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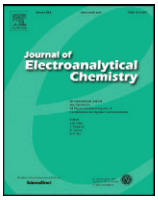

Mineralization of chlorobenzene in aqueous medium by anodic oxidation and electro-Fenton processes using Pt or BDD anode and carbon felt cathode

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ABSTRACT

This study focuses on the in situ destruction of pesticide chlorobenzene (CB) by using two electrochemical advanced oxidation processes, namely anodic oxidation and electro-Fenton. Influence of several operating parameters such as applied current, catalyst concentration and supporting electrolytes was assessed to optimize oxidation and mineralization of CB. Kinetics study showed that CB is quickly oxidized by •OH following a pseudo first-order reaction kinetics. The rate constant of oxidative degradation of CB by hydroxyl radicals was determined by competition kinetics method and found to be 4.35×10^9 M^{-1} s^{-1}. The quasi complete mineralization (95% TOC removal) of 0.1 mM CB aqueous solution was achieved at 4 h treatment. Formation and evolution of aromatic and aliphatic (short-chain carboxylic acids) intermediates during treatment were monitored by HPLC analysis and a mineralization pathway was proposed. The results obtained highlight the great efficiency of electro-Fenton process in effective destruction of a very persistent pollutant such as CB that can be extrapolated to other toxic/persistent organic pollutants.

1. Introduction

The intensive use of pesticides in the environment constitutes a threat to living beings [1–3]. Chlorobenzene (CB) is one of the most common organic pollutants in industrial wastewaters [4] since it is involved in the synthesis of many chemicals, particularly in the field of pesticides [5]. Therefore, CB is considered as a hazardous waste and a prior toxic pollutant by the U.S. Environmental Protection Agency [4]. Chlorinated aromatic compounds are considered as the most problematic categories of environmental pollutants because they are mostly non-biodegradable or very slowly degradable by microorganisms [6]. It is therefore important to assess the fate of these compounds in the environment and develop effective methods to remove them from water.

Recently, there is great interest in the remediation of waters containing toxic and organic pollutants with different methods such as chemical, photochemical, photocatalytical and electrochemical processes [7–11]. In this work we focus on electrochemical advanced oxidation processes (EAOPs) like electro-Fenton (EF) and anodic oxidation (AO) for removal of CB from water. These processes enable efficient degradation of persistent organic pollutants in aqueous medium by in situ generating highly reactive oxidizing agents such as hydroxyl radicals (•OH), which are able to oxidize efficiently almost all organic contaminants [11–17]. This radical is the second most strong oxidant known, after fluorine, having a very high standard potential ($E^\circ(\bullet OH/H_2O) = 2.80$ V/SHE) that makes it able to non-selectively react with organics to give hydroxylated or dehydrogenated derivatives until their mineralization (transformation into CO_2, water and inorganic ions) [18–22]. One of the most popular EAOPs is the EF process based on the continuous supply of H_2O_2 from reaction (1) [23–25]. Formation of homogeneous •OH starts via Fenton reaction (2) once a catalytic amount of ferrous iron salt added to the solution [2,23,26]. The process is electrocatalytic since Fe^{2+} ions is electro-regenerated according to the reaction (3) from ferric iron produced by reaction (2) [20,27,28]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + {}^\bullet OH \qquad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (3)$$

Other popular EAOP is the AO process in which organics pollutants in a contaminated solution are oxidized by direct charge transfer on the anode (M) from heterogeneous hydroxyl radicals (M(•OH)) formed

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from oxidation of water (reaction (4)) [28–30]. The availability and efficiency of these radicals is depending to the anode material (M) [29, 30]. The boron-doped diamond (BDD) anode appears as the most effective anode because of the high O_2 evolution overpotential and physisorption on the surface [28–32].

$$M + H_2O \rightarrow M\left(^{\bullet}OH\right) + H^+ + e^- \quad (4)$$

The use of a high overpotential anode material like BDD in EF process enhances strongly the efficiency of the process since this operation is consisting of a coupling between EF and AO processes: •OH and BDD(•OH) are generated simultaneously [33]. Therefore the oxidative degradation of CB was carried out by EF comparatively with AO. The electrolyses were carried out with both anode materials: Pt and BDD. A three-dimensional electrode material, carbon felt, was used as the cathode in all experiments [33,34]. The influence of the applied current and the kind of supporting electrolytes on the effectiveness of the treatment were evaluated. The degradation kinetics was followed by high performance liquid chromatography (HPLC). The mineralization efficiency was studied for the two processes following the evolution of the total organic carbon (TOC) content. Identification of aromatic intermediates, short-chain carboxylic acids and TOC results enabled us to propose a plausible mineralization pathway for mineralization of CB by hydroxyl radicals. Although the oxidative degradation of CB has been carried out already by Liu et al. [35] and Hsiao and Kobe [36], the present work provides new data on the degradation and mineralization of CB. Hsiao and Kobe reported, in a pioneer work the oxidation of CB in a packed bed flow reactor by electrochemically generated Fenton's reagent with a low degradation (40% in 40 min) rate. More recently Liu et al. [35] gave a more interesting work investigating the electro-oxidation of CB by AO using Pt and BDD anodes. A degradation kinetic model was developed and identification of number aromatic intermediates was carried out. The present study aims to complete the work of Liu et al. and Hsiao and Kobe investigating the oxidation and mineralization of CB by electro-Fenton process and elucidating the mineralization kinetics through TOC removal measurements as a function of electrode material, current applied. And supporting electrolyte used. Results obtained in this study were then compared with those reported in [35,36].

2. Experimental

2.1. Chemicals

Chlorobenzene (CB, C_6H_5Cl) was obtained from Sigma-Aldrich. Iron (II) sulfate heptahydrate used as Fe^{2+} (catalyst) source was analytical grade from Fluka. Hydroxybenzoic acid was obtained from Merck. Acetic, maleic, oxalic, fumaric, formic, succinic and malonic acids were of analytical grade and supplied by Fluka. Anhydrous sodium sulfate and sodium chlorate used as supporting electrolytes were obtained by Across. The pH was adjusted with analytical grade sulfuric acid purchased from ACS reagent Across. Sodium nitrate (Merck), ammonium nitrate and sodium phosphate (Aldrich) were used as standards for ionic chromatography (IC) analysis. Organic solvents and other chemicals used were either of HPLC or analytical grade purchased from Merck and Fluka.

2.2. Procedures and equipment

All electrolyses were conducted in an open and undivided cylindrical glass cell of 250 mL capacity, equipped with two electrodes. The working electrode was a 70 cm^2 (14 cm × 5 cm) piece of carbon-felt (from Mersen, France), placed on the inner wall of the cell covering the internal perimeter. The counter electrode was cylindrical Pt grid or BDD plate (6 cm × 4 cm) (from CONDIAS GmbH, Germany) placed at the center of the cell. Prior to the electrolysis, compressed air was bubbled through the aqueous solutions, which were stirred continuously by magnetic stirrer (500 rpm). A catalytic quantity of ferrous ion (0.1 mM) was introduced into the solution before the beginning of electrolysis. The supporting electrolytes were Na_2SO_4 (50 mM) and NaCl (100 mM). Different currents intensities were applied in the degradation and the mineralization experiments, these currents were measured and displayed continuously throughout electrolysis using a DC power supply (HAMEG Instruments, HM 8040-3). Before starting electro-oxidation treatment, the initial solutions were adjusted to pH 3.0 with analytical grade 1 M sulfuric acid.

2.3. Instruments and product analysis procedures

The solution pH was measured with a glass electrode calibrated with standard buffers at pH values of 4, 7 and 10. The concentration decay of CB was monitored by HPLC using a Merck-Hitachi Lachrom chromatograph equipped with a diode array UV–Vis detector (model L-7455) fitted with a reverse phase purospher RP-18, 5 μm, 4.6 × 250 mm column purchased from Merck (France). The column was eluted at isocratic mode for all experiments with a mobile phase composed of 70:30 (v/v) methanol/water at a flow rate of 0.8 mL min^{-1}. The column was thermostated at 40 °C. Detection was performed at 230 nm for kinetic studies. The short-chain carboxylic acids were identified and quantified using an ion-exclusion column (Supelcogel H column; $\phi =$ 7, 8 mm × 300 mm) with a mobile phase of 4 mM H_2SO_4 at 210 nm. Inorganic ions were analyzed by ionic chromatography from Thermo-Fisher (Dionex-100 equipped with a conductivity detector). An anionic exchanger column (IonPac AS14-Dionex) was used for Cl^- analysis. The TOC content of initial CB solutions and its evolution during electrolysis was performed at pH 3. The CB samples were filtered (0.22 μm) and acidified with HCl (1% HCl 2 mM). The injection volumes were 50 μL. TOC values were determined with Shimadzu VCSH TOC analyzer. From these data, the mineralization current efficiency (MCE) was estimated as follows [23,34]:

$$\text{MCE}\ (\%) = \frac{n\ F\ V_S\ \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7\ m\ I\ t} \times 100 \quad (5)$$

where F is the Faraday constant (96,487 °C mol^{-1}), V_S is the solution volume, $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC change at a given time (mg L^{-1}), 4.32×10^7 is an homogenization factor (3600 s h^{-1} × 12,000-mg mol^{-1}), m is the number of carbon atoms of CB (6 atoms), I is the applied current (A) and t is the electrolysis time (h). The number of electrons (n) consumed per mole of CB was taken as 28 considering total mineralization according to the following reaction [2,18,35]:

$$C_6H_5Cl + 12H_2O \rightarrow 6CO_2 + 29H^+ + Cl^- + 28e^- \quad (6)$$

3. Results and discussion

3.1. Effect of experimental parameters on oxidative degradation of MC

The performance of electrode pairs Pt/carbon felt and BDD/carbon felt was tested for EF and AO processes. The efficiency of the anodes was analyzed and compared in the same conditions in order to optimize the degradation of MC solutions. All experiments were carried out with 230 mL of 0.1 mM MC solutions at pH 3.0. The decay kinetics of MC concentration with the generated oxidant (•OH)/M(•OH) was studied at different current values from 50 to 500 mA, using 50 mM of Na_2SO_4 or 100 mM of NaCl and 0.1 mM of catalyst (Fe^{2+}) concentration for EF process.

Fig. 1 shows the effect of the current applied to the profile of the kinetic curves of the oxidation of CB by •OH/M(•OH). The electrolysis time required for complete disappearance of CB is becoming shorter when