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Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode

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Abstract

Oxidation of phenol in aqueous media by electro-Fenton process using carbon felt cathode has been studied. The salts of iron, cobalt, manganese, and copper were used to provide the metal cations as catalyst of Fenton reaction to produce hydroxyl radicals. 10^{-4} M of soluble iron(II) sulfate salt supplied the optimum catalytic condition, allowing to remove 100% of total organic carbon (TOC) of aqueous phenol solutions. The main reaction intermediates formed during electro-Fenton treatment were identified as hydroquinone, *p*-benzoquinone, and catechol. Carboxylic acids such as maleic, fumaric, succinic, glyoxylic, oxalic, and formic were predominantly identified as end products, before complete mineralization. The absolute rate constant of phenol degradation by hydroxyl radicals was obtained in acid medium ($2.5 < \mathrm{pH} < 3.0$), being equal to $(2.62 \pm 0.23) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$. Experiments with electro-Fenton oxidation of each aromatic intermediate allowed to propose a complete mineralization pathway.

Keywords: Advanced oxidation process; Electro-Fenton; Phenol; Mineralization; Catalysts

1. Introduction

Among the various wastes, phenolic compounds constitute a family of pollutants particularly toxic to the aquatic fauna and flora. These compounds are released in the surface water by a considerable number of industries, mainly, by pharmaceutical plants, oil refineries, coke plants, pulp, and food-processing industries and several other chemical plants [1,2], constituting an environmental hazard. Phenol is also a typical molecule present in most of aromatic products, emphasizing its relevance. It is toxic to fish at a 1–2-ppm concentration level [3], being considered lethal to most of aquatic organisms exposed to concentrations of 10–100 ppm [4]. Moreover, it presents an acute toxicity for man [5]. Consequently, phenol removal from wastewater is an environmental concern.

Phenol belongs to the recalcitrant pollutants to conventional physicochemical and biological treatments. On the other hand, the advanced oxidation processes (AOPs) have been defined as effective processes for treatment of wastewater containing toxic and persistent organic pollutants. These processes use hydroxyl radical, a powerful oxidizing agent, which is able to destruct target pollutants [6]. The oxidative degradation of phenol in aqueous media has been the subject of several AOPs studies such as Fenton's reagent [7], Fenton like process using zero valence iron [8], ozonation [9], H_2O_2-mediated photodegradation [10], photo-Fenton [10,11], and heterogeneous photocatalysis [12,13]. However, high cost of chemical products, parasite reactions, strict applying conditions and/or moderate mineralization efficiency limit most of the AOPs. Esplugas et al. [14], for instance, studied the mineralization of synthetic samples of phenol (1 mM) by different advanced oxidation processes. In best conditions, low total organic carbon (TOC) decreases of 10, 37, 45, and 65% were obtained for Fenton, O_3/H_2O_2, O_3/H_2O_2/UV, and O_3/UV systems, respectively. The chemical oxygen demand (COD) abatement was 30% in optimum conditions in the study of Poulopoulos et al. [15] during the degradation of 3.2 mM phenol aqueous solution by H_2O_2/UV system.

Electrochemistry offers new ways for organic waste treatment. The advanced electrochemical oxidation processes (AEOPs) such as anodic oxidation [16–18], electro-Fenton

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[19–22], electro-Fenton coupled to anodic oxidation [23–25], solar photo-electro-Fenton [26], and other electro-Fenton like processes [27,28] developed during the last decade constitute emergent and promising AOPs. Moreover numerous works have been conducted by anodic oxidation to degrade phenol in aqueous solution using various anodes such as Pt [29], PbO_2 [16], bismuth-doped PbO_2 [30], Ti/SnO_2–Sb [31], and boron-doped diamond [32,33]. Fockedey and Van Lierde [34] studied the electrochemical oxidation of phenol by the coupling of anodic and cathodic reactions, provided by Sb-doped-SnO_2-coated titanium anode and a reticulated vitreous carbon cathode.

In this work, we have studied the oxidative degradation of aqueous phenols solutions in acidic medium by electro-Fenton process using a carbon felt cathode and a platinum anode in order to evaluate the mineralization efficiency of this process. The process is based on the electrochemical in situ production of the Fenton's reagent, a mixture of ferrous ions (used as catalyst) and hydrogen peroxide which is able to generate hydroxyl radicals [35,36]. Hydrogen peroxide is continuously generated in acidic-contaminated medium from the two-electron reduction of dissolved O_2. New catalysts have been used in other electrochemical experiments with carbon felt cathode to assure Fenton like reactions. These studies evidenced that pH 3 enhances hydrogen peroxide electrochemical production [27,37]. In fact, considering saturated concentration of oxygen in experimental conditions ($0.45\ mM < [O_2] < 0.58\ mM$), pH 3 assures ideal conditions ($[H^+]/[O_2] \cong 2$) to optimize electrochemical production of hydrogen peroxide according to the following equation, avoiding the formation of peroxo and sulfate complexes in higher acid mediums [38]:

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

Addition of a catalytic amount of ferric or ferrous ions in the solution to be treated allows an enhancement of the oxidation power of electrogenerated H_2O_2 according to the Fenton's reaction (reaction (2)):

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

At pH 3 (optimal value for reaction (1)), the predominant species of Fe(III) is $Fe(OH)^{2+}$ and the electrochemical reduction is written according to reaction (3):

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

The sum of reactions (2) + (3) indicates the electrocatalysis of the Fenton's reaction.

On the other hand, the production of H_2O_2 is also electrocatalyzed because the oxygen required by reaction (1), can be produced by water oxidation at the Pt anode (reaction (4)):

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (4)$$

Hydroxyl radicals are produced in a catalytic and controlled way, allowing the mineralization of organic pollutants (transformation to CO_2, H_2O and/or mineral ions) [16–28].

The classical electro-Fenton process is carried out with one of the forms of the Fe^{3+}/Fe^{2+} redox couple ($E^0 = 0.77$ V/NHE). However, any appropriate homogeneous redox couple $M^{(n+1)+}/M^{n+}$ can be used according to reaction (5):

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + {}^{\bullet}OH \qquad (5)$$

Several metal cations have been tested as catalysts [39,40]. In this case, electro-Fenton process efficiency is influenced by the standard potential of $M^{(n+1)+}/M^{n+}$ redox couple used and by scavenging catalyst effect.

This paper reports an investigation concerning the effect of catalyst nature and concentration on the electro-Fenton degradation of phenol and the mineralization efficiency of this technique to treat phenol aqueous solutions. We have carried out a detailed study in aqueous medium to show the viability of the electro-Fenton process to remove phenol and its hydroxylated and/or quinoid metabolites from wastewater. The effect of the nature of catalyst was studied by comparative treatments with several metal cations such as Fe^{2+} ($E^0_{(Fe^{3+}/Fe^{2+})} = 0.77\,V$), Co^{2+} ($E^0_{(Co^{3+}/Co^{2+})} = 1.92\,V$), Cu^{2+} ($E^0_{(Cu^{2+}/Cu^{+})} = 0.16\,V$), and Mn^{2+} ($E^0_{(Mn^{3+}/Mn^{2+})} = 1.50\,V$). The aromatic and aliphatic intermediates formed during current-controlled electrolyses were identified by chromatographic techniques. The follow of the phenol decay and evolution of its oxidation reaction intermediates during electro-Fenton treatment as well as the TOC removal measurements permitted to propose a plausible mineralization pathway of phenol, including hydroxyl radical reactions which controlled the destruction of phenol and predominant aromatics. Competitive kinetics method [37,41] using equal initial concentrations of phenol and 4-hydroxybenzoic acid (4-HBA) allowed to obtain the absolute rate constant of phenol degradation by hydroxyl radicals in pH 3. The effect of current density and initial volume on mineralization rates was also studied.

2. Experimental

2.1. Chemicals

Phenol (Aldrich, 99.5%) was used as soon as purchased. The salts used to obtain catalyst ions (iron(II) sulfateheptahydrate, 99.75%, copper(II) sulfate pentahydrate, 98%, cobalt(II) sulfate heptahydrate, 99%, and manganese(II) sulfate monohydrate, 98%) were supplied by Acros Organics and Fluka and were used without further purification. Catalyst concentrations used in different experiments are outlined in Table 1. All other products used, including intermediates, were obtained with purity higher than 99%.

All solutions were prepared with pure water obtained from a Millipore Simplicity 185 system (conductivity $< 6 \times 10^{-8}\ S\ cm^{-1}$ at 25 °C). The pH of solutions was adjusted using analytical grade sulfuric acid (Merck).