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Degradation of chlorophenol by in-situ electrochemically generated oxidant*

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Abstract: A novel in-situ electrochemical oxidation method was applied to the degradation of wastewater containing chlorophenol. Under oxygen sparging, the strong oxidant, hydrogen dioxide, could be in-situ generated through the reduction of oxygen on the surface of the cathode. The removal rate of chlorophenol could be increased 149% when oxygen was induced in the electrochemical cell. The promotion factor was estimated to be about 82.63% according to the pseudo-first-order reaction rate constant (min^{-1}). Important operating parameters such as current density, sparged oxygen rate were investigated. Higher sparged oxygen rate could improve the degradation of chlorophenol. To make full use of oxygen, however, sparged oxygen rate of 0.05 m^3/h was adopted in this work. Oxidation-reduction potential could remarkably affect the generation of hydrogen peroxide. It was found that the removal rate of chlorophenol was not in direct proportion to the applied current density. The optimum current density was 3.5 mA/cm^2 when initial chlorophenol concentration was 100 mg/L and sparged oxygen rate was 0.05 m^3/h.

Key words: In-situ electrochemical oxidation, Chlorophenol, Oxygen, Hydrogen peroxide
Document code: A **CLC number:** TQ150.9; O646.5; X783

INTRODUCTION

With the development of industry, more and more pollutants are discharged into environment, among them, phenolic wastes are typical contaminants considered to be hazardous and top priority toxic pollutants listed by the USEPA. They are toxic even at low concentration. Due to their biorefractory, bioaccumulation and carcinogenic potential, the treatment of these contaminants is very important in environmental protection.

Various technologies and processes have been tried for treating phenolic contaminants. Advanced oxidation processes (AOPs) are attractive methods involving production of the hydroxyl radical (·OH) as a primary oxidant to remove organic matter and to purify water. However, some strong oxidants such as Fenton reagent (Fe^{2+}+H_2O_2) must be added to accelerate the removal of contaminants in AOPs reaction. Moreover, these strong oxidants cannot be generated in the field and easily decompose, which will result in higher treatment cost (Gau and Chang, 1996; Casero *et al.*, 1997).

Recently, advanced electrochemical oxidation processes (AEOPs) have been extensively applied to treat various wastewaters (Comninellis and Nerini, 1995; Wu *et al.*, 2002a; 2002b). They can produce the hydroxyl radicals directly or indirectly by electrode reactions at ambient temperature and atmospheric pressure and provide promising approaches for the prevention of pollution problems. Another

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advantage is their environmental compatibility because the main reagent, the electron, is a “clean reagent”. In addition, they are also attractive because of their versatility for treating various wastewaters, amenability to automation, and high selectivity to prevent the production of unwanted by-products (Juttner *et al*., 2000).

Degradation of phenolic compounds in wastewater is the rather costly part of water treatments. In this work, oxygen was induced in the electrochemical cell. Cheap oxygen was activated and could be reduced to hydrogen peroxide on the surface of the electrode, which has strong oxidation ability. Thus, the strong oxidant could be in-situ yielded. Moreover, in-situ produced hydrogen peroxide is more efficient than that added. The aim of this study was to explore the feasibility of the electrocatalysis process wherein oxygen is sparged. Important operating parameters such as current density and sparged oxygen rate were investigated to determine the optimal values and conditions.

MATERIAL AND METHODES

Apparatus

Electrochemical degradation of 4-chlorophenol was carried out in the electrochemical reactor shown in Fig.1. The anode used here was a *β*-PbO_2 electrode modified with fluorine resin. The details of the anode preparation and the characteristics of the anode are given in Wu and Zhou (2001). The cathode was a Ni-Cr-Ti alloy net concentrically assembled in the reactor with a volume of 1 L. The active area of the electrode was 220 cm^2. The simulated wastewater contained a certain amount of chlorophenol and Na_2SO_4. In every run, oxygen was sparged in suitable quantity into the cathode zone. The wastewater was pumped through the reactor.

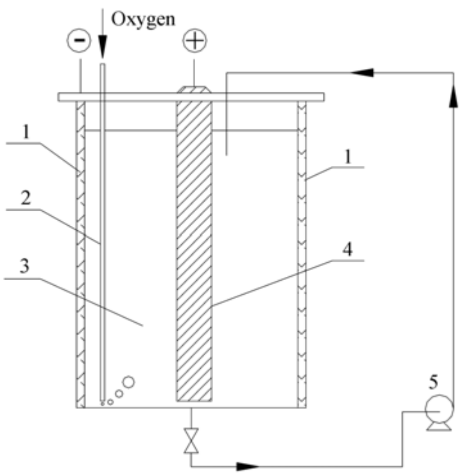


Fig.1 The schematic diagram of electrochemical reactor
1. cathode; 2. oxygen inlet; 3. wastewater; 4. *β*-PbO_2 anode; 5. pump

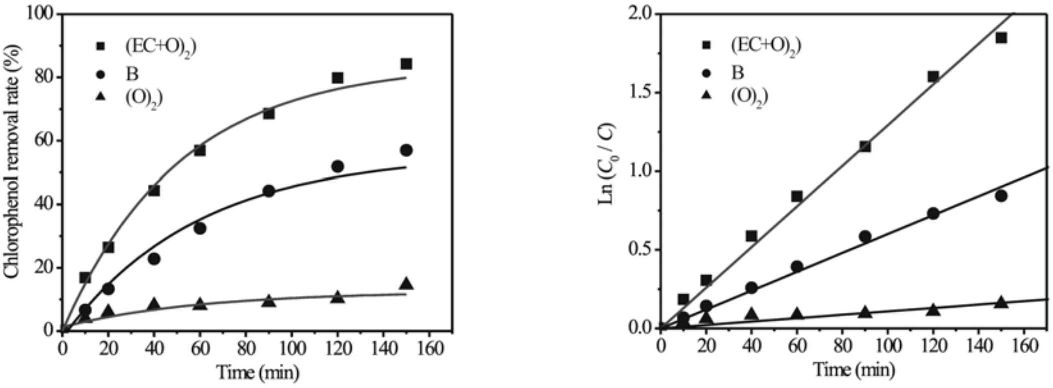
Analysis

The determination of chlorophenol and its stable degradation products were carried out on high-performance liquid chromatograph (HPLC, Gilson) by comparing the retention time of the standard compounds. To determine the concentration of chlorophenol and degradation products, 25 μl aliquots of samples were injected into the HPLC running on mobile phase of acetonitrile / water / concentrated H_3PO_4 (v/v/v) at 45/55/0.2. The separation was performed using an ODS-18 reversed phase column at flow rate of 1.5 ml/min and column temperature of 25 °C. A UV detector was used with the wavelength set at 254 nm. All samples were immediately analyzed to avoid further reaction. Chloride produced was determined by ion chromatography (Techcomp IC 1000) with DS-plus^{TM} auto suppressor (Alltech, USA). The COD (chemical oxygen demand) was measured according to the standard methods for examination of water and wastewater (APHA, etc., 1995). The concentration of H_2O_2 was analyzed by the standard titration method of potassium permanganate.

RESULTS AND DISCUSSIONS

Improvement of electrocatalysis method with oxygen sparged

Oxygen was applied to the treatment of wastewater containing 4-chlorophenol during the electrocatalysis. Fig.2a shows the improvement of chlorophenol removal rate by three processes: electrocatalysis (EC), electrocatalysis with oxygen sparged (EC+O_2) and oxidation by oxygen without electrocatalysis (O_2). Fig.2a shows that chlorophenol degradation rate was notably enhanced in the order EC+O_2> EC > O_2. For instance, after 150 min



(a) (b)

Fig.2 Effect of different processes on the chlorophenol conversion
Operating conditions: initial chlorophenol concentration: 100 mg/L; pH=6; Na_2SO_4 = 5 g/L; current density = 3.5 mA/cm^2; volume =1000 ml, sparged oxygen rate = 0.05 m^3/h.
(a) chlorophenol removal rate of three processes: EC+O_2, EC and O_2;
(b) line fitted by the apparent first-order kinetics

treatment, chlorophenol removal rate by O_2 was only 15%; the rate by EC was about 57%, while it could reach 85% by EC+O_2. This indicated that it was very difficult to oxidize the chlorophenol if only oxygen was applied and that electrocatalysis was the main contributor during the degradation of chlorophenol. When electrocatalysis and oxygen were used together, the removal rate could be increased 149% that of electrocatalysis and 567% that of oxidation by oxygen. This indicated that some strong oxidants could be formed during the electrocatalysis and that oxygen could be activated to generate some stronger oxidants under electrocatalysis. Quantitative titration of $KMnO_4$ indicated that hydrogen peroxide was formed during the electrocatalysis with oxygen sparged. The main reactions on the anode and cathode surfaces are given below.

Anodic reaction:

In the case of anodic polarization, the positive hole of [PbO_2 (h^+)] on the anode react with absorbed water molecules, resulting in hydroxyl radical:

$$PbO_2\ (h^+) + H_2O_{ads} \rightarrow PbO_2\ (OH)_{ads} + H^+$$

Cathodic reaction:

On sparging oxygen, the dissolved oxygen was adsorbed onto the active sites of the cathode and then was reduced to hydrogen peroxide which could generate hydroxyl radical:

$$O_2\ (g) \rightleftharpoons O_2\ (aq)$$

$$O_2\ (aq) \rightleftharpoons O_2\ (ads)$$

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

Therefore, the oxidizing agent could be formed both on the anode and the cathode. The combination of anode and cathode could greatly improve the efficiency of chlorophenol degradation.

To evaluate the feasibility of the in-situ electrochemical degradation process, the kinetics of chlorophenol degradation by the three processes were researched. As shown in Fig.2a, the tendency of chlorophenol degradation could be fitted well by the following apparent first-order kinetics:

$$\ln (c_0/c) = k\,t \qquad (1)$$

where, c_0 and c are the concentrations of chlorophenol at the initial time (mg/L) and at the reaction time t, respectively; k is the pseudo-first-order reaction rate constant (min^{-1}). The k values of the three different processes could be obtained from the data-fitting in Fig.2a. The line fitted according to the Eq.(1) is shown in Fig.2b and the k values are listed in Table 1. The reaction rate constant in the electrocatalysis process with oxygen sparged was $2.16\times10^{-4}s^{-1}$. It was $1.0\times10^{-4}s^{-1}$ and $0.18\times10^{-4}s^{-1}$ for anodic electrocatalysis and oxygen oxidation, respectively. The value of k in electrocatalysis process

Table 1 First-order reaction rate constants by three processes

Processes	k (10^4 s^{-1})
O_2	0.18
Electrocatlysis	1.00
Electrocatalysis + O_2	2.16

with oxygen sparged was much greater than the sum of the value of k in the anodic electrocatalysis and in the oxidation by oxygen without electrocatalysis. The promoting factor (f) was estimated to be about 82.63% using the following definition:

$$f = \frac{k_{EC+O_2} - \left(k_{EC} + k_{O_2}\right)}{k_{EC} + k_{O_2}} \times 100\% \qquad (2)$$

This result is consistent with the analysis given above. Therefore, in-situ electrochemical degradation of chlorophenol is superior to the single electrocatalysis or the oxidation by oxygen.

Intermediates of degradation

The main intermediates of degradation were benzoquinone, hydroquinone, fumaric acid and oxalic acid. Fig.3 shows the concentration of chlorophenol, benzoquinone and organic acids during the electrochemical degradation. It is well known that benzoquinone is one of the rather persistent intermediates very difficult to degrade (Tahar and Savall, 1998). The toxicity of wastewater mainly depended on the concentration of chlorophenol and benzoquinone formed. Fig.3 shows that benzoquinone concentration reached the maximum after 40 min degradation, and then slowly decreased with time. The maximum concentration of benzoquinone was less than 0.05 mmol/L and it was less than one-tenth of the concentration of the initial chlorophenol concentration. Organic acids have less toxicity and can be degraded by biological methods. Thus the toxicity of wastewater would be enormously decreased after 100 min treatment. Considering the economy, it was not necessary to degrade chlorophenol to CO_2 and H_2O. This was discussed in detail in our previous work (Wu and Zou, 2001). Therefore, partial degradation of chlorophenol is feasible for practical application.

Effect of sparged oxygen rate

Fig.4 of the effect of sparged oxygen rate on chlorophenol degradation shows that chlorophenol removal rate was improved with the enhancement of sparged oxygen rate. At 150 min, chlorophenol removal rate was only 67% at sparged oxygen rate of 0.04 m^3/h, while it was around 92% at sparged oxygen rate of 0.075 m^3/h. The enhancement was about 137%. However, it is not advisable to adopt too high sparged oxygen rate. Fig.4 shows that the removal rate reached 92% at 150 min when sparged oxygen rate was 0.075 m^3/h. That is to say, the removal rate would have less enhancement with the increase of sparged oxygen rate. If sparged oxygen

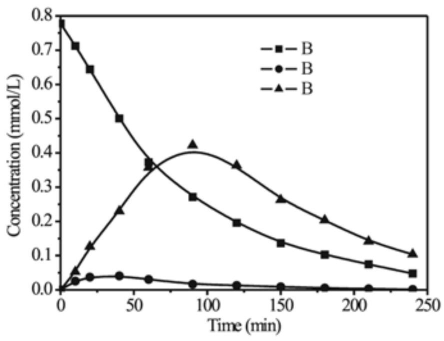


Fig.3 Degradation of chloropohenol
Operating conditions: initial chlorophenol concentration: 100 mg/L; pH=6; Na_2SO_4 = 5 g/L; current density = 3.5 mA/cm^2; volume =1000 ml

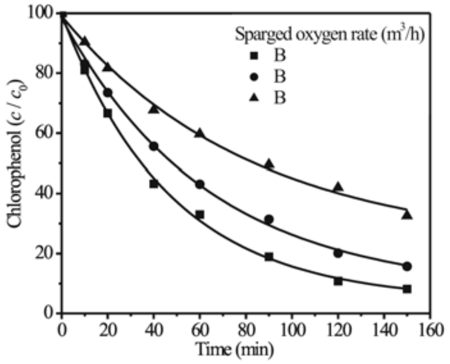


Fig.4 Effect of sparged oxygen rate on the chlorophenol degradation
Operating conditions: initial chlorophenol concentration: 100 mg/L; pH=6; Na_2SO_4 = 5 g/L; current density = 3.5 mA/cm^2; volume =1000 ml

rate was increased continually, some oxygen would escape and would not be reduced to hydrogen peroxide, the important oxidant. Thus oxygen would not be sufficiently utilized. Therefore, a suitable sparged oxygen rate is suggested in the in-situ electrochemical degradation of chlorophenol.

Effect of current density

Fig.5 of the effect of current density on the chlorophenol degradation shows that chlorophenol removal rate was not in direct proportion to current density, which had an optimum value during the degradation of chlorophenol. Under the experimental conditions given in Fig.5, chlorophenol removal efficiency was increased with the enhancement of current density and reached the maximum of 85% when current density was 3.5 mA/cm^2. However, the removal efficiency began to decrease when current density was enhanced continuously. This could be due to the fact that oxidation-reduction potential could remarkably affect the generation of hydrogen peroxide. H_2 evolution occurs as a possible side reaction when the current density exceeds the transport limited value of O_2 reduction. Therefore, too high or too low oxidation-reduction potential is disadvantageous for generation of hydrogen peroxide. Optimal current density is very important for achieving maximal removal rate of contaminants.

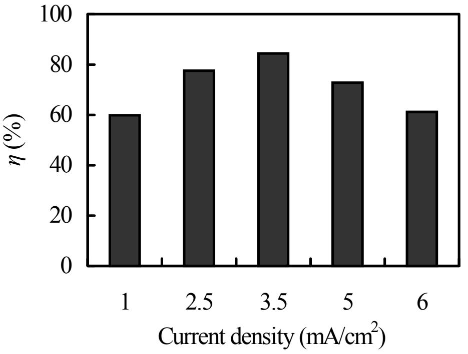


Fig.5 Effect of current density on chloropohenol removal
Operating conditions: initial chlorophenol concentration=100 mg/L; pH=6; Na_2SO_4=5 g/L; volume=1000 ml; sparged oxygen rate=0.05 m^3/h

CONCLUSIONS

An in-situ electrochemical method was applied to the degradation of chlorophenol in wastewater. Under suitable conditions, strong oxidant, hydrogen peroxide, could be in-situ generated through the reduction of oxygen on the surface of the cathode. It was found that the removal rate could be increased 149% that by electrocatalysis and 567% that by oxygen oxidation when oxygen was induced into the electrochemical cell. The promoting factor was calculated to be about 82.63% according to the pseudo-first-order reaction rate constant. Hydrogen peroxide was detected in the cathode zone. In-situ electrochemical degradation of chlorophenol was superior to that by electrocatalysis alone or by oxygen.

The main intermediates of degradation were benzoquinone, hydroquinone, fumaric acid and oxalic acid. During the degradation, chlorophenol and benzoquinone could be degraded rapidly to organic acids that could be removed by the economical biological method. Considering the economy, partial degradation of chlorophenol is suggested.

It is very important to operate under suitable conditions to make the main reactions occur in harmony on the surface of the anode and cathode. Higher sparged oxygen rate was helpful for degradation of chlorophenol. However, the capacity of oxygen reduction on the cathode was finite; it is not appropriate to adopt too high sparged oxygen rate. A suitable sparged oxygen rate is suggested. It was found that chlorophenol removal rate was not in direct proportion to current density, which has an optimum value during the degradation of chlorophenol. Oxidation-reduction potential can remarkably affect the generation of hydrogen peroxide. An appropriate current density is very important for achieving higher removal rate of contaminants.

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