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Electrochemical incineration of cresols: A comparative study between PbO_2 and boron-doped diamond anodes

Cristina Flox [a], Conchita Arias [a], Enric Brillas [a], André Savall [b], Karine Groenen-Serrano [b,*]

[a] Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[b] Laboratoire de Génie Chimique, CNRS, Université Paul Sabatier 118, Route de Narbonne, 31062 Toulouse Cedex 9, France

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ABSTRACT

The electrooxidation of aqueous solutions containing 5 mM of *o*-, *m*- and *p*-cresol at pH 4.0 has been investigated using a flow filter-press reactor with a boron-doped diamond (BDD) under galvanostatic electrolysis. All cresols are degraded at similar rate up to attaining overall mineralization. Comparable treatment of the *m*-cresol effluent on PbO_2 leads to partial electrochemical incineration. However, this pollutant is more rapidly removed with PbO_2 than with BDD. The decay kinetics of all cresols follows a pseudo-first-order reaction. Aromatic intermediates such as 2-methylhydroquinone and 2-methyl-*p*-benzoquinone and carboxylic acids such as maleic, fumaric, pyruvic, malonic, tartronic, glycolic, glyoxylic, acetic, oxalic and formic, have been identified and followed during the *m*-cresol treatment by chromatographic techniques. From these oxidation by-products, a plausible reaction sequence for *m*-cresol mineralization on both anodes is proposed. The energy consumption for the corresponding electrochemical process is also calculated.

1. Introduction

Phenol and its derivatives are the major constituents of industrial wastewater produced by oil refineries, petrochemicals, polymeric resins, pharmaceuticals, coal conversion plants and chemical industries (Rajkumar and Palanivelu, 2003; Ródenas-Torralva et al., 2005; Wu et al., 2006). Their high aqueous solubility and weak adsorption to most soils result in a quick entry into groundwater due to leaching (Rao and Asolekar, 2001). The concentration of these compounds in agro-industrial wastewaters can vary from 0.05 to 10 g L^{-1} depending on the type and origin of the effluent. In a contaminated aquifer of Fredensborg (Denmark), for example, phenol, *o*-cresol and *m*-cresol contents of 2.00, 0.65 and 0.78 mg L^{-1}, respectively, were detected (Flyvbjerg et al., 1993). For a low temperature coal carbonization wastewater, about 2.5 g L^{-1} phenol, 250 mg L^{-1} resorcinol, 5.3 g L^{-1} catechol, 480 mg L^{-1} *o*-cresol, 200 mg L^{-1} *m*-cresol, 470 mg L^{-1} *p*-cresol, 2.0 g L^{-1} pyrogallol and 400 mg L^{-1} xylenol were found (Rajkumar et al., 2005). High phenol, *p*-cresol and resorcinol concentrations were also determined in wastewaters coming from the oil shale treatment process.

At concentrations above some threshold levels, phenolic compounds are toxic to microorganisms and refractory to biodegradation. Cresols are classified by the US EPA as persistent, priority and toxic chemicals, showing chronic effects at 12 mg L^{-1} of the quantitative structure–activity relationship (Kavitha and Palanivelu, 2005). Unfortunately, the high contamination of industrial wastewaters of these compounds, their seasonal production and the presence of other organic pollutants such as lipids usually render these effluents inappropriate for direct biological treatment. Alternative powerful oxidation technologies are then needed to be developed for achieving total destruction of cresols from wastewaters.

Advanced oxidation processes (AOPs) based on the in situ generation of hydroxyl radical ($^{\cdot}OH$) are promising environmentally friendly techniques for water remediation. $^{\cdot}OH$ is the second strongest oxidant known after fluorine, with a high standard potential ($E^{\circ} = 2.80$ V vs. SHE) that makes feasible its fast non-selective reaction with organics to give dehydrogenated or hydroxylated by-products up to total mineralization, i.e., conversion into CO_2 and water.

Several papers have reported the rapid removal of *o*-, *m*- and/or *p*-cresol from waters by photocatalysis with TiO_2/UV. Hatipoğlu et al. (2004) found that *m*-cresol undergoes a 74% decay after 160 min of treatment by this AOP following a pseudo-first-order kinetics and proposed the initial generation of 3-methylcathecol from quantum mechanical calculations. In contrast, mixtures of hydroxylated and benzoquinone derivatives have been detected by gas chromatography–mass spectrometry (GC–MS) from the photocatalytic degradation of all cresols (Wang et al., 1998; Sivalingam et al., 2004). The treatment of wastewaters of these

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* Corresponding author. Tel.: +33 561558677; fax: +33 561556139.
E-mail address: serrano@chimie.ups-tlse.fr (K. Groenen-Serrano).

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compounds by other AOP such as Fenton's reagent (H_2O_2/Fe^{2+}) only allows attaining 42% mineralization, because of the production of acetic and oxalic acids as major by-products, which are difficulty destroyed by $^{\cdot}OH$ formed in the bulk (Kavitha and Palanivelu, 2005). In this scenario, we previously reported that total mineralization of cresols is feasible using the solar photoelectro-Fenton method in which complexes of Fe(III) with generated carboxylic acids are efficiently photodecomposed by UV irradiation of sunlight (Flox et al., 2007).

Electrochemical oxidation or electrooxidation is the most popular electrochemical treatment for wastewaters containing low contents of organics. This AOP allows the electrochemical incineration of pollutants from their mediated oxidation with hydroxyl radical formed at a high O_2-overvoltage anode (M) from water oxidation (Panizza and Cerisola, 2005):

$$M(H_2O) \rightarrow M(^{\cdot}OH) + H^+ + e^- \tag{1}$$

Recently, electrooxidation has received great attention due to the use of non-active boron-doped diamond (BDD) thin film electrodes, which possess so high O_2-overvoltage that favors the production of great quantity of reactive BDD($^{\cdot}OH$) with ability to completely mineralize organics, as shown for several aromatics (Panizza et al., 2001; Marselli et al., 2003; Polcaro et al., 2003; Brillas et al., 2005; Flox et al., 2006; Nava et al., 2007; Zhao et al., in press) and carboxylic acids (Martinez-Huitle et al., 2004; Weiss et al., 2007). Thus, Nava et al. (2007) described the efficient electrochemical incineration of 2 mM *p*-cresol and *o*-cresol in 1 M H_2SO_4 using a filter-press-type FM01-LC cell with a BDD anode and a Ti/Pt cathode, both of 64 cm^2 area. After 3 h of electrolysis at 10 mA cm^{-2}, *p*-cresol reached 90% mineralization, with 71% current efficiency and an energy consumption of 7.84 kW h m^{-3}; whereas *o*-cresol was mineralized to 84%, with 67% current efficiency and 6.56 kW h m^{-3} energy cost. However, no intermediates were detected in these trials. These results evidence the good performance of a BDD anode for treating cresols wastewaters. In contrast, a poor electrochemical degradation for *o*-, *m*- and *p*-cresol in alkaline medium with generation of hypochlorite ion as oxidant has been found by Rajkumar and Palanivelu (2003) using an undivided cell with a $Ti/TiO_2–RuO_2–IrO_2$ anode and a graphite cathode. At pH 9 the optimum operating conditions yielding maximum degradation, shorter electrolysis time and less energy consumption were achieved with 2.5 g L^{-1} chloride as electrolyte and cresols concentration >300 mg L^{-1} at 54 mA cm^{-2} (1.5 A). The chemical oxygen demand decreased in the sequence: *m*-cresol > *o*-cresol > *p*-cresol, but total organic carbon (TOC) removal values as low as 50–60% were obtained after the consumption of high specific charges of 40–50 Ah L^{-1}. Adsorbable organic halogens analysis of treated solutions revealed the production of chloroderivatives as intermediates.

The good performance of other potent anodes such as PbO_2 in electrooxidation for the removal of phenol and other organics has been confirmed previously and compared with the oxidation power of BDD anodes (Belhadj Tahar and Savall, 1998; Belhadj Tahar et al., 2008; Martinez-Huitle et al., 2008; Sirés et al., 2008; Weiss et al., 2008; Zhu et al., 2008). To gain a better knowledge on the ability of these anodes to oxidize phenolic compounds, we have undertaken the present study on the electrochemical incineration of cresols in acid medium using a flow filter-press reactor under galvanostatic conditions. Our research was focused to determine the degradation rate of *o*-, *m*- and *p*-cresol effluents with BDD to be further compared with that of *m*-cresol with PbO_2. A concentrated (5 mM) solution of each pollutant was treated to clarify the role of aromatic intermediates and carboxylic acids formed on the degradation process. The decay kinetics of all cresols and the evolution of by-products for *m*-cresol were then followed by chromatographic techniques, allowing the proposal of a reaction pathway for *m*-cresol mineralization. The energy consumption for the electrochemical treatment of this compound on each anode was also calculated.

2. Experimental

2.1. Chemicals

o-Cresol (99% purity), *m*-cresol (99% purity) and *p*-cresol (97% purity) were purchased from Sigma and used in the electrochemical trials as received. 2-Methylhydroquinone, 2-methyl-*p*-benzoquinone and maleic, fumaric, malic, malonic, tartronic, pyruvic, glycolic, glyoxylic, acetic and oxalic acids were either reagent or analytical grade from Sigma–Aldrich, Merck and Avocado. Solutions were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm at 25 °C). Analytical grade sulfuric acid from Prolabo was used to adjust its initial pH to 4.0. Anhydrous sodium sulfate employed as background electrolyte was analytical grade supplied by Prolabo. Other chemicals and organic solvents were either HPLC or analytical grade from Sigma–Aldrich, Merck and Prolabo.

2.2. Electrochemical reactor

Electrolyses were conducted in a one-compartment flow filter-press reactor (Diacell) under galvanostatic conditions and in batch operation mode. Electrodes were two discs of 63 cm^2 of active surface separated 10 mm. The anode was either a Si wafer coated with a 1 μm BDD thin layer or a titanium disc covered with a PbO_2 film supplied by De Nora. The BDD electrode from Centre Suisse d'Électronique et de Microtechnique (Neuchâtel, Switzerland) was elaborated by chemical vapour deposition on a conductive substrate of polysilicium. The cathode was a 1 mm thick disc of zirconium. The current was supplied by an ELC AL 924 power supply. Details on the electrochemical system are reported elsewhere (Weiss et al., 2007).

Comparative degradation of cresols was studied by electrolyzing 1 L of solutions containing 5 mM of initial pollutant and 0.05 M Na_2SO_4 of pH 4.0. In all trials, a constant current density of 40 mA cm^{-2} was applied. The solution temperature was maintained at 25 °C and the effluent was recirculated at a constant flow rate of 126 L h^{-1}.

2.3. Analysis procedures

The solution pH was determined with a Schott pH-meter CG 837. Samples withdrawn from original and treated solutions were filtered with Whatman 0.45 μm PTFE filters before analysis. The mineralization of cresols solutions was monitored from the decay of their dissolved organic carbon (DOC), determined on a Shimadzu 5050A TOC analyzer with 2% accuracy.

The organic components of about 100 mL of the 5 mM *m*-cresol solution treated with a BDD anode for 60 min were extracted three times with 25 mL of CH_2Cl_2. The collected organic solution was dried with anhydrous Na_2SO_4, filtered and rotavaporated up to ca 2 mL. The remaining aromatic intermediates were further identified by GC–MS using a Hewlett-Packard 5890 Series II gas chromatograph fitted with an Elite-5MS 0.25 μm, 30 m × 0.25 mm (i.d.), column, and a Hewlett-Packard 5989A mass spectrophotometer operating in electron impact mode at 70 eV. The temperature ramp for this column was 70 °C for 1 min, 20 °C min^{-1} up to 250 °C and hold time 1 min. The evolution of all cresols and aromatic intermediates from *m*-cresol were followed by reversed-phase HPLC chromatography using a Hewlett-Packard 1100 Series liquid chromatograph, fitted with a Spherisorb ODS2 5 μm, 150 mm ×