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Technical Note

Homogeneous oxidation of aqueous solutions of atrazine and fenitrothion through dark and photo-Fenton reactions

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ABSTRACT

The homogeneous catalytic oxidation of atrazine and fenitrothion in single compound-containing solutions and in mixture, in pure water, was investigated in dark and light-driven oxidation systems using H_2O_2 as the oxidant and Fe(II) as the catalyst. It was shown that the degradation during the dark Fenton reactions takes place during the first 2 h and further prolongation of the reaction time does not lead to enhanced removals. The same holds true for the light-driven reactions. With the photo-Fenton reaction, fenitrothion was completely mineralized while the TOC contained in the atrazine solution was removed by 57%. Both compounds in their parent form were completely eliminated from the first 5 min of the oxidation both when being in the single-containing solutions and in their binary mixture. The oxidation of the TOC in the atrazine solution follows a two-stage second-order kinetic behavior which is attributed to the complex reaction pathways occurring during the oxidation while that of the TOC in the fenitrothion solutions follows a pseudo-first order degradation kinetic and that of binary mixture a two-stage degradation kinetics. The results obtained in this study, clearly indicate that the light-driven Fenton oxidation can be very efficient for the removal of atrazine and especially fenitrothion from polluted waters.

1. Introduction

Agrochemicals constitute one of the most important synthetic chemical families that are bio-resistant and continuously released in the environment as a result of their industrial use and agricultural applications. The majority of these compounds either in their parent form or in other forms resulting from their participation in various biotic or abiotic processes in the environment can exhibit dangerous behavior towards organisms including among others endocrine disruption activity and mutagenicity. Pesticides, insecticides, acaricides, herbicides, etc., are found in the environment all over the word, and numerous studies have focused on the presence of such compounds in fresh waters (Claver et al., 2006; Konstantinou et al., 2006; Fatta et al., 2007; Darko et al., 2008; Serrano et al., 2008; Terzić et al., 2008).

Atrazine (ATZ) belongs to the *s*-triazine ring herbicides and therefore is characterized as bio-recalcitrant. Its potential environmental hazard for polluting drinking water has led some countries to ban this herbicide (Chan and Chu, 2003). As such, it is classified as a possible human carcinogen by the USEPA (Belluck et al., 1991), and human exposure mostly comes from the use of contaminated groundwater (USEPA, 1990). In Europe, ATZ belongs to a group of 76 substances that have been phased out and is also included in the list of priority hazardous substances of the Water Framework Directive (Directive, 2000/60/EC).

Fenitrothion (FNT) is a contact insecticide and selective acaricide. It belongs to the organophosphate family of insecticides. FNT residues in natural water undergo both hydrolysis and photodegradation resulting in the release of many toxic intermediate products some of which are more toxic than the parent compound (Derbalah et al., 2004).

In the last several years, studies have been focused on the use of advanced oxidation processes for the treatment of bio-resistant chemical compounds and liquid waste streams since biological methods are not capable of sufficiently eliminating bio-recalcitrant organic loads. Till now, ATZ has been completely degraded by microwave-assisted electrodeless discharge mercury lamp (Ta et al., 2006), removed by more than 99% by an electro-Fenton treatment (Pratap and Lemley, 1998) and eliminated by more than 98% by TiO_2-photocatalysis/ozonation (Farré et al., 2005). In addition, the degradation of ATZ has been extensively studied under the Fenton and Fenton-like processes (Huston and Pignatello, 1999; Gallard and De Laat, 2000; Chan and Chu, 2003; Bandala et al., 2007; Chu et al., 2007) and under sonolysis by Bianchi et al. (2006). Concerning FNT, complete mineralization of the compound was achieved by Fe(III)-Fenton-like process (Derbalah et al., 2004) and by TiO_2 photocatalysis (Topalov et al., 2003; Kormali et al., 2004) while Badawy et al. (2006) achieved approximately 89% TOC removal by the photo-Fenton process.

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The Fenton process is proved to be advantageous if compared with other oxidation processes due to the following facts: (i) it appears to decompose agrochemicals faster; (ii) the reagents employed are readily available and not expensive; (iii) no special equipment is required for the application of the process, and (iv) it can utilize the sunlight (when photo-Fenton process is applied) for the acquisition of the photons required and therefore the cost required can be reduced.

The kinetics of the degradation of ATZ and FNT through dark Fenton oxidation was studied before and is given elsewhere (Kassinos et al., 2008). That study investigated the degradation behavior of four pesticides (ATZ, FNT, 2-methyl-4-chlorophenoxyacetic acid, 4-chlorophenoxyacetic acid) under dark Fenton oxidation using Fe(II) and H_2O_2 concentrations in the range 0.088–0.45 mM and 1.74–33.2, respectively. That study included a preliminary examination of the degradation potential of the single compounds under photo-Fenton as well.

The present study based on the previous one, investigated the degradation of ATZ and FNT in single solutions but also and most importantly in a binary mixture through the application of the dark and photo-Fenton reaction. The selection of the oxidation process was based on the advantageous characteristics of the Fenton system described above. The aim of the study was to determine the efficiency of the process in oxidizing the single compound-containing solutions but also the mixture of the two recalcitrant compounds (i.e. ATZ and FNT) and to elucidate the kinetics of their oxidation under photo-Fenton oxidation. In this study chromatography was also used to assess the behavior of the two compounds.

2. Materials and methods

2.1. Chemicals

ATZ of 99.0% purity and FNT of 97.7% purity were purchased from Laboratories Dr. Ehrenstorfer-Schäfers GmbH. Ferrous salt ($FeSO_4{\cdot}7H_2O$, 98.0% purity) and hydrogen peroxide (35% solution) were purchased from Merck. Sulphuric acid (95–98%, extra pure, Merck) was used to adjust the pH of the system. Milli-Q water system (Millipore) was used for the preparation of solutions. Na_2SO_3 (>98%, Fluka) was used to terminate the reaction. Merckoquant peroxide–test strips (0.5–25 mg L^{-1} H_2O_2) were used to monitor the elimination of non-reacted hydrogen peroxide. These analytical test strips were used for the detection and semiquantitative determination of residual concentrations of hydrogen peroxide (colorimetric method).

2.2. Experimental procedures and methods

2.2.1. Dark Fenton process

Dark Fenton reactions took place in Erlenmeyer flasks at ambient temperature. In a typical run, the appropriate volume of H_2O_2 was first added to the 100 mL aqueous pesticide-containing solution, then its pH was adjusted to 3–3.5 (optimum pH range for the dark Fenton reactions carried out in the present study) with 0.1 M H_2SO_4 and finally the appropriate amount of Fe(II) was added to start the reaction. The concentrations of the H_2O_2 and Fe(II) used are given in Table 1. The reaction mixture was magnetically stirred to ensure the homogeneity of the solution, while the flask was enclosed by aluminum foil to prevent any light-driven side reactions.

Table 1
Experimental conditions employed in this study.

Combination No.	H_2O_2 (mM)	Fe(II) (mM)	H_2O_2/Fe(II) ratio
1	16.6	0.45	36.9
2	33.2	0.45	73.8
3	49.9	0.45	110.9
4	16.6	0.89	18.7
5	33.2	0.89	37.3
6	49.9	0.89	56.1
7	16.6	1.79	9.3
8	33.2	1.79	18.5
9	49.9	1.79	27.9

2.2.2. Photo-Fenton process

Similar procedures were followed for photo-Fenton reactions, where a 125 W Osram lamp (HQV), with a black-glass bulb emitting in the range 315–400 nm was used as the irradiation source. The photo-Fenton reactions took place in Erlenmeyer flasks in closed chambers under controlled temperature between 35 and 40 °C. The chamber used is equipped with air-cooling system in order to avoid any potential thermal decomposition of the pesticides due to increases in the temperature. The initial reaction pH was 2.5; this pH was found to be the optimum for the photo-Fenton reactions in the present study. The lamp was activated 30 min before the irradiation of the solution in order to secure a stabilized photon flow.

2.2.3. Methodology and conditions applied for dark and photo-Fenton processes

Several experiments were conducted at various initial concentrations of Fenton's reagents as summarized in Table 1. The Fe(II) and H_2O_2 solutions were freshly prepared. Three different pesticide-containing solutions were tested as follows: 30 mg L^{-1} ATZ, 30 mg L^{-1} FNT and a mixture of ATZ and FNT at 15 mg L^{-1} each. The initial concentration of each compound in the solution corresponds to its maximum solubility in water under the investigated conditions. At the end of each run, a proper volume of a Na_2SO_3 solution (20% w/v) was added to the reaction solution to quench residual, non-reacted hydrogen peroxide and then the solution was analyzed with respect to its TOC content according to the standard methods for the examination for water (APHA, 1998). An OI Analytical TOC analyzer (Model 1010) was used in this study. The pH of the final solution was between 9 and 10. The measurements were carried out immediately after the addition of Na_2SO_3 in order to avoid any potential interference due to coagulation. Before the TOC measurement all samples were filtrated using Whatman filters (0.45 μm) in order to remove any iron that might had precipitated. The existence of residual hydrogen peroxide was monitored using Merckoquant peroxide–test strips. All runs were performed in duplicate and mean values are quoted herewith as results.

2.2.4. Actinometry

The estimation of the photon flow of the lamp towards the reaction solution was performed with chemical actinometry based on the photoreduction of potassium iron(III) oxalate, $K_3(Fe(C_2O_4)_3){\cdot}3H_2O$. The photon flow ($\Phi_P$) was calculated using Eq. (1) and following the experimental process described in Kuhn et al. (1989).

$$\Phi_P = \frac{\Delta A V_1 10^{-3} V_3}{\Phi_\lambda \varepsilon_{510} V_2 t} \text{mol photons s}^{-1}. \tag{1}$$

2.2.5. Chromatographic analysis of ATZ and FNT

The reference method that was followed is based on EPA Method 507 (USEPA, 1995). Solid phase extraction using discs filled with octadecyl-C18-bonded silica was used for sample preparation. For the measurement, a GC Shimadzu 17A equipped with a Flame Thermionic Detector was used. For the GC, the following program was applied: From 60 (5 min) to 210 °C (5 min) at 15 °C min^{-1} and to 300 °C (3 min) at 5 °C min^{-1}. The injector and detector