WATER RESEARCH 41 (2007) 2015–2027

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Oxidation of two organophosphorous insecticides by the photo-assisted Fenton reaction

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ARTICLE INFO

Article history:
Received 16 October 2006
Received in revised form
18 January 2007
Accepted 23 January 2007
Available online 13 March 2007

Keywords:
Photo-Fenton
Dimethoate
Parathion
Toxicity
Degradation products

ABSTRACT

The photocatalytic degradation of two selected insecticides (dimethoate and methyl parathion) has been studied using the photo-assisted Fenton reaction. The degradation kinetics were studied under different conditions such as iron's and oxidant's concentration, temperature and inorganic ions. The degradation rates proved to be strongly influenced by these parameters. The replacement of hydrogen peroxide with peroxydisulfate was also tested in a photo-Fenton-like reaction. This system achieved high degradation rates of the selected compounds. Intermediate products formed during photocatalytic treatment were identified by means of solid-phase extraction (SPE) coupled to gas chromatography–mass spectroscopy techniques (GC–MS). Eight possible by-products were identified for parathion methyl and three for dimethoate formed through mainly oxidation and dealkylation reactions. Mineralization studies showed also that the photo-Fenton and the photo-Fenton-like systems are able to achieve mineralization of the insecticides. However, complete detoxification is achieved only in the presence of the photo-Fenton reagent.

1. Introduction

Pesticide pollution of surface waters and wastewaters has increased sharply and it constitutes a major pollutant problem due to an extensive use of these substances. In response, the European Community has implemented programs for the development of technologies which are useful for reducing pesticide input into water runoff. Their concentration in water can vary between a few ppb to ppm levels that have to be removed in order to achieve drinking water quality or to protect the water resources (Floesser-Mueller and Schwack, 2001). This situation stimulated the development of new water and wastewater treatment processes that are able to promote complete mineralization of potentially toxic compounds, with feasible implementation and at low cost. In recent years, advanced oxidation processes (AOPs) have been intensively investigated. They are considered very promising alternatives to conventional treatments of wastewaters due to their efficiency to oxidize a great variety of organic contaminants by the generation of highly reactive hydroxyl radicals ($OH^{\bullet}$) (Chiron et al., 2000; Andreozzi et al., 1999).

In the recent years, the Fenton process has been extensively used with success for the oxidation of many classes of organic compounds due to its high efficiency to generate hydroxyl radicals during decomposition of H_2O_2 by Fe^{2+} in acidic medium (Penuela and Bercelo, 1998). A disadvantage of this process is that it requires stoichiometric amounts of Fe^{2+}. However, the process can be made catalytic, by photoreducing the Fe^{3+} to Fe^{2+}, which can react with hydrogen peroxide establishing a cycle besides of generating additional hydroxyl radicals. The combined process (Eqs. (1) and (2)) is known as

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doi:10.1016/j.watres.2007.01.027

the photo-assisted Fenton (photo-Fenton) reaction (Huston and Pignatello, 1999).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}, \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^{\bullet}. \quad (2)$$

The main advantage of this process is the ability of using sunlight with light sensitivity up to 700 nm, thus avoiding the high costs of UV lamps and electrical energy. Moreover, the depth of light penetration is high and the contact between pollutant and oxidizing agent is close, since homogenous solution is used. The disadvantages of the process are the low pH values which are required, since iron precipitates at higher pH and the iron removal after treatment. However, late studies showed that these problems could be solved with immobilization of iron on membranes (Bauer et al., 1999).

The purpose of this study was to evaluate the $Fe^{3+}/H_2O_2/UV$ system for oxidizing two organophosphorous pesticides: dimethoate (*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate) and methyl parathion (*O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate) (Scheme 1). The influence of various factors, like iron and hydrogen peroxide concentration, temperature and inorganic ions, on the photocatalytic rate was examined. Comparison between the dark and the illuminated system was also carried out. The degree of mineralization was evaluated while changes in toxicity during treatment were also measured. Finally, the intermediates that are formed during the photocatalytic degradation of the selected compounds were identified.

Previous studies have used the Fenton reaction for the degradation of other organophosphorous compounds (Lu et al., 1999, 1997), while the photo-Fenton reaction has been used with success on the degradation of methyl parathion (Pignatello and Sun, 1995). However, the use of the alternative system $UV/Fe^{3+}/K_2S_2O_8$ along with the examination of three different homogenous photocatalytic systems, in order to evaluate their ability to mineralize the selected insecticides and to detoxify the treated solution, are first presented in this study.

2. Materials and methods

2.1. Reagents

Dimethoate and methyl parathion, all analytical grade (99.9% purity), were purchased from Riedel-de-Haen (Germany) and they were used without any further purification. HPLC-grade solvents (acetonitrile and water) were supplied by Merck. Hydrogen peroxide (30%) was obtained from Panreac and $K_2S_2O_8$ was purchased from Merck. Ferric sulfate $Fe_2(SO_4)_3 7$-H_2O, ferric chloride $FeCl_3$ and ferric perchlorate $Fe(ClO_4)_3$ were supplied by Riedel-de-Haen and were used as received. Stock solutions of dimethoate ($1000\,mg\,L^{-1}$) and methyl parathion ($40\,mg\,L^{-1}$) were prepared in ultra pure water, protected from light and stored at 4 °C.

2.2. Irradiation procedure

Irradiation experiments were carried out in a 500 mL Pyrex UV reactor equipped with a diving Philips HPK 125 W high-pressure mercury lamp. The lamp was jacked with a water-cooled Pyrex filter restricting the transmission of wavelengths below 290 nm. The tap water cooling circuit maintained the temperature at 30–35 °C.

The pesticide solution ($10\,mg\,L^{-1}$, unless otherwise stated) with the appropriate amount of iron was put into the reactor and was magnetically stirred before and during the illumination. The solution was acidified using sulfuric, hydrochloric or perchlorate acid (initial pH was 2.9–3 in all cases) depending on the type of iron salt that has been used. The lamp was warmed up for 10 min to reach constant output. The reaction was initiated by adding the appropriate amount of hydrogen peroxide followed by inserting the lamp into the reactor.

2.3. Analyses

2.3.1. Kinetic studies

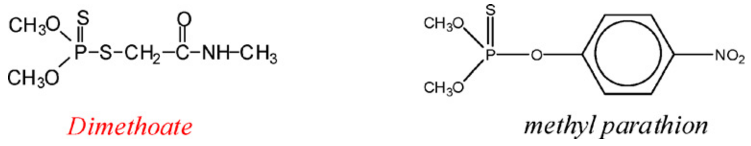
At specific time intervals, the samples were withdrawn from the reactor. Pesticides concentrations were determined by a Shimadzu 10AD liquid chromatograph equipped with a variable-wavelength UV detector using a $250 \times 4.6\,mm^2$, C18 nucleosil 100-S column. The mobile phase was a mixture of acetonitrile and water (40/60 v/v for dimethoate and 65/35 v/v for methyl parathion) with a flow rate of $1\,mL\,min^{-1}$. The detection was realized at 210 nm for dimethoate and at 270 nm for methyl parathion.

2.3.2. Mineralization studies

In order to evaluate the extent of mineralization, dissolved organic carbon (DOC) measurements were carried out by a Shimadzu V-csh TOC analyzer. Phosphate, sulfate, nitrate and ammonium ions were analyzed spectrophotometrically (with a WTW spectrophotometer) using cuvette tests supplied by WTW.

2.3.3. Toxicity studies

For the examination of the toxic properties of the samples collected at specific time intervals throughout the photocatalytic treatment, the luminescent bacteria *V. ficheri* were used. Luminescent bacteria emit light as a by-product of their



Scheme 1 – Chemical structures of the selected insecticides.