Electrochemical removal of pentachlorophenol in a lab-scale platinum electrolyzer

Ting-Nien Wu

ABSTRACT

This study is focused on the removal of pentachlorophenol from its aqueous phase by electrochemically induced degradation with Pt electrodes. The objective of this study was to contrast the electrochemical removal of pentachlorophenol at the oxidative and the reductive potentials, and further to understand how to apply the electrochemical treatment on PCP degradation. Lab experiments were conducted in a Pt electrolyzer, and the voltage source was supplied and precisely controlled by an electrochemical analyzer. In these experiments, the variables including electrolyte species, pH, voltage supply, and reaction time were examined to compare the efficiency of pentachlorophenol removal. Experimental results showed that pentachlorophenol was completely degraded after being electrolyzed for 1 h at $-1.5\,\text{V}$ in a 0.5 M KCl solution, while the removal of pentachlorophenol is negligible under the similar condition when 0.5 M NaNO$_3$ or Na$_2$CO$_3$ was used as the electrolyte. The electrolyte concentration below 0.5 M is unfavourable for the electrochemical removal of pentachlorophenol. The removal efficiency of pentachlorophenol is slightly affected by pH, and the strong basic environment might impede the degradation of pentachlorophenol. Comparing with those under positive potentials, the experiments conducted under negative potentials have shown a better removal of pentachlorophenol with a higher current efficiency. It implies that pentachlorophenol degradation followed the reductive pathway. Based on the analysis of GC/MS, the intermediates of pentachlorophenol degradation were identified as 1,2-dichlorocyclohexane and 2-chlorocyclohexanol.

Key words | dechlorination, electrochemical reaction, intermediate, pentachlorophenol, Pt electrode, reduction

INTRODUCTION

Pentachlorophenol (PCP) possesses a stable cyclic molecular structure, and it has been widely used in bactericides, fungicides, herbicides, disinfectant and wood preservatives in agriculture and industries for several decades. PCP is toxic to most creatures, and its recalcitrance to biological processes makes PCP prevalent in most natural environments. There are several regulated sites contaminated with PCP in Taiwan. Several remedy schemes have been proposed for the removal of chlorophenols from their adsorbed or dissolved phases including biodegradation (Yang & Lee 2007), carbon adsorption (Subha & Namasivayam 2008), microwave decomposition (Abramovitch & Capracotta 2003; Wu 2008), sonolysis (Ku et al. 2006a), ozonation (Ku et al. 2006b; Anotai et al. 2007), photocatalysis (Chang & Lu 2007), Fenton process (Oturan et al. 2001) and electrochemical oxidation (Ureta-Zanartu et al. 2001; Wang 2008). Comparing with other proposed remedy schemes, the biological process is relatively slow and sometimes inhibited at a high concentration of chlorophenols. Carbon adsorption is an expensive alternative, plus the generated waste may potentially cause secondary pollution without proper disposal. Advanced oxidation processes (AOPs) generate...
hydroxyl radicals or oxidizing agents that are capable of destructing organic pollutants. Besides, the advantages of rapid reaction and easy control make AOPs more attractive. Electrochemical technology is a clean treatment scheme that employs the electrons to initiate serial electrochemical reactions for the breakdown of organic pollutants. Electrochemical oxidation approach has been proven as a successful remedy scheme for several poorly biodegradable compounds such as MTBE (Wu et al. 2006; Wu 2007; Wu & Lin 2007) and phenolic compounds (Ammar et al. 2007; Polcaro et al. 2008).

By mediated electrochemical treatment, organic pollutants can be selectively oxidized to certain extent. The selection of suitable anodic materials and the control of appropriate operative conditions are crucial for practical application of electrochemical treatment. In this study, a platinum electrode was employed as the working electrode, which gave good performance on breakdown of MTBE (Wu et al. 2006) and degradation of methomyl (Wu 2005) through electrochemical oxidation. Depending on the operative condition, the organic pollutant may be adsorbed on the anodic surface and degraded through direct oxidation. The other mechanism of electrochemical oxidation, indirect oxidation, is to diffuse the electrogenerated radicals or strong oxidizing agents in solution that can attack organic pollutants rapidly. Besides, degradation of pollutants may be accomplished by means of electrochemical reduction of chlorinated compounds. The platinum electrode has been successfully applied on electrochemical degradation of many organic pollutants (Zor et al. 1998; Guinea et al. 2008; Liu et al. 2009). In this study, the platinum electrode was employed as working electrode to demonstrate its electrocatalytic performance on removing PCP. The objective of this study was to contrast the electrochemical removal of PCP at the oxidative and the reductive potentials. Also, the influence of main operation factors such as voltammetric charge, electrolyte, and pH on PCP degradation was examined in the Pt-electrolytic system. Based on the intermediate determination, the degradation pathway of PCP dechlorination was proposed as well. Thus, experimental data of a lab-scale platinum electrolyzer might be valuable for understanding how to apply the electrochemical method on the treatment of PCP contaminated water.

MATERIALS AND METHODS

Chemicals

Analytical grade of sodium pentachlorophenate (99%) was purchased from Merck Ltd., which was used to prepare PCP contaminated water. Three electrolytes were of reagent grade, including potassium chloride (99%), sodium nitrate (99%), and sodium carbonate (99%) obtained from Shimakyu Chemical Co. (Japan). All reagents were prepared with de-ionized water, which was made by Mili-Q system (Millipore TK-10, USA). Analytical grade of acetonitrile (99%) purchased from Merck Ltd. was utilized as a mobile-phase elute in the analysis of high performance liquid chromatography (HPLC). Analytical grade of dichloromethane (99%) purchased from Merck Ltd. was applied to the extraction of sampled liquor.

Experimental setup

The bench-scale electrolysis apparatus comprised an electrolytic reactor, an electrochemical analyzer, an electrical multimeter, and a thermostatic water bath. A 50 ml double-jacketed glass vial with a Teflon cap was used as the splitless electrolytic reactor, which was equipped with a Pt electrode as the working electrode (WE), a Pt wire as the counter electrode (CE) and a saturated Ag/AgCl electrode as the reference electrode (RE). A constant voltammetric potential was supplied and precisely controlled by a Bio Analytical System (BAS) 100B electrochemical analyzer, and the alteration of passing current between WE and CE was monitored by a Keithley 2,000 multimeter. During the experiment, the temperature of the electrolytic reactor was controlled by recirculating cooling water from a thermostatic water bath, and the liquor of the reactor was completely mixed with a mini magnetic stirrer to attain the homogeneous state.

Electrolysis experiments

Based on the consideration of PCP saturation, the initial concentration of 14 mg l\(^{-1}\) PCP was prepared at room temperature for the batch experiments. Electrolysis experiments were conducted in the electrolytic reactor, and the electrolyte concentration was maintained at 0.5 M to
facilitate the electron transfer. Potassium chloride, sodium nitrate, and sodium carbonate were selected as electrolyte and examined their suitability in the Pt-electrolytic system. Before each experiment, the Pt electrode was cleaned with 0.05 μ alumina powder, polished 1 min with a fine polishing paper, and rinsed with de-ionized water to remove adsorbed deposits on the surface. RE was immersed in a 3 M KCl solution to maintain its saturated status while not in use. Each run was operated at a constant potential for 120 min and sampled with a syringe at 10, 20, 30, 60, 120 min. The sampled liquor (1 ml) was analyzed by HPLC for the determination of PCP concentration. At the end of electrolysis experiments, the remaining solute was extracted by dichloromethane and subsequently subjected to the analysis of gas chromatography/mass spectrometry (GC/MS) for the identification of intermediate products. The pH of the reaction solution was measured in the beginning and the end of electrolysis experiments. The online monitoring of the passing current was recorded to calculate the passage of charge in the Pt-electrolytic system as well.

Analytical methods

HPLC analysis

The decreases of PCP concentration in the reactor during electrolysis experiments were measured by a Hitachi L-7100 HPLC system equipped with a Hitachi L-7420 diode array UV-Vis detector and fitted with a reverse phase RP-18, 5 μm, 4.6 × 250 mm column. The operative condition of HPLC analysis was set at the isocratic mode and eluted with a mobile phase composed of acetonitrile, water, and acetic acid at a 60:39:1 ratio. The flow rate of elution was 1 ml min⁻¹, and UV detection was performed at 228 nm.

GC/MS analysis

Prior to GC/MS analyses, the solvent extraction procedures should be undertaken. The remaining reaction solute was subjected to sample extraction by dichloromethane at the end of electrolysis experiments. The sampled liquor (40 ml) was acidified by HCl, mixed 2 min with 3 ml of dichloromethane on a vortex mixer, and settled for at least 10 min until two immiscible layers formed. The bottom layer of two immiscible fluids was taken using a Pasteur pipette, which was continually subjected to the extraction procedures three times. The top layer of the two immiscible fluids was collected after each extraction. The prepared aqueous extracts were analyzed using Perkin Elmer model Clarus 500 GC/MS system equipped with a SUPELCO Equity-5 capillary column (30 m L × 0.25 mm ID × 0.25 μm thick). In this study, operating condition was set up as: N₂ carrier gas at 1 ml min⁻¹, split ratio at 30:1, injector temperature at 50°C, and detector temperature at 250°C. The column was isothermal at 50°C for 1 min, ramped at 10°C min⁻¹ to 200°C, held for 2 min, continually ramped at 10°C min⁻¹ to 250°C, and held for 2 min. The intermediate products of PCP degradation were identified according to MS ion fragments with mass-to-charge ratio.

Quality assurance/ quality control

The reliability and consistency of the PCP analysis were checked using parallel analyses of a QC standard sample and a standard-spike sample. The recovery values were 94.3% for the QC sample and 109.2% for the spike sample. A duplicate analysis was conducted as well to check the reproducibility of the PCP analysis, and the relative standard deviation (RSD) was 7.0%. Besides, the blank electrolysis experiment was conducted without any electricity supply to confirm the attenuation of PCP through the mechanisms other than electrochemical reaction. The loss of PCP from the dissolved phase was less than 5% in the system during 2 h. The electrolysis experiments were repeated three times to examine the reproducibility of the PCP removals under the optimum controls. The PCP removals were between 98% and 100% after electrolyzing 30 min, and the complete removals of PCP were attained for all reproducibility experiments after electrolyzing 60 min.

RESULTS AND DISCUSSION

Effect of voltammetric potential on PCP degradation

Figure 1 displays the cyclic voltammogram for the Pt electrode dipped in a 1 M KCl solution at a scan rate of 100 mV s⁻¹ with the presence of 14 mg l⁻¹ PCP. There are two pairs of clear peaks at 1,200 and −800 mV in the positive sweep and at 200 and −400 mV in the negative
sweep. The occurrence of oxygen and hydrogen evolution was observed above 1,500 mV and below −1,000 mV, respectively. In order to trigger some complicate electrochemical reactions, the electrolysis experiments were conducted at different levels of potential strength. As can be seen in Figure 2, the decrease in PCP concentration was less than 5% when electrolyzing at 1,000 or 1,800 mV. Comparatively, the removal of PCP was complete within 20 min when electrolyzing at 3,000 mV. The anodic oxygen evolution resulted in a decrease of solution pH initially from pH 7 to 5.8. In the presence of chloride ion, the involved electrochemical reactions can produce strong oxidants (such as Cl₂, HOCl, HClO₂ and O₃) or radicals to oxidize aqueous pollutants (Panizza et al. 2000; Chen 2004). Because these electrogenerated oxidants or radicals have stronger oxidizing potentials than oxygen, the observed degradation of PCP was negligible when electrolyzing below 1,800 mV. The involved electrochemical reactions may be given by the following:

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad E_0 = -1.36 \text{ V} \tag{1}
\]

\[
\frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + e^- \quad E_0 = -1.63 \text{ V} \tag{2}
\]

\[
\text{HOCl} + \text{H}_2\text{O} \rightarrow \text{HClO}_2 + 2\text{H}^+ + 2e^- \quad E_0 = -1.645 \text{ V} \tag{3}
\]

\[
\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_3 + 2\text{H}^+ + 2e^- \quad E_0 = -2.07 \text{ V} \tag{4}
\]

\[
\text{H}_2\text{O} \rightarrow \text{OH}^- + H^+ + e^- \quad E_0 = -2.85 \text{ V} \tag{5}
\]

When electrolyzing at negative potentials, all experiments gave a satisfactory performance on PCP removal. In Figure 3a, PCP was completely removed within 30 min through electrolysis at overpotential of hydrogen reduction. The cathodic hydrogen evolution resulted in a slight rise of solution pH initially from pH 6.9 to 7.1. Figure 3b shows the coulometric efficiency under different electrolysis potentials. The coulomb is calculated by integrating the recorded current with time, while the recorded current is contributed by PCP degradation and water electrolysis. The endpoint of the progressive curve in Figure 3b records the ultimate efficiency of PCP removal and the accumulated charge at each controlled potential, and the slope of the progressive curve explains the associated response of PCP degradation and water electrolysis. PCP degradation is regarded as the major Faradaic process, and the slopes at −1,500 and −3,000 mV become less due to the occurrence of hydrogen evolution. Figure 3b gives the best coulometric efficiency of PCP removal at −1,000 mV, but the complete removal of PCP was not achieved in Figure 3a. Thus, the electrolysis experiments would be better to operate at −1,500 mV for balancing PCP removal and coulometric efficiency.

**Effect of supporting electrolyte on PCP degradation**

The purpose of adding supporting electrolyte in the electrolytic system is to provide a conductive medium and minimize the voltage drop in the reactor. Three species of electrolytes including KCl, Na₂CO₃, and NaNO₃ were examined by comparing the efficiency of PCP degradation at −1,500 mV. The decrease in PCP concentration was less than 5% when 0.5 M Na₂CO₃ or NaNO₃ was used as
the electrolyte, and KCl was found to be the only suitable electrolyte for PCP electrolysis among the tested electrolytes. The better efficiency on PCP degradation in the KCl solution is primarily ascribed to the formation of oxidative chlorine species or radicals. Our experimental observation is similar to other electrolyte comparison that use of NaCl showed 2 orders of magnitude faster on phenol degradation than uses of Na₂SO₄, Na₃PO₄, or Na₂CO₃ (Park et al. 2008). Three levels of KCl concentrations were tested for their effectiveness in facilitating PCP electrolysis. In Figure 4a, the ascending trend of PCP degradation is obvious with intensifying electrolyte concentration as expected. The slopes of the progressive curves in Figure 4b became steeper with increasing electrolyte concentrations as well. Complete removal of PCP and better coulometric efficiency were achieved when concentrated electrolyte (0.5 M or 1 M KCl) was used. Accordingly, the electrolyte concentration greater than 0.5 M was suggested to support the undergoing of electrochemical reactions. Chen (2004) suggested that a high chloride concentration larger than 3 g l⁻¹ was typically employed in order to effectively oxidize many inorganic and organic pollutants.

**Effect of solution pH on PCP degradation**

The effect of solution pH on PCP degradation was examined under basic, neutral, and acidic conditions through electrolysis at −1,500 mV in 0.5 M KCl solutions. The solution pH varied during the electrolysis experiments, and the initial and final pHs were measured each run. In the acidic or neutral environment, a slight increase in solution pH was observed after the experiment. This observation can be explained by the consumption of hydrogen atoms in the reductive system. During the experiments, hydrogen...
atoms can be reduced to H₂ or extracted from the solution to participate the dechlorination reaction. The probable reactions in the reductive system were given in reactions (6) to (8). Figure 5a shows that complete removal of PCP was attained through electrolysis at both neutral and acidic conditions. It also implied that the basic environment is unfavorable for the extraction of hydrogen atom on electrode surface, which can initiate PCP degradation in a reduction pathway. Figure 5b was also consistent with the above deduction that the coulometric efficiency of PCP removal improved with decreasing solution pH. As a result, PCP degradation is effective and efficient when electrolyzed in a neutral or acidic solution.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{OH}^+ + \text{H}^+ \quad (6) \\
\text{H}^+ + \text{H}^+ & \rightarrow \text{H}_2 \quad (7) \\
\text{C}_6\text{H}_5\text{Cl}_n\text{OH} + n\text{H}^+ & \rightarrow \text{product} + n\text{Cl}^- \quad (8)
\end{align*}
\]

**Intermediate and pathway of PCP degradation**

Depending on the applied voltammetric potential, the breakdown of PCP may follow the oxidative degradation pathway or the reductive dechlorination pathway through electrolysis. Torres *et al.* (2003) has pointed out that the electrooxidation of chlorophenols or phenolic compounds may form some aromatic intermediates, such as hydroquinone, benzoquinone, and pyrocatecol. Lin & Tseng (1999) have determined intermediate products of reductive PCP dechlorination as 2,3,4,5-tetrachlorophenol, 2,4,5- and 2,4,6-trichlorophenol. As illustrated in Figures 2 to 5, the complete removal of PCP was attained after electrolyzing 60 min. However, the disappearance of PCP after electrolyzing 60 min did not indicate that the final mineralization of PCP was achieved. In order to examine the intermediate products of reductive PCP degradation, the sampled liquor was analyzed by GC/MS after being electrolyzed for 60 min and 120 min at −1,500 mV. In Figure 6, the peak of PCP occurs at 16.7 min on the GC/MS chromatogram. The chromatograms after 60 min and 120 min electrolysis illustrate the disappearance of PCP and the occurrence of two new peaks at 6.55 and 7.19 min, which are identified as trans-2-chlorocyclohexanol and 1,2-dichlorocyclohexane. Based on the identification of MS ion fragments with mass-to-charge ratios during electrolysis, the reductive dechlorination of PCP (C₆H₅Cl₅O) was initiated by atomic hydrogen, gradually dechlorinated to form C₆H₄Cl₂OCl or C₆H₄Cl₂, and the ring structure was then broken down to produce C₆H₆. As illustrated in reaction (9), our proposed electrochemical dechlorination pathway of PCP is somewhat diverting to the traditional dechlorination pathway that PCP was reduced to tetra-, tri-, di-, mono-chlorophenol and phenol step by step (Cui *et al.* 2005). To determine the extent of electron transfer during a reaction, the first task is to determine the oxidation state of each atom before and after the reaction. In reaction (9), hydrogen in all compounds has an oxidation state +1, the oxidation state of oxygen in all compounds is always −2, and the oxidation state of chlorine is −1.
state of chloride is always $-1$. Thus, the oxidation state of carbon can be increased through the oxidative reaction or decreased through the reductive reaction. The oxidation state of carbon in PCP is $+1$, and its carbon oxidation state is $-4/3$ in both $\text{C}_6\text{H}_{11}\text{OCl}$ and $\text{C}_6\text{H}_{10}\text{Cl}_2$. If six carbons in PCP were reduced to form $\text{C}_6\text{H}_{11}\text{OCl}$ and $\text{C}_6\text{H}_{10}\text{Cl}_2$, then one molecule intermediate formation decreased carbon oxidation state summing up $-14$ that required 10 protons and 14e. Following our proposed pathway, the oxidation state of carbon was decreased from $+1$ to $-4/3$ that might be closely linked to the strength of reduction potential. The presence of 1,2-dichlorocyclohexane as the major intermediate product is consist with the finding that the release of chloride may reach 52% through the reductive degradation of PCP in a KI solution.

$$\text{C}_6\text{Cl}_5\text{OH} + 10\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_6\text{H}_{10}\text{Cl}_2 + 3\text{Cl}^- + \text{OH}^- \text{(9)}$$

**CONCLUSIONS**

When compared to $\text{Na}_2\text{CO}_3$ and $\text{NaNO}_3$, KCl has demonstrated its superiority as an electrolyte for PCP removal through electrolysis. The KCl concentration should be greater than 0.5 M for the ease of electrochemical reactions. The complete removal of PCP was achieved within 30 min by electrolyzing either at 3,000 mV or below $-1,500$ mV, but its degradation may follow different pathways. The oxidative degradation pathway counts on the electro-generated OH radicals to oxidize PCP, while the reductive dechlorination pathway is initiated by the participation of atomic hydrogen during water electrolysis. Considering both PCP removal and coulometric efficiency, the electrolysis experiments at $-1,500$ mV has the best performance. The basic environment was found unfavourable for the extraction of atomic hydrogen on electrode surface, so PCP degradation in a neutral or acidic solution is more effective and efficient through electrolysis. Based on the identification of MS ion fragments with mass-to-charge ratios during electrolysis, the major intermediate products of PCP degradation were trans-2-chlorocyclohexanol ($\text{C}_6\text{H}_{11}\text{OCl}$) and 1,2- dichlorocyclohexane ($\text{C}_6\text{H}_{10}\text{Cl}_2$). The continual electrolysis of PCP at overpotential of hydrogen evolution may cause the breakdown of the ring structure to produce $\text{C}_6\text{H}_8$. Accordingly, PCP can be successfully dechlorinated and degraded through appropriate control of electrolysis.
REFERENCES


Wang, J. W. 2008 Removal of pentachlorophenol in water by electrochemical treatment process, MS Thesis, Department of Environmental Engineering, Kun Shan University, Tainan, Taiwan.


