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Mineralization of p-methylphenol in aqueous medium by anodic oxidation with a boron-doped diamond electrode

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ABSTRACT

The electrochemical oxidation of pesticide, p-methylphenol (PMP) as one kind of pesticide that is potentially dangerous and biorefractory, was studied by galvanostatic electrolysis using boron-doped diamond (BDD) as anode. The influence of several operating parameters, such as applied current density, supporting electrolyte, and initial pH value, was investigated. The best degradation occurred in the presence of Na_2SO_4 (0.05 M) as conductive electrolyte. After 8 h, nearly complete degradation of p-methylphenol was achieved (95%) using BDD electrodes at pH = 3 and at current density equals 60 mA cm^{-2}. The decay kinetics of p-methylphenol follows a pseudo-first-order reaction. Aromatic intermediates such as 3-methylcatechol, methylhydroquinone and methylbenzoquinone and carboxylic acids such as maleic, formic, fumaric, acetic, succinic, glyoxylic and oxalic, have been identified and followed during the PMP treatment by chromatographic techniques. From these anodic oxidation by-products, a plausible reaction sequence for PMP mineralization on BDD anodes is proposed.

1. Introduction

It is well known that a lot of wastes are formed during the production of pesticides and their application processes [1] Most of these compounds pose environmental problems due to their ecotoxicity and stability. The aqueous effluents contaminated by these pollutants must thus be treated before their injection in the natural environment. There are various methods for the treatment of these wastes such as activated carbon adsorption, chemical oxidation, and biological treatment [2]. But these classical processes are not generally sufficiently efficient in the elimination of these pollutants. For example, activated carbon adsorption involves phase transfer of pollutants without decomposition and thus induces another pollution problem. Chemical oxidation is unable to mineralize the persistent organic pollutants. Concerning the biological treatment, the main drawbacks are non-efficiency in presence of non-biodegradable and toxic pollutants, slow reaction rates, disposal of sludge and the need for strict control of proper pH and temperature. In order to overcome these disadvantages, more powerful oxidation methods are required than those currently applied in wastewater treatments for achieving their complete destruction. The development of new technologies such as advanced oxidation processes (AOPs) has attracted great attention during the last two decades for the treatment of toxic and persistent organic pollutants in aqueous media because of their ability to reach the total mineralization [3–5]. These processes involve chemical, photochemical or electrochemical techniques to bring about chemical degradation of organic pollutants. Among them, electrochemical advanced oxidation processes (EAOPs) offer many advantages such as low operational cost and high mineralization efficiency of pollutants compared to other known chemical and photochemical ones [6–10]. In this sense, anodic oxidation is a very common EAOP. In this process pollutants can be oxidized by direct electron transfer reaction from organics to the electrode surface or the action of highly oxidizing radical species (i.e. hydroxyl radicals) formed on the high O2-overvoltage anode surface. In this manner, a wide variety of electrode materials such as dimensionally stable anodes (RuO_2 or IrO_2-coated Ti) [11], thin film oxide anodes (PbO_2, SnO_2) [12], noble metals (platinum) [13] and carbon- based anodes [14] have been investigated. On the other hand, these electrodes have some drawbacks in the electrochemical oxidation of pollutants. The usage of the boron-doped diamond (BDD) as anode material in wastewater treatment processes has attracted great attention recently because of its high stability and efficiency

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[15–17]. This electrode allows the in-situ production of hydroxyl radicals from water (Eq. (1)) or hydroxide ion (Eq. (2)) oxidation on the electrode surface at large quantities [18–21]. These radicals are very powerful oxidizing agents and they react unselectively with organics giving dehydrogenated or hydroxylated by products until their total conversion into CO_2, water and inorganic ions:

$$H_2O \rightarrow {}^{\cdot}OH_{ads} + H^+ + e^- \quad (1)$$

$$OH^- \rightarrow {}^{\cdot}OH_{ads} + e^- \quad (2)$$

The removal of p-methylphenol from aqueous solution was performed previously by using TiO_2 as heterogeneous photocatalyst, $Ti/TiO_2–RuO_2–IrO_2$ anode and a graphite cathode and fenton's reagent (H_2O_2/Fe^{2+}) [22–24].

To the best of our knowledge, there is no study on the electrochemical oxidation of p-methylphenol by anodic oxidation with a BDD anode. In this study, we examined the removal of p-methylphenol pesticide from its aqueous solution by electrochemical oxidation using a BDD anode for the first time in the literature. The effects of important operating parameters such as anode material, applied current, pH and types of the supporting electrolyte on the degradation rate and mineralization efficiency were investigated. The oxidation by-products such as aromatics and short-chain carboxylic acids were determined by high-performance liquid chromatography (HPLC) method. Finally, an oxidative degradation pathway of p-methylphenol by $^{\cdot}OH$ radicals generated on BDD anode in aqueous medium was proposed.

2. Materials and methods

2.1. Electrodes preparation

PbO_2 was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid solution (100 g L^{-1}) at 25 °C. This acid solution was electrolyzed galvanostatically for 30 min at ambient temperature using an anodic current density of 100 mA cm^{-2}. The cathode was stainless steel (austenitic type), the two electrodes were concentric with the lead electrode as axial. This arrangement gave the formation of a regular and uniform deposit [25].

BDD films were provided by CSEM and synthesized on a conductive *p*-Si substrate (1 mm, Siltronix) via a hot filament, chemical vapor deposition technique (HF-CVD). The temperature of the filament was from 2440 to 2560 °C and that of the substrate was monitored at 830 °C. The reactive gas used was 1% methane in hydrogen containing 1–3 ppm of trimethylboron. The gas mixture was supplied to the reaction chamber at a flow rate of 5 L min^{-1} to give a growth rate of 0.24 μm h^{-1} for the diamond layer. This procedure gave a columnar, randomly textured, polycrystalline diamond film, with a thickness of about 1 μm and a resistivity of 15 mΩ cm (±30%) onto the conductive *p*-Si substrate [26].

2.2. Electrolysis of p-methylphenol solutions

Galvanostatic electrolyses were carried out at BDD and PbO_2 electrodes, with current density ranging from 0 to 60 mA cm^{-2}. Runs were performed at 20 °C. Solutions of 216 mg L^{-1} of pure p-methylphenol were used. Electrolysis was done with 0.05 M of different types of electrolytes NaCl and Na_2SO_4 with pH around 3.0–10.0. All electrolyses were conducted in an open, one-compartment and thermostated cylindrical cell containing a 150 mL solution stirred with a magnetic bar. The anode was a 42 cm^2 BDD. For comparative purposes, a 42 cm^2 PbO_2 and Pt were also employed as anode. The cathode was always a 42 cm^2 graphite bar from Sofacel. The interelectrode gap was about 3 cm. The current and potential measurements were carried out using digital multimeter.

2.3. Analytical techniques

The used compounds were either reagent or analytical grade from Sigma-Aldrich. Anhydrous sodium sulphate used as background electrolyte was analytical grade from Fluka. All solutions were prepared with water from a Millipore Milli-Q system (conductivity $<6 \times 10^{-8}$ S cm^{-1}). The temperature of the electrolyte was fixed by using a water thermostat. The current density for the electrolysis was kept at the desired level with an Amel 2053 potentiostat-galvanostat. The solution pH was measured with a Crison 2000 pH-meter. Total Organic Carbon (TOC) amounts in aqueous solutions were obtained with a Shimadzu VCSH carbon analyzer. During all experiments, samples were collected and immediately measured without using any filter. Chemical oxygen demand (COD) data were obtained with a Merck Model SQ118 spectrophotometer after digestion of samples in a Merck Model TR-300 thermoreactor. p-Methylphenol and all other intermediates were identified by reversed-phase chromatography with a water system composed of a Waters 600 HPLC liquid chromatography fitted with a Spherisorb ODS2 5 μm, 150 × 4.6 mm column, at room temperature, and coupled with a waters 996 photodiode array detector selected at 256 nm, controlled through a Millennium-32 program®. These analyses were made by injecting 20 μL aliquots into the chromatograph and circulating a 39/59/2 (v/v/v) Methanol/water/acetic acid mixture at 0.7 mL min^{-1} as mobile phase. Generated carboxylic acids were followed by ion-exclusion chromatography by injecting 20 μL samples into the above HPLC system with a SUPELCOGEL C-610H, 250 × 4.6 mm column, at 35 °C from Bio-Rad. For these measurements, the photodiode detector (L-2400) was selected at 210 nm and the mobile phase was 4 mM H_2SO_4 at 0.2 mL min^{-1}. Inorganic ions were analysed by ion chromatography using a Dionex ICS-1000 Basic Ion Chromatography system fitted with an IonPac AS4A-SC, 25 cm × 4 mm anion-exchange column. These measurements were conducted by injecting 25 μL samples and using a mobile phase composed of 1.8 mM of sodium carbonate and 1.7 mM of sodium bicarbonate at the flow rate of 0.8 mL min^{-1}.

3. Results and discussion

3.1. Effect of experimental parameters on p-methylphenol mineralization

3.1.1. Effect of the anode material

In anodic oxidation, pollutants are mineralized by direct electron transfer reactions or action of radical species (i.e. hydroxyl radicals) formed on the electrode surface. In this manner, a wide variety of electrode materials have been investigated recently, but the mixed metal oxide, PbO_2 or boron doped diamonds BDD, is used as anode because of its high O2 evolution overvoltage, high stability and efficiency [20]. Within this context, for comparing the oxidation ability of BDD, PbO_2 and Pt, a commercially and more available material, a series of electrolyses have been performed applying a constant current of 60 mA cm^{-2} and the results are reported in Fig. 1.

Fig. 1 shows the evolution of COD as a function of specific charge (Q in Ah l^{-1}) in BDD, Pt, and PbO_2 anodes cells under the same electrolysis conditions. As can be seen, the COD removal rate in BDD anode cell was much greater than those in PbO_2 and Pt anodes cells. At the end of treatment, COD was almost completely removed in BDD anode cell, while COD were only removed by 52% in Pt anode cell and by 72% in PbO_2 anode cell. It meant that the