

Comparative study on electrochemical 4-chlorophenol degradation in different diaphragm systems with combined reduction and oxidation properties

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ABSTRACT

Two diaphragm electrolysis systems, two-electrode (anode–cathode) and three-electrode (cathode–anode–cathode), were compared for the electrochemical degradation of 4-chlorophenol. The performance of these systems was improved by feeding with hydrogen gas and then with air, in aid of the combined processes of reduction and oxidation. The 4-chlorophenol degradation, dechlorination, and total organic carbon removal were monitored to characterize the difference between the two systems. The results indicated that the three-electrode system exhibited higher degradation percentages for 4-chlorophenol compared with that of the two-electrode system. The dechlorination property of the three-electrode system was stronger than that of the two-electrode system. In addition, the total organic carbon removal percentage of the anodic compartment in the three-electrode system was higher than that of the two-electrode system. The three-electrode system showed excellent treatment properties for 4-chlorophenol.

Key words | chlorophenols, combined process, diaphragm system, Pd/graphene gas-diffusion cathode

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INTRODUCTION

Chlorophenols are one of the toxic organic compounds listed by the US Environmental Protection Agency as priority pollutants (Lin & Tseng 1999). They are mainly leaked into the environment during the manufacture of various products such as pesticides, pharmaceuticals and dyes, and through the chlorination of municipal waters and the degradation of other chemicals. Their resistance to degradation and the toxicity of chlorophenols increase with the number of chlorine substituents (Christoforidis *et al.* 2010). As the accumulation of chlorophenols in the environment has become a serious problem, it is essential to develop an effective method to degrade these contaminants.

However, traditional treatment processes, such as biological treatments, are not very effective for the degradation of chlorophenols. Therefore, more efficient electrochemical oxidation has attracted considerable attention when it is used to effectively treat wastewater-containing chlorophenols, due to its ease of control, amenability to automation, high efficiency and environmental compatibility (Comninellis 1994). In the electrolysis system, wastewater could be treated by anodic oxidation (Liu *et al.*

2013). At present, dimensionally stable anodes, which are typically prepared by thermal deposition of a thin layer of metal oxide on a base metal, have been used for the oxidation of chlorophenols (Chu *et al.* 2012). However, electrochemical oxidation usually opens the aromatic nucleus of chlorinated compounds and then forms chlorinated aliphatic intermediates (Hirvonen *et al.* 2000). The accumulation of chlorinated intermediates may be even more toxic than their parent compounds (Brinzila *et al.* 2013). In addition, an electrochemical reductive approach to gain exhaustive dechlorination of chlorinated aromatic compounds was disclosed in the 1970s. This approach ensured the selective removal of chlorine atoms from various chlorinated aromatic compounds under mild conditions (Lin & Tseng 2000). Electrochemical reduction could be increased by using carbon materials as the cathodes, such as carbon/polytetrafluoroethylene (Harrington & Pletcher 1999), carbon nanotubes (Murugesan *et al.* 2011), graphite (Do & Chen 1994), carbon felt (Oturán *et al.* 2011), and reticulated vitreous carbon (De Leon & Pletcher 1995). Since graphene was fabricated successfully

in 2004 (Novoselov *et al.* 2004), it has been widely applied in the field of electrochemistry because of its unique properties. However, most electrochemical reductive studies focus on the removal of chlorine atoms from the aromatic structure without further processes being applied simultaneously to treat the organic intermediates. Therefore, an effective and environmentally friendly method has been developed to treat contaminants of chloride compounds by using a combination process of electrochemical reduction and oxidation (Pang *et al.* 2013).

Electrochemical systems have many types, such as column type and box type. Uchibori *et al.* (2010) used the column type electrochemical system to treat high turbidity wastewater. However, researchers prefer to use the box type electrochemical system, which includes two or more electrodes. Recently, some researchers have used the combination process of electrochemical reduction and oxidation to degrade chlorinated organic pollutants in the two-electrode diaphragm system (Wang *et al.* 2010).

In this paper, a three-electrode (cathode–anode–cathode) diaphragm system was designed and investigated for the degradation of 4-chlorophenol compared with the reported two-electrode (anode–cathode) diaphragm system. Prepared Pd/graphene gas-diffusion cathode and Ti/IrO₂/RuO₂ anode were constructed in the systems. In the cathodic compartment, the chlorine atoms were released from chlorophenols and formed non-chlorinated intermediates, which were further oxidized and degraded in the anodic compartment and the cathodic compartment.

METHODS

Preparation of Pd/graphene gas-diffusion cathodes

Pd/graphene catalysts with a Pd load of 1.0 wt% were prepared by sodium borohydride reduction, and characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, and cyclic voltammetry (CV). In the catalyst, Pd particles with an average diameter size of 4.5 nm were highly dispersed in the graphene with an amorphous structure. The Pd/graphene gas-diffusion cathodes were prepared according to the reported procedure (Wang *et al.* 2012).

Procedures

According to the two-electrode diaphragm system (anodic single and cathodic single) (Wang *et al.* 2010), the three-

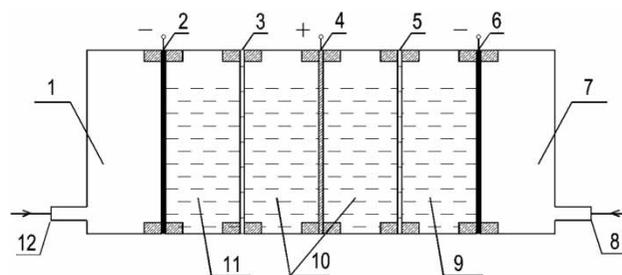


Figure 1 | Schematic diagram of apparatus in the three-electrode system 1,7. Gas compartment; 2,6. Pd/graphene gas-diffusion cathode (cathodic 1 and cathodic 2); 3,5. Diaphragm; 4. Ti/IrO₂/RuO₂ anode; 8,12. Sparged-gas setup; 9,11. Cathodic compartment 1 and cathodic compartment 2; 10. Anodic compartment.

electrode diaphragm system (anodic, cathodic 1, and cathodic 2) (Figure 1) was designed and made (Beijing Plexiglass Plant, Beijing, China). The diaphragm system was made with plexiglass and comprised cathodic compartment, anodic compartment, gas compartment, air intake, cathode, anode, board, diaphragm. A Ti/RuO₂/IrO₂ electrode (Wuhan Kaida Technology Engineering Co., Ltd, Wuhan, China) was used as the anode, a Pd/graphene gas-diffusion electrode as the cathode, and polyester fabric (Tangshan Fengrun Jinxiang Chemical Fiber Co., Ltd, Tangshan, China) as the diaphragm; the distance between the electrodes was 2 cm. Electrolysis was conducted in the three-electrode diaphragm system of 100 mL. A laboratory direct current power supply with current–voltage monitor (GD1791 Guodian Ya Guang Power Technology (BJ) Co., Ltd, Beijing, China) was employed to provide electric power. Synthetic wastewater was used. The initial concentration of 4-chlorophenol was 100 mg L⁻¹. The current density was 45 mA cm⁻²; the concentration of the supporting electrolyte (Na₂SO₄) was 0.03 mol L⁻¹; the initial pH was 7.0. Before the experiment started, hydrogen gas feeding took place for 5 min in order to maintain dissolved gas saturation, and the rate of gas feeding was 25 mL s⁻¹. Hydrogen gas was fed into the gas compartment during 0–60 min electrolysis. After 60 min electrolysis, air was fed into the gas compartment, and electrolysis was carried out at room temperature.

Analysis methods

The determination of the concentration of 4-chlorophenol was carried out using a high-performance liquid chromatograph (HPLC, Shimadzu, Japan) with a column of Zntertsil ODS-SP C18 (250 mm × 4.6 mm, 5 μm). The mobile phase is a mixture of methanol and water (80/20v/v) with a flow rate of 1.0 mL min⁻¹. A UV detector was used with the wavelength of 280 nm. Total organic carbon (TOC) was detected with an

Elementar High TOC analyzer, Kyoto, Japan. The concentration of chloride ions in the reaction solution was determined using an ion chromatograph (ICS-3000, Dionex, California, USA). The H_2O_2 concentration accumulated during electrolysis was determined by titration with permanganate using a standard procedure. All data are the averages from three parallel experiments.

RESULTS AND DISCUSSION

Degradation percentage

The degradation percentage of 4-chlorophenol in the three-electrode system compared with that in the two-electrode system is shown in Figure 2. The degradation percentage of 4-chlorophenol in different systems increased gradually with electrolysis time. In the initial 60 min, the removal percentage of 4-chlorophenol was notably enhanced by feeding hydrogen gas into the two systems. This trend is attributed to the fact that the hydrogen atom is a powerful reducing agent that reductively dechlorinates chlorophenols. After 120 min, the degradation percentages in cathodic compartment 1, cathodic compartment 2, and the anodic compartment of the three-electrode system were 94.8, 94.9, and 94.6%, respectively, while the degradation percentage of the cathodic compartment and the anodic compartment in the two-electrode system were 91.9 and 91.0%, respectively. The results indicated that the three-electrode systems exhibited higher degradation

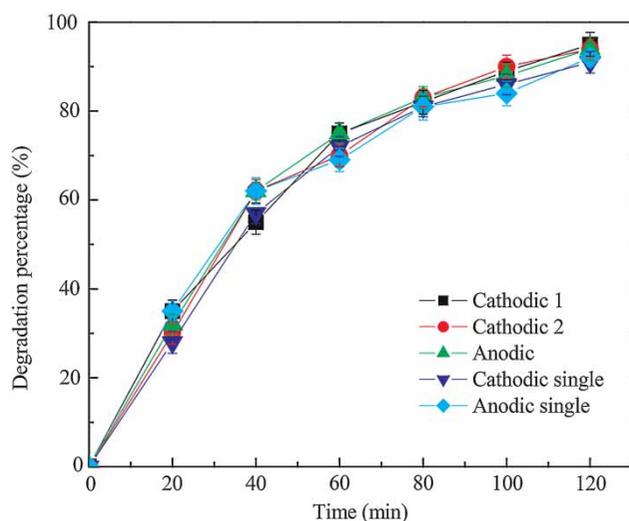


Figure 2 | Degradation percentage of different cells.

percentages for 4-chlorophenol compared with that of the two-electrode system.

TOC removal percentage

The TOC removal percentage in the three-electrode system compared with that in the two-electrode system is shown in Figure 3. The concentration of TOC in different cells decreased gradually with the electrolysis time. In the initial 60 min, TOC removal of the cathodic compartment increased slightly with prolonged electrolysis time in the two systems. This was attributed to no notable H_2O_2 formation during the feeding of hydrogen gas. After 60 min, air was used for feeding instead of hydrogen gas, and TOC removal in cathodic compartment markedly increased. The TOC removal percentages in cathodic compartment 1, cathodic compartment 2, and the anodic compartment of the three-electrode diaphragm cell reached 93.0%, 92.4%, and 90.3%, respectively. While the TOC removal percentage of the cathodic compartment and the anodic compartment in the two-electrode system reached 89.7 and 85.3%, respectively. In addition, TOC concentrations in the anodic compartments decreased steeply in the initial 40 min. It was believed that the degradation of aromatic compounds in the anodic compartment was supposed to be oxidized by $\text{MO}_x(\text{OH})$ or MO_{x+1} produced on the anode surface. In the three-electrode system, the TOC removal percentage was higher than that of the two-electrode system in the anodic compartment, due to the oxidation of the anode promoted by one or more cathodes. This is one of the advantages of the three-electrode system.

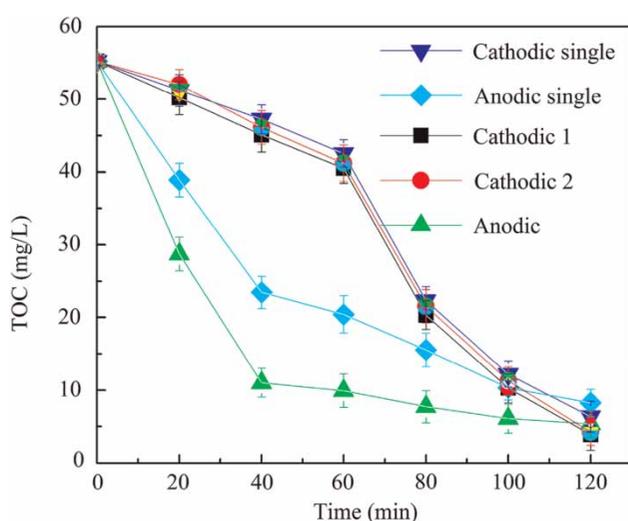


Figure 3 | Variation of TOC concentration with the electrolysis time.

Dechlorination degree

The dechlorination degree of 4-chlorophenol in the three-electrode system compared with that in the two-electrode system is shown in Figure 4. In the initial 60 min, the concentration of the chloride ion in the anodic compartment increased gradually with electrolysis time and was significantly higher than the cathodic compartments. It indicated that hydrogen gas feeding promoted the reductive dechlorination of 4-chlorophenol and the chloride ion generated by cathodic reduction entered the anode compartment due to the electric field effect. Then, the concentration of the chloride ions began to decrease slightly, which indicated that chloride ions were gradually oxidized to generate Cl_2 and released from the system. The same trend could be observed in the cathodic compartment. In the three-electrode system, the dechlorination percentage of 4-chlorophenol could reach 93.7% and higher than the 90.2% in the two-electrode system. Hence, using the three-electrode system could promote the dechlorination degree of 4-chlorophenol.

Degradation mechanism of 4-chlorophenol

The degradation mechanism of 4-chlorophenol in the cathodic compartment was described by the following equations (Wang *et al.* 2010).

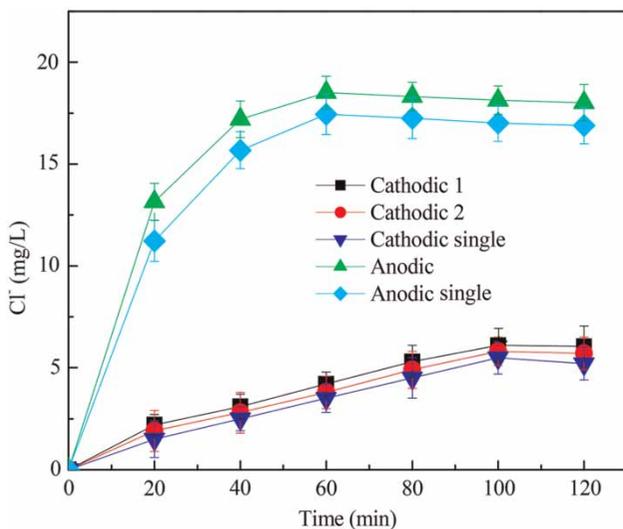
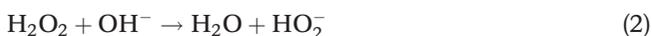
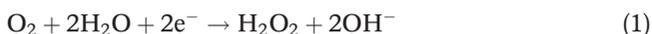


Figure 4 | Variation of the chloride ion concentration with the electrolysis time.



Figure 5 shows the variation of accumulated H_2O_2 concentration with the electrolysis time. In the initial 60 min, there was no measurable H_2O_2 in the cathodic compartments under the present monitoring system. It could be that there was no H_2O_2 formation during hydrogen gas feeding due to the absence of dissolved oxygen. After 60 min, the concentration of H_2O_2 increased gradually with the electrolysis time. It was obvious that the electrodes catalyzed the two-electron reduction of O_2 to H_2O_2 with air feeding. The concentration of H_2O_2 gradually increased and reached a platform (28.0 and 27.5 mg L^{-1} for the cathodic compartments of the three-electrode system; 20.0 mg L^{-1} for that of the two-electrode system). H_2O_2 could transfer to HO^\bullet and $\text{O}_2^{\bullet-}$ which can oxidize the 4-chlorophenol and its degraded intermediates to CO_2 and H_2O . Hence, the higher H_2O_2 concentration in the three-electrode system showed excellent oxidation and degradation properties compared with the two-electrode system.

CONCLUSIONS

Two types of diaphragm electrolysis system (using self-made Pd/graphene gas-diffusion electrodes as the cathodes and a Ti/RuO₂/IrO₂ electrode as the anode) were compared to degrade 4-chlorophenol in aid of a combined process of reduction and oxidation. Some electrolysis effects, such as degradation, dechlorination, and TOC removal were compared in the three-electrode system and the two-electrode

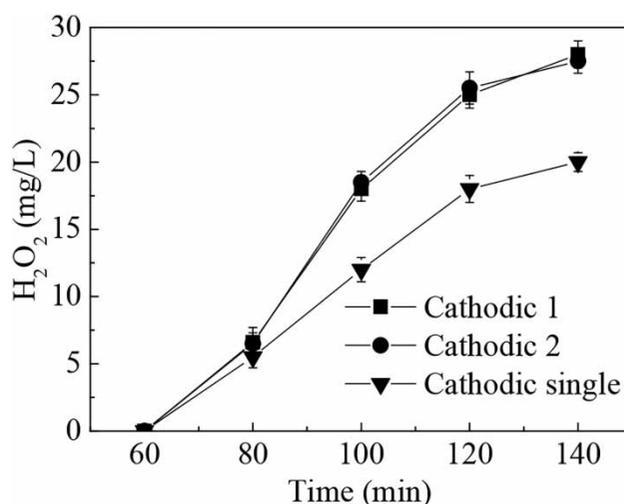


Figure 5 | Variation of accumulated H_2O_2 concentration with the electrolysis time.

system. The three-electrode system exhibited higher degradation percentages for 4-chlorophenol compared with that of the two-electrode system. In addition, in the three-electrode system, the TOC removal percentage was higher than that of the two-electrode system in the anodic compartment, due to the oxidation of the anode promoted by having one more cathode. The dechlorination percentage of 4-chlorophenol in the three-electrode system could reach 93.7%, which is higher than the 90.2% in the two-electrode system. Two types of diaphragm electrolysis systems could take advantage of the reduction and oxidation properties from cathodic and anodic compartments to degrade chlorinated organic compounds. The three-electrode system showed excellent 4-chlorophenol treatment properties. There is wide potential to use the combined process of reduction and oxidation in the three-electrode system.

ACKNOWLEDGEMENTS

This work was supported by the Beijing Excellent Talents Project (No. 2013D009046000005), the Beijing Higher Education Young Elite Teacher Project (No. YETP0773), the Fundamental Research Funds for the Central Universities (No. 2012LYB33), the National Natural Science Foundation of China (Nos 51278053 and 21373032), and the Beijing Natural Science Foundation (No. 8122031).

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First received 25 July 2014; accepted in revised form 11 November 2014. Available online 24 November 2014