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Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes

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ABSTRACT

Laboratory experiments were carried out on the kinetic of the electrochemical degradation of aqueous solutions containing chlorpyrifos as model compounds of organophosphorus pesticides. The process was studied under galvanostatic polarization mode in acidic medium using boron-doped diamond (BDD) anodes and graphite carbon bar as cathode. The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the instantaneous current efficiency. The results showed that the degradation of this pesticide is dependent on its initial concentration, current density and temperature. COD decay follows a pseudo first-order kinetic and the process was under mass transport control within the range studied, regardless of the experimental conditions. The removal rate of COD increases with applied current density until 20 mA cm^{-2} and decreases for higher values. The degradation rate increased significantly with increasing temperature and initial concentration of chlorpyrifos. The best obtained conditions for COD removal on the BDD anode to degrade chlorpyrifos solutions (COD(0) = 456 mg L^{-1}) include operating at 20 mA cm^{-2} and 70 °C. This arrangement allows to completely degrade chlorpyrifos in just 6 h. Compared with PbO_2, BDD anode has shown more performance and rapidity in the COD removal in the same electrolysis device.

1. Introduction

The intensive use of pesticides in agriculture and the improper storage or disposal of obsolete pesticides are a source of contamination of soil, ground water, rivers, lakes, rainwater and air. Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electrochemical processes constitute the emergent methods for the degradation of pesticides. These methods are environmentally friendly and they do not form new toxic wastes.

In anodic oxidation, organic pollutants are directly destroyed by reaction with hydroxyl radical ($HO^•$) formed at the anode surface from water oxidation [1–4]:

$$H_2O \rightarrow HO^• + H^+ + e^- \quad (1)$$

Several anode materials such as Pt [5–10], SnO_2 [11,12], PbO_2 [12–14] and BDD [10,12,15,16] have been used for pesticides removal. The new anode material (BDD) possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium [17,18]. BDD anode has much higher O_2 overvoltage than that of conventional anodes such as PbO_2, doped SnO_2, IrO_2 and Pt, then producing larger amount of $HO^•$ on the anode surface by reaction (1) giving a more rapid destruction of pollutants [14,17,18].

Some investigations have also intended to compare the behaviour of BDD with other electrodes, such as SnO_2, PbO_2 and IrO_2 for the oxidation of organic pollutants. Chen et al. [19] reported that the current efficiency obtained with Ti/BDD in oxidizing acetic acid, maleic acid, phenol, and dyes was 1.6–4.3-fold higher than that obtained with the typical $Ti/Sb_2O_5–SnO_2$ electrode. Other papers showed that Si/BDD electrodes are able to achieve faster oxidation and better incineration efficiency than PbO_2 in the treatment of naphthol [20,21], 4-chlorophenol [22] and chloranilic acid [23].

Recently, Martínez-Huitle et al. [12] demonstrated that the pesticide methamidophos can be electrochemically removed from aqueous solutions using Pb/PbO_2, Ti/SnO_2, and Si/BDD electrodes. They found that current density influence is remarkably clear on the Si/BDD electrodes where it was evident that the most efficient current density toward a complete methamidophos mineralization was reached with the application of 50 mA cm^{-2}.

Chlorpyrifos is one of the most widely used organophosphorus pesticides in agriculture (Fig. 1). The use of chlorpyrifos has been vastly restricted in U.S. and some European countries, even for agricultural purposes. However, it is still widely used in about 100 other countries. Like other organophosphorus pesticides, chlorpyrifos inhibits the cholinesterase enzyme systems essential in the normal

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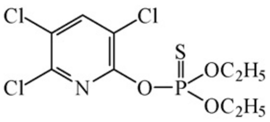

Fig. 1. Chemical structure of chlorpyrifos.

functioning of the nervous system. The most commonly reported effects of chlorpyrifos poisoning include: headache, nausea, dizziness, salivation, excess sweating, blurred vision, muscle weakness, abdominal cramps, diarrhoea, and in some extreme cases even death [24].

Various innovative technologies have been proposed for wastewater treatment containing chlorpyrifos. These include the use of the ionizing radiation [25], photocatalytic degradation using TiO_2 as catalyst [26], photo-Fenton process [27], high-pressure arc discharge plasma process [28], biodegradation [29,30] and chemical oxidation using hypochlorous acid (HOCl) as the primary oxidant [31]. However, there is no work related to the electrochemical degradation of chlorpyrifos. This article therefore, aims to study the electrochemical process for the total degradation of chlorpyrifos in aqueous solutions. The process was studied under galvanostatic polarization mode in acidic media using BDD anodes. The degradation rate of the studied pesticide and the efficiency and limits of such a technique were investigated according to experimental parameters such as the initial concentration of chlorpyrifos, the anodic current density and the temperature.

2. Experimental

2.1. Chemicals

In this work, all solutions were prepared in the laboratory. These solutions contain quantities of chlorpyrifos taken from an emulsifiable concentrate (DURSBAN* 4, from Dow Agrosciences) containing 480 g L^{-1} (44.6%, w/w) chlorpyrifos. All solutions were freshly prepared with double distilled water. Sulfuric acid and sodium hydroxide of analytical grade were employed as conductive electrolytes and for pH adjustment.

2.2. Boron-doped diamond Si/BDD electrodes

The boron-doped diamond electrodes were provided by CSEM (Centre Suisse d'Electronique et de Microtechnique, Neuchâtel, Switzerland). It was synthesized by the hot filament chemical vapour deposition technique (HF-CVD) [32] on single-crystal p-type Si ⟨1 0 0⟩ wafers (1–3 mΩ cm, Siltronix). The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm. The resulting diamond film thickness was about 1 μm with a resistivity of 10–30 mΩ cm. The electrode area is 6 cm^2. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 30 min with a 1 M H_2SO_4 solution at 50 mA cm^{-2} to remove any kind of impurity from its surface.

2.3. Preparation of Nb/PbO_2 electrode

The electrode used for a comparison with the BDD anode was made of niobium rectangular plates (70 mm × 10 mm × 1 mm) covered with a layer of lead dioxide obtained by electrochemical oxidation of a lead nitrate aqueous solution. In order to obtain a rough substrate surface to ensure the adhesion of PbO_2 deposits, the niobium plates underwent sandblasting using silica grains with an average diameter of 0.3 mm projected under 5 bar pressure. The substrate was then ultrasonically rinsed in doubly distilled water and chemically etched with HF 40% (weight) for 30 s at room temperature. The lead dioxide was then galvanostatically deposited using a two-compartment cell ($V = 500\ cm^3$) containing a lead nitrate solution (1 mol L^{-1}). The cathode is a graphite carbon-PTFE bar ($\phi = 5$ mm; $L = 60$ mm) placed in a porous ceramic cylinder (Norton, RA 84) containing 1 mol L^{-1} sulfuric acid solution. The deposition of PbO_2 was carried out for 2.5 h, at 65 °C and using an anodic current density of 20 mA cm^{-2}. The average mass of PbO_2 deposited per unit of surface area was 0.22 g cm^{-2}. The deposit obtained was mat grey, adherent, regular and uniform. The surface of this electrode was 6 cm^2.

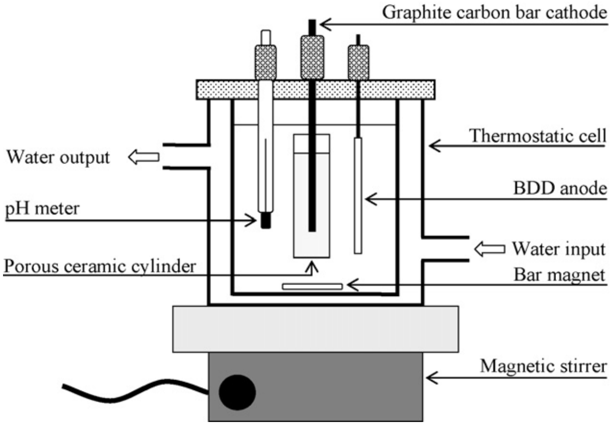

Fig. 2. Electrolytic cell.

2.4. Bulk electrolysis

Galvanostatic electrolyses of chlorpyrifos aqueous solutions (150 cm^3) have been carried out in a two-compartment thermostatted cell (Fig. 2). The cathode is a graphite carbon-PTFE bar ($\phi = 5$ mm; $L = 60$ mm) placed in a porous ceramic cylinder (Norton, RA 84) containing a 1 M sulfuric acid solution. The anode is 6 cm^2 Si/BDD or PbO_2 plate placed in front of the cathode. Chlorpyrifos solutions were electrolyzed in galvanostatic mode by applying current densities of 10–30 mA cm^{-2} using a DC power supply (model ABTP 530 Française d'Instrumentation, France). The pH of the solution was kept constant (pH = 2) by the continuous introduction of concentrated sulfuric acid or sodium hydroxide solutions to the cell.

2.5. Analysis

The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the instantaneous current efficiency. COD was determined by the dichromate method. The appropriate amount of sample was introduced into prepared digestion solution (0–1500 mg L^{-1}) containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 2 h at 150 °C in a WTW CR 2200 thermoreactor (Germany) for COD and thermal digestions. COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of the organic compounds. ICE during electrolysis can be performed from the decrease of COD by means of the following relation [1]:

$$\mathrm{ICE} = FV\frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{8I\,\Delta t} \qquad (2)$$

where F is the Faraday constant (96,487 C mol^{-1}), V the volume of the solution (L), COD_t and $COD_{t+\Delta t}$ are the chemical oxygen