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Effect of Fe^{2+} on the degradation of the pesticide profenofos by electrogenerated H_2O_2

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ABSTRACT

The purpose of the study was to evaluate the degradation of the organophosphate pesticide profenofos in acidic medium using a gas diffusion electrode (GDE) modified with 5.0% cobalt phthalocyanine (CoPc). The degradation of profenofos was based on oxidation by H_2O_2 electrogenerated *in situ*, and experiments were performed in the absence or presence of Fe(II) catalyst. Removal of the pesticide by anodic oxidation was minimal (~20%), and reached only 36% when H_2O_2 was electrogenerated in the absence of catalyst. However, in the presence of 0.15 mmol L^{-1} $FeSO_4 \cdot 7H_2O$ (electro-Fenton reaction), profenofos removal attained 91% after 60 min of process time while total organic carbon (TOC) was reduced by 37%. Prolonged electrolysis under similar electro-Fenton conditions showed that 100% profenofos removal could be achieved after 2 h and a 89.9% reduction in TOC could be attained after 4 h. Analysis by gas chromatography–mass spectrometry of the by-products formed during the process revealed the progressive degradation of profenofos to *o*- and *p*-benzoquinone, with subsequent rupture of the aromatic ring to form oxalic acid and, ultimately, CO_2 and H_2O. It is concluded that wastewater treatments involving H_2O_2 electrogeneration in a CoPc-modified GDE were effective in removing profenofos and TOC from commercial formulations of profenofos.

1. Introduction

Organophosphates exhibit a wide range of biological activities and are used extensively in the control of insects and weeds in diverse agricultural settings [1]. However, most organophosphorus compounds are extremely toxic, and handing these agents without adequate protective equipment or in the absence of proper supervision can be highly detrimental to human health [2,3]. Additionally, organophosphate pesticides often possess extended half-life times in the environment, and their inappropriate and indiscriminate application can give rise to serious ecological issues, particularly with regard to aquatic biota. Since the global use of organophosphates continues to rise, it is increasingly important to employ effective methods for the treatment of wastewaters and watercourses that have been contaminated with these pesticides.

In this context, the elimination of organophosphates can be achieved through biological processes [4], incineration [5] chemical oxidation [6] and other synergistic degradation process [7–16]. Unfortunately, none of these techniques can be classified as highly efficient, and all have limited application since they do not bring about the complete mineralization of organic load. On the other hand, electrochemical advanced oxidation processes (EAOPs) based on the formation of the highly reactive hydroxyl radical (•OH) promote the oxidation of organic compounds and are particularly efficient in removing effluents contaminated with pesticides [17–19]. In EAOPs, the non-selective oxidant is typically obtained from H_2O_2 through diverse methods including irradiation of organic compounds in aqueous solution [20], high-pressure reaction with a mixture of O_2/N_2 in the presence of metallic catalysts [21], direct synthesis in the presence of Pd/SiO_2 [22], and irradiation of aerated suspensions containing different metals [23]. However, these methods suffer from a variety of shortcomings, including the use of heterogeneous catalysts and the need for different gases to be solubilized in the medium. In contrast, electrochemical technologies involving the use of gas diffusion electrodes (GDEs) allow the generation of H_2O_2 directly in the reaction medium [24–26], under acid [27] or alkaline [28] conditions, at different temperatures and ambient pressure. Furthermore, a number of reports confirm that the *in situ* electrogeneration of H_2O_2 proceeds efficiently and with low energy consumption when GDEs comprising conductive carbon black are

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employed [29–31]. These versatile electrodes also exhibit high efficiency when applied to the electrodegradation of organic compounds [30].

In consideration of the serious environmental problems caused by wastewaters contaminated with organophosphorus pesticides, we have evaluated the electro-Fenton degradation of a commercial agrochemical formulation containing the organophosphate insecticide profenofos (4-bromo-2-chloro-1-[ethoxy(propylsulfanyl)phosphoryl]oxybenzene) in acidic medium using a GDE constructed with carbon black containing 5.0% cobalt phthalocyanine (CoPc) as redox modifier.

2. Experimental methods

The preparation of organophosphate insecticide employed in this study was the emulsifiable concentrate Curacron 500 commercialized by Syngenta Brasil (São Paulo, SP, Brazil) under registration number 00,868,698 issued by the Ministério da Agricultura, Pecuária e Abastecimento, Brasilia, DF, Brazil. The formulation is described as containing 500 g L^{-1} of profenofos and 500 mg L^{-1} of unidentified compounds that are claimed to be *inert* but constitute a source of organic matter that must be considered in the degradation process.

Degradation experiments were performed in a single compartment electrochemical cell containing the GDE working electrode, an Ag/AgCl reference electrode and a platinum screen as counter electrode [29–31]. Printex 6L modified with CoPc was used to construct the GDE according to methods described in the literature [25,26,31] in which the catalytic mass was hot pressed (320 °C; 7.5 ton) for 2 h.

The degradation of profenofos was investigated using solutions containing 10–12 mg L^{-1} of active ingredient in 400 mL of electrolyte (K_2SO_4 0.1 mol L^{-1} + H_2SO_4 0.1 mol L^{-1}). The influence of anodic oxidation was established by delivering N_2 at a pressure of 0.2 bar to the external layer of the GDE. The oxidation of analyte by H_2O_2 electrogenerated *in situ* was evaluated by supplying the GDE with O_2 at a pressure of 0.2 bar in the presence of 0, 0.05, 0.10 and 0.15 mmol L^{-1} of $FeSO_4 \cdot 7H_2O$. In these experiments, electrolysis was performed for 60 min at −0.7 V (*vs.* Ag/AgCl) and samples of electrolyte were collected every 15 min. A further degradation experiment was performed with 0.15 mmol L^{-1} of $FeSO_4 \cdot 7H_2O$ present in the electrolyte and O_2 supplied to the GDE for a period of 240 min with sample monitoring every 60 min.

Samples of electrolytes collected during the experiments were analyzed by high performance liquid chromatography (HPLC) using a Shimadzu (Kyoto, Japan) Prominence LC20-AT chromatograph equipped with a Phenomenex (Torrance, CA, USA) Luna C-18 column (250 × 4.6 mm i.d.; 5 μm). The mobile phase comprised water and acetonitrile (20:80 v/v) supplied at a flow rate of 1 mL min^{-1}, and the separated components were detected at 277 nm. Quantification of organic load was performed using a Shimadzu TOC-VCPN total organic carbon (TOC) analyzer equipped with an automatic sampler. Complementary analysis by gas chromatography–mass spectrometry (GC–MS) was performed using a Varian (Agilent Technologies, Palo Alto, CA, USA) CP-3800 chromatograph fitted with an Agilent DB-5 column (30 m × 0.25 m i.d.) and coupled to a Varian Saturn 2200 spectrometer and for this analysis each sample were extracted using Omix pipettes tips C18 (100 mm), each sample was extracted five times from aqueous medium and the sequence was eluted just one single time using methanol and this procedure was performed even the extraction of all organic phase to achieve the volume required for analysis in GC–Ms. The chromatographic conditions were: injector temperature - initially 35 °C then increased to 250 °C at 200 °C min^{-1}; oven temperature - initially 35 °C then increased to 250 °C at 100 °C min^{-1}; electron ionization emission current 7 μA; mass range recorded - 50 to 400 *m/z*.

3. Results and discussion

The efficient degradation of profenofos by H_2O_2 electrogenerated *in situ* in a carbon black GDE depends on the capacity of the electrode to promote the reduction of O_2. According to Barros et al. [31]., the maximum concentration of H_2O_2 that can be electrogenerated in an unmodified carbon black GDE is around 176 mg L^{-1} at −1.0 V (*vs.* Ag/AgCl). In contrast, carbon black GDEs modified with CoPc are more effective and can generate up to 331 mg L^{-1} (4.4 mg L^{-1} min^{-1}) of H_2O_2 at −0.7 V (*vs.* Ag/AgCl). In the present study, the degradation of profenofos was performed in acidic medium by electrolysis at −0.7 V (*vs.* Ag/AgCl) using a carbon black GDE modified with 5% CoPc.

Although the degradation process was based on the electrogeneration of H_2O_2, the investigation was carried out using a single compartment electrochemical cell containing both the working electrode and the counter electrode. In order to determine the influence of the Pt anode on the degradation of profenofos, the external layer of the GDE was initially supplied with N_2, thereby preventing the formation of H_2O_2. Fig. 1A shows the removal of analyte from solution during electrolyses performed without H_2O_2 generation (GDE supplied with N_2) and with H_2O_2 generation (GDE supplied with O_2) but in the absence of Fe^{2+} catalyst. Interestingly, the profiles of profenofos removal during the first 15 min of electrolysis were similar under both sets of experimental conditions, with 10% of analyte degraded by anodic oxidation and 11% by the H_2O_2 process. However, after 60 min of electrolysis, profenofos removal had attained only 20% by anodic oxidation but had risen to 36% by the H_2O_2 process.

The differences in degradation of profenofos under the two sets of conditions can be explained by considering the type of mechanism operating in each case. Anodic degradation occurs at the electrode surface, but the diffusion of molecules of analyte to the anode is limited by mass

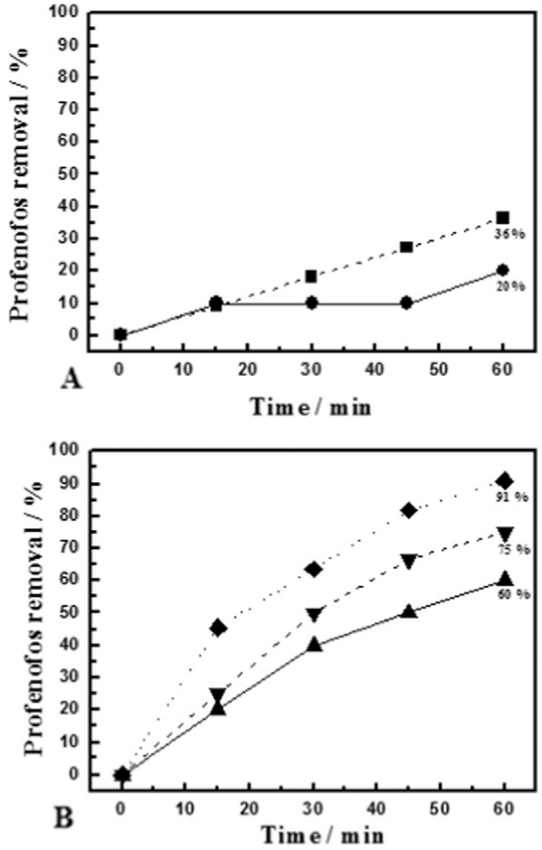

Fig. 1. Percentage removal of profenofos, as determined by high performance liquid chromatographic analysis, during 60 min of electrolysis performed under conditions of: (A) anodic oxidation (–●–) and H_2O_2 electrogeneration (– –■– –) in the absence of catalyst, and (B) the electro-Fenton reaction in the presence of 0.05 (–▲–), 0.10. (– –▼– –), and 0.15 (···♦···) mmol L^{-1} of FeSO4·$7H_2O$. Experiments conducted at an applied potential of −0.7 V (*vs.* Ag/AgCl) with N_2 (anodic oxidation) or O_2 (electrogeneration of H_2O_2) supplied at a pressure of 0.2 bar to the external layer of the modified gas diffusion electrode.