrogen containing compounds give rise to both ammonium and nitrate atoms. The NH_4^+/NO_3^- ratio depends on the irradiation time, the pH of the solution and the oxidation

state of nitrogen (Konstantinou and Albanis, 2004). In all the photocatalytic systems studied, the overall yield of NH_4^+ ions produced was greater than the corresponding amount of NO_3^- ions while nitrites were not detected; in agreement with other reports (Antonopoulou *et al.*, 2013). However, at prolonged irradiation times the ammonium ions were converted into nitrate ions in both systems, achieving much lower concentrations (3.2 mg l^{-1} and 1.6 mg l^{-1} in the presence of $S_2O_8^{2-}$ and H_2O_2, respectively) than the limits established in drinking water as well as in discharges by the US Environmental Protection Agency and European regulatory authorities. Thus, TiO_2 photocatalysis besides the organic pollutants removal can also be employed with success for the treatment of inorganic pollutants.
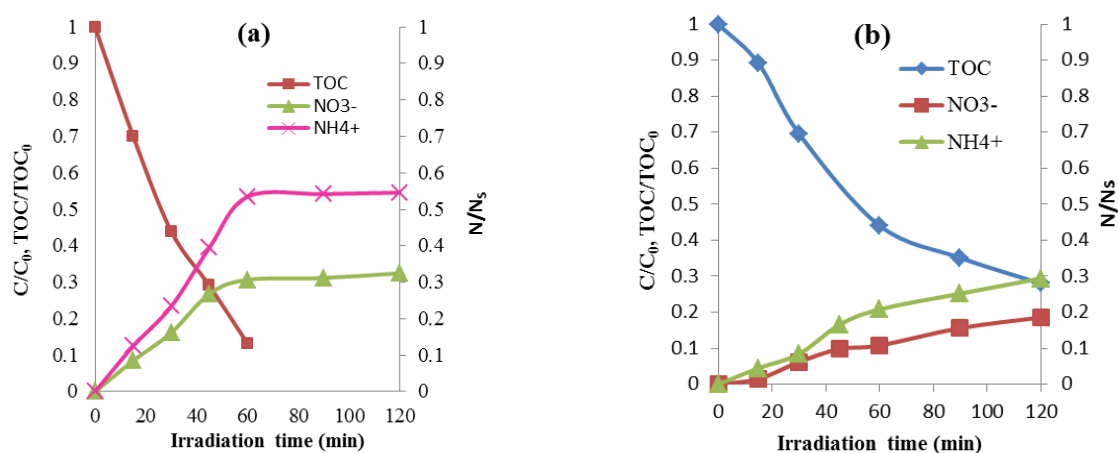

Figure 4. Kinetics of degradation of TOC and evolution of NO_3^-/NH_4^+ versus irradiation time in the presence of a) $S_2O_8^{2-}$ (500 mg l^{-1}) and b) H_2O_2 (100 mg l^{-1})

4.   Conclusions

The results of this study clearly showed that the presence of oxidants could have an important impact on the photocatalytic degradation efficiency of the parent compound as well as on the transformation rate of the organic intermediates. The degradation rates were found to be strongly influenced by the concentration levels of the oxidants and the solution pH. The initial concentration of oxidants showed an obviously positive effect on the degradation process appreciably enhancing photodegradation efficiency of DEET. However, it was observed that above a certain level of oxidants' concentration the reaction rate becomes constant or even decreases due to their ability to acts as scavenger of valence band holes and HO$^\bullet$ radicals. Among the oxidants used, $S_2O_8^{2-}$ showed the most pronounced effect on the decomposition of DEET, followed by H_2O_2. The degradation of DEET follows pseudo-first order kinetics in all cases. Acid environment (pH=3) was favorable for the photocatalytic degradation of DEET for both oxidants studied. The optimum concentrations of H_2O_2 and $S_2O_8^{2-}$ were found equal to 100 and 500 mg l^{-1} respectively. Similarly to the degradation rate of the substrate, the overall mineralization is markedly improved in the presence of the selected oxidants at acidic pH range and nitrates concentrations lower than the maximum permitted concentrations in drinking water and wastewater were achieved. Finally, the study contributes significantly to the improvement and better understanding of photocatalytic processes in the presence of oxidants in order to establish a thoughtful photocatalytic oxidation design to treat pollutants in natural waters and wastewaters.

References

Ahmed S, Rasul M.G., Marten W.N., Brown R. and Hashib M.A. (2010), Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, *Desalination,* **261**, 3–18.

Antonopoulou M. and Konstantinou I. (2013), Optimization and modeling of the photocatalytic degradation of the insect repellent DEET in aqueous TiO_2 suspensions. *Clean, Soil, Air, Water* ,**41 (6),** 593–600.

Antonopoulou M., Giannakas A., Deligiannakis Y. and Konstantinou I. (2013), Kinetic and mechanistic investigation of photocatalytic degradation of the N,N-diethyl-m-toluamide, *Chemical Engineering Journal,* **231**, 314–325.

Bahnemann W., Muneer M. and Haque M.M. (2007), Titanium dioxide-mediated photocatalysed degradation of few selected organic pollutants in aqueous suspensions, *Catalysis Today*, **124**, 133-148.

Chen J., Wang D., Zhu M. and Gao, C. (2007), Photocatalytic degradation of dimethoate using nanosized TiO_2 powder, *Desalination,* **207**, 87-94.

Chen S. and Liu Y. (2007), Study on the photocatalytic degradation of glyphosate by TiO_2 photocatalyst, Chemosphere, **67**, 1010-1017.

Chiou C.H., Wu C.Y. and Juang R.S. (2008), Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO_2 process, *Chemical Engineering Journal*, **139,** 322–329.

Evgenidou E., Bizani E., Christophoridis C. and Fytianos K. (2007), Heterogeneous photocatalytic degradation of prometryn in aqueous solutions under UV-Vis Irradiation, *Chemosphere*, **68,** 1877-1882.

Hazime R., Nguyen Q.H., Ferronato C., Huynh T.K.X., Jaber F. and Chovelon J.-M. (2013), Optimization of imazalil removal in the system $UV/TiO_2/K_2S_2O_8$ using a response surface methodology (RSM), *Applied Catalysis B: Environmental*, **132–133**, 519– 526.

Hazime R., Nguyen Q.H., Ferronato C., Salvador A., Jaber F. and Chovelon J.-M. (2014), Comparative study of imazalil degradation in three systems: $UV/TiO2$, $UV/K_2S_2O_8$ and $UV/TiO_2/K_2S_2O_8$, *Applied Catalysis B: Environmental*, **144**, 286– 291.

Konstantinou I.K. and Albanis T.A. (2004), TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, *Applied Catalysis B*, **49**(1), 1–14.

Liang C. and Su H.-W. (2009), Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate, *Industrial & Engineering Chemistry Research,* **48**, 5558–5562.

Liu W., Chen S., Zhao W. and Zhang S. (2009a), Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase, *Journal of Hazardous Materials*, **164**, 154-160.

Liu W., Chen S., Zhao W. and Zhang S. (2009b), Study on the photocatalytic degradation of trichlorfon in suspension of titanium dioxide, *Desalination*, **249,** 1288–1293.

Malato S., Fernández-Ibáñez P., Maldonado M.I., Blanco J. and Gernjak W. (2009), Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, *Catalysis Today*, **147**, 1–59.

Selvam K., Muruganandam M., Muthuvel I. and Swaminathan M. (2007), The influence of inorganic oxidants and metal ions on semiconductor sensitized photodegradation of 4-fluorophenol, *Chemical Engineering Journal,* **128**, 51–57.

Solorzano L. (1969), Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method, *Limnology* and *Oceanography*, **14 (5)**, 799–801.

Sun J., Wang X., Sun J., Sun R., Sun S. and Qiao L. (2006), Photocatalytic degradation and kinetics of Orange G using nano-sized $Sn(IV)/TiO_2/AC$ photocatalyst, *Journal of Molecular Catalysis A: Chemical*, **260**, 241–246.

Wei L., Shifu C., Wei Z. and Sujuan Z. (2009), Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase, *Journal of Hazardous Materials*, **164**, 154–160.

Yu C-H., Wu C.-H., Ho T.-H. and Andy Hong P.K. (2010), Decolorization of C.I. Reactive Black 5 in UV/TiO_2, $UV/oxidant$ and $UV/TiO_2/oxidant$ systems: A comparative study, *Chemical Engineering Journal*, **158**, 578–583.