WATER RESEARCH 44 (2010) 1809–1818

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes

Sandra Sanches[a], Maria T. Barreto Crespo[a,b], Vanessa J. Pereira[a,b,*]

[a] Instituto de Biologia Experimental e Tecnológica, Apartado 12, 2781-901 Oeiras, Portugal
[b] Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal

ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form
29 October 2009
Accepted 2 December 2009
Available online 4 January 2010

Keywords:
LP/UV
Hydrogen peroxide
Titanium dioxide
Real water matrices
Pesticides
Mixtures

ABSTRACT

This study reports the efficiency of low pressure UV photolysis for the degradation of pesticides identified as priority pollutants by the European Water Framework Directive 2000/60/EC. Direct low pressure UV photolysis and advanced oxidation processes (using hydrogen peroxide and titanium dioxide) experiments were conducted in laboratory grade water, surface water, and groundwater.

LP direct photolysis using a high UV fluence (1500 mJ/cm^2) was found to be extremely efficient to accomplish the degradation of all pesticides except isoproturon, whereas photolysis using hydrogen peroxide and titanium dioxide did not significantly enhance their removal. In all matrices tested the experimental photolysis of the pesticides followed the same trend: isoproturon degradation was negligible, alachlor, pentachlorophenol, and atrazine showed similar degradation rate constants, whereas diuron and chlorfenvinphos were highly removed. The degradation trend observed for the selected compounds followed the decadic molar absorption coefficients order with exception of isoproturon probably due to its extremely low quantum yield.

Similar direct photolysis rate constants were obtained for each pesticide in the different matrices tested, showing that the water components did not significantly impact degradation. Extremely similar photolysis rate constants were also obtained in surface water for individual compounds when compared to mixtures. The model fluence and time-based rate constants reported were very similar to the direct photolysis experimental results obtained, while overestimating the advanced oxidation results. This model was used to predict how degradation of isoproturon, the most resilient compound, could be improved.

1. Introduction

In recent years, a large group of organic compounds have been labelled as water emerging contaminants by the Environmental Protection Agency (U.S.A.) and the European Union. The European Water Framework Directive 2000/60/EC identifies 33 priority substances that present high toxicity, high environmental persistence, and bioaccumulation potential. This directive includes pesticides such as atrazine, diuron, isoproturon, alachlor, pentachlorophenol, and chlorfenvinphos, which are of special interest due to their easy transport in the environment as well as potential for seriously threatening the aquatic environment and human health (Hincapié et al., 2005). The adverse health effects of these

---

* Corresponding author at: Instituto de Biologia Experimental e Tecnológica, Apartado 12, 2781-901 Oeiras, Portugal. Tel.: +351 21 4469568; fax: +351 21 4421161.
E-mail address: vanessap@itqb.unl.pt (V.J. Pereira).

0043-1354/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2009.12.001

compounds include increased cancer risk as well as anemia, eye, liver, kidney, spleen cardiovascular system, and reproductive problems (EPA, 2003). Among these pesticides, alachlor, atrazine, and pentachlorophenol are also known to have endocrine disrupting capabilities.

These xenobiotics have been detected in drinking water sources such as surface water and groundwater at levels in the range of 2–13 000 ng/L (Planas et al., 2006; Field et al., 2003).

Low pressure (LP) ultraviolet (UV) radiation, that emits primarily monochromatic light at 254 nm, is widely used for drinking water disinfection due to its effectiveness against a wide range of waterborne pathogens (Linden et al., 2002). The use of high UV fluences (1000–2000 mJ/cm^2) can also promote the degradation of photolabile organic compounds by direct photolysis due to their potential to absorb light (Sharpless and Linden, 2003; Pereira et al., 2007a,b). However, some molecules do not strongly absorb the LP/UV radiation. For these stable micropollutants, advanced oxidation processes (AOPs), using hydrogen peroxide (H_2O_2) and titanium dioxide (TiO_2), may be used to remove them from drinking water, due to the production of highly reactive, unselective, and short-lived hydroxyl (OH) radicals (Pereira et al., 2007b). H_2O_2 has been widely described for water disinfection and degradation of pollutants (Sharpless and Linden, 2003; Schwarzenbach et al., 1993; von Gunten, 2003). TiO_2 recently emerged as a promising material to efficiently degrade pesticides in water. It presents several advantages related to its chemical and biological inertness, photostability, absence of toxicity, and low cost. To be catalytically active, TiO_2 requires irradiation with a wavelength lower than 380 nm, which induces the photoexcitation of an electron since it has an energy band gap of about 3.2 eV. Therefore, light sources such as low and medium pressure ultraviolet lamps as well as solar radiation are suitable to induce TiO_2 activity (Balasubramanian et al., 2004).

Several authors reported the degradation of the selected pesticides (atrazine, diuron, isoproturon, alachlor, pentachlorophenol, and chlorfenvinphos) by UV photolysis and AOPs (such as UV/H_2O_2 and UV/TiO_2), using solar (Hincapié et al., 2005; Malato et al., 2003; Haque and Muneer, 2003) and UV–Vis radiation (Haque and Muneer, 2003; Wong and Chu, 2003a). Both direct photolysis and AOPs photolysis have proven to be very efficient although AOPs were usually more efficient (Haque and Muneer, 2003; Wong and Chu, 2003a).

LP lamps are the most commonly used lamps in drinking water facilities due to their extremely effective disinfection potential. To date, few studies have been conducted addressing the efficiency of LP lamps for the removal of the priority pesticides mentioned above and therefore further research is needed to address their degradation potential. LP/UV lamps have been reported to promote high degradation levels of some of the selected pesticides: atrazine by direct photolysis, UV/TiO_2, and UV/H_2O_2 (e.g. Bianchi et al., 2006); pentachlorophenol by direct photolysis (Vollmuth et al., 1994); diuron by direct and Photo-Fenton photolysis (Djebbar et al., 2008); and chlorfenvinphos by direct and UV/H_2O_2 (Acero et al., 2008).

Authors often describe the degradation of xenobiotics only as a function of time. These results provide insight on the efficiency of different systems to degrade the compounds, but cannot be compared directly with results obtained under different experimental setups. Reporting degradation in terms of UV fluence permits a standardization of bench-scale UV testing providing increased confidence in the data generated and the ability to compare results with other authors that report their results using the same method (Bolton and Linden, 2003). The photolysis of xenobiotics is often studied for individual compounds and few studies compared these results to those obtained with mixtures where a competition effect could probably decrease the rate of degradation. In addition, studies addressing AOPs potential for the removal of the selected pesticides from water have been conducted mainly in laboratory grade water and synthetic water matrices spiked with natural organic matter (NOM). Few studies concerning the removal of the selected micropollutants using real water matrices such as surface water and groundwater have been conducted to date (e.g. Acero et al., 2008; Rosenfeldt et al., 2006; Song et al., 2008). More studies using real source waters with different characteristics should therefore be conducted to address the potential of direct photolysis and AOPs to degrade organic compounds that may be present in those waters.

This study reports the effectiveness of LP/UV direct photolysis and AOPs (using H_2O_2 and TiO_2) for the degradation of the selected pesticides (isoproturon, alachlor, atrazine, pentachlorophenol, diuron, and chlorfenvinphos) identified as priority pollutants by the European Water Framework Directive 2000/60/EC. The degradation of these compounds was studied in laboratory grade water, surface water, and groundwater. The pesticides were spiked individually in the different matrices and as mixtures in surface water to address if in real water systems, where a wide combination of compounds is expected to be present, different degradation trends could be expected. Several kinetic photolysis parameters were determined and used to model the photolysis results.

2. Materials and methods

2.1. *Reagents*

All pesticides and *para*-chlorobenzoic acid (pCBA) were purchased as solutions or solids of the highest grade commercially available (Sigma Aldrich, Germany). Aqueous suspension of bovine liver catalase with 40 000–60 000 units/mg protein was also obtained from Sigma Aldrich (1 unit decomposed 1 μmol of H_2O_2). Hydrogen peroxide (30% w/w) was obtained from Panreac (Spain). Titanium dioxide Degussa P25, a mixture of 70% anatase and 30% rutile, with an average particle size of 20 nm and a reactive surface area of 35–65 $m^2\ g^{-1}$ from Evonik Degussa, Germany, was kindly supplied by Dr. Paula Passarinho (LNEG, Portugal). HPLC grade acetonitrile and methanol from Lab Scan Analytical Sciences (Poland) were used for the chromatographic analysis and preparation of stock solutions. Laboratory grade water was produced by a Milli-Q water system (Millipore, CA, USA) and the real water samples were collected in brown glass bottles, filtered through 0.45 μm mixed esters of cellulose filters (Millipore, CA, USA) and stored at 4 °C until used.

2.2. Experimental setup

2.2.1. UV photolysis experiments

UV photolysis experiments were conducted in a collimated beam bench-scale reactor (Trojan Technologies Inc., Canada) using a low pressure Hg lamp that emits mainly monochromatic light at 254 nm.

100 mL of laboratory grade water and two natural water matrices – surface water and groundwater – were spiked with the appropriate volume of the pesticides stock solutions to achieve concentrations of 1 mg/L. This concentration was set in order to follow the degradation of the compounds, spiked individually (in laboratory grade water, surface water, and groundwater) and as mixtures (in surface water), by direct injection using high pressure liquid chromatography (HPLC). 50 mL of sample were placed in a Petri dish and continuously stirred beneath the LP/UV source. The remaining 50 mL were used as control and kept in the dark under identical experimental conditions in order to determine possible pesticide losses due to evaporation or adsorption to the Petri dish walls. All experiments were conducted at room temperature (21 $\pm$ 2 °C).

The lamp irradiance was measured using a calibrated radiometer (IL1700, International Light, Newburyport, MA) which was placed at the same height of the water level in the Petri dish and the solution transmittance was measured by a UV photometer (P254C, Trojan Technologies Inc.). UV fluences of approximately 0, 40, 100, 500, 750, 1000, and 1500 mJ/cm^2 were selected, taking into account the radiometer meter reading as well as Petri, reflection, water, and divergence factors (Bolton and Linden, 2003), to establish the corresponding exposure times at which 200 μL of sample were taken to quantify the concentration of the compounds by HPLC analysis.

2.2.2. UV/H_2O_2 photolysis experiments

UV/H_2O_2 photolysis experiments were conducted similarly to direct photolysis experiments with the addition of 40 mg/L H_2O_2 and 500 μg/L pCBA to laboratory grade water and surface water spiked with the individual pesticides and mixtures. pCBA was added to the solution in order to determine indirectly, by competition kinetics, the second-order rate constants between the selected pesticides and the hydroxyl radicals (Elovitz and von Gunten, 1999). At determined exposure times, 200 μL of sample were taken to vials containing catalase to quench the residual hydrogen peroxide. The residual H_2O_2 was determined at the beginning and end of each experiment using the I_3^- method described by Klassen et al. (1994).

2.2.3. UV/TiO_2 photolysis experiments

UV/TiO_2 photolysis experiments were conducted similarly to direct photolysis experiments with the addition of 2.5 mg/L TiO_2 and 500 μg/L pCBA to laboratory grade water spiked with the individual pesticides and surface water spiked with a mixture of the pesticides. During the degradation, samples (200 μL) were taken at each defined exposure time and filtered using 0.2 μm filters made of regenerated cellulose (Whatman, USA) to remove TiO_2 particles.

Even though different types of TiO_2 particles are available, Degussa P25 TiO_2 (Evonik Degussa, Germany) was selected because it has been referred by many authors as being the most efficient type of TiO_2 due to the presence of the more reactive anatase form (70%), surface area, and average particle size (Haque and Muneer, 2003; Wong and Chu, 2003b).

The UV/TiO_2 photocatalysis experiments in surface water were only conducted using a mixture of the pesticides isoproturon, alachlor, atrazine, diuron, and chlorfenvinphos. Pentachlorophenol was not added to the samples containing the mixture of pesticides due to analytical constrains and was not analyzed individually because it was found to be significantly retained in the filters used to remove the TiO_2 particles from the solutions.

2.2.4. Analytical methods

The selected pesticides and pCBA were analyzed by reverse-phase high performance liquid chromatography (HPLC) using a Waters system equipped with an ultraviolet absorbance detector (Waters Chromatography, Milford, MA, USA).

The individual compounds, mixtures of each pesticide with pCBA, as well as mixtures containing all the selected pesticides were analyzed using a Luna 5μ C18(2) 100A (150 × 3.0 mm) column (Phenomenex Inc., Torrance, CA, USA), different mobile phase compositions, and monitored at compromise maximum absorbance wavelengths (detailed in the Supplementary Material Section SM Table 2). Pentachlorophenol was not added to the mixture samples because it could not be detected using the chromatography conditions used for the detection of the other pesticides. The Temperature Control Module was set at 34 °C for all analysis except the pesticide mixture samples that need to be analyzed at room temperature to ensure appropriate separation of atrazine, diuron, and isoproturon.

3. Results and discussion

3.1. Direct photolysis

LP direct photolysis experiments were conducted to evaluate the degradation potential of pesticides with very different structures (described in the Supplementary Material Section SM Table 1), considered as priority pollutants.

Fig. 1 and Table 1 present the experimental and model direct photolysis results obtained using two real water matrices with very different compositions: surface water (Fig. 1a) and groundwater (Fig. 1b). The characterization of the water matrices used was described elsewhere (Pereira et al., 2009). In summary, the surface water matrix showed higher levels of total organic carbon and turbidity, whereas the groundwater samples presented higher alkalinity and total hardness.

Different matrix compositions were taken into account in the fluence calculations. For the same UV fluence, different matrices were therefore subjected to different exposure times calculated taking into account the absorbance of each matrix used. The direct photolysis fluence and time-based rate constants obtained in LGW, surface water, and groundwater

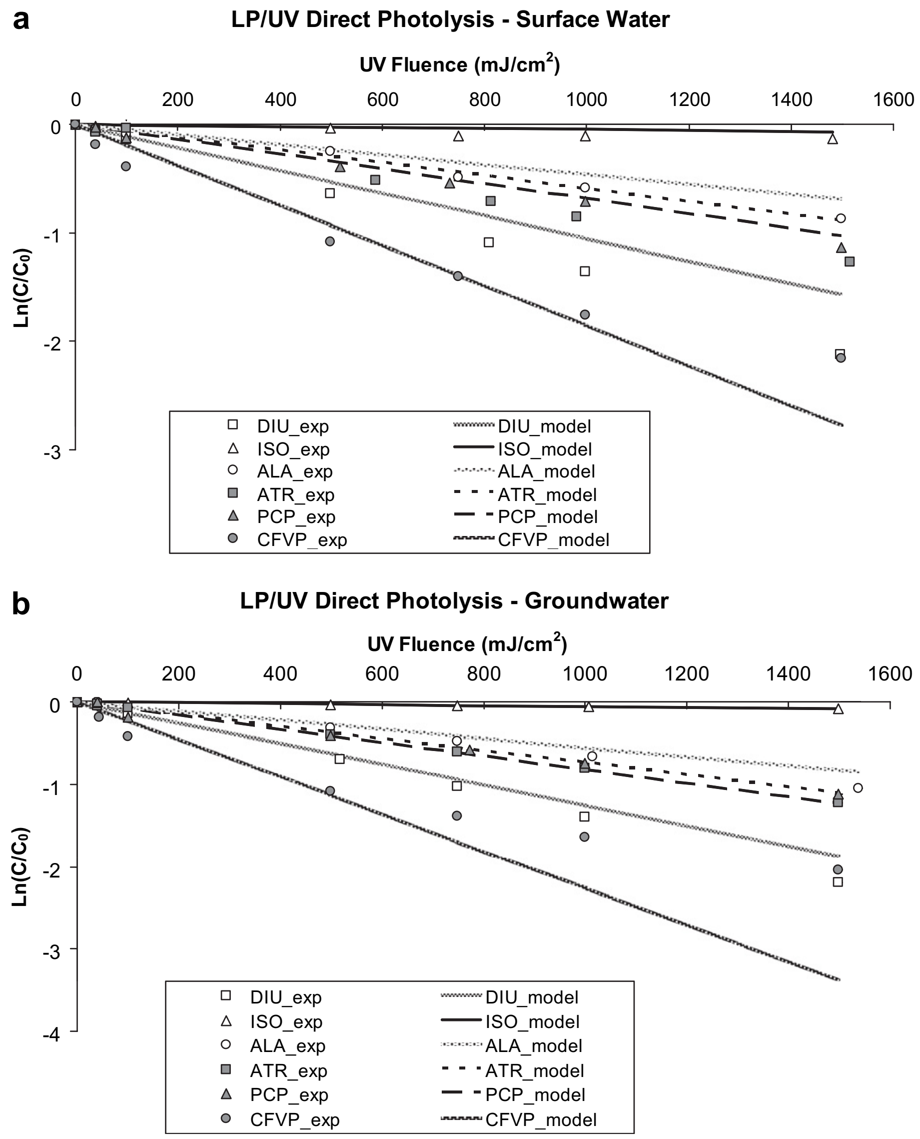

Fig. 1 – Experimental (exp) and model low pressure direct photolysis of diuron (DIU), isoproturon (ISO), alachlor (ALA), atrazine (ATR), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) in (a) surface water and (b) groundwater; experimental values are represented by symbols with error bars whereas the lines show the model results.

(Table 1 and Supplementary Material Section SM Table 3) show that for all the selected compounds except pentachlorophenol and chlorfenvinphos the rates slightly increased in surface water and groundwater. However, very similar time and fluence-based rate constants were obtained in all the tested matrices for all the compounds except chlorfenvinphos that presented lower rate constants in the real water matrices. Extremely similar rate constants were also obtained in surface water for the individual compounds and the mixtures.

In all matrices tested the degradation of the pesticides followed the same trend (Table 1 and Fig. 1). Isoproturon degradation was negligible, alachlor, pentachlorophenol, and atrazine showed similar degradation rate constants, whereas diuron and chlorfenvinphos were highly removed. The same trend was observed when a mixture of the pesticides was degraded using direct photolysis.

There are two parameters – decadic molar absorption coefficient (ε) and quantum yield (ϕ) – that highly impact direct photolysis. Table 2 shows the decadic molar absorption coefficient and the quantum yield obtained for each pesticide. The decadic molar absorption coefficient presented represents the probability of the selected pesticides to absorb UV light at 254 nm, whereas the quantum yield can be defined as the ratio between the total number of molecules of compound degraded to the total number of photons absorbed by the solution due to the compound's presence (Schwarzenbach et al., 1993). The degradation trend observed for the selected compounds followed the decadic molar absorption coefficients order with exception of isoproturon probably due to its extremely low quantum yield. All the decadic molar absorption coefficients and quantum yields obtained agree very well with previously reported values (Table 2).

Table 1 – Fluence-based direct photolysis (LP/UV) and AOPs (LP/UV/H_2O_2 and LP/UV/TiO_2) rate constants obtained for the selected pesticides in different water matrices: laboratory grade water (LGW), surface water (SW), and groundwater (GW) as individual compounds (ind) and mixtures (mix); standard errors given in parenthesis and modeled results given in square brackets.

Compound	$k_f \times 10^4$ (cm^2/mJ)								
	LP/UV				LP/UV/H_2O_2 – 40 mg/L			LP/UV/TiO_2 – 2.5 mg/L	
	LGW_{ind}	GW_{ind}	SW_{ind}	SW_{mix}	LGW_{ind}	SW_{ind}	SW_{mix}	LGW_{ind}	SW_{mix}
Atrazine	7.56 (0.08) R^2= 0.999	8.21 (0.03) $R^2 = 0.999$ [7.40]	8.51 (0.16) $R^2 = 0.996$ [5.94]	5.85 (0.04) $R^2 = 0.999$	7.43 (0.11) $R^2 = 0.997$ [59.4]	8.64 (0.06) $R^2 = 0.999$ [48.8]	6.16 (0.09) $R^2 = 0.997$	9.15 (0.06) $R^2 = 0.999$ [22.2]	10.17 (0.11) $R^2 = 0.999$ [17.3]
Isoproturon	0.56 (0.07) $R^2 = 0.850$	0.53 (0.02) $R^2 = 0.983$ [0.55]	1.06 (0.17) $R^2 = 0.769$ [0.45]	0.12 (0.02) $R^2 = 0.963$	1.23 (0.04) $R^2 = 0.987$ [6.05]	0.16 (0.02) $R^2 = 0.880$ [4.95]	0.12 (0.03) $R^2 = 0.843$	0.47 (0.07) $R^2 = 0.780$ [1.73]	0.25 (0.05) $R^2 = 0.920$ [1.41]
Diuron	13.05 (0.20) $R^2 = 0.99$	14.49 (0.15) $R^2 = 0.999$ [12.46]	14.04 (0.15) $R^2 = 0.999$ [10.47]	12.15 (0.09) $R^2 = 0.999$	13.52 (0.13) $R^2 = 0.999$ [91.6]	16.21 (0.10) $R^2 = 0.999$ [75.0]	12.96 (0.13) $R^2 = 0.999$	18.14 (0.29) $R^2 = 0.997$ [43.6]	14.59 (0.16) $R^2 = 0.999$ [33.0]
Alachlor	5.42 (0.16) $R^2 = 0.991$	6.80 (0.08) $R^2 = 0.998$ [5.47]	5.76 (0.18) $R^2 = 0.988$ [4.57]	6.71 (0.08) $R^2 = 0.998$	6.08 (0.11) $R^2 = 0.996$ [43.9]	6.20 (0.06) $R^2 = 0.999$ [36.9]	5.23 (0.07) $R^2 = 0.998$	7.03 (0.17) $R^2 = 0.993$ [8.63]	7.30 (0.18) $R^2 = 0.993$ [9.36]
Pentachlorophenol	8.38 (0.07) $R^2 = 0.999$	7.26 (0.22) $R^2 = 0.989$ [8.29]	7.34 (0.14) $R^2 = 0.996$ [6.86]	nd	9.57 (0.21) $R^2 = 0.994$ [69.9]	8.60 (0.33) $R^2 = 0.983$ [56.8]	nd	nd	nd
Chlorfenvinphos	22.52 (0.61) $R^2 = 0.993$	13.51 (0.85) $R^2 = 0.955$ [22.51]	14.44 (0.81) $R^2 = 0.964$ [18.50]	16.30 (0.47) $R^2 = 0.990$, –	20.16 (0.79) $R^2 = 0.985$ [152]	15.81 (0.67) $R^2 = 0.979$ [125]	16.96 (0.45) $R^2 = 0.992$	15.17 (0.56) $R^2 = 0.984$ [70.2]	18.54 (0.36) $R^2 = 0.996$ [56.7]

nd – Not determined.

The experimental results obtained in Fig. 1 were modeled using equations (1)–(4) detailed in the Supplementary Material Section (Sharpless and Linden, 2003; Schwarzenbach et al., 1993). The model used predicted extremely well the results obtained in groundwater for all the pesticides except chlorfenvinphos. In the surface water degradation experiments, the model slightly underestimated the experimental results for alachlor, atrazine, and diuron. However, as can be seen in Table 1 the modeled direct photolysis fluence-based rate constants were similar to the experimental rate constants obtained.

3.2. *Advanced oxidation processes*

Experimental and model AOPs photolysis of the selected pesticides was also tested using hydrogen peroxide and titanium dioxide (Table 1 and Fig. 2). The experimental results represent, in these experiments, a combination of direct photolysis and AOP results, and were modeled using equations (1)–(11) presented in the Supplementary Material Section (Sharpless and Linden, 2003; Schwarzenbach et al., 1993; Klassen et al., 1994; Buxton et al., 1988; Huber et al., 2003; Neta and Dorfman, 1968; Larson and Zepp, 1988).

The LP/UV/H_2O_2 photolysis fluence-based rate constants obtained for atrazine, diuron, and alachlor slightly increased in surface water compared to laboratory grade water similarly to what was observed in the LP/UV experiments (Table 1). Likewise, very similar time (Supplementary Material Section SM Table 3) and fluence-based rate constants were obtained in both tested matrices for all the compounds except chlorfenvinphos that presented lower photolysis rate constants in the real water matrix. In the LP/UV/TiO_2 photolysis experiments similar time and fluence-based rate constants were obtained for all compounds in LGW and surface water. In addition, the exact same degradation trend was observed for the mixtures in the surface water matrix when comparing the LP/UV, the LP/UV/H_2O_2, and the LP/UV/TiO_2 results. The following order of degradation was observed: isoproturon, alachlor, atrazine, pentachlorophenol, diuron, and chlorfenvinphos. The results obtained when a mixture of the pesticides was subjected to AOPs were again in agreement with the results obtained for the individual compounds.

Different concentrations of hydrogen peroxide (20, 60, 80, and 120 mg/L) and titanium dioxide (0.5, 5 and 10 mg/L) were tested but the results obtained showed no significant improvement in the photolysis rates obtained relatively to 40 mg/L H_2O_2 and 2.5 mg/L TiO_2.

The second-order rate constants for reaction of the pesticides with OH radicals, $k_{OH,P}$ (Table 2) were determined by competition kinetics using pCBA as a reference compound (Elovitz and von Gunten, 1999) according to equations (10) and (11) detailed in the Supplementary Material Section and are similar to reported literature values.

The modeled results overestimated the AOP experimental values (Fig. 2a and b and Table 1) especially when hydrogen peroxide was used to produce the OH radicals.

The model tested was also used to predict the degradation behaviour of the selected pesticides under different experimental conditions. The change in the direct photolysis

Table 2 – Decadic molar absorption coefficient (ε), quantum yield (ϕ), and second-order rate constants for reaction of the pesticides with OH radicals, ($k_{OH,P}$) for the selected pesticides; literature values given in square brackets (Acero et al., 2008; Song et al., 2008; Wong and Chu, 2003b; Benitez et al., 2003,2006; De Laat et al., 1999; Beltrán et al., 1993; Haag and Yao, 1992).

Compound	ε (M^{-1} cm^{-1})	ϕ (mol $einstein^{-1}$)	$k_{OH,P}$ ($\times 10^9$ M^{-1} s^{-1})	
			LP/UV/H_2O_2	LP/UV/TiO_2
Atrazine	2647	0.060	7.3	35.0
	[2847–3860]	[0.041–0.05]	[18]	
Isoproturon	5944	0.002	0.8	3.3
	[6068]	[0.0037]	[5.2]	
Diuron	16 162	0.019	12.7	87.0
	[15 699]	[0.0115]	[4.6]	
Alachlor	543	0.210	5.4	6.1
	[428–467]	[0.095—0.140]	[7.0]	
Pentachlorophenol	7400	0.025	9.0	nd
	[8500]	[0.0525]	[4.0]	
Chlorfenvinphos	8656	0.056	18.5	132.5
	[7287]	[0.089]	[3.2]	

nd – Not determined.

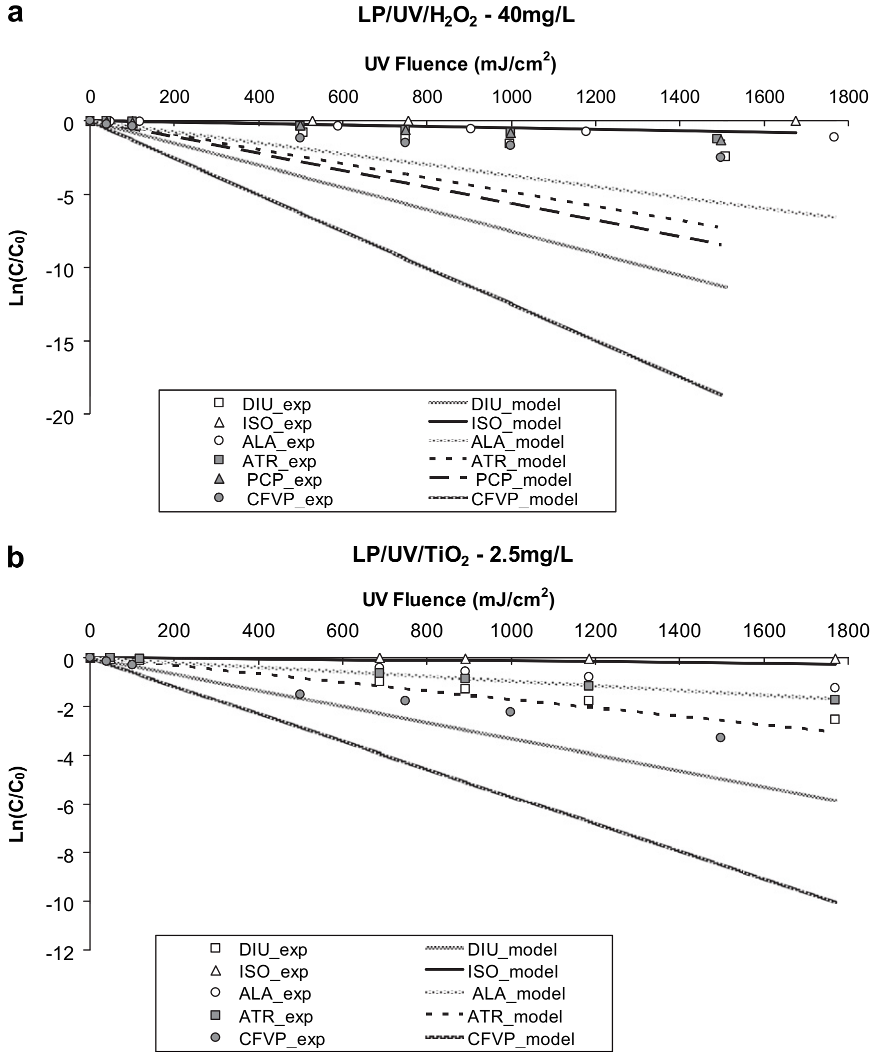

Fig. 2 – Experimental (exp) and model low pressure photolysis of diuron (DIU), isoproturon (ISO), alachlor (ALA), atrazine (ATR), pentachlorophenol (PCP), and chlorfenvinphos (CFVP) in surface water using (a) hydrogen peroxide (H_2O_2) and (b) titanium dioxide (TiO_2); experimental values are represented by symbols with error bars whereas the lines show the model results.

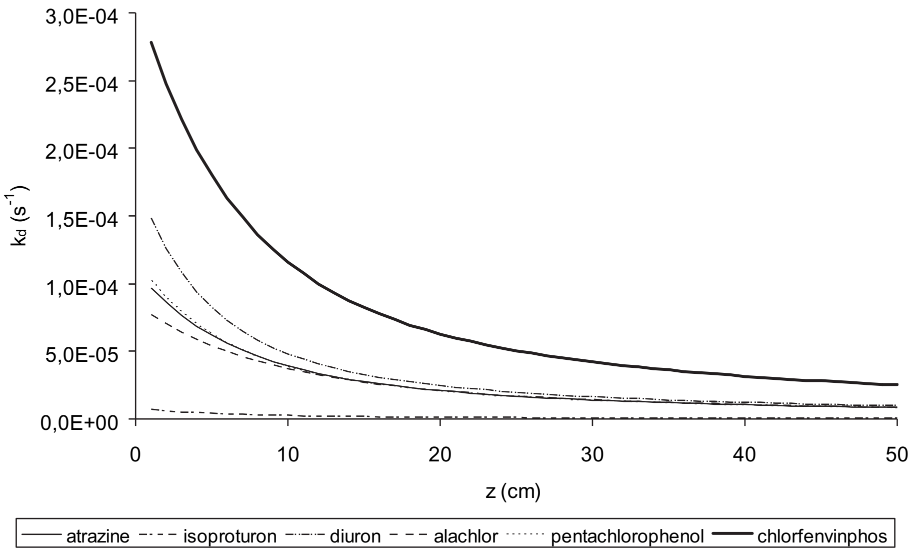

Fig. 3 – Modeled time-based direct photolysis rate constants.

time-based rate constants was therefore predicted at different distances from the UV source (Fig. 3). As expected, the distance to the UV source highly affects the degradation of the compounds at shorter pathlengths (up to approximately 20 cm), remaining almost constant at higher distances.

Fig. 4 shows the AOPs time-based rate constants predicted for isoproturon, the most resilient compound, in surface water as a function of changes in the distance to the UV source and the hydrogen peroxide (Fig. 4a) and titanium dioxide (Fig. 4b) concentrations. At the distance to the source used in our collimated beam reactor (29 cm), the overall AOPs rate constants predicted were found to be fairly independent of the H_2O_2 and TiO_2 concentrations. However, under different experimental setups, the overall degradations rate constants obtained are likely to be more efficient using higher hydrogen peroxide and titanium dioxide concentrations at lower pathlengths.

Fig. 5 presents a final comparison of the results obtained in the surface water matrix at a UV fluence of 1500 mJ/cm^2 that was achieved after approximately 4–5 h of degradation.

All the pesticides except isoproturon are expected to degrade significantly using LP/UV. Due to its extremely low quantum yield at 254 nm, isoproturon degradation using LP lamps will probably be very low even at higher UV fluences. Medium pressure lamps, that emit light at a broader range of wavelengths, have also proven to be inefficient for the degradation of isoproturon (Haque and Muneer, 2003). To achieve isoproturon degradation, much higher H_2O_2 or TiO_2 concentrations would probably need to be used with a different reactor configuration that would allow shorter distances to the lamp (Fig. 4).

The photolysis results obtained when mixtures of pesticides were degraded in surface water were extremely similar to the results obtained for the LP direct photolysis and AOPs using H_2O_2 of the individual compounds. The slight decrease in degradation of the pesticides in most of the mixture samples may be due to competition between compounds for the UV light and the OH radicals produced. For all the selected pesticides, AOPs did not seem to enhance significantly their degradation using LP lamps. This tendency was already observed by other authors whenever direct

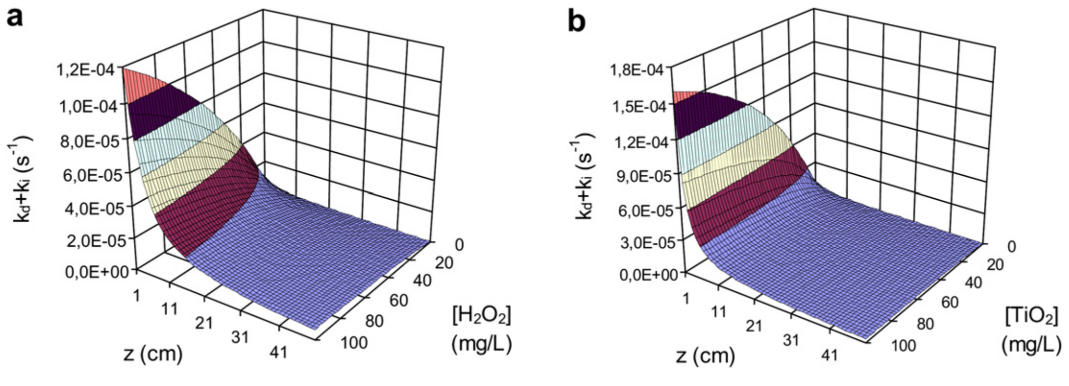

Fig. 4 – Modeled time-based direct photolysis and AOPs rate constants obtained for isoproturon.

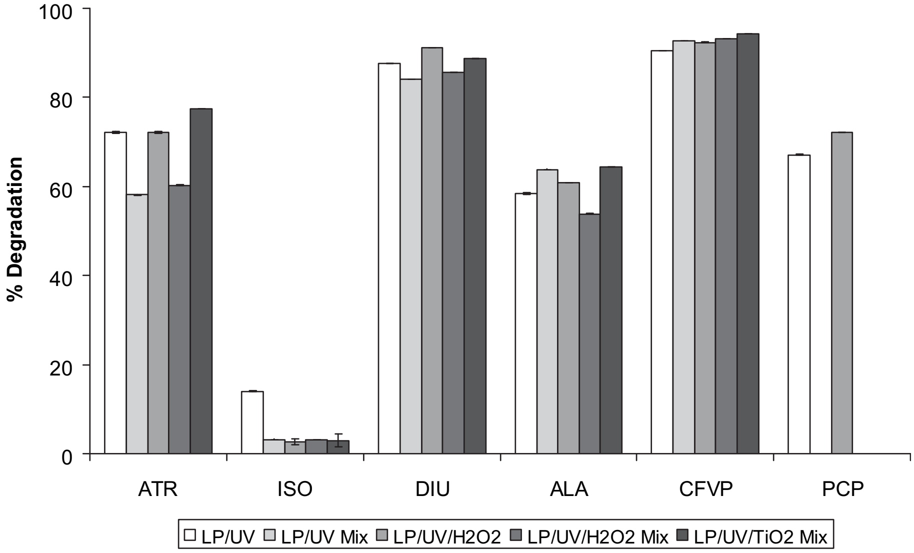

Fig. 5 – LP/UV, LP/UV/H_2O_2, and LP/UV/TiO_2 percent degradation of atrazine (ATR), isoproturon (ISO), diuron (DIU), alachlor (ALA), chlorfenvinphos (CFVP), and pentachlorophenol (PCP) spiked in surface water as individual compounds and mixtures (Mix) using a UV fluence of 1500 mJ/cm^2.

photolysis efficiently degraded compounds such as alachlor (Wong and Chu, 2003b), N-nitrosodimethylamine (Sharpless and Linden, 2003), clofibric acid and iohexol (Pereira et al., 2007b). Even though no significant enhancement of pesticides degradation was observed using AOPs, the two processes should be compared in terms of the levels of mineralization achieved. Therefore, future studies should address if the LP photolysis of these priority pollutants accomplishes the mineralization of pesticides or if by-products may form as described by other authors for different light sources (Malato et al., 2003; Wong and Chu, 2003a; Bianchi et al., 2006; Mills and Hoffmann, 1993). The identified compounds may be different according to the UV systems used. The HPLC results obtained showed that as the UV fluence increased, the alachlor peak area decreased and a by-product peak was formed (Fig. 6).

This compound is probably similar in structure to alachlor since it was detected using the same HPLC chromatographic method. Even though this was the only by-product detected in our results, many other by-products may have been formed and could be identified using mass spectrometry analysis.

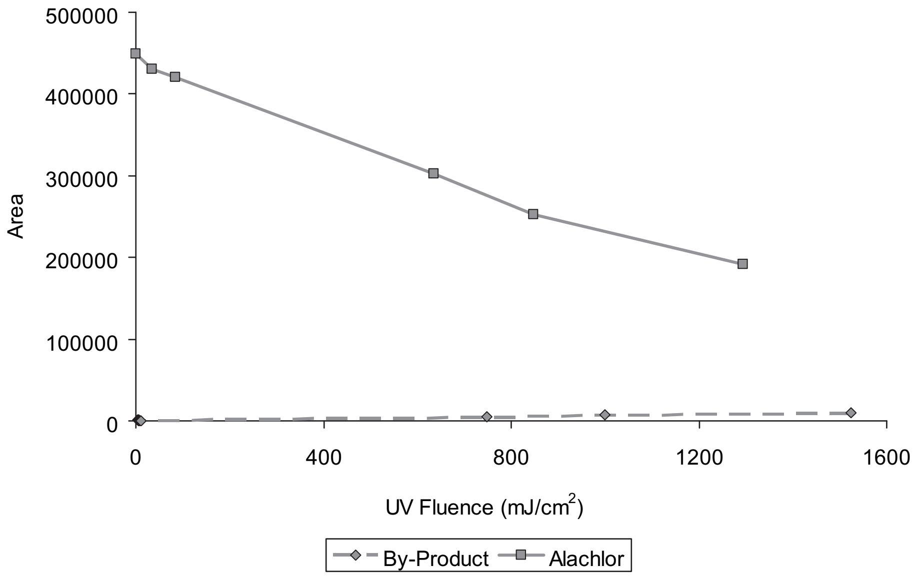

Fig. 6 – Alachlor by-product detected by HPLC.

4. Conclusions

LP/UV was found to be extremely efficient to degrade the pesticides atrazine, diuron, alachlor, pentachlorophenol, and chlorfenvinphos. Besides being known as an extremely efficient process to inactivate microorganisms, the results of this work show that LP direct photolysis using high UV fluences may also prove to be very effective to ensure the degradation of several priority substances with different structures and it is therefore a promising technology for drinking water treatment.

Acknowledgments

We thank Cristina Leitão and Joana Ricardo for their technical assistance. This work was financed by Fundação para a Ciência e a Tecnologia (PTDC/AMB/66024/2006) and the European Economic Area Financial Mechanism, Empresa Portuguesa de Águas Livres, Município de Almada, and Instituto de Biologia Experimental e Tecnológica (through project PT0012). Vanessa J. Pereira acknowledges the financial support provided from Fundação para a Ciência e a Tecnologia through the grant SFRH/BPD/26990/2006. Empresa Portuguesa de Águas Livres is acknowledged for providing the real water matrices. We thank Dr. Paula Passarinho (LNEG, Portugal) for supplying the titanium dioxide catalyst.

Appendix.
Supplementary material

Additional information provided in the supplementary Material section includes a description of the selected pesticides, details concerning the HPLC methods used, the time-based photolysis rate constants obtained in different water matrices, and the direct photolysis and AOP modeling equations used.

Note: Supplementary data associated with this article can be found in the online version at doi:10.1016/j.waters.2009.12.001.

REFERENCES

Acero, J.L., Real, F.J., Benitez, E.J., Gonzalez, A., 2008. Oxidation of chlorfenvinphos in ultrapure and natural waters by ozonation and photochemical processes. Water Research 42 (12), 3198–3206.

Balasubramanian, G., Dionysiou, D.D., Suidan, M.T., Baudin, I., Audin, B., Laine, J.M., 2004. Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water. Applied Catalysis B – Environmental 47 (2), 73–84.

Beltran, F.J., Ovejero, G., Acedo, B., 1993. Oxidation of atrazine in water by ultraviolet-radiation combined with hydrogen-peroxide. Water Research 27 (6), 1013–1021.

Benitez, F.J., Acero, J.L., Real, F.J., Garcia, J., 2003. Kinetics of photodegradation and ozonation of pentachlorophenol. Chemosphere 51 (8), 651–662.

Benitez, F.J., Real, F.J., Acero, J.L., Garcia, C., 2006. Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters. Journal of Hazardous Materials 138 (2), 278–287.

Bianchi, C.L., Pirola, C., Ragaini, V., Selli, E., 2006. Mechanism and efficiency of atrazine degradation under combined oxidation processes. Applied Catalysis B – Environmental 64 (1–2), 131–138.

Bolton, J., Linden, K., 2003. Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. Journal of Environmental Engineering – ASCE 129 (3), 209–215.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals $({}^{\bullet}OH/{}^{\bullet}O^{-})$ in aqueous-solution. Journal of Physical and Chemical Reference Data 17 (2), 513–886.

De Laat, J., Gallard, H., Ancelin, S., Legube, B., 1999. Comparative study of the oxidation of atrazine and acetone by H_2O_2/UV, Fe(III)/UV, Fe(III)/H_2O_2/UV and Fe(II) or Fe(III)/H_2O_2. Chemosphere 39 (15), 2693–2706.

Djebbar, K.E., Zertal, A., Debbache, N., Sehili, T., 2008. Comparison of diuron degradation by direct UV photolysis and advanced oxidation processes. Journal of Environmental Management 88 (4), 1505–1512.

Elovitz, M.S., von Gunten, U., 1999. Hydroxyl radical/ozone ratios during ozonation processes. I. The Rct concept. Ozone: Science & Engineering 21 (3), 239–260.

EPA, 2003. List of Drinking Water Contaminants & Their Maximum Contaminant Levels (MCLs). Environmental Protection Agency – Office of Water. http://www.epa.gov/safewater/contaminants.

Field, J.A., Reed, R.L., Sawyer, T.E., Griffith, S.M., Wigington, P.J., 2003. Diuron occurrence and distribution in soil and surface and ground water associated with grass seed production. Journal of Environmental Quality 32 (1), 171–179.

von Gunten, U., 2003. Ozonation of drinking water: part I. Oxidation kinetics and product formation. Water Research 37 (7), 1443–1467.

Haag, W., Yao, C., 1992. Rate constants for reaction of hydroxyl radicals with several drinking-water contaminants. Environmental Science & Technology 26 (5), 1005–1013.

Haque, M.M., Muneer, M., 2003. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. Journal of Environmental Management 69 (2), 169–176.

Hincapié, M., Maldonado, M., Oller, I., Gernjak, W., Sanchez-Perez, J., Ballesteros, M., Malato, S., 2005. Solar photocatalytic degradation and detoxification of EU priority substances. Catalysis Today 101 (3–4), 203–210.

Huber, M.M., Canonica, S., Park, G.Y., Von Gunten, U., 2003. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environmental Science & Technology 37 (5), 1016–1024.

Klassen, N.V., Marchington, D., McGowan, H.C.E., 1994. H_2O_2 determination by the I_3^- method and by $KMnO_4$ titration. Analytical Chemistry 66 (18), 2921–2925.

Larson, R.A., Zepp, R.G., 1988. Reactivity of the carbonate radical with aniline derivatives. Environmental Toxicology and Chemistry 7 (4), 265–274.

Linden, K., Shin, G., Faubert, G., Cairns, W., Sobsey, M., 2002. UV disinfection of *Giardia lamblia* cysts in water. Environmental Science & Technology 36 (11), 2519–2522.

Malato, S., Caceres, J., Fernandez-Alba, A., Piedra, L., Hernando, M., Aguera, A., Vial, J., 2003. Photocatalytic treatment of diuron by solar photocatalysis: evaluation of main intermediates and toxicity. Environmental Science & Technology 37 (11), 2516–2524.

Mills, G., Hoffmann, M., 1993. Photocatalytic degradation of pentachlorophenol on TiO_2 particles – identification of intermediates and mechanism of reaction. Environmental Science & Technology 27 (8), 1681–1689.

Neta, P., Dorfman, L.M., 1968. Pulse radiolysis studies. XIII. Rate constants for reaction of hydroxyl radicals with aromatic compounds in aqueous solutions. Advances in Chemistry Series 81, 222–230.

Pereira, V.J., Basílio, M.C., Fernandes, D., Domingues, M., Paiva, J. M., Benoliel, M.J., Crespo, M.T., San Romão, M.V., 2009. Occurrence of filamentous fungi and yeasts in three different drinking water sources. Water Research 43 (15), 3813–3819.

Pereira, V.J., Linden, K.G., Weinberg, H.S., 2007a. Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. Water Research 41, 4413–4423.

Pereira, V.J., Weinberg, H.S., Linden, K.G., Singer, P.C., 2007b. UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. Environmental Science & Technology 41 (5), 1682–1688.

Planas, C., Puig, A., Rivera, J., Caixach, J., 2006. Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction – estimation of the uncertainty of the analytical results. Journal of Chromatography A 1131 (1–2), 242–252.

Rosenfeldt, E.J., Linden, K.G., Canonica, S., von Gunten, U., 2006. Comparison of the efficiency of center dot OH radical formation during ozonation and the advanced oxidation processes O_3^-/H_2O_2 and UV/H_2O_2. Water Research 40 (20), 3695–3704.

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 1993. Environmental Organic Chemistry. John Wiley & Sons, Inc., New York.

Sharpless, C., Linden, K., 2003. Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H_2O_2 assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water. Environmental Science & Technology 37 (9), 1933–1940.

Song, W., Ravindran, V., Pirbazari, M., 2008. Process optimization using a kinetic model for the ultraviolet radiation–hydrogen peroxide decomposition of natural and synthetic organic compounds in groundwater. Chemical Engineering Science 63 (12), 3249–3270.

Vollmuth, S., Zajc, A., Niessner, R., 1994. Formation of polychlorinated dibenzo-P-dioxins and polychlorinated dibenzofurans during the photolysis of pentachlorophenol-containing water. Environmental Science & Technology 28 (6), 1145–1149.

Wong, C., Chu, W., 2003a. The hydrogen peroxide-assisted photocatalytic degradation of alachlor in TiO_2 suspensions. Environmental Science & Technology 37 (10), 2310–2316.

Wong, C., Chu, W., 2003b. The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources. Chemosphere 50 (8), 981–987.