JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) · SHORT COMMUNICATION

SHORT COMMUNICATION

# Hydroxylation of chlorobenzene and phenol in a packed bed flow reactor with electrogenerated Fenton's reagent

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Received 25 August 1992; revised 17 December 1992

## 1. Introduction

Fenton's reagent is an aqueous mixture of ferrous ions and hydrogen peroxide [1]. In the presence of ferrous ions, the oxidation power of $H_2O_2$ is enhanced significantly due to the formation of hydroxyl radicals:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \quad (1)$$

The hydroxyl radical is the actual oxidizing agent in Fenton's system [2] and is an effective oxidant for a wide variety of organic chemicals [3–15]. A recent study has shown its potential for waste water treatment [11].

The generally accepted mechanism for Fenton's reaction is as follows:

$$\cdot OH + RH \rightarrow H_2O + \cdot R \quad (2)$$

$$\cdot R + Fe^{3+} \rightarrow Fe^{2+} + \text{ product} \quad (3)$$

where RH is the reactant with $\cdot OH$ to form a radical $\cdot R$. This radical then reduces $Fe^{3+}$ to $Fe^{2+}$ to continue the catalytic production of $\cdot OH$, Reaction 1. Therefore, regeneration of $Fe^{2+}$ is a prerequisite for the propagation of the catalytic Fenton's reaction. The importance of the effective conversion of $Fe^{3+}$ back to $Fe^{2+}$ also lies in the fact that $Fe^{3+}$ catalyses $H_2O_2$ decomposition to $H_2O$ and $O_2$ [3], thus greatly reducing the oxidation strength of the peroxide.

In Fenton's system, $Fe^{2+}$ is regenerated by reacting with free radicals formed in Reactions 2 and 3 [3]. However, the two major limitations associated with the conventional Fenton's system are: (i) that the regeneration of $Fe^{2+}$ via Reaction 3 is less efficient than electrochemical reduction of $Fe^{3+}$ [4], and (ii) that a continuous supply of $H_2O_2$ is essential. A modified process for generating Fenton's reagent has been reported, in which $H_2O_2$ was electrochemically produced by oxygen reduction at selected cathodes [4]. In this modified Fenton's system, in addition to the electrochemical generation of $H_2O_2$, Reaction 4, the reduction of $Fe^{3+}$ to $Fe^{2+}$ also occurs at the cathode, Reaction 5. That is,

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (4)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (5)$$

This approach, however, requires constant sparging with oxygen. In order to eliminate this requirement, electrolysis is carried out in an undivided flow reactor where oxygen is produced *in situ* by $H_2O$ oxidation at the platinum anode and then reduced downstream to $H_2O_2$ at a reticulated vitreous carbon (RVC) cathode. Chlorobenzene and phenol have been selected as model compounds to test the effectiveness of this electrochemically generated Fenton's reagent.

## 2. Experimental details

### 2.1. Apparatus

An EG&G PAR model 173 Potentiostat/Galvanostat and EG&G PAR model 175 Universal programmer were used to control the potential or the current. Optimal conditions for the oxidation of chlorobenzene and phenol by electrochemically generated Fenton's reagent was examined using a three-compartment, three-electrode cell. A two-electrode, undivided packed-bed flow reactor was then used to carry out the electrolysis. The schematic diagram for the flow reactor is shown in Fig. 1. The reactor was constructed of plexiglass with a platinum wire anode upstream and RVC porous cathode (45 pores per 2.54 $cm^2$) downstream. The RVC cathode (1.63 cm diam., 2.54 cm length) had a surface area of 153 $cm^2$. Flow rates were controlled with a Cole–Parmer MasterFlex computerized drive (model 7550-90).

Identification of reaction products was performed with an HPLC system (Spectra–Physics) using a reverse-phase (ODS spheri-5 $\mu$m) 100 mm × 2.1 mm column (Brownlee Labs) with a model SP8800 ternary pump, a model Spectra Chrom 200 programmable wavelength detector, and a model SP4270 integrator. Concentrations were assumed to be a linear function of peak areas under the chromatograms.

### 2.2. Reagents

The solvent $CH_3CN$ was HPLC-grade, and all other chemicals were of analytical reagent grade. Solutions were prepared by distilled-deionized water. The pH of 0.1 M $H_2SO_4$ was adjusted by addition of NaOH.

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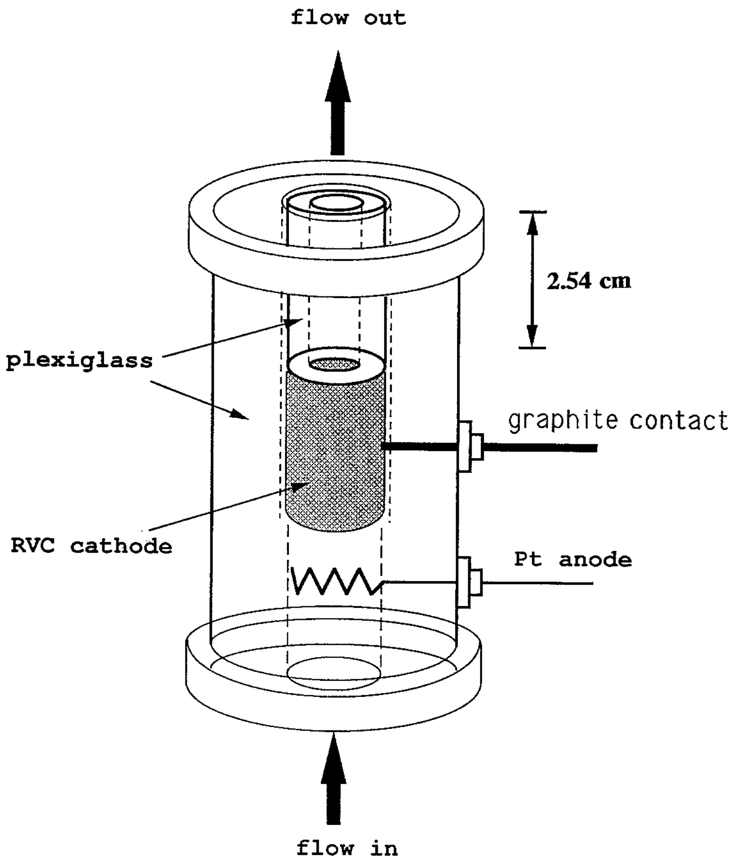

Fig. 1. Schematic diagram of the flow reactor.

### *2.3. Procedure*

Prior to electrolysis, the RVC cathode was washed with chromic-sulphuric acid cleaning solution and rinsed with copious amounts of deionized water. Solutions were maintained at room temperature unless otherwise specified.

A solution pH of 3.8 was chosen for the flow reactor experiments according to the results obtained with the three-compartment electrolysis cell. The solution, which contained 4 mM chlorobenzene (or 1 mM phenol), 5 mM $FeSO_4$ and 0.1 M $Na_2SO_4$, was pumped through the reactor at a flow rate of $50\,cm^3\,min^{-1}$. The reactor was first presaturated with the flowing solution to preclude a concentration decrease due to chlorobenzene (or phenol) adsorption in the reactor system. Electrolysis was at a current density of $0.7\,mA\,cm^{-2}$. The reactor was operated in a recycled mode, and total volume of the stream was $50\,cm^3$. An aliquot of $0.5\,cm^3$ was taken each time for product analysis, which resulted in a total volume of $2.5\,cm^3$ being withdrawn from the reactor for each experiment.

Products of chlorobenzene and phenol oxidation were identified using retention time matching with chromatograms of standard samples. The u.v.-detector was operated at 210 nm for maximum detection sensitivity of chlorobenzene, phenol and some of their products. The composition of the mobile phase was a mixture of $CH_3CN : H_2O$ (60 : 40) for chlorobenzene and its products, and $CH_3CN : H_2O$ (20 : 80) for phenol and its products. The flow rate of the mobile phase was maintained at $0.2\,cm^3\,min^{-1}$ for both chlorobenzene and phenol.

## 3. Results and discussion

As shown in Fig. 1, the solution was pumped into the reactor from below and out the top. This particular configuration offers a novel feature for electrochemical generation of Fenton's reagent, which takes advantage of convective transport of the oxygen generated at the anode followed by electroreduction to $H_2O_2$ at the RVC cathode.

### *3.1. Flow reactor results*

Figure 2 shows the flow reactor results for 4 mM chlorobenzene reacting with electrogenerated Fenton's reagent in the presence of 5 mM $FeSO_4$ at pH 3.8. Curves (a)–(c) show the concentration change of chlorobenzene, *p*-chlorophenol, and phenol, respectively, as a function of time. A 38% decrease in chlorobenzene concentration was obtained within 38 min. Note that the concentrations of both products reached maximum values at $t = 10$ min, indicating that hydroxylation and dehalogenation were not the final steps in the Fenton's reaction. Identification of byproducts was not pursued further.

Figure 3 shows the results of 1 mM phenol reacting with electrochemically generated Fenton's reagent in 5 mM $FeSO_4$ at pH 3.5. The concentration of phenol decreased to 20% of its initial value within

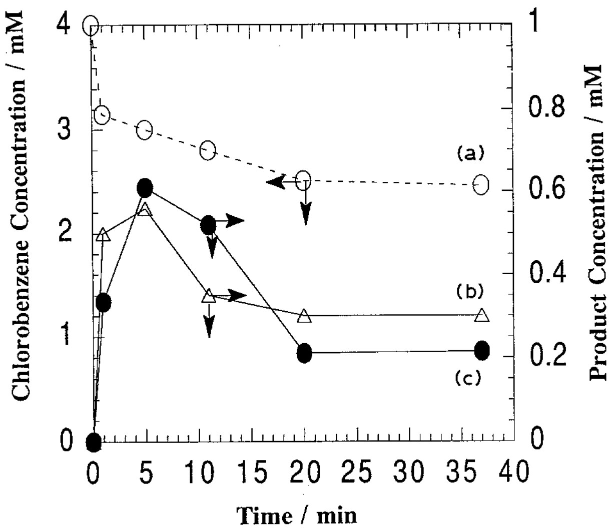

Fig. 2. Flow reactor results of 4 mM chlorobenzene reacting with electrochemically generated Fenton's reagent with 5 mM $FeSO_4$ at pH 3.8. Flow rate: 50 $cm^3 min^{-1}$; current density at RVC: 0.7 $mA cm^{-2}$. (a) Chlorobenzene, (b) *p*-chlorophenol and (c) phenol.

60 min. Three hydroxylated products were catechol (curve a), resorcinol (curve b), and hydroquinone (curve c). Catechol was the dominant product.

### 3.2. Electrochemistry at the Pt anode

Three reactions can occur at the platinum anode:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (6)$$

$$2Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (7)$$

$$\text{Chlorobenzene or phenol} \rightarrow \text{oxidation products} \quad (8)$$

Rapid oxygen evolution was observed. On the other hand, experimental results indicated that direct electrochemical oxidation of either chlorobenzene or phenol, Reaction 8, was negligible at the platinum anode, since virtually no current was obtained under the particular conditions applied here.

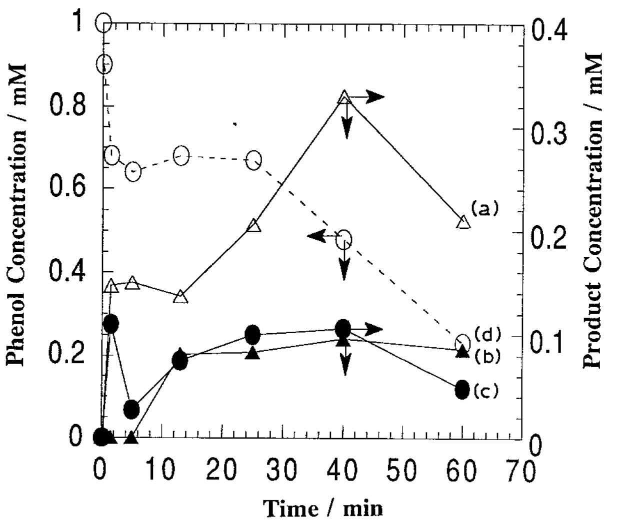

Fig. 3. Flow reactor results of 1 mM phenol reacting with electrochemically generated Fenton's reagent with 5 mM $FeSO_4$ at pH 3.5. Flow rate and current density are the same as in Fig. 2. (a) Catechol, (b) resorcinol, (c) hydroquinone and (d) phenol.

### 3.3. Electrochemistry at the RVC cathode

The $O_2$ and $Fe^{3+}$ formed at the platinum anode were transported to the RVC cathode and reduced to $H_2O_2$ and $Fe^{2+}$, respectively, according to Reactions 4 and 5. Meanwhile, chlorobenzene and phenol can react with $\cdot OH$ formed by Reaction 1 to generate their respective products. Two identified u.v.-active products were *p*-chlorophenol and phenol for chlorobenzene, where phenol is actually the dehalogenated product of chlorobenzene. The solubilities of *p*-chlorophenol and phenol were 54 times and 164 times, respectively, that of chlorobenzene (0.05% v/v in water). The reactions not only reduced the toxicity of chlorobenzene but also converted the contaminant to more water-soluble products. The appreciable increase in product solubility makes this system potentially applicable for waste water treatment. Some products identified for phenol oxidation include hydroquinone, catechol, and resorcinol.

The electrochemical operation mode offers two advantages over the conventional one: (i) regeneration of $Fe^{2+}$ is effectively achieved electrochemically at the RVC cathode, and (ii) constant sparging of the solution with oxygen is not required. This Fenton's system offers a promising method to treat large volumes of aqueous waste streams.

## Acknowledgements

This work received support from the UC Toxic Substance Research & Teaching Program and NSF Biotechnology Program (grant no. BCS 8807418). The authors thank Professor A. K. Cho and Dr W. Li for helpful discussions.

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