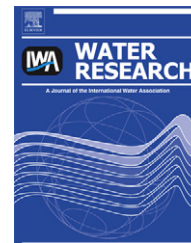


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Complete removal of the insecticide azinphos-methyl from water by the electro-Fenton method – A kinetic and mechanistic study

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ABSTRACT

The removal of organophosphorous insecticide azinphos-methyl (AZPM) from water has been investigated by the electro-Fenton method which produces hydroxyl radicals electrocatalytically. The reaction between these radicals and AZPM has led to the oxidation of AZPM up to carbon dioxide and inorganic ions indicating its complete removal from water. The oxidation kinetics was fitted to pseudo-first order reaction and absolute rate constant of the second order reaction kinetic was determined as $(6.82 \pm 0.18) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by using competitive kinetics method. The oxidation of AZPM by hydroxyl radicals leads to the formation of different intermediates species; such as aromatic derivatives, short-chain carboxylic acids and inorganic ions as end products. The identification and quantification of these intermediates were deeply investigated by HPLC, GC–MS and ion chromatography analyses. Based on the identified intermediates, a general oxidation mechanism was proposed. Mineralization ability of the process was also tested by using aqueous AZPM solutions and its commercial formulation, Gusathion M WP 25 (GMWP25). Mineralization efficiency was followed by the chemical oxygen demand (COD) analysis of treated solutions. The overall mineralization of synthetic AZPM solution and that of commercial formulation at the end of treatment highlights the outstanding mineralization power of the electro-Fenton process.

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1. Introduction

The runoff, leaching and improper application of pesticides allow pollution of the environment and water resources. Their intensive usage enhances their occurrence in the environment. The combination of their toxicities and widespread use result in an increased threat to wild life and human health (Casida, 2009). Therefore, there is considerable interest in avoiding or reducing the entry of such kind of substances into the environment. The commonly used traditional methods for

this purpose remain often inefficient in the case of persistent and or toxic pollutants such as pesticides (Oturan and Brillas, 2007). In order to effective treatment of pesticide containing wastewaters, new efficient methods are developed during last decays. Advanced oxidation processes (AOPs) can be considered as potentially powerful methods in this field. These processes involve chemical, photochemical or electrochemical techniques. The principal active species in such processes is the hydroxyl radical, ($\cdot\text{OH}$), a highly oxidizing agent of organic contaminants (Oturan, 2000; Dutta et al., 2001;

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Malik and Saha, 2003; Özcan et al., 2008a,b, Brillas et al., 2009; Sires et al., 2010; Isarein-Chavez et al., 2010; Oturan et al., 2011; Garcia-Segura et al., 2012). These radicals react with organic pollutants and thus lead to their oxidative degradation by hydrogen atom abstraction reaction, electron transfer, or electrophilic addition to π systems (Oturan, 2000; Brillas et al., 2009). For effective oxidations of refractory organic compounds, the hydroxyl radicals must be generated continuously in situ through chemical or photochemical or electrochemical processes due to their instability. The Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has been widely used for this purpose (Barbeni et al., 1987; Kang et al., 2002). However, this reaction has some limitations in application such as the use of a large quantity of chemical reagents, large production of ferric hydroxide sludge and very slow catalysis of the ferrous ions generation (Walling and Goosen, 1973; De Laat and Gallard, 1999). It was suggested that this reaction can be performed catalytically via electrochemistry (Oturan, 2000; Oturan et al., 2000, 2001, 2012; Boye et al., 2003; Sirés et al., 2007a,b; Özcan et al., 2008a; Brillas et al., 2009) avoiding the drawbacks of the Fenton process. This emergent method is called as electro-Fenton method.

Electro-Fenton method is an advanced electrochemical oxidation process based on the continuous supply of H_2O_2 which is electrochemically generated (Eq. (1)) in the contaminated acid solution containing a catalytic amount of Fe^{2+} or Fe^{3+} as catalyst (Boye et al., 2002; Gözmen et al., 2003; Guivarch et al., 2003; Brillas et al., 2004). $\cdot\text{OH}$ is then produced in homogeneous medium by the Fenton's reaction between ferrous ion and hydrogen peroxide (Eq. (2)).



At the optimal pH of about 3, the ferric ion formed by Fenton reaction (Eq. (2)) is mainly found as $\text{Fe}(\text{OH})^{2+}$ form and it was reduced at the cathode (Eq. (3)) to catalyze continuously the Fenton reaction (Eq. (2)). Thus, catalytic and continuous generation of homogeneous $\cdot\text{OH}$ radicals can be achieved (Guivarch et al., 2003). Since $\cdot\text{OH}$ production does not involve the use of harmful chemicals which can be hazardous for the environment, this process is environmentally friendly for wastewater treatment and seems to be promising for the purification of water polluted by persistent and/or toxic organic pollutants including the pesticides (Oturan, 2000; Oturan et al., 2001; Brillas et al., 2003; Gözmen et al., 2003; Guivarch et al., 2003; Özcan et al., 2008c,d).

Azinphos methyl (AZPM) is an organophosphorous non-systemic pesticide widely used to control a variety of insects in food and non-food crops, ornamentals and forest trees. It is mainly applied as a foliar spray during the growing season. Although its high toxicities and widespread usage, limited number of studies was reported in the literature for the removal of AZPM from water resources. In this concept, Kralj et al. (2007) have studied the photo-degradation behavior of AZPM. Flocco et al. (2004) used hydroponic cultures of alfalfa (*Medicago sativa* L., var *Romagnola*) as a model system for the removal of AZPM. When they exposed these cultures to

a nutrient medium containing 10 mg L^{-1} of AZPM, the initial amount of AZPM was reduced to non-detectable levels after 20 days. Hernandez et al. (1998) used chloroperoxidase from *Caldariomyces fumago* for the enzymatic degradation of AZPM. They observed that AZPM was converted to its oxon-derivative instead of its complete mineralization.

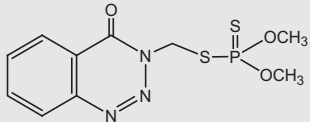
To the best of our knowledge, the degradation of AZPM by the electro-Fenton method was not reported previously in the literature. This study intends to perform two objectives. First one is determination of the oxidation intermediates of AZPM formed during the electro-Fenton treatment. Last one is to assess the mineralization ability of the electro-Fenton process in the case of a commercial formulation, Gusathion M WP 25 (GMWP25), containing AZPM as the active ingredient. The concentration decay of AZPM was followed by high performance liquid chromatography (HPLC). The identification and evolution of degradation intermediates was performed by HPLC, gas chromatography–mass spectrometry (GC–MS) and ion chromatography (IC) analysis. By using these intermediates, a general reaction sequence was proposed for the degradation of AZPM in acidic media. The mineralization ability of electro-Fenton process was followed by the chemical oxygen demand (COD) analysis.

2. Materials and methods

2.1. Materials

AZPM was obtained from Riedel-de Haën. Its physicochemical properties were shown in Table 1. Iron(III)sulfate pentahydrate (97%, Aldrich), sodium sulfate (anhydrous, 99%, Across) and potassium sulfate (99%, Fluka) were used as catalyst and supporting electrolytes, respectively. Benzoic acid (99.9%, Merck), sulfuric acid, (ACS reagent grade, Across), acetic acid (glacial p.a., Across), and potassium hydrogen phthalate (Nacalai tesque Inc.) were obtained as a reagent grade. Sodium nitrate (99%, Merck), ammonium nitrate (99%) and sodium phosphate (96%, Aldrich) were used as standard for the IC analysis. Sodium hydroxide (ACS reagent grade, Aldrich), methanesulfonic acid ($\geq 99.0\%$, Fluka) and tetrabutylammonium hydroxide (40%, Fluka) were used as eluents and

Table 1 – Physical and chemical properties of AZPM.

Molecular formula	$\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_3\text{PS}_2$
Chemical structure	
Molecular weight	$317.32 \text{ g mol}^{-1}$
Solubility	28 mg L^{-1} in water at 20°C , 250 g L^{-1} in dichloroethane, acetone, acetonitrile, ethyl acetate and dimethyl sulfoxide at 20°C , 1.2 g L^{-1} in <i>n</i> -heptane and 170 g L^{-1} in xylene at 20°C
^a Log Kow	2.75
^a Log Kow : Octanol/water partition coefficient.	

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