



Removal of protham from water by using electro-Fenton technology: Kinetics and mechanism

Ali Özcan^a, Yücel Şahin^{a,*}, Mehmet A. Oturan^b

^aAnadolu University, Faculty of Science, Department of Chemistry, 26470 Eskişehir, Turkey

^bUniversité Paris Est, Laboratoire Géomatériaux et Géologie de l'Ingénieur, 5 bd Descartes, Champs-sur-Marne, 77454 Marne la Vallée Cedex 2, France

ARTICLE INFO

Article history:

Received 11 March 2008

Received in revised form 10 June 2008

Accepted 11 June 2008

Available online 27 July 2008

Keywords:

Protham

Electro-Fenton

AOP

Hydroxyl radical

Degradation pathway

Mineralization

ABSTRACT

The removal of a carbamate herbicide, protham, from aqueous solution has been carried out by the electro-Fenton process. Hydroxyl radical, a strong oxidizing agent, was generated catalytically and used for the oxidation of protham aqueous solutions. The degradation kinetics of protham evidenced a pseudo-first order degradation. The absolute rate constant of second order reaction kinetics between protham and $\cdot\text{OH}$ was determined as $(2.2 \pm 0.10) \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$. The mineralization of protham was followed by the organic carbon (TOC) removal. The optimal Fe^{3+} concentration was found as 0.5 mM at 300 mA. The 94% of initial TOC of 0.25 mM protham solution was removed in 8 h at the optimal conditions by using the cathode area to solution volume ratio of 3.33 dm^{-1} . The maximum mineralization current efficiency values were obtained at 60 mA in the presence of 0.5 mM Fe^{3+} . During the electro-Fenton treatment, several degradation products were formed. These intermediates were identified by using high performance liquid chromatography, liquid chromatography–mass spectrometry, gas chromatography–mass spectrometry and ion chromatography analysis. The identified by-products allowed proposing a pathway for the protham mineralization.

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1. Introduction

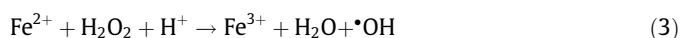
Pesticides have been used extensively to increase the agricultural productivity for last fifty years. Food and Agriculture Organization reported that more than 1.2 million metric tons of pesticides were sold to the agricultural sectors during the middle of the last decade (Schulze et al., 2002). These substances are in fact very effective against the harmful microorganisms and insects; however, because of their hazardous nature, the waste and rinsate from spray and storage equipment have been considered as one of the major threats to the environment.

Carbamate compounds were introduced as pesticides in the early 1950s and are still used extensively in pest control due to their relatively short lifetime, effectiveness and broad spectrum of biological activity (Sole et al., 2003). Protham is a pre and post emergence carbamate herbicide for the control of weeds in alfalfa, clover, flax, lettuces, afflow, spinach, sugar beets and pees. It prevents cell division and act on meristematic tissues. It is also an acetylcholinesterase inhibitor and could be degraded into aniline metabolites which are in fact more dangerous than the parent molecule (Orejuela and Silva, 2004). To avoid the dangerous accumulation of these types of pollutants in the aquatic environment, research efforts are underway to develop more powerful oxidation

methods than those currently applied in wastewater treatments for achieving their complete destruction.

Recent progress in the removal of pesticides from water has led to the development of advanced oxidation processes (AOPs). These processes involve chemical, photochemical or electrochemical techniques. The most commonly used oxidation processes have H_2O_2 , O_3 or O_2 as the bulk oxidant. The principal active specie in such systems is the hydroxyl radical, $\cdot\text{OH}$ (Lin and Lo, 1997; Huston and Pignatello, 1999; Oturan, 2000; Dutta et al., 2001; Malik and Saha, 2003; Swaminathan et al., 2003). These radicals react with organic pollutants and thus lead to their degradation by hydrogen abstraction reaction, redox reaction or electrophilic addition to π systems (Oturan, 2000).

Electro-Fenton is an advanced electrochemical oxidation process based on the continuous supply of H_2O_2 generated from reaction (1) to a contaminated acid solution containing 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 the medium by the Fenton's reaction between ferrous ion and hydrogen peroxide (Eq. (3)).



* Corresponding author. Tel.: +90 222 3350580x5786; fax: +90 222 3204910.
E-mail address: ysahin@anadolu.edu.tr (Y. Şahin).

This catalytic reaction is propagated from Fe^{2+} regeneration, which mainly takes place by the reduction of Fe^{3+} at the cathode (Eq. (2)) (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 (Oturán, 2000; Oturán et al., 2001; Brillas et al., 2003; Gözmen et al., 2003; Guivarch et al., 2003; Özcan et al., 2008a).

The removal of propham from aqueous solutions was performed by using membrane separation technique (Kosutic and Kunst, 2002) and TiO_2 photocatalysis (Muneer et al., 2005; Bahne-mann et al., 2007). Moreover, we have investigated the degradation of propham by using boron doped diamond (BDD) electrode in the anodic oxidation process (Özcan et al., 2008b). In this study, we have investigated the removal of propham from water through complete conversion to carbon dioxide and water by using electro-Fenton technology.

2. Materials and methods

2.1. Materials

Propham was obtained from Riedel-de Haën. Iron(III)sulphate pentahydrate (97%, Across) and sodium sulphate (anhydrous, 99%, Across) were used as catalyst and supporting electrolyte, respectively. Benzoic acid (99.9%), sodium nitrate (99%) and ammonium nitrate (99%) were obtained from Merck. Oxalic, maleic, fumaric, lactic, glyoxylic, acetic, formic and oxamic acids were obtained from Fluka and used without further purification. All solutions were prepared by using pre-distilled $18\ \mu\text{S cm}^{-1}$ deionized water (Sartorius).

2.2. Electrochemical system

Experiments were performed at room temperature in a 0.175 L undivided cylindrical glass cell of diameter of 5 cm equipped with two electrodes. The working electrode was a $50\ \text{cm}^2$ piece of carbon-felt ($10 \times 5\ \text{cm}$). It is placed on the inner wall of the cell covering the totality of the internal perimeter. The counter electrode was cylindrical Pt gauze placed on the centre of the cell. Prior to the electrolysis, compressed air was bubbled through the aqueous solutions, which were agitated continuously by a magnetic stirrer (500 rpm). A catalytic quantity of ferric ion was introduced into the solution before the beginning of electrolysis. The applied current was 60 mA for degradation kinetics and 100 mA for by-products determination. The current and the amount of charge passed through the solution were measured and displayed continuously throughout electrolysis by using a DC power supply. Prior to electro-Fenton reaction, the pH of initial solutions was set at 3 by the addition of aqueous H_2SO_4 (1 M). The pH values were measured by a pH glass electrode calibrated with standard buffers at pH values of 4, 7 and 10. The ionic strength was maintained constant by addition of 50 mM Na_2SO_4 .

2.3. HPLC and LC–MS analysis

The degradation of propham and its by-products were monitored by high performance liquid chromatography (HPLC) and liquid chromatography–mass spectrometry (LC–MS) using an Agilent 1100 system equipped with a diode array detector and an Agilent 6300 mass spectrometer with an electron spray ionization interface and a heated nebulizer, in the positive mode, respectively. Reversed phase Inertsil ODS-3 $5\text{-}\mu\text{m}$, $4.6 \times 250\text{-mm}$ and $3\text{-}\mu\text{m}$, $4.6 \times 150\ \text{mm}$ columns were used in HPLC and LC–MS

experiments, respectively. The columns were thermostated at $40\ ^\circ\text{C}$. Twenty microliters of the sample was injected. The columns were eluted with a mixture of water–methanol–acetic acid at 44:54:2 and 54:44:2 (v/v/v) with flow rates of 0.8 and $0.5\ \text{mL min}^{-1}$ in HPLC and LC–MS experiments, respectively. HPLC detections were performed at 254 and 280 nm. Carboxylic acids compounds were identified and quantified by a Supelcogel H column ($\phi = 7.8 \times 300\ \text{mm}$) with a mobile phase of 4 mM H_2SO_4 at 210 nm by the same HPLC system. The identification of carboxylic acids was conducted by the retention time comparison and adding standard of the related carboxylic acids to the analysis solution.

2.4. Gas chromatography–mass spectroscopy (GC–MS) analysis

GC–MS analysis was performed by using a Thermo Finnigan PolarisQ GC–MS analyzer. Electro-Fenton treated solution of the propham was extracted three times with dichloromethane and ethyl acetate and then the extracts were concentrated by a rotavapor to 2 mL. The final solutions were analyzed by using a 25 m SE-54 column. The column was held at $50\ ^\circ\text{C}$ for 2 min, and then a gradient temperature program at $10\ ^\circ\text{C min}^{-1}$ was used between 50 and $280\ ^\circ\text{C}$. *N,O*-bis-(trimethylsilyl)trifluoroacetamide was used to prepare the trimethylsilyl derivatives of the aromatic intermediates.

2.5. Ion chromatography (IC) analysis

The concentration of ammonium and nitrate ions released during electrolysis was measured by IC (Dionex-100 equipped with a conductivity detector). A cationic (IonPac[®] CS12A-Dionex) and anionic (IonPac[®] AS14-Dionex) exchanger columns were used for ammonium and nitrate ions, respectively. The volume of injections was 25 μL . The mobile phase and regenerant solutions were 20 mM methanesulfonic acid (Fluka, 70%) with a flow rate of $0.85\ \text{ml min}^{-1}$ and 100 mM tetrabutylammonium hydroxide (Aldrich, 40%) in the cation analysis, respectively. On the other hand, 30 mM sodium hydroxide (Fluka, 99%) with a flow rate of $0.80\ \text{ml min}^{-1}$ and 22 mM H_2SO_4 (Across, 98%) was used in the anion analysis as mobile phase and regenerant, respectively.

2.6. The total organic carbon (TOC) analysis

The TOC of the initial and electrolyzed samples was determined with a Shimadzu TOC-V analyzer. The platinum catalyst was used in the combustion reaction. The carrier gas was oxygen with a flow rate of $150\ \text{mL min}^{-1}$. The detector of the TOC system was a non-dispersive infra-red detector, NDIR. Calibration of the analyzer was achieved with potassium hydrogen phthalate (99.5%, Merck) and sodium hydrogen carbonate (99.7%, Riedel-de Haën) standards for total carbon (TC) and inorganic carbon (IC), respectively. The difference between TC and IC analysis gives TOC data of the sample.

3. Results and discussion

3.1. The degradation kinetics of propham

The degradation behavior of propham was investigated by electrolyzing aqueous solution of propham at acidic media. The decay of its concentration was followed by HPLC, where it displayed a well-defined peak at a retention time of 15.24 min. The degradation of propham was firstly investigated at 60 mA in the presence of 0.01 mM Fe^{3+} . The obtained concentration–time curve showed that the degradation of propham followed pseudo-first order reaction kinetics. In order to verify this result, experiments were re-

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