DEGRADATION OF PESTICIDES IN WATER USING SOLAR ADVANCED OXIDATION PROCESSES

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ABSTRACT

Alachlor, atrazine and diuron dissolved in water at 50 mg/L, 25 mg/L and 30 mg/L, respectively were photodegraded by Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2, TiO_2 and $TiO_2/Na_2S_2O_8$ treatments driven by solar energy at pilot-plant scale using a compound parabolic collector (CPC) photoreactor. All the Advanced Oxidation Processes (AOPs) employed mainly compared the TOC mineralisation rate to evaluate treatment effectiveness. Parent compound disappearance, anion release and oxidant consumption are discussed as a function of treatment time. The use of Fe^{2+} or Fe^{3+} showed no influence on the reaction rate under illumination and the reaction using 10 or 55 mg/L of iron was quite similar. $TiO_2/Na_2S_2O_8$ showed a quicker reaction rate than TiO_2 and a similar rate compared to photo-Fenton. The main difference found was between $TiO_2/Na_2S_2O_8$ and photo-Fenton, detected during atrazine degradation, where pesticide transformation into cyanuric acid was confirmed only for $TiO_2/Na_2S_2O_8$.

Key words: Alachlor, Atrazine, Diuron, Photodegradation, Photocatalysis, Photo-Fenton.

1. INTRODUCTION

Fresh water shortage is a severe problem, particularly in arid and semi-arid areas. The problems encountered in trying to achieve economical water sanitation in these regions have led to the conclusion that success depends to a large extent on the ability to develop effective, rational and affordable wastewater (WW) treatment strategies. Partial or complete closure of the water cycle is an essential part of sustainable water-resource management and WW and its reuse should be considered within the wider context of sustainable development [European Commission, 2003]. The increasing scarcity of a clean drinking-water supply and the growing consumption of water by industry and agriculture should be countered by efficient, rational utilization of water resources. One of the options is to widen the reuse of reclaimed water to variety of purposes. Its planned direct reuse, treated to a greater or less extent, with no dilution in agro/food production (irrigation water) has become a necessity. Such direct reuse, eliminating intermediate delivery to a reception volume, reduces WW treatment and discharge costs, and avoids the delivery of pollutants to a water stream (prevention of pollution is better than removal). And it postpones, reduces and can even omit additional plant units for water supply treatment. However, health risks associated with both physico-chemical and bioactive pollutants, including persistent organic chemicals, need to be addressed where reclaimed water is reused. Because of the high cost of the end-of-pipe approach (i.e., drinking water treatment), indirect reuse of effluents requires efficient treatment of wastewater prior to discharge into the aquatic environment. Although adopted as the best available technology, biological treatment does not remove polar, toxic or non-biodegradable pollutants.

The most recent and comprehensive initiative of the European Union in the area of water protection [http://europa.eu.int/comm/environment/water/index.html] is the Water Framework

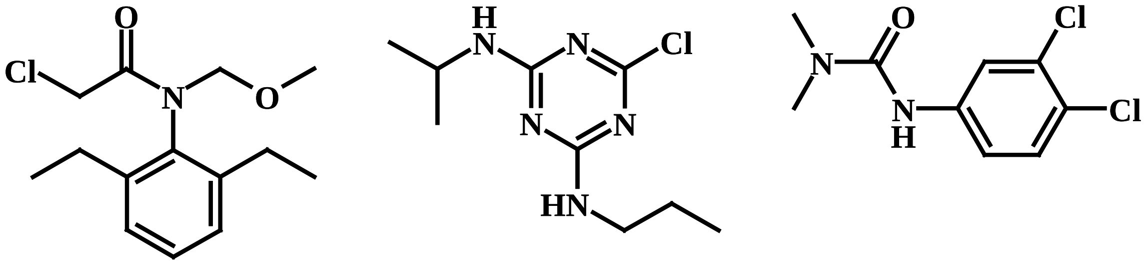
Directive (WFD) (2000/60/EC). The WFD calls for conservation of the aquatic ecosystems, sustainable use of water and preservation of water resources, such as groundwater. This is to be obtained by reducing emissions of environmental pollutants into bodies of water, improving water quality and controlling pollution at its source [Barceló, 2003]. The WFD includes a list of 33 priority substances (PS) which represent a significant risk to or through the European aquatic environment [European Commission, 2001]. Cessation or phasing out of discharges, emissions and losses of these substances must follow an appropriate timetable not to exceed 20 years. Alachlor, Atrazine and Diuron, the water-soluble pesticides studied in this paper, are included among these substances.

Alachlor is soluble in water (240 mg/L, 25ºC), it is moderately toxic to fish and highly toxic to aquatic invertebrates: EC_{50} (48 h) water flea (*Daphnia magna*) 10 mg/L; TL_{50} (72 h) algae (*selenastrum capricornutum*) 0.012 mg/L. Furthermore, it is a persistent herbicide with a half-life in soil and water of over 70 and 30 days, respectively [Tomlin, 1997]. Atrazine is also soluble in water (30 mg/L, 25ºC) and is moderately toxic to fish and highly toxic to aquatic invertebrates: EC_{50} (48 h) water flea (*Daphnia magna*) 87 mg/L; EC_{50} (72 h) algae (*selenastrum capricornutum*) 0.012 mg/L and (*Desmodesmus subspicatus*) 0.043 mg/L). It is also a persistent herbicide with a half-life in soil and water of over 41 and 55 days, respectively. Diuron is soluble in water (36.4 mg/L, 25ºC) as well. It is moderately toxic to fish and highly toxic to aquatic invertebrates EC_{50} (48 h) water flea (*Daphnia magna*) 1.4 mg/L; EC_{50} (96 h) green algae (*Desmodesmus subspicatus*) 0.022 mg/L. Moreover, it is a highly persistent herbicide with a half-life in soil of over 300 days. All three of these pesticides are classified by the EPA (Environmental Protection Agency, USA) as Type III, that is, toxic and slightly hazardous, and all of them are labelled PS by the European Commission (EC) [http://europa.eu.int/comm/environment/water/water-dangersub/pri_substances.htm]. Degradation of these pesticides dissolved in water by TiO_2 and photo-Fenton has already been described, included the toxicity reduction during the treatment [Hincapié et al., 2005].

Traditional physical techniques (coagulation, adsorption on activated carbon, reverse osmosis, etc.) can generally be used for the removal of such pollutants. Nevertheless, these methods are usually non-destructive, and the post-treatment of the adsorbent materials or solid wastes is necessary and expensive. Advanced Oxidation Processes (AOPs) may be used for decontamination of water containing these compounds and many reviews about them have recently been published [Devipriya and Yesodharan, 2005; Gogate and Pandit, 2004; Konstantinou and Albanis, 2004; Pera-Titus et al., 2004]. Although there are several different reacting systems, all of them are characterised by the same chemical feature: production of free OH radicals ($^\bullet OH$), which are able to oxidise and mineralise almost any organic molecule, yielding CO_2 and inorganic ions. Due to the reactivity of free hydroxyl radicals, their attack is unselective, which is useful for treatment of wastewater containing many different pollutants. Despite AOPs having shown their suitability for degradation of persistent organic compounds, they may involve considerable energy consumption, due to the UVA lamps used to provide photons to the system. Cleaning up waste water in this way thus comes at the price of consuming scarce resources and generating pollutant emissions and waste associated with electricity. On the other hand, it is well known that several AOPs can be performed with solar irradiation, as the sun provides photons with the wavelength required for these processes [Malato et al., 2002; Malato et al., 2004a]. With a typical UV flux near the surface of the earth of 20 to 30 W m^{-2}, the sun makes 0.2 to 0.3 mol photons m^{-2} h^{-1} within the 300 to 400 nm range available to the process

[Bahnemann, 2004], suggesting the sun as an economical and ecologically sensible light source. This is a key point, since solar irradiation is a clean renewable energy source.

This work is a comparative pilot-plant study of treatment of three PS by four different solar AOPs: heterogeneous photocatalysis using TiO_2, heterogeneous photocatalysis plus $S_2O_8^{2-}$, photo-Fenton using Fe^{2+} and photo-Fenton using Fe^{3+}. All these AOPs were applied under the same experimental conditions and the corresponding degradation studies compared not only their kinetics, but also operating parameters and chemical consumption.


Alachlor Atrazine Diuron

Scheme 1. Structures of the pesticides studied.

2. EXPERIMENTAL

2.1 Chemicals

Alachlor (2-chloro-2′,6′-diethyl-N-methoxymethylacetanilide, CAS n. 15972-60-8, 95% technical grade, Aragonesas Agro S.A.), Atrazine (6-chloro-N-ethyl-N’-isopropyl-1,3,5-triazine-2,4-diamine, CAS n. 1912-24-9, 95%, technical grade, Ciba-Geigy) and Diuron (1-(3,4-dichlorophenyl)amino-N,N-dimethyl-formamide, CAS n. 330-54-198.5%, technical grade

Aragonesas Agro S.A.) were used as received. Initial concentrations of the pesticides were 50 mg/L of alachlor, 25 mg/L of atrazine and 30 mg/L of diuron. Analytical standards of all pesticides and atrazine intermediates (Ammeline, 2-hydroxy-4,6-diamino-s-triazine CAS n. 645-92-1; Ammelide, 2-amino-4,6-dihydroxy-s-triazine, CAS n. 645-93-2; Cyanuric acid, 2,4,6-trihydroxi-s-triazine, CAS n. 108-80-5) for chromatographic analyses were purchased from Sigma-Aldrich. Water used in the pilot plant was obtained from the Plataforma Solar de Almería (PSA) distillation plant (conductivity<10microS/cm, Cl^- = 0.7-0.8 mg/L, organic carbon <0.5 mg/L). Iron sulphate ($FeSO_4.7H_2O$), hydrogen peroxide (30% w/v), sodium peroxydisulphate and sulphuric acid for pH adjustment (around 2.7-2.8) were reagent grade. TiO_2 (200 mg/L) was Degussa P-25.

2.2 Analytical determinations.

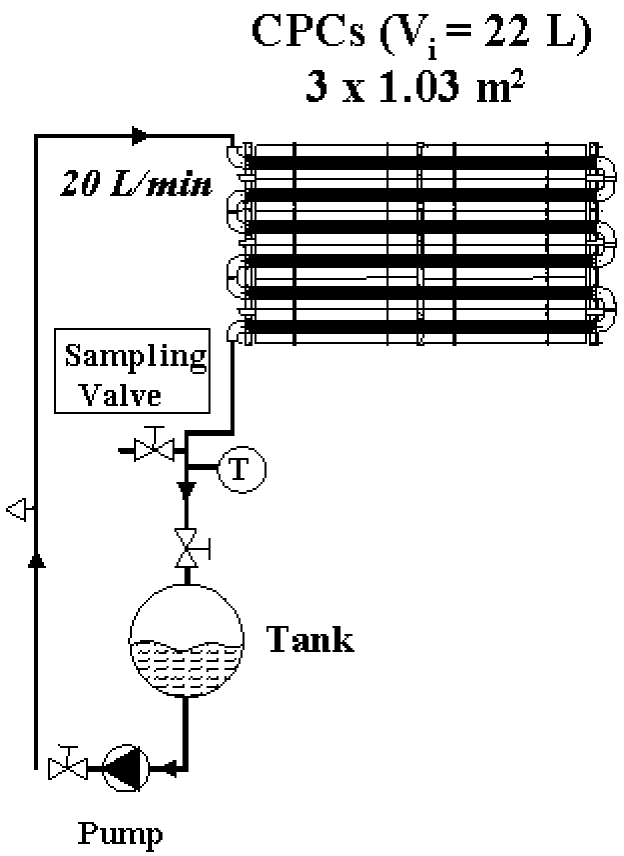
Mineralization was monitored by measuring the Total Organic Carbon (TOC) by direct injection of filtered samples into a Shimazu-5050A TOC analyser provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. Pesticide concentration was analysed using reverse-phase liquid chromatography (flow 0.5 mL/min) with UV detector in a HPLC-UV (Agilent Technologies, series 1100) with a C-18 column (LUNA 5 micron, 3x150 mm, from Phenomenex): Alachlor (H_2O/Acetonitrile 40/60, 225 nm), Atrazine (H_2O/ACN 55/45, 240 nm) and Diuron (H_2O/ACN 40/60, 254 nm). Ammeline, ammelide and cyanuric acid are detected at 220 nm and separated in a modified stationary phase. The C-18 column is loaded with di-dodecyl methyl ammonium bromide by flushing 10^{-2} M of it and ACN (25/75) for 30 min, washing with water (30 min) and then conditioning with a $5x10^{-3}$ M phosphate buffer (pH = 7.7) after baseline becomes stable. The phosphate buffer is used as an eluent for separating atrazine intermediates. Ultra pure distilled-deionized water from a Milli-Q (Millipore Co) system and HPLC-grade organic solvents were used to prepare all the solutions. Formation of inorganic anions was monitored by LC-IC (Dionex-120, anions column IonPac AS14, 250 mm long). The eluent was $Na_2CO_3/NaHCO_3$ (3.5 mM/1mM). TOC, LC-IC and HPLC-UV are provided with autosamplers and specific control programs for managing the samples, guarantying 5% accuracy of the analytical results. The Nessler method was used for ammonium determination. The concentration of peroxide in the reactor was found by iodometric titration. Concentration of peroxydisulphate was calculated by adding a known initial quantity to the photoreactor and by sulphate determination throughout testing ($S_2O_8^{2-} \rightarrow 2SO_4^{2-}$).

2.3 Experimental set-up.

All experiments were carried out under sunlight, in a pilot plant at the PSA (latitude 37ºN, longitude 2.4ºW). Each experiment has been repeated twice and the data used for kinetic calculations (and figures drawing) correspond to the average of two different tests. The pilot plant (see Scheme 2) operates in batch mode and has three compound parabolic collectors (CPCs), one tank and one recirculation pump. Each collector (1.03 m^2 each) is mounted on a fixed platform tilted 37º (local latitude). The water flows at 20 L/min directly from one module to another and finally into the tank, from which the pump recirculates the fluid back to the CPCs. The total volume (V_T) of 35 litres is separated into two parts, 22 litres (borosilicate glass-transparent tubes in the CPC) of total irradiated volume (V_i) and the dead reactor volume (tank + High Density Polyethylene tubes), which is not illuminated, as recently described in detail elsewhere [Kositzi et al., 2004]. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3), mounted on a platform tilted 37º (the same as the CPCs), which provides data in terms of incident W_{UV} m^{-2}. In this way, the energy reaching any surface in the same position with regard to the sun can be measured. With Eq. 1, combination of the data from several day's experiments and their comparison with other photocatalytic experiments is possible.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and t_{30W} is the "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon). As the system is outdoors and is not thermally controlled, the temperature inside the reactor is continuously recorded by a PT-100. Temperature never reached more than 40ºC. The characteristics (mainly water solubility) of the pesticides tested, made the use of "simulated wastewater" preparation procedures necessary. The alachlor solutions were prepared by mixing for several hours to achieve a 50-mg/L concentration in the pilot plant. Atrazine and diuron are soluble in water at less than 50 mg/L at ambient temperature. In order to test them at the maximum initial concentration, a saturated solution was prepared in the auxiliary 100-L tank and mixed for a further 24 hours. Then the pilot plant was completely filled with water from the auxiliary tank, avoiding the transfer of any undissolved solids.



Scheme 2. Schematic representation of the photoreactor.

3. RESULTS AND DISCUSSION

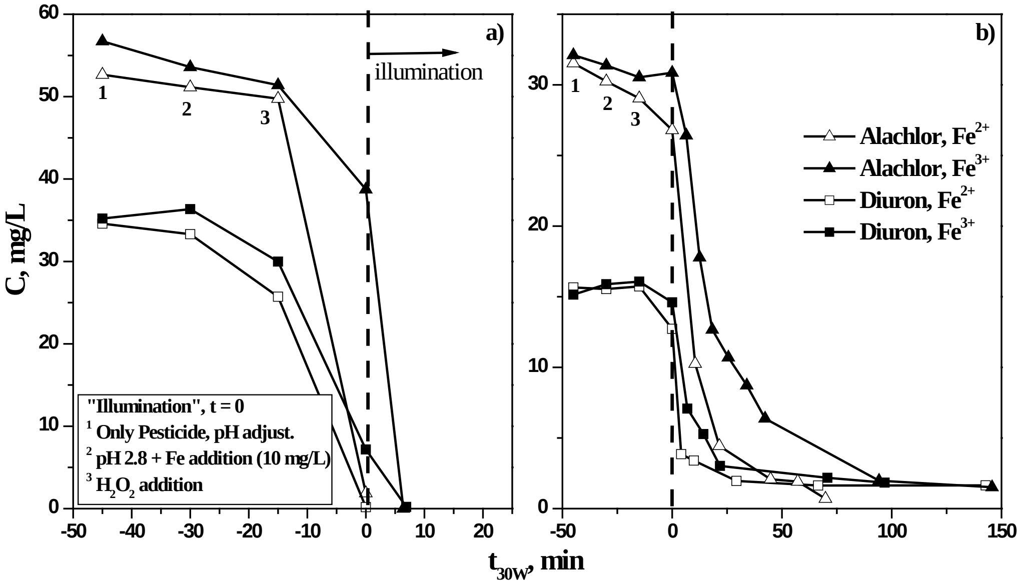


Figure 1. Disappearance of pesticide (a) and evolution of TOC (b) as a function of t_{30w} for 10 mg/L of Fe^{2+} and Fe^{3+}, respectively.

Figure 1 shows the evolution of pesticide concentration and the corresponding TOC using Fe^{2+} or Fe^{3+} in the photo-Fenton process. In this figure, it is clear that photo-Fenton based on Fe^{2+} or Fe^{3+} is an effective treatment, even with a small amount of iron (10 mg/L). Among the advantages of this method are that Fe is abundant and nontoxic, the hydrogen peroxide is easy to handle and environmentally-friendly and there are no mass transfer limitations. It has been demonstrated before [Malato et al., 2004b] that the amount of iron necessary for carrying out these processes in solar photoreactors with a light-path length of a few centimetres (diameter of the cylindrical photoreactor) is in the range of a few tens of mg/L. Eqs. 2-7 show the most important reactions involving iron and hydrogen peroxide. The rate constants listed in parenthesis are those reported by Sychev and Isaak [Sychev and Isaak, 1995]. In this system, iron is a true catalyst, as it is recycled, while hydrogen peroxide is continuously consumed. The rate-limiting step is the regeneration of ferrous iron. During the oxidation process, carboxylic acids are produced, which form rather stable complexes with ferric iron, further slowing down the regeneration of ferrous iron. Eqs. 6 and 7 also show that excess ferrous iron and hydrogen peroxide themselves can act as hydroxyl radical scavengers. Ferric iron complexes can be photolysed upon irradiation in a ligand-to-metal charge transfer reaction by passing through a photo-excited transition state before charge transfer and complex dissociation. Especially worthy of mention is the photolysis of ferric iron-aquo complexes, which apart from regenerating ferrous iron efficiently, generates further hydroxyl radicals. The excitation of $[Fe(OH)(H_2O)_5]^{2+}$, the dominant monomer species of aqueous ferric ion at pH = 2.5-2.8, is known to yield $^{\bullet}OH$ with a quantum yield of 0.075 at 360 nm [Benkelberg and Warneck, 1995]. Ferric iron-carboxylic acid complexes can also be photolysed, often with very high quantum yields and also at wavelengths up to around 580 nm [Bauer et al., 1999]. Ferrous iron regeneration and pollutant decarboxylation take place as a result. Consequently, as shown in Figure 1, there is a wide difference between Fe^{2+} and Fe^{3+} at the beginning of the process (in the dark), but not under illumination. Indeed, mineralisation rates (TOC decrease, considering TOC at t = 0 as the initial TOC) under illumination were in the same range: $k_{TOC,alachlor(Fe^{2+})} = 0.046$ min^{-1}, $k_{TOC,diuron(Fe^{2+})} = 0.050$ min^{-1}, $k_{TOC,alachlor(Fe^{3+})} = 0.038$ min^{-1}and $k_{TOC,diuron(Fe^{3+})} = 0.069$ min^{-1}. This was the only case in which conventional kinetics calculations were possible, as TOC kinetics data could be fitted to an apparent first order kinetics constant. This was not the case under other photo-Fenton conditions or for comparing photo-Fenton and TiO_2 photocatalysis, as explained below. Of course, pesticide disappearance and TOC mineralisation, triggered by “dark” Fenton, took less time with Fe^{2+}, (Eq. 2). If photo-Fenton is performed at low Fe concentration (which is often very useful, mainly for simplifying iron removal at the end of the process and/or for discharging the water into a subsequent biological treatment without removing iron), the decision on whether to use both Fe oxidation stages should be based only on economic reasons (iron salt prices). For the rest of the work, Fe^{2+} was used, but the main conclusions obtained could also be considered pertinent for Fe^{3+}.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (53 - 76\ M^{-1}\ s^{-1}) \qquad (2)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+ \qquad (1 – 2{\cdot}x\ 10^{-2}\ M^{-1}\ s^{-1}) \qquad (3)$$

$$Fe^{2+} + {}^{\bullet}HO_2 \longrightarrow Fe^{3+} + HO_2^- \qquad (0.72 – 1.5{\cdot}x\ 10^{6}\ M^{-1}\ s^{-1}) \qquad (4)$$

$$Fe^{3+} + {}^{\bullet}HO_2 \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (0.33 – 2.1{\cdot}x\ 10^{6}\ M^{-1}\ s^{-1}) \qquad (5)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow H_2O + {}^{\bullet}HO_2 \qquad (1.7 – 4.5{\cdot}x\ 10^{7}\ M^{-1}\ s^{-1}) \qquad (6)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \qquad (2.6 - 5{\cdot}x\ 10^{8}\ M^{-1}\ s^{-1}) \qquad (7)$$

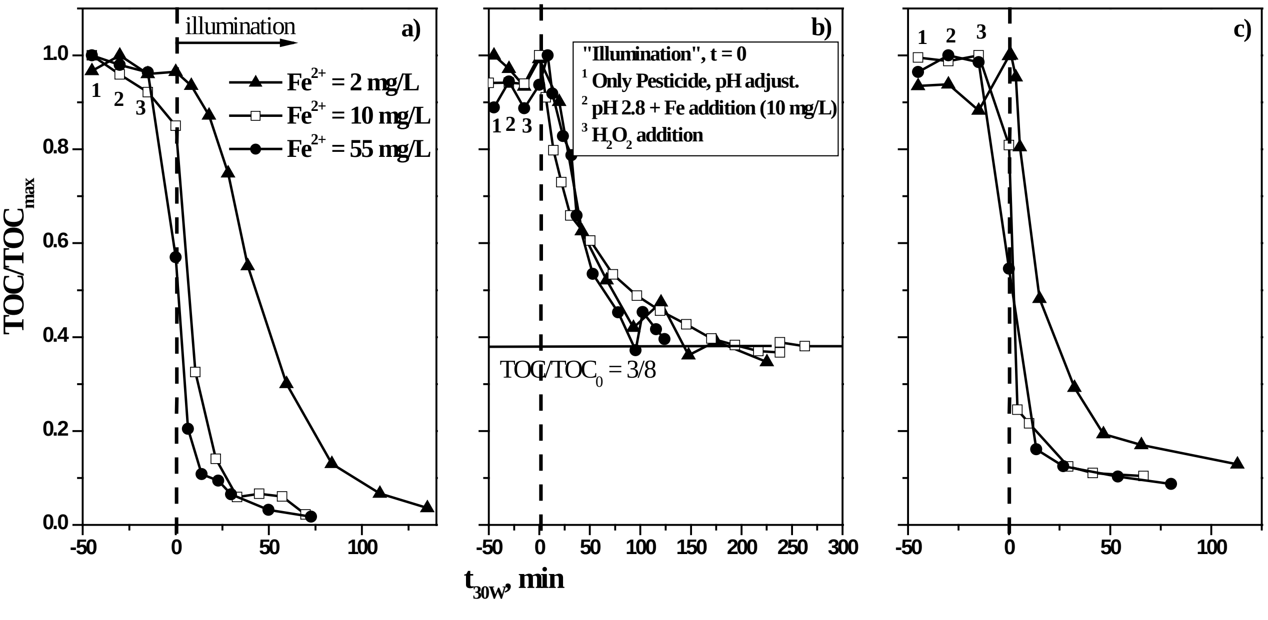


Figure 2. Mineralisation of 50 mg/L of alachlor (a), 25 mg/L of atrazine (b) and 30 mg/L of diuron (c) as a function of t_{30W} during photo-Fenton treatment using Fe^{2+}. 3/8 TOC line for atrazine represents the non-degradable triazine ring.

Figure 2 shows results obtained at three different iron concentrations. Only TOC is used for comparison, as due to the dark Fenton reaction, disappearance of the parent compound was so quick (less than 25 min for the slower conditions with Fe = 2 mg/L) that no kinetics calculation was possible. Indeed, the mineralisation rate (decrease in TOC, with TOC at t = 0 taken as initial TOC) under illumination did not follow simple first or zero order kinetics models and overall reaction rate constants cannot be calculated. The complexity of the results, of course, is caused by the fact that TOC is a parameter which is often the sum of several hundred products undergoing a multitude of reactions. Two different parameters have been chosen to get a practical grip on the experiments for their comparison. On one hand, the time necessary for a certain amount of degradation ($t_{90\%TOC}$ is defined as the time necessary to mineralise 90% of the initial TOC) and, on the other hand, the maximum gradient of the degradation curve, formally the gradient of the tangent at the inflection point (r_0), which has a zero-order rate constant (mg L^{-1} min^{-1}) and therefore appears to be easy to handle. Furthermore, this gradient can be considered roughly the initial rate of the photo-Fenton reaction, as calculated taking t = 0 as the starting point.

	Fe^{2+}, 2 mg/L		**Fe^{2+}, 10 mg/L**		**Fe^{2+}, 55 mg/L**	
	$t_{90\%,TOC}$	r_0/$r_{0,D}$	$t_{90\%,TOC}$	r_0	$t_{90\%,TOC}$	r_0
	min	mg L^{-1} min^{-1}	min	mg L^{-1} min^{-1}	min	mg L^{-1} min^{-1}
Alachlor	105	0.33/0.0	40	0.99/0.15	29	0.93/0.80
Atrazine	155	0.091/0.0	170	0.085/0.0	135	0.11/0.0
Diuron	127	0.23/0.0	65	0.43/0.20	68	0.38/0.42

Table 1. Comparison of pesticide degradation at different Fe^{2+} concentrations under illumination ($t_{90\%, TOC}$ and r_0) and in the dark ($r_{0,D}$). In the case of atrazine, $t_{90\%,TOC}$ refers to time necessary for reaching TOC = 3/8 TOC_0.

It may be observed that the higher the initial iron concentration was, the more pronounced mineralisation in the dark. However, it can also be seen that the photo-Fenton reaction rate was quite similar between Fe = 55 mg/L and Fe = 10 mg/L after illumination began. This is in agreement with the comment above on optimal Fe loading in solar photoreactors (with light path length of a few centimetres) and regeneration of ferrous iron as the rate-limiting step. It should also be mentioned that initial TOC (just before t = 0) during atrazine and diuron tests, concentration was unstable because both pesticides were added at their solubility limits. Changes in pH and degradation during dark Fenton have produced a slight precipitation and subsequent re-dissolution. Indeed, TOC results were consistent only after t= 0. On the other hand, atrazine is not completely mineralised, because it is well-known that it cannot be mineralised by photo-Fenton until the end due to the stability of the triazine ring. Around 10% of the initial TOC in diuron was also difficult to degrade. This TOC must be only from aliphatic compounds, as HPLC diode array detector scans did not show any signal above 210 nm. The very slow degradation of TOC in phenylurea pesticides after 80-90% mineralisation [Muneer et al., 1999; Parra et al., 2002] and the very slow mineralisation of urea [Maletzky and Bauer, 1998], which can be predicted as an intermediate of diuron, have also been reported previously. Urea contains only 1 C atom and 2 N atoms, which could justify not only the remaining 10% of the initial TOC, but also the incomplete release of N, as commented below.

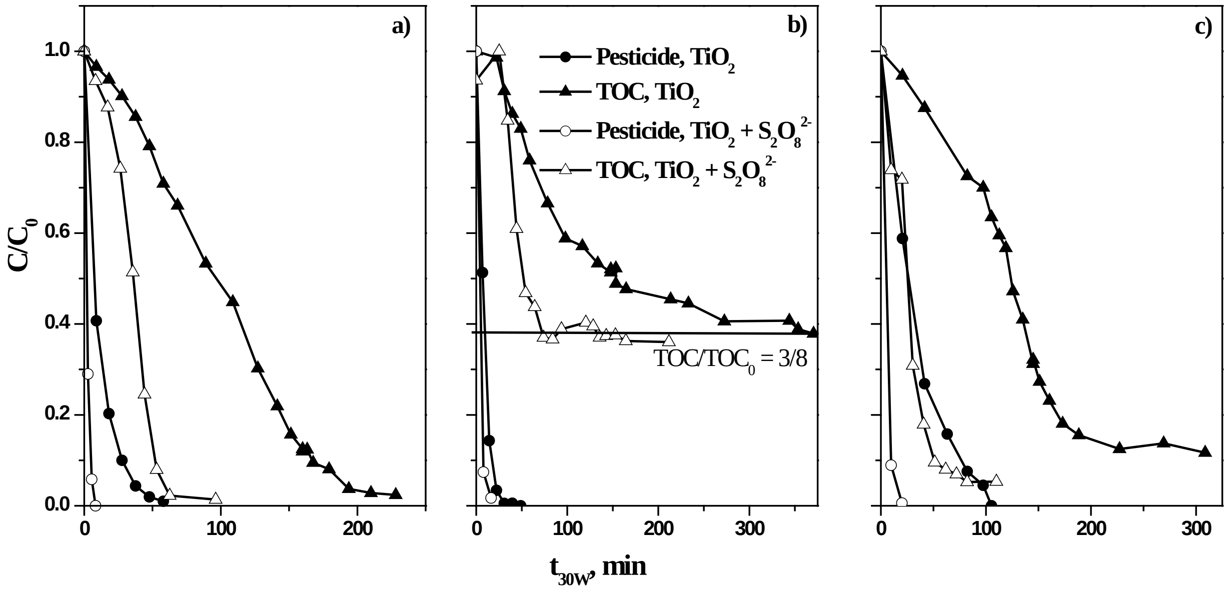


Figure 3. Disappearance of pesticide and evolution of TOC as a function of t_{30w} for TiO_2 200 mg/L (with and without 10 mM $S_2O_8^{2-}$) of alachlor (a), atrazine (b) and diuron (c). 3/8 TOC line for atrazine represents the non-degradable triazine ring.

The TiO_2 photocatalytic redox process is based on electron and hole migration to the semiconductor surface, and two further oxidation and reduction steps. It is widely argued that the reduction step may be rate-limiting since electrons react (with dissolved oxygen from water) much more slowly than holes. Two basic lines of R&D have been working on balancing the rates of the two halves of the reaction, one by modifying catalyst structure and composition and the other by adding electron acceptors. Both have tried to promote competition for electrons and avoid recombination of e^-/h^+ pairs. A third approach has focused not only on increasing quantum yield, but finding new catalysts able to work with band-gaps which better overlap the solar spectrum (mainly using dye sensitised TiO_2 [Chatterjee et al., 2004]). There have been many attempts within the first approach, such as improving specific surface, doping and deposition with metal ions and oxides [Blake D.M, 1994, 1995, 1997, 1999, 2001]. Successful innovative catalyst compositions have been developed during recent years, but they have not been used in large-size solar plants (where P-25 suspensions continue being the more reliable solution) because no “cheap” solution has yet been developed. Our experience in testing at large solar facilities and with different contaminants qualifies the use of electron scavengers as the most versatile and useful way of improving TiO_2 reaction rates (for the moment), opening the opportunity to extend the utilisation of heterogeneous photocatalysis to complicated waste water [Malato et al, 2002]. Hydrogen peroxide is the obvious candidate and has been tested with a large number of compounds. Also, it is very cheap and commonly used. But in the literature there is huge disparity in results concerning the effect of H_2O_2. Sometimes it is beneficial and others detrimental, but the optimum concentration usually depends on the H_2O_2/contaminant molar ratio. This produces additional problems when working with complex mixtures, because the molar concentration is usually different for each compound in the mixture. Our experience with H_2O_2 has not been successful [Malato et al., 2000], not only for the reasons above, but also because of the enormous consumption of H_2O_2 required for only a slight increase in degradation rate. Based on those results, we have therefore selected peroxydisulphate for this work instead of hydrogen peroxide [Malato et al., 2000] for comparison with other solar AOPs under the same conditions. With peroxydisulphate, the mineralization reaction rate was clearly enhanced (compared to TiO_2 alone, as shown in Figure 3). The reactions peroxydisulphate is involved in and responsible for its efficiency are expressed in Eqs. 8-11, where e^-_{CB} is the electron generated in the TiO_2 conduction band. Obviously reactions 8 and 9 enhanced the photocatalytic reaction rate by avoiding e^-/h^+ recombination (the major cause of the low quantum yield of TiO_2 photocatalysis). This leaves a larger number of holes (h^+) able to produce $^{\bullet}OH$. Photolysis of peroxydisulphate also produces two sulphate radical anions (Eq. 12) with unity quantum efficiency. Though it absorbs from the deep UV region up to 350 nm, light absorption above 300 nm (beginning of solar-light spectrum at earth surface) is very scarce [Hori et al., 2005]. Indeed, in the photoreactors, which are made of borosilicate glass, transmission of light below 350 nm is incomplete. Therefore, the influence of reaction 12 on the overall process efficiency may be considered irrelevant. In a previous paper [Malato et al., 2000], we have already demonstrate by performing adequate blanks that: temperature (< 40ºC) in the dark, temperature under illumination (< 40ºC) and the solar UV radiation itself did not produced any effect.

$$S_2O_8^{2-} + e^-_{CB} \longrightarrow SO_4^{2-} + SO_4^{\bullet -} \qquad (8)$$

$$SO_4^{\bullet -} + e^-_{CB} \longrightarrow SO_4^{2-} \qquad (9)$$

$$SO_4^{\bullet -} + H_2O \longleftrightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \qquad (10)$$

$$SO_4^{\bullet -} + \text{Pollutant} \longrightarrow SO_4^{2-} + \text{oxidised species} \qquad (11)$$

$$S_2O_8^{2-} + h\upsilon \longrightarrow 2SO_4^{\bullet -} \qquad (12)$$

In Figure 3, it is evident that the addition of this oxidant is quite beneficial, suggesting that the additive strongly accelerates degradation of intermediates. It increases the photocatalytic reaction rate because it avoids and reduces the probability of recombination, generating additional hydroxyl radicals and produces $SO^{\bullet -}_4$ radicals, which are also strongly oxidizing species (E^o = 2.6 V). This leads to a very significant reduction in treatment time, at least 6 times faster than necessary for total disappearance of the initial compound (in all three cases) with TiO_2 alone. As a detailed kinetics comparison for the degradation of the parent compound is difficult because the reaction rate with peroxydisulphate is so quick, it is better to compare TOC mineralisation in the same way as described for the photo-Fenton tests (see Table 1). These results are included in Table 2.

	TiO_2		**$TiO_2 + S_2O_8^{2-}$**	
	$t_{90\%,TOC}$	r_0	$t_{90\%,TOC}$	r_0
	min	mg L^{-1} min^{-1}	min	mg L^{-1} min^{-1}
Alachlor	165	0.19	50	0.61
Atrazine	370	0.074	75	0.19
Diuron	250	0.095	50	0.37

Table 2. Comparison of pesticide degradation for TiO_2 200 mg/L (with and without 10 mM $S_2O_8^{2-}$). In the case of atrazine, $t_{90\%,TOC}$ refers to time necessary for reaching TOC = 3/8 TOC_0.

Results presented in Figure 2, Figure 3, Table 1 and Table 2 lead to the conclusion that photo-Fenton using Fe = 55 mg/L and TiO_2 with peroxydisulphate are the two processes where highest degradation rate is obtained. Another important parameter related with both processes and necessary for comparing them is the consumption of both hydrogen peroxide and peroxydisulphate. In Figure 4 peroxydisulphate consumption is always observed to be related to TOC mineralisation. When TOC has been mineralised, oxidant consumption is clearly slower. In any case, this effect has enormous significance for photocatalytic plant operation with peroxydisulphate because the sulphate production rate can be used to find out exactly when organics are mineralised. TOC analysis is not a cheap technique and the cost of the equipment (around 30.000 Euro) may be higher than the cost of solar collectors in medium size plants

(100 m^2 around 50.000 Euro). Sulphate analysis is very cheap indeed and could be installed on-line. This is very important for automating the plant and reducing operating costs. It can also be stated that consumption of hydrogen peroxide is higher than peroxydisulphate. It should be noted that, from a practical point of view, the molecular weight of these two oxidants is very different. Therefore, any economic comparison should be done taking this into consideration, as chemicals are usually sold by unit of "weight". With these results, the best choice could not be ascertained, and a case-by-case economic comparison taking the main parameters related to each treatment into account would be necessary. Peroxydisulphate has several drawbacks (in addition to consumption), such as the large amount of sulphate generated during the process (2 moles of sulphate per mol of peroxydisulphate) and pH decrease. Catalyst separation, neutralisation of acid pH (pH = 2 is reached if 10 mM peroxydisulphate are consumed), cost of peroxydisulphate, and reaction rate should be taken into account when TiO_2 (with $S_2O_8^{2-}$) is used. Neutralisation of acid pH (pH = 3) and hydrogen peroxide costs should be taken into account when photo-Fenton is used.

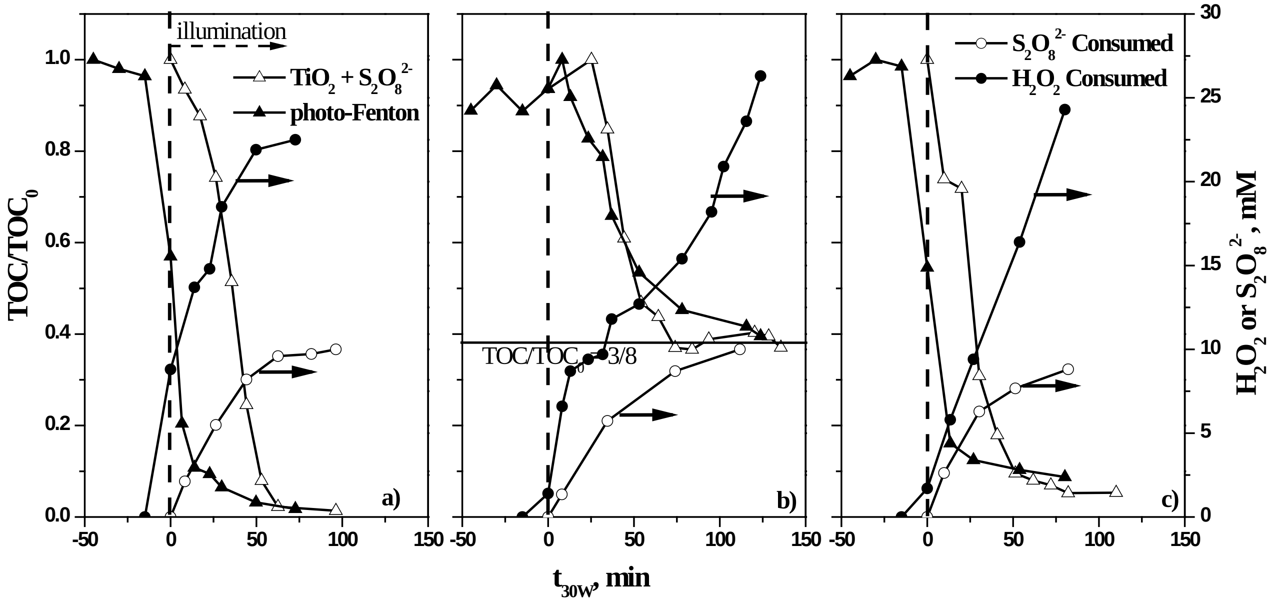


Figure 4. Evolution of TOC as a function of t_{30w} for 200 mg/L TiO_2 (with $S_2O_8^{2-}$) and for photo-Fenton (Fe^{2+} = 55 mg/L) of alachlor (a), atrazine (b) and diuron (c). Consumption of hydrogen peroxide and peroxydisulphate is also shown. 3/8 TOC line for atrazine represents the non-degradable triazine ring.

Apart from TOC evolution and oxidant consumption, it might be of interest to compare inorganic release of heteroatoms, such as chlorine, ammonia and/or nitrate. Ammonia and nitrate were detected in different relative concentrations, and total balance of N was obtained only in the case of alachlor, mainly as ammonia. The nitrogen mass balance of atrazine was unclear, considering that 2 N atoms would have to be mineralised (the other 3 atoms are contained in the ring). Release of nitrogen from diuron was incomplete . As commented above, around 10% of the initial TOC was difficult to degrade (see Figures 2 and 3) in all the AOPs applied (with only TiO_2-peroxydisulphate it seems to be nearly 5% of the initial TOC). Therefore, results for nitrogen mineralisation as ammonia and/or nitrate were inconclusive. Chloride release was complete in all cases. Figure 5 shows the results obtained using TiO_2 (200 mg/L) and Fe (2 mg/L). In all other cases, inorganics evolution was quicker, reaching a maximum concentration similar to that shown in Figure 5, but in a shorter time. Chloride analyses showed dechlorination to be faster than disappearance of TOC. Therefore, residual TOC remaining in the water at the end of experiments did not correspond to any chlorinated compound. Alachlor has the lowest dechlorination rate. In fact, alachlor is the only pesticide studied here that has non-aromatic chlorine atoms (aliphatic chlorines are released at slower rates than aromatic chlorines). It has been demonstrated before that dechlorination usually causes decreased toxicity [Hincapié et al., 2005]. Under these circumstances, monitoring of water toxicity before total mineralisation is more than justified in order to stop the AOP treatment just after detoxification requirements are met.

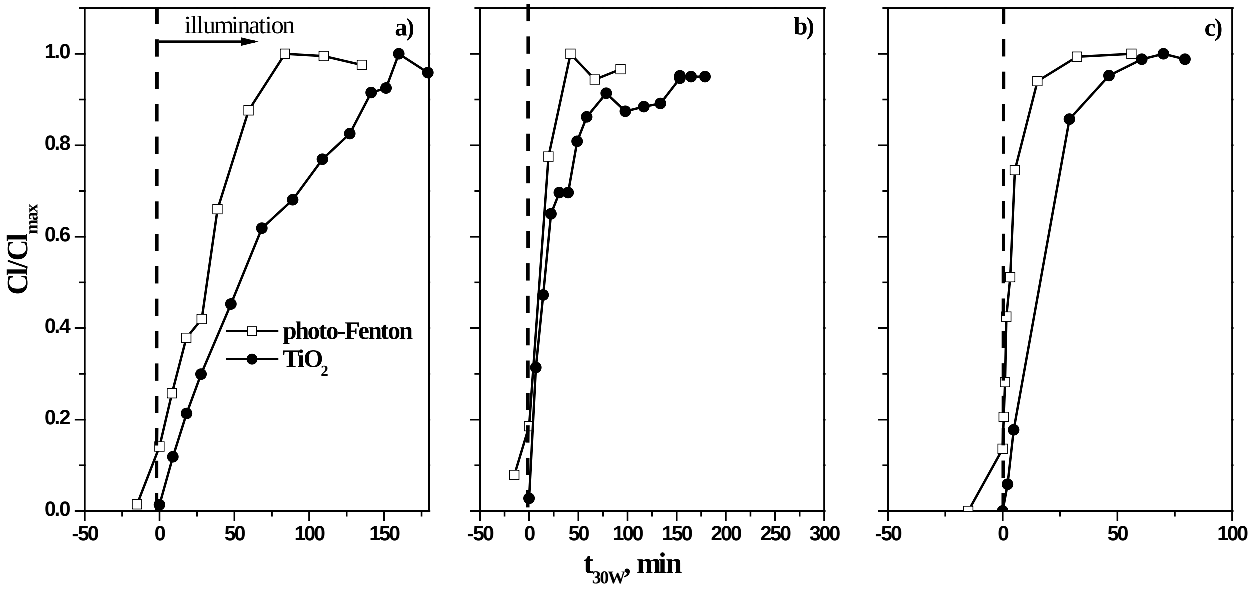


Figure 5. Evolution of chloride as a function of t_{30w} for TiO_2 200 mg/L and for photo-Fenton (Fe^{2+} = 2 mg/L) of alachlor (a), atrazine (b) and diuron (c). Cl/Cl_{max} refers to all chloride values divided by the expected from initial concentration of each pesticide.

Atrazine intermediates generated by all the processes employed have been studied in some detail. This pesticide is of interest because complete mineralisation is not attained as oxidation only affects the lateral chains with 5 of the 8 carbons removed as CO_2. The photocatalytic degradation of s-triazine herbicides was first studied by Pelizzetti et al., [Pelizzetti et al., 1990] and since then several studies have been published about the photocatalysed oxidation of s-triazines and the pathways of the photoproducts, most of them recently reviewed by Konstantinou and Albanis

[Konstantinou and Albanis, 2003]. It has been concluded that the oxidation of the lateral chains and subsequent disappearance of the initial compound is very fast, but the formation of the final product (cyanuric acid) may require a long irradiation time. It is of interest to note that cyanuric acid is reported to have lower toxicity than atrazine and its degradation products [Hiskia et al., 2001]. Substitution of the amino groups linked to the triazine ring by hydroxyl groups in particular is a very slow process. With this in mind, we have attempted to compare TiO_2 (with $S_2O_8^{2-}$) and photo-Fenton under identical experimental conditions to find out whether there is any difference in cyanuric acid release. Figure 6 shows the results. It can be seen that ammeline and ammelide are the main intermediates during photo-Fenton treatment, with more than 80% of atrazine converted into these two compounds. Indeed, nearly 40% of atrazine was converted into ammeline during the "dark-Fenton". But cyanuric acid is only produced very slowly after more than 10 hours. Atrazine treatment by Fenton and/or photo-Fenton has been reported several times [Arnold et al., 1995; Balmer and Sulzberger, 1999; De Laat et al. 1999] as well as comparison between Fe and TiO_2 [Krisova et al. 2003], but in no case is cyanuric described as the final product, or if so, only after a very long time. On the contrary, TiO_2 with peroxydisulphate produces a complete release of cyanuric acid in around two hours. Therefore, the results shown in Figure 6, where photo-Fenton and 200 mg/L TiO_2 (with $S_2O_8^{2-}$) are compared for atrazine degradation, should be carefully observed, because when $TOC/TOC_0 = 3/8$, the intermediates present in the treated water are completely different. Cyanuric acid is biodegradable and with negligible eco-toxicity, and therefore the best treatment for atrazine should have complete transformation of atrazine into cyanuric acid as its final goal.

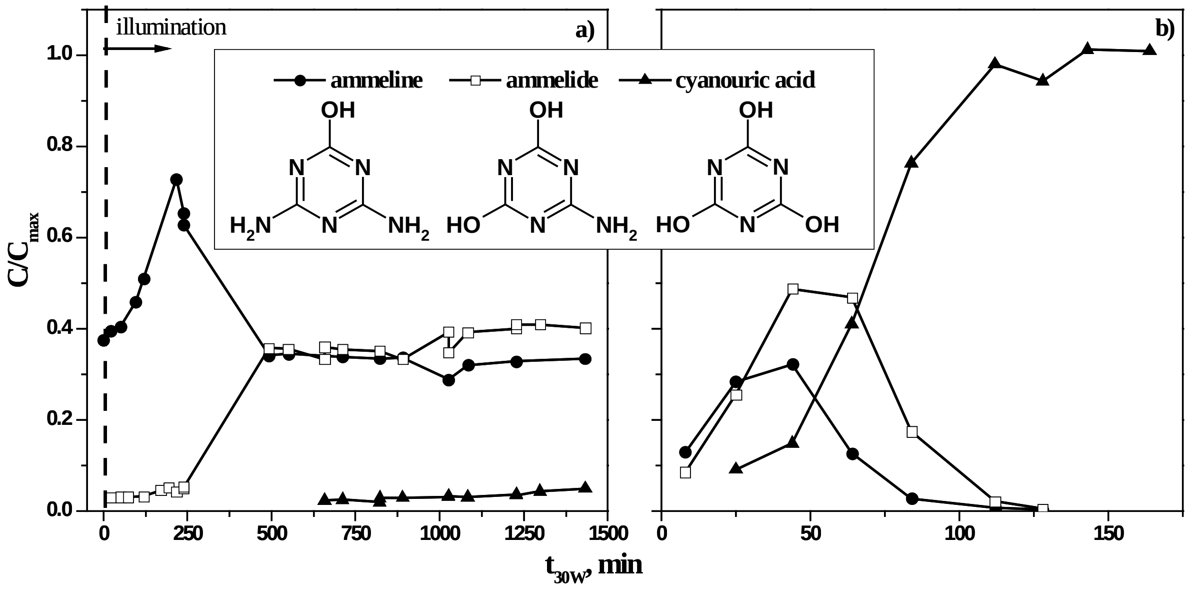


Figure 6. Evolution of main intermediates of atrazine as a function of t_{30w} for (a) photo-Fenton (Fe^{2+} = 10 mg/L) and for (b) 200 mg/L TiO_2 (with $S_2O_8^{2-}$). C/C_{max} refers to the contribution of each intermediate to the overall mass balance at any given moment.

4. CONCLUSIONS

It has been demonstrated that photo-Fenton using iron at low concentrations is a suitable treatment for water containing pesticides at mg/L level, as it is always quicker than TiO_2 photocatalysis. Mineralisation was attained in all cases, and complete release of chloride. The decision as to whether to use Fe^{2+} or Fe^{3+} salts should be for economic reasons, since with small quantities of iron, “dark Fenton ” does not much influence overall treatment time. In the case of photoreactors with a path length of a few centimetres, use of more than a few tens of mg/L of iron is not recommended.

Peroxydisulphate-TiO_2 may be a suitable alternative to photo-Fenton, so a case-by-case comparative economic study should be done taking the main parameters of each treatment into account. Catalyst separation, neutralisation of acid pH (pH = 2 is attained with 10 mM peroxydisulphate), peroxydisulphate costs, reaction rate (plant size will depend on it) should be taken into account when TiO_2 (with $S_2O_8^{2-}$) is used. Neutralisation of acid pH (pH = 3), hydrogen peroxide costs, and reaction rate should be taken into account with photo-Fenton.

Although mineralisation of atrazine was expected to be incomplete, it was also decomposed by all the AOPs applied. Complete release of cyanuric acid was attained in a reasonable time only by treatment with Peroxydisulphate-TiO_2.

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