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Dechlorination by combined electrochemical reduction and oxidation*

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Abstract: Chlorophenols are typical priority pollutants listed by USEPA (U.S. Environmental Protection Agency). The removal of chlorophenol could be carried out by a combination of electrochemical reduction and oxidation method. Results showed that it was feasible to degrade contaminants containing chlorine atoms by electrochemical reduction to form phenol, which was further degraded on the anode by electrochemical oxidation. Chlorophenol removal rate was more than 90% by the combined electrochemical reduction and oxidation at current of 6 mA and pH 6. The hydrogen atom is a powerful reducing agent that reductively dechlorinates chlorophenols. The instantaneous current efficiency was calculated and the results indicated that cathodic reduction was the main contributor to the degradation of chlorophenol.

Key words: Electrochemical reduction, Electrochemical oxidation, Dechlorination, Combined process
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INTRODUCTION

Chlorinated phenols compounds used widely in industry were intentionally or inadvertently released into environment in large quantities. These chlorinated aromatic compounds have strong resistance to physical, chemical and biological treatments and have been listed as a priority pollutant by the U.S. Environmental Protection Agency (Lin and Tseng, 1999). Wastewater containing chlorophenols has malodorous odor, high toxicity, bioaccumulation and carcinogenic potential. As the accumulation of chlorinated aromatic compounds in the environment has become a serious problem nowadays, it is very urgent to develop effective method to treat these contaminants.

Traditional treatment processes such as biological treatments were not very effective for degradation of chlorinated phenols. Recently, advanced oxidation processes (AOPs) have attracted much attention as they can be used to effectively treat wastewater containing chlorophenols. Electrochemical methods for degrading chlorophenol compounds have been widely studied (Brillas *et al*., 1995; Tahar and Savall, 1998; Houk *et al*., 1998; Polcaro *et al*., 1999; Cong *et al*., 2004).

The electrochemical reduction approach was suggested in the 1970s as a promising method for detoxification of chlorine-containing aromatic hydrocarbons. This method ensured the selective removal of chlorine atoms from various chloroaromatics under mild experimental conditions without using the highly reactive reducing agents (Huang and Rusling, 1995; Tsyganok *et al*., 1999). Reductive dechlorination promoted by zero-valent metals has been a very active research area (Zhang *et al*., 2001; Cheng and Wu, 2001). However, metal catalyst fouling by some oxide precipitates was a problem, which decreased the effectiveness of the catalyst over time (Li and Farrell, 2000). Most reductive approaches focus on the removal of chlorine atoms from the aromatic structure but no further measures were applied simultaneously to treat the organics after the dechlorination.

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Electrochemical oxidation has also been used for the treatment of chlorinated compounds. Some high oxygen over-potential anodes have shown potential for rapid oxidation of organics (Comninellis and Pulgarin, 1993; Wu *et al.*, 2002a). Hydroxyl radicals formed in the process of oxidation are very powerful oxidizing agents that can open the aromatic nucleus of chlorinated compounds and bring out the chlorinated aliphatic intermediates (Oturan *et al.*, 2001). It is well known that most chlorinated compounds are toxic due to the chlorine contained in their structure. Therefore, the toxicity of intermediates containing chlorine might not decrease or even increase.

The objective of this study was to probe the feasibility of using a combination process of reduction and oxidation and to develop an effective and friendly method for treating contaminants in chlorine compounds. Simulated wastewater containing chlorophenols was introduced into cathodic region where the chlorine atoms of chlorophenols were removed from the aromatic structure and chlorophenols were reduced to non-chlorinated intermediates. Then the wastewater from the cathodic region was introduced into anodic region where the non-chlorinated intermediates were oxidized and degraded.

MATERIAL AND METHODE

Experimental apparatus

Simulated wastewater containing a certain concentration chlorophenols and supporting electrolyte of Na_2SO_4 was circulated between electrolytic cell and reservoir by a circulating pump. The electrolytic cell was divided into three sections. First, the wastewater was slowly pumped into the cathodic region for reduction reaction, then passed through the middle part for homogenization and entered the anodic region for oxidation reaction. The anode used was carbon, and the cathode was porous nickel with effective area of 5 cm^2.

Analysis

The determination of chlorophenol and its stable degradation products were carried out on high-performance liquid chromatography (HPLC, Gilson) by comparison with the retention time of the standard compounds. Aliquots of 25 μl were injected into the HPLC to determine the concentration of chlorophenol and degradation products, running with mobile phase of acetonitrile/water/concentrated H_3PO_4 (v/v/v) at 45/55/0.2. The separation was performed using an ODS-C18 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.

RESULT AND DISCUSSION

Intermediate comparison of chlorophenol degradation by single electrochemical reduction and single oxidation

A systematic comparison of chlorophenol degradation was carried out between the single electrochemical reduction and the single electrochemical oxidation. Fig.1 shows the typical chromatograms of chlorophenol degradation. HPLC analysis and comparison of the retention times of the peaks with retention times of standard samples expected to appear in the chlorophenol degradation intermediates identified the six major intermediates listed in Table 1.

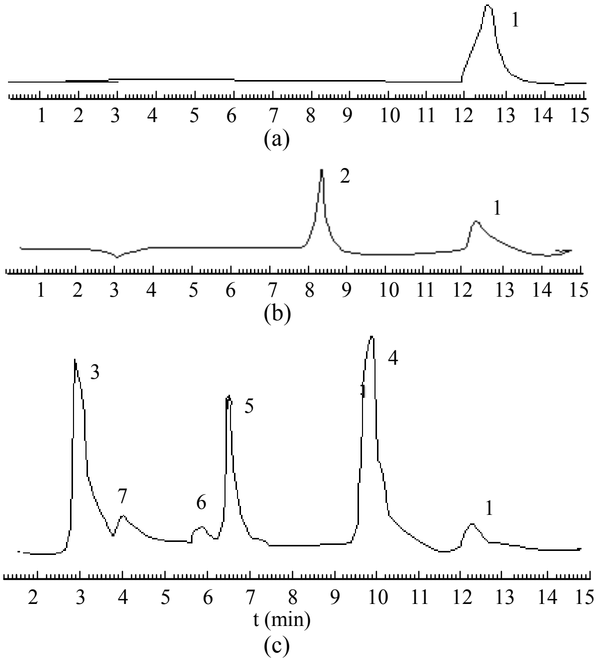


Fig.1 Chromatogram of degradation by single electrochemical reduction and oxidation (a) The initial 2-chlorophenol; (b) Treatment by the single electrochemical reduction; (c) Treatment by the single electrochemical oxidation

Table 1 Identification of 2-chlorophenol degradation intermediates

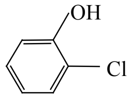
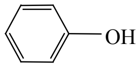
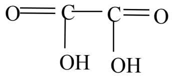
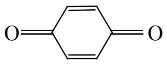
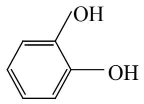
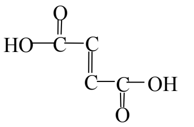
HPLC peaks	Identification	Chemical structure
1	2-chlorophenol	
2	Phenol	
3	Oxalic acid	 $O{=}C(OH){-}C(OH){=}O$
4	Intermediate containing chlorine atom (unidentified)	R-Cl
5	Benzoquinone	
6	Catechol	
7	Fumaric acid	 $HO{-}C({=}O){-}C{=}C{-}C({=}O){-}OH$

Fig.1b shows that there was only phenol intermediate during the degradation of chlorophenol by the single electrochemical reduction. That is to say, 2-chlorophenol was degraded to phenol and no other intermediates were generated. The chlorophenol intermediate obtained by the single electrochemical reduction was quite simple, but there were many intermediates during the degradation of chlorophenol by single electrochemical oxidation. Fig.1c and Table 1 show that benzoquinone, catechol, organic acids and a chlorinated intermediate were produced during the oxidation of chlorophenol. Apparently the intermediates were much more complicated by the electrochemical oxidation than by the electrochemical reduction. This observation result was similar to that of other investigations by the electrochemical oxidation methods. Hirvonen *et al.*(2000) noticed that chlorophenols could be treated efficiently, but the dechlorination of the compounds was insufficient. Hydroxylation of chlorophenols and the formation of dimeric products were involved in the oxidation of chlorophenols. Other investigators also detected the complex intermediates including those containing the chlorine during the degradation of chlorophenols by oxidation method (Mylonas and Papaconstantinou, 1996; Antonaraki *et al.*, 2002). The presence of a complex mixture of intermediates suggested that the toxicity of wastewater could not be but might even be increased.

Fig.1 shows that phenol was generated by the electrochemical reduction, but no phenol peak was observed under electrochemical oxidation. On the other hand, benzoquinone, organic acids and intermediate containing chlorine were detected by electrochemical oxidation and they did not occur during electrochemical reduction. In view of the two cases, it may be better to remove the chlorine atom from the benzene ring and degrade chlorophenol to phenol through electrochemical reduction as the phenol produced during electrochemical reduction can be degraded easily by electrochemical oxidation. Through the combination of reduction and oxidation, chlorophenol can be removed efficiently. Therefore, it is feasible to degrade contaminants containing chlorine by electrochemical reduction before electrochemical oxidation.

Chlorophenol degradation by single electrochemical reduction

Fig.2 shows the removal of 2-chlorophenol and its intermediate by electrochemical reduction. From Fig.2, it can be seen that the removal rate of 2-chlorophenol was nearly 90% in 5 h under 6 mA current. The concentration of intermediate increased

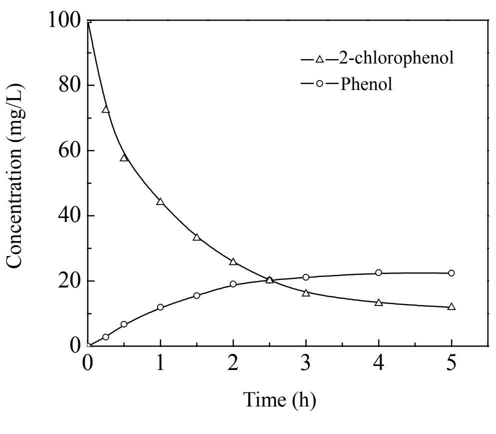


Fig.2 Chlorophenol degradation by electrochemical reduction
Operating conditions: initial 2-chlorophenol concentration 100 mg/L; pH 6; Na_2SO_4 5 g/L; current 6 mA; volume 60 ml

with time and the tendency to increase slowed down after 3 h. This indicated that 2-chlorophenol can be degraded rapidly by electrochemical reduction dechlorination. However, the concentration of intermediate phenol was maintained at certain level and did not decrease in 5 h. This means that it was difficult to degrade the intermediate phenol by the single electrochemical reduction method. More time might be necessary to degrade chlorophenol, while it would not be possible for phenol to be degraded if only electrochemical reduction was used.

Chlorophenol degradation by electrochemical oxidation

Fig.3 showed the concentration of 2-chlorophenol and its intermediates during chlorophenol degradation by the electrochemical oxidation method. Fig.3 shows that the removal rate of 2-chlorophenol was only 60% in 5 h under 6 mA current by the electrochemical oxidation method. The concentration of benzoquinone increased in the first 3 h and then began to decrease with time. The concentration of organic acid increased with time and the removal rate tended to slow down in 5 h. This indicated that benzoquinone formed was further oxidized and turned to organic acids. Comparison of Fig.2 and Fig.3 shows that the removal rate of chlorophenol by electrochemical reduction and by oxidation was different. The removal rate could reach 90% in 5 h by electrochemical reduction, but was only 60% by electrochemical oxidation in the same time duration. This result accorded with the fact that cathodic reduction was mainly used to simply reduce chlorophenol to phenol and anodic oxidation was mainly used to oxidize phenol and chlorophenol to their further products.

Chlorophenol degradation by the combination of reduction and oxidation

Chlorophenol degradation by the combination of reduction and oxidation is shown in Fig.4 showing that chlorophenol can be degraded more than 90% in 5 h. According to Figs.2, 3 and 4, it was obvious that the effect of chlorophenol degradation by the combination of reduction and oxidation was better than the single electrochemical reduction or oxidation. This further confirmed that high degradation efficiency could be achieved by the combination of reduction and oxidation discussed above.

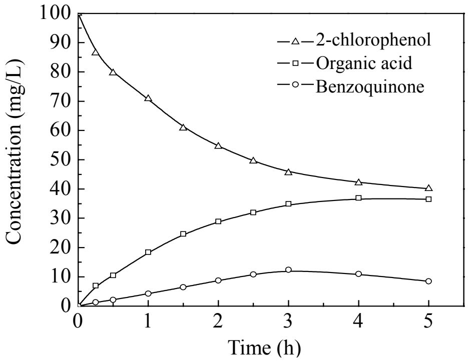


Fig.3 Chlorophenol degradation by electrochemical oxidation

Operating conditions: initial 2-chlorophenol concentration 100 mg/L; pH 6; Na_2SO_4 5 g/L; current 6 mA; volume 60 ml

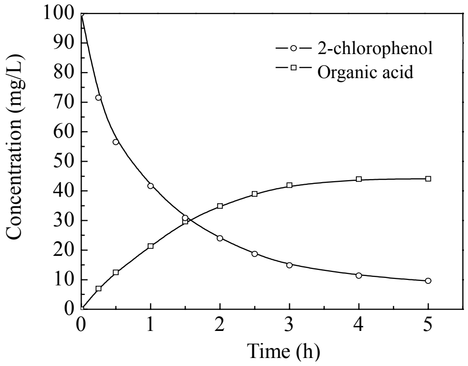


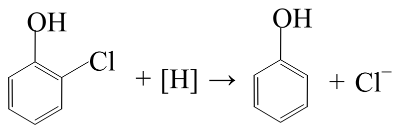
Fig.4 Chlorophenol degradation by combination of reduction and oxidation

Operating conditions: initial 2-chlorophenol concentration 100 mg/L; pH 6; Na_2SO_4 5 g/L; current 6 mA; volume 60 ml

Current efficiency

The electrochemical mechanism of dechlorination of chlorophenol was proposed in our previous work (Wu *et al.*, 2002b). Hydrogen atom played a key role in the dechlorination of chlorophenols. The atomic hydrogen was formed on the surface of the nickel cathode and could mediate the reduction of the chlorinated compounds.

$$H^+ + e \rightarrow [H]$$



The current efficiency for the degradation of CP could be calculated using the following Eq.(1):

$$CE=\frac{N}{N_0}\times 100\%=\frac{nVF}{I}\times\frac{C_t-C_{t+\Delta t}}{\Delta t}\times 100\% \quad (1)$$

where N is the number of electrons used for degrading chlorophenol (mol/(s·cm^2)), N_0 is the total electron numbers per electrode area per time supplied by power source (mol/(s·cm^2)), n is the number of electrons required for degrading one mole chlorophenol (here it was 1), V is the volume of wastewater of chlorophenol (L), I is the current (A), t is the reaction time (s), F is the Faraday constant (96480 C), C_t and $C_{t+\Delta t}$ are the concentration of chlorophenol at the reaction time t and Δt, respectively.

Table 2 lists the current efficiency of anodic oxidation, cathodic reduction and their combination process calculated according to the Eq.(1). Table 2 shows that cathodic reduction had a higher current efficiency than anodic oxidation at the identical time span of degradation. The efficiency of the combination process was higher than that of anodic oxidation and was close to that of cathodic reduction alone. These results show that cathodic reduction made a large contribution to the degradation of chlorophenol. However, the current efficiency decreased very rapidly with time. Comparison of Figs.2, 3 and 4 shows that the concentration of chlorophenol decreased after 3 h degradation, while the concentration of organic acids was still high after 5 h. In fact, low toxicity organic acids can be degraded by the economical biological method. Therefore, it is not advisable to completely degrade chlorophenol to CO_2 and H_2O. The detailed discussion was given in our previous work (Wu and Zhou, 2001) which suggested partial degradation.

Table 2 Current Efficiency of 2-Chlorophenol Degradation

Time (h)	*CE* (%)		
	Anodic oxidation η (%)	Cathodic reduction η (%)	Combination of reduction and oxidation η (%)
0	–	–	–
0.25	11.27	23.04	23.77
0.5	5.70	12.38	12.49
1.0	3.67	5.58	6.19
1.5	4.20	4.56	4.52
2.0	2.61	3.13	2.86
2.5	2.08	2.32	2.20
3.0	1.67	1.68	1.60
4.0	0.71	0.60	0.73
5.0	0.41	0.27	0.37

CONCLUSION

Anodic oxidation, cathodic reduction and the combined process of reduction and oxidation were used to degrade the wastewater of chlorophenol. Results indicated that the combination of electrochemical reduction and oxidation was better than single reduction and single oxidation for the degradation of chlorophenol and intermediates. More than 90% chlorophenol could be degraded in 5 h. Cathodic reduction had better effect on the degradation of chlorophenol than anodic oxidation. Hydrogen atoms played an important role in reducing chlorophenol. It was found that cathodic reduction had higher current efficiency than anodic oxidation. Results showed that the energy cost of anodic oxidation was greater than that of cathodic reduction. Cathodic reduction was the main contributor to the degradation of chlorophenol. The combination of electrochemical reduction and oxidation was effective and feasible method for degrading contaminants containing chlorine.

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