Electrochemical degradation of pentachlorophenol on a palladium modified gas-diffusion electrode
H. Wang and J. L. Wang

ABSTRACT

Pd/C catalyst was prepared by a hydrogen reduction method and used for making a Pd/C gas-diffusion electrode. It was fully characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). In the catalyst, Pd particles with an average size of 4.0 nm were highly dispersed in the activated carbon with an amorphous structure; Pd content on the surface of the Pd/C catalyst reached 1.3 at% (atomic concentration). The Pd/C gas-diffusion electrode was then used as the cathode to investigate the electrochemical degradation of pentachlorophenol (PCP) in a diaphragm electrolysis device, feeding firstly with hydrogen gas then with air, compared with the carbon/polytetrafluoroethylene (C/PTFE) gas-diffusion cathode. The Pd/C gas-diffusion cathode can not only reductively dechlorinate PCP by feeding hydrogen gas, but also accelerate the two-electron reduction of O₂ to hydrogen peroxide (H₂O₂) by feeding air. Therefore, both the removal efficiency and the dechlorination degree of PCP exceeded 80% after 100 min, and the average removal efficiency of PCP in terms of total organic carbon (TOC) was more than 75% after 200 min by using Pd/C gas-diffusion cathode, which was better than that of the C/PTFE gas-diffusion cathode. Phenol was identified as the dechorination product using high-performance liquid chromatography (HPLC).

Key words | chlorophenol, electrochemical oxidation, gas-diffusion cathode, Pd/C catalyst, priority pollutant

INTRODUCTION

Chlorophenols are one kind of the toxic organic compounds listed by Environmental Protection Agency (EPA) as Priority pollutants (Lin & Tseng 1999). They are released into the environment mainly by the chlorination of municipal water, the degradation of some chemicals, and the manufacturing of various products such as pesticides, pharmaceuticals, and dyes. The strong resistance to physical, chemical, and biological treatments of chlorophenols causes hazardous influence on living organisms including human beings. As the accumulation of chlorinated aromatic compounds in the environment has become a serious problem nowadays, it is very urgent to develop an effective method to remove these contaminants.

The electrochemical oxidation for the treatment of such kind of wastewater has attracted a great deal of attention recently, mainly because of its ease of control, amenability to automation, high efficiency, and environmental compatibility (Comninellis 1994). Very recently, more potent indirect electro-oxidation methods for the wastewater treatment involving H₂O₂ electrogeneration have been developed. Carbon materials such as C/PTFE, graphite felt and reticulated vitreous carbon are classified electrode materials for the electrochemical production of H₂O₂ (Do & Chen 1994; Leon & Pletcher 1995; Brillas et al. 1998). Generally, the electro-Fenton process can be realized in the undivided electrolytic cell, where H₂O₂ is produced on the...
cathode in an acid medium and Fe$^{2+}$ is added (Harrington & Pletcher 1999; Oturan et al. 2001). In our previous work (Wang et al. 2005, 2006), we have explored a novel electrochemical oxidation system to treat the aqueous organic pollutant without adding metal catalysts. It was performed in the diaphragm cell with the C/PTFE gas-diffusion cathode. In the cathodic compartment, the decomposition of H$_2$O$_2$ in the warm alkaline solution can produce the highly reactive hydroxyl radicals (HO$^-$) during the electrolysis. The degradation of organic pollutants was attributed to the cooperatively oxidization processes including direct and/or indirect electrochemical oxidations at the anode and H$_2$O$_2$ and free radicals produced by the reduction of oxygen at the cathode.

It is well known that most chlorinated compounds are toxic due to the chlorine contained in their structure. Electrochemical oxidation based on oxidation processes mostly could open the aromatic nucleus of chlorinated compounds and bring out the chlorinated aliphatic intermediates (Otur 2001). The accumulation of chlorinated intermediates may be even more toxic than their parent compounds. The possibility to gain exhaustive dechlorination of chlorinated aromatic compounds by electrochemical reductive approach was disclosed in the 1970s. This method ensured the selective removal of chlorine atoms from various chlorinated aromatic compounds under mild experimental conditions. However, in many cases, the effective process required the use of non-aqueous reaction media or environmental unpleasant cathode material (mercury or lead) (Connors & Rusling 1983; Merica et al. 1998; Birkin et al. 2004), which made such methods unattractive for the possible practical application. The latter obstacle could be overcome by using carbon materials as the cathodes (Tsyanok et al. 1999; Chen et al. 2004) while the suitable composition of reaction medium has been under consideration. The exhaustive dechlorination of chlorinated aromatic compounds in aqueous medium was by using carbon materials loaded with Pd metals (Cheng et al. 1997; Tsyanok & Otsuka 1999; Calvo et al. 2006). 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 compounds after the dechlorination.

In this paper, we present a detailed study on the degradation of PCP in the diaphragm cell with an organic synthesized diaphragm, a Ti/IrO$_2$/RuO$_2$ anode, and homemade Pd/C gas-diffusion cathodes. In addition, we have developed an effective and friendly method to treat contaminants of chlorine compounds by using a combination process of reduction and oxidation. In the cathodic compartment, the chlorine atoms of chlorophenols were removed from the aromatic structure till to achieve non-chlorinated intermediates. Then, the non-chlorinated intermediates were oxidized and degraded in the anodic and cathodic compartments. Pd/C catalyst used for the Pd/C gas-diffusion electrode was prepared and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). The evolution intermediate during the degradation of PCP has been followed by chromatographic techniques. The electrochemical degradation of PCP by using the Pd/C gas-diffusion electrode as a cathode was compared with that by using the C/PTFE gas-diffusion cathode.

**METHODS**

**Preparation of Pd/C catalyst**

Activated carbon powder was used as the catalyst support, and was subjected to a pretreated with nitric acid. Nitric acid treatment was carried out by heating the activated carbon in 10% nitric acid solution (the ratio of grams of activated carbon/volume of 10% nitric acid at 1/10) at 95°C for 2 h. After that, the sample was washed with distilled water until neutrality and dried overnight at 100°C. Palladium chloride (0.04 g, 0.22mmol) was first dissolved in a hydrochloric acid aqueous solution (35%, 3 mL) and then diluted with 15 mL of water. The solution of PdCl$_2$ (18 mL) was dropped to a vigorously stirred activated carbon suspension (4 g in 150 mL of water) at 80°C. The mixture was kept at 80°C for 2 h and evaporated to dryness. The dried catalyst was further reduced at 250°C in a stream of hydrogen gas with a rate of 30 mL/min for 2 h, and then cooled to room temperature under the hydrogen atmosphere. Pd/C catalyst with a Pd load of 0.5 wt% was obtained and stored in a desiccator.
Preparation of Pd/C gas-diffusion cathode

A suspension for the catalyst layer was prepared with a mixture of 1.2 g of 0.5% Pd/C catalyst (activated carbon powder instead of Pd/C catalyst in the C/PTFE gas-diffusion cathode), 5.0 mL of ethanol as a dispersant, and 3 g of 10% PTFE as a wet-proofing agent and binder. This above suspension was vigorously mixed at 80°C, and the resulting wet paste was pressed into a thin catalyst layer (5 cm × 6 cm, 0.4 mm thick). The gas-diffusion layer was prepared according to the procedure for making the catalyst layer except a mixture of 0.75 g of activated carbon powder, 0.05 g of acetylene black, 0.5 g of Na2SO4, 3 g of 10% PTFE, and 5.0 mL of ethanol was used. Furthermore, a cathode composed of both the catalyst layer and the gas-diffusion layer was stacked onto a stainless steel screen (200 mesh) as current collector was finally cold-pressed at 10 MPa for 1 min. The resulting electrode was then cut to obtain gas-diffusion electrodes of 5 cm × 6 cm and about 0.4 mm thick.

Procedures

Electrolysis was conducted in a terylene diaphragm cell of 100 mL. The anode was a Ti/IrO2/RuO2 net of 16 cm². A schematic diagram of the experimental setup was shown in Figure 1. A laboratory direct current power supply with current-voltage monitor was employed to provide the electric power. The synthetic wastewater was used. The initial PCP was 100 mg/L. The current density was 39 mA/cm²; the concentration of supporting electrolyte (Na2SO4) was 0.1 mol/L; the distance between electrodes was 2 cm; the initial pH was 7.0. Before experiment started, feeding gas was 5 min in order to keep dissolved gas saturation. The feeding rate was 25 mL/s. Hydrogen gas was fed into the gas compartment during 0 ~ 100 min electrolysis. After 100 min electrolysis, air was fed into the gas compartment.

Analytical methods

The XRD patterns were used to determine the identity of any phase present and their crystallite size. The Pd/C catalyst was characterized by XRD with a Rigaku D/max-III A X-ray power diffractometer using Cu Kα radiation with a Ni filter. The Pd particle morphology and size distributions were determined by TEM (JEM-2100F TEM microscope) operated at an accelerating voltage of 200 kV.
The surface composition of catalyst and Pd surface concentration were investigated by XPS on PHI5300 Electron Spectrometer (Mg Kα radiation; $\hbar \nu = 1253.6$ eV). XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard.

The CV spectra were recorded on a potentiostat/galvanostat (EG&G Model 273A) with a standard three-compartment cell consisting of a Pt wire as a counter electrode, a Ag/AgCl electrode as a reference one, and the Pd/C catalyst (or activated carbon) modified electrode as a working electrode. Five milligram of Pd/C catalyst (or activated carbon) was suspended in a mixture of 1 mL ethanol and 50 $\mu$L of Nafion® solution (5 wt% Aldrich solution) to prepare a catalyst ink. Then 10 $\mu$L of ink was transferred with an injector to the surface of a clean glassy carbon disk electrode (with area of 0.126 cm$^2$). After the ethanol evaporated, the electrode was heated at 75°C for 10 min. 0.5 mol/L Na$_2$SO$_4$ solution was used as an electrolyte, which was saturated with oxygen (or nitrogen) by feeding oxygen gas (or nitrogen gas) to the cell for 30 min before the electrochemical measurements, and gas was continued to feed throughout the electrolysis. During the experiment process, the temperature was kept at 25°C. The scanning rate was 100 mV/s.

The determination of PCP and phenol in electrolyzed solutions were carried out using high-performance liquid chromatography (HPLC, Shimadzu, Japan) by comparing the retention time of the standard compounds. Samples of 20 $\mu$L previously filtered with PTFE filters of 0.45 μm were injected to the HPLC. The separation was performed using a Znertisl ODS-SP C18 column (250 mm × 4.6 mm, 5 μm) at the flow rate of 1.0 mL/min and at column temperature of 25°C. PCP was determined by HPLC, running with mobile phase of methanol/water (v/v) at 85/15, and an UV detector was used with the wavelength set at 320 nm. Phenol was determined by HPLC, running with mobile phase of methanol/water (v/v) at 80/20, and an UV detector (280 nm) was employed.

The total organic carbon (TOC) was detected by an Elementar High TOC analyzer. The concentration of chloride ion in electrolyzed solutions was determined by titration with mercury nitrate using a standard procedure.

RESULTS AND DISCUSSION
Characterization of Pd/C catalyst

The XRD patterns of the Pd/C catalyst are shown in Figure 2. The characteristic diffraction peak of a Pd particle at about 40.6° was observed in the catalyst reduced by H$_2$ (Cui et al. 2005). When the diameter of the Pd particles became larger, the Pd peak became narrower and sharper. There were no other distinct reflection peaks in the spectra, indicating that the self-made Pd/C catalyst had prevailed Pd particles. XRD analysis showed that there was no detectable crystal structure of Pd particles over the 0.5 wt% Pd/C catalyst, as shown in Figure 2, which indicated that only the Pd species were present. These observations suggested that Pd particles less than 4.0 nm were amorphous and highly dispersed over the activated carbon supports.

In order to estimate the geometry and the particle size of the Pd species, TEM image of Pd/C catalyst was obtained (Figure 3). It was clear that Pd species, as spherical and half-spherical grains, were homogeneously dispersed on the supports. Pd/C catalyst was characterized by a narrow distribution of smaller Pd particles to give a surface area weighted mean particle diameter $= 3.9 \pm 0.8$ nm, which was smaller than the previous observation (Chen et al. 2006). This conclusion agreed quite well with the XRD results.

Chemical states of surface atoms in the catalysts were investigated by XPS and the results are showed in Figure 4. It can be seen that the binding energies of Pd3d in the reduced catalyst are 355.1 and 336.2 eV, which were
almost similar to the data in the previous observation (Venezia et al. 2001) and can be assigned to Pd (0) and Pd (II), respectively. Pd particles content on the surface of Pd/C catalyst reached 1.3 at%.

Figure 5 depicts the CV curves of the catalyst in a 0.5 mol/L Na$_2$SO$_4$ solution (pH = 12.8 adjusted with NaOH) bubbled with different gas. There are the high reduction peak (a, b: O$_2$) at about −0.30 V in the presence of oxygen in a basic solution, however, this peak disappeared in the absence of oxygen (c: N$_2$). According to redox potential, the two-electron reduction of O$_2$ to peroxide anion (HO$_2^-$) led the formation of reduction current peaks at the catalyst modified electrodes in a basic solution at oxygen gas. The reduction current peak of the Pd/C catalyst modified electrode was higher than that of the no catalyst modified electrode. This can be attributed to that Pd/C catalyst accelerates the two-electron reduction of O$_2$ to H$_2$O$_2$.

**Removal and dechlorination degree of PCP**

Figure 6 shows the removal of PCP and the residual TOC with electrolysis time in the cathodic and anodic compartments in the Pd/C gas-diffusion electrode system and C/PTFE gas-diffusion electrode system.
As shown in Figure 6, in the first 100 min, the removal efficiency of PCP was increased with electrolysis time in the cathodic compartment of two gas-diffusion electrode systems by feeding hydrogen gas. The removal efficiency of PCP reached about 83.5% at 100 min by using Pd/C gas-diffusion electrode system, which was higher than that of C/PTFE gas-diffusion electrode system.

The mechanism of the electro-catalytic cleavage of carbon-chlorine bond (R-Cl molecule) was described by the following equations. First, chemisorbed hydrogen atom \([H]\) was formed on the cathodes surface by the reduction of water (Dabo et al. 2000).

\[
\text{H}_2\text{O} + e^- \rightarrow [H] + \text{OH}^- \quad (1)
\]

\[
\text{RCl} + [H] + e^- \rightarrow \text{RH} + \text{Cl}^- \quad (2)
\]

Hydrogenolysis of the C–Cl bond was then processed. In the first 100 min, the removal efficiency of PCP was remarkably enhanced in two systems by feeding hydrogen gas. This trend is attributed to the fact that hydrogen atom is a powerful reducing agent that can reductively dechlorinates chlorophenols, and largely produced in the hydrogen atmosphere is in favor of improving the removal efficiency of PCP.

Palladium is not only a catalyst for hydrogen evolution but also a facilitator for the reductive dechlorination of organic compounds. The high reactivity of the Pd/C gas-diffusion electrode system can be attributed to the following sequence of reactions (Cheng et al. 1997): (1) the evolution of hydrogen gas by the reduction of water molecules; (2) the adsorption of the evolved hydrogen gas by Pd, and the formation of the powerful reducing species, Pd–H2; and (3) the reduction of the chlorinated organic compound that is adsorbed on the surface of the Pd/C gas-diffusion electrode. Therefore, the removal efficiency of PCP in the Pd/C gas-diffusion electrode system was better than that of the C/PTFE gas-diffusion electrode system by feeding hydrogen gas.

As shown in Figure 6, in the first 100 min, TOC removal of the cathodic compartment increased slightly with prolonged electrolysis time in two systems. After 100 min, feeding air was used instead of feeding hydrogen gas, and TOC removal in the cathodic compartment markedly increased.

In the diaphragm cell, where the terylene diaphragm was used, it could keep pH > 12 in cathodic compartment and pH < 1 in anodic compartment whether the original solution was acidic, neutral or alkaline solution. In basic electrolyte of the cathodic compartment in the terylene diaphragm cell, C/PTFE O2-fed electrode catalyzed the two-electron reduction of O2 to H2O2 and HO2–, and then H2O2 and HO2– may be converted to HO– and \(\text{O}_2\)–. The electrochemical reaction mechanisms of the generation of HO– and H2O2 by reduction of dissolved oxygen in the cathodic compartment was proved previously (Wang et al. 2006).

In the first 100 min, it was believed that the non-chlorinated intermediates were not be further oxidized to CO2 and H2O in the cathodic compartment, which did not produce H2O2 by the electro-reduction of dissolved oxygen during feeding hydrogen gas. After 100 min, it was obviously that gas-diffusion electrode catalyzed the two-electron reduction of O2 to H2O2 and HO2–, and then H2O2 and HO2– may be converted to HO– and O2– by feeding air. As shown in Figure 6, TOC removal of the Pd/C gas-diffusion electrode system was higher than that of C/PTFE gas-diffusion electrode system in the cathodic compartment. This can be attributed to that Pd/C catalyst in Pd/C gas-diffusion electrode system accelerated the two-electron reduction of O2 to H2O2 when feeding air, which was consistent with CV conclusions (Figure 5).

As shown in Figure 6, in Pd/C gas-diffusion electrode system, TOC removal increased with an increase in electrolysis time in the anodic compartments. But after 100 min, TOC removal in the cathodic compartment was better than that in the anodic compartment in the same system. The degradation of PCP in the anodic compartment was supposed to be oxidized by MOx(OH) or MOx+1 produced on the anode surface (Canizares et al. 1999). However for anodic oxidation, it was difficult to achieve total mineralization because of low MOx(OH) or MOx+1 concentration on the anode. However, the oxidizing power of H2O2, HO– and O2– existed in the catholyte during O2-electroreduction on the C/PTFE cathode are very strong, which can oxidize organic compounds to smaller molecule intermediates or to CO2 and H2O. Therefore, the mineralization of organic...
compounds in the cathodic compartment was better than that in the anodic compartment.

In two systems, the changes of the concentration of chloride ion with electrolysis time in the cathodic and anodic compartments were illustrated in Figure 7.

As shown in Figure 7, the changing trend of the chloride ion concentration in the anodic and cathodic compartments was similar in two systems. The concentration of chloride ion increased in both anodic and cathodic compartment with an increasing of electrolysis time, but the concentration of chloride ion in the anodic compartment was higher than that in the cathodic compartment in the same system. This attributed to the fact that in the initial period of the experiment, the chloride ions of the cathodic compartment could diffuse to the anodic compartment through the terylene diaphragm, due to the electro-static repulsion from the negatively charged cathode. Therefore, their concentration in the anodic compartment was high. The concentrations of chloride ion increased with an increase of electrolysis time, and reached the highest values, then decreased in two compartments. Results indicate that chloride ion was already oxidized to Cl\textsubscript{2} at the anode, as reported for the electrolysis of chlorophene with BDD anode (Sirés et al. 2007), and Cl\textsubscript{2} was immediately driven away from the reaction system.

However, the electrolysis time needed to reach the highest chlorine ion concentration in the Pd/C gas-diffusion cathode system was shorter than that in the C/PTFE gas-diffusion cathode system (the former was 120 min, and the latter was 140 min). Here, the dechlorination degree of PCP reached 82.3% in the Pd/C gas-diffusion electrode system. This can be attributed to that Pd promotes the cleavage of carbon-chlorine bonds and facilitates hydrogenation by feeding hydrogen gas. Therefore, it was feasible to degrade chlorinated contaminants by electrochemical reduction to non-chlorinated intermediates in the Pd/C gas-diffusion electrode system.

**Identification of intermediates and their evolution**

It is noteworthy that the dechlorination of chlorophenols to phenol has been reported by other researchers (Tsyganok et al. 1999; Yasman et al. 2006). It is well known (Brillas et al. 2003) that electrochemical degradation of the generated aromatic compounds leads to a mixture of carboxylic acids. The formed intermediates of PCP have many kinds, and the dechlorination processes are complex. Hence, phenol of the complete dechlorination product was selected to study the dechlorination effect of PCP. Figure 8 shows phenol detected in the cathodic compartment during the degradation of PCP by Pd/C gas-diffusion electrode systems.

During the electrolysis process, PCP decreased steeping and disappeared from the solution in 200 min. The concentration of phenol increased at the first 100 min and then began to decrease till complete removal within 200 min. These results indicated that in the Pd/C gas-diffusion electrode system the intermediate were
transformed into carboxylic acids, because they reacted rapidly with the larger amount of HO' formed from the cathodic compartment. The principal reaction had been turned to the mineralization of aliphatic carboxylic acids to CO₂ after 200 min in the Pd/C gas-diffusion electrode system. Owing to its low current efficiency, in practical use, it was not necessary to degrade PCP to the final products of CO₂. It may be more worthwhile to treat PCP to the biodegradable stage aliphatic carboxylic acids followed by an economical biological process.

CONCLUSIONS

A novel Pd/C gas-diffusion cathode was prepared and used to degrade PCP in an aqueous solution. In the Pd/C catalyst, Pd particles with an average size of 4.0 nm were highly dispersed in the activated carbon with amorphous structure. Additionally, the Pd content on the surface of Pd/C catalyst reached 1.3 at%. In the Pd/C gas-diffusion electrode system feeding firstly with hydrogen gas then with air, the removal efficiency and the dechlorination degree of PCP exceeded 80% after 100 min, and the average removal efficiency of PCP in terms of TOC was more than 75% after 200 min. The Pd/C gas-diffusion cathode can not only reductively dechlorinate PCP by feeding hydrogen gas, but also accelerate the two-electron reduction of O₂ to H₂O₂ by feeding air. Hence, the removal efficiency of PCP by using the Pd/C gas-diffusion cathode was better than that of the C/PTFE gas-diffusion cathode. The main intermediate of PCP dechlorination in the cathodic compartment was determined as phenol. The further oxidation of phenol, after ring opening, led to the formation of aliphatic carboxylic acids. The combined process of reduction and oxidation was in favor of improving PCP degradation efficiency in the Pd/C gas-diffusion electrode system.

ACKNOWLEDGEMENTS

This work was supported by the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 200800221007) and Beijing Nova Program (Grant No. 2008B21), which are greatly acknowledged.

REFERENCES


Harrington, T. & Pletcher, D. 1999 The removal of low levels of organics from aqueous solutions using Fe(II) and hydrogen...
peroxide formed in situ at gas diffusion electrodes. 


