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Electrochemically Reductive Dechlorination of Pentachlorophenol Using a High Overpotential Zinc Cathode

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Abstract

Electrochemically reductive dechlorination of pentachlorophenol (PCP) on a zinc electrode in both propylene carbonate solvent and water is investigated. In propylene carbonate system, the reductive dechlorination of PCP occurred at two different potentials: -2.4 V and -1.7 V. In water system, two reductions were also found at -1.95 V and -1.6 V. The mechanism of PCP reduction in propylene carbonate was mediated by adsorbed atomic hydrogen. The current efficiency decreased with the electrolysis time from 84% to 38%. The reason for low current efficiency was that the rate of the formation of hydrogen was faster than the diffusion of PCP to the surface of zinc electrode.

Introduction

Chlorinated phenols are of environmental concern due to anthropogenic inputs from industrial waste, and the use of pentachlorophenol as a wood preservative. In addition, chlorinated hydrocarbons of environmental concern, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) are transformed by anaerobic bacteria to chlorophenols (CPs) [1]. As a result of being extensively used, CPs are widely formed in the environment and are significant contaminants at many sites selected for cleanup on the National Priorities List of the Superfund program [2]. Sites contaminated with PCP are numerous. It is important to treat such contaminant in groundwater aquifers.

Several options are currently available for the remediation of PCP. The degradation of pentachlorophenol via bioremediation was investigated under aerobic and anaerobic conditions. Anaerobic degradation of chlorinated phenolic compounds are desired to mineralize of PCP to CO_2 and CH_4 as completely as possible [3,4]. However, it is necessary to take several days or weeks to reduce this contaminant. In addition, the utilization of bioremediation is restricted to the inhibition of anaerobic culture by toxic chemical [5].

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Reductive dechlorinations catalyzed by bacterial transition-metal coenzymes, vitamin B_{12}, coenzyme F_{430}, and hematin were investigated in the last few years [6]. It was found that the regiospecificity of dechlorination by transition-metal coenzymes depended upon the environmental factors. Titanium (III) citrate which had a lower redox potential than dithiothreitol (DTT) could reduce vitamin B_{12a} [Co (III)] to the vitamin B_{12s} [Co (I)]. Vitamin B_{12s} is a more effective electron transfer mediator to react with PCP. Reductive dechlorination of PCP was not observed by using the vitamin B_{12r} [Co (II)] when DTT worked as the electron donor [7,8]. Lower redox potential is necessary for the dechlorination of PCP using this approach, but it is difficult to control the redox potential in contaminated sites.

The use of metal in environmental remediation has been found to degrade many chlorinated aromatic compounds to non-toxic forms [9,10]. Reductants such as iron, zinc or aluminum powders have been used in effecting treatment of converting the toxicants such as 2,4-D, 2,4,5-T and chlorobenzene to an innocuous compound [9,10]. This is an electrochemical method, in which many of redox cells formed on the metal surface. The reduction reaction proceeds primarily to replace halogen atom with hydrogen.

The transformation of halogenated aliphatic compounds was also studied in the presence of metallic particles [11,12]. Zinc and tin were successfully used to degrade carbon tetrachloride and behaved quite differently with the final carbon-containing product [11]. The degradation of carbon tetrachloride by iron also occurred in several hours, but no significant reduction of methylene chloride was observed over one month [12]. The electrochemical method is not restricted by toxicant and environmental factor. Therefore, it is of special interest to electrochemically degrade chlorinated organic compound using these active metals as the electrode.

In this study, we first investigate the cathodic reduction of PCP on a zinc cathodic electrode. Zinc metal is chosen as the working electrode because of its high overpotential of hydrogen reduction. Propylene carbonate is selected as solvent because cathodic breakdown for this compound is known to occur typically at more negative potentials than water does [13,14]. This solvent is used to prevent the reduction of water from competing with PCP reduction. In this paper, the mechanism of reduction of PCP on a zinc cathode was discussed, and current efficiency was also reported. Subsequently, the electrochemical reduction of PCP in water by zinc electrode is also under progress.

Experimentals

Electrochemical study : The degradation of PCP was investigated using cyclic voltammetry. Figure 1 shows the schematic diagram of electrochemical cell. The cathode and anode compartments are separated by a Nafion membrane. Zinc metal plate (99.9% purity, from the Fan Chern Co., Ltd., Taiwan) was used as a working electrode because it possessed high overpotential for the reduction of proton. A platinum plate worked as the counter electrode. The potential of working electrode was applied verus a saturated calomel electrode (SCE) by using a luggin probe. All of potentials were reported with respect to SCE, unless otherwise noted. A copper rod was attached to the zinc electrode for electrical contact, and platinum wire was attached as the counter electrode. The heat clothes were used to envelop the wire in order to isolate from solvent.

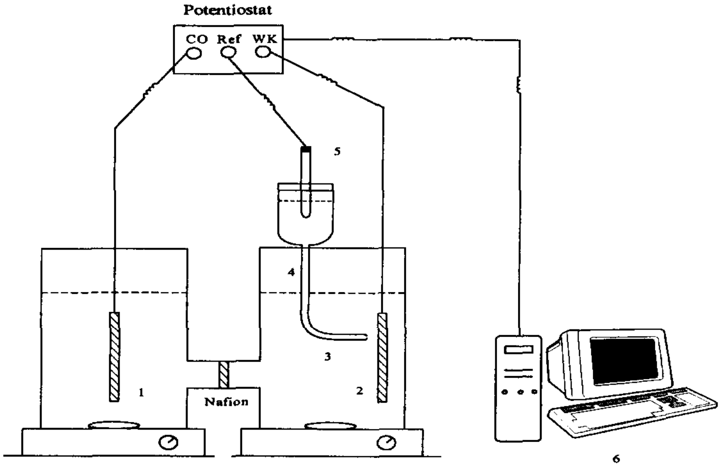


Figure 1. Diagram of the three compartment cell used for studying electrochemical reduction of PCP: 1. Pt electrode, 2. Zn electrode, 3. Luggin probe, 4. Salt bridge, 5. Saturated calomel electrode, 6. Output data recorder

The dimension of the zinc electrode was 3 cmx 5 cmx 3 mm. The working cell contained a volume of 500 cm^3. Cyclic voltammetry was conducted with a scanning potentiostat, EG&G Model 273A. Voltage sweeped from -1.3 V to -2.8 V in propylene carbonate and from -1.1 V to -2.2 V in water. The scan rates were 5 mV/s, 20 mV/s, 50 mV/s and 100 mV/s. The output data were stored in the EG&G Model 230/250 Research Electrochemistry software 4.23.

The experiments of cyclic voltammetry were carried out in both propylene carbonate solvent and water systems. Tetraethylammonium chloride (TEACl) of 0.25 M in propylene carbonate and water was used as the supporting electrolyte. PCP of 1 to 30 mM was added in the cathodic compartment. Current-voltage curves were obtained for PCP solution of varying concentration in the range described above.

In addition to cyclic voltammetry, controlled potential electrolysis was carried out on the same working electrode with the potential held at -2.3 V. PCP of 20 mM and TEACl of 0.25 M in the propylene carbonate of 250 mL were prepared to study the degradation of PCP at controlled potential electrolysis. The solution was sampled at 30 min interval over a period of 7 hrs. Aliquots of these samples were analyzed by HPLC. The currents were also recorded during the electrolysis period in which could be used to calculate the instantaneous current efficiency as a function of electrolysis time.

Analysis: PCP and other chlorinated phenols were determined by using a XPER-CHROM Model 400 HPLC with a Bio Rad Model 1706 uv/vis detector and a Phemonex Spherisorb octadecyl-silane (ODS) reversed-phase column (4.6mm inner diameter by 25 cm). The samples were injected by using a Bio Rad Model AS-100 HRLC autosampler. The volume of sample loop was 20 μL. The mobile phase was acetonitrile-water-acetic acid (600:400:5.7 [vol/vol/vol]) and ran at a flow rate of 1 mL/min. UV detector was operated at 280 nm for trichlorophenol and 300 nm for tetrachlorophenol and PCP, respectively. Authentic PCP, tetrachlorophenol and trichlorophenol dissolved in propylene carbonate were used as standards to verify the retention time of suspected intermediates. The output signals were recorded with a HP 3396 integrator.

Chemicals: All reagents were of analytical grade. Chlorophenols were obtained as follow: PCP and 2,3,4,6-tetrachlorophenol (Nacacai Tesque, Japan) ; 2,3,5,6-tetrachlorophenol (Tanssen Chemica, Japan); 2,4,5-trichlorophenol (Merck, Germany). Propylene carbonate was obtained from Ferak Berlin or Merck, Inc. The solvent for HPLC was obtained from J. T. Baker, Inc. All of other chemicals were reagent or HPLC grade as necessary.

Results and Dissusion

Cyclic voltammetric studies

Figure 2 shows the typical cyclic voltammogram for the background behaviour of 0.25 M TEACl in propylene carbonate. No wave was observed in the range of -1.3 V to -2.8 V. The solvent started to break down at -2.5 V. This result suggested that zinc electrode exhibits a high overpotential for the reduction of propylene carbonate. This characteristic was suitable for studying the mechanism of electrochemically reductive dechlorinarion of chlorinated phenol compounds.

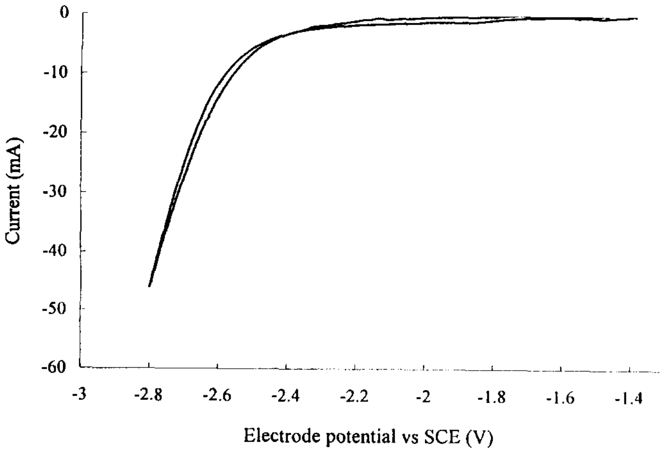


Figure 2. Cyclic voltammograms record in 0.25 M TEACl/propylene carbonate on a zinc electrode at a voltage scan rate 20 mV/s. The voltage of initial solvent breakdown is at -2.5 V.

In this study, cyclic voltammetry was obtained for PCP solution of varying concentration in the range of 1 to 30 mM. The scan rates were 5 mV/s, 20 mV/s, 50 mV/s, and 100 mV/s, respectively. The data showed that no wave was observed for the concentrations less than 5 mM. However, plateaus were observed for higher concentration. Figure 3 shows a typical cyclic voltammogram obtained for the zinc electrode in the presence of 20 mM PCP in 0.25 M TEACl/propylene carbonate system and scan rate of 20 mV/s. The voltage sweeps from -1.3 V to -2.8 V. Two irreversible reductions, -1.4 V and -2.1 V, were observed prior to the onset of solvent breakdown. The reduction of PCP was first found at –1.4 V, and limiting current occurred at –1.7 V (C_1). The further reduction of PCP was observed at –2.1 V, and limiting current took place at –2.4 V (C_2).

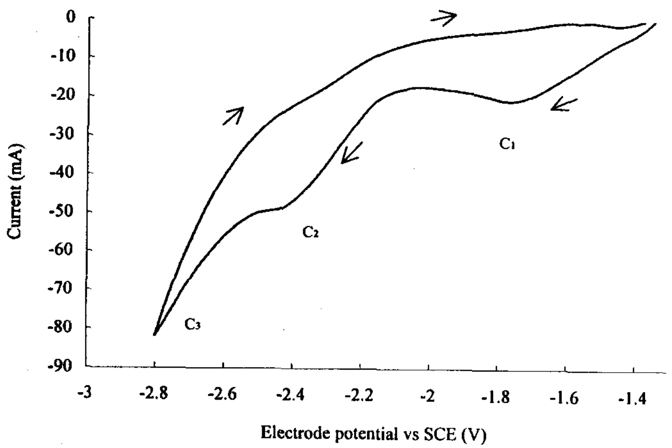


Figure 3. Cyclic voltammogram for reduction of 20 mM PCP in 0.25 M TEACl/propylene carbonate on a zinc electrode at a voltage scan rate 20 mV/s. C_1 and C_2 are irreversible reductions at -1.7 V and -2.4 V, and C_3 is solvent breakdown.

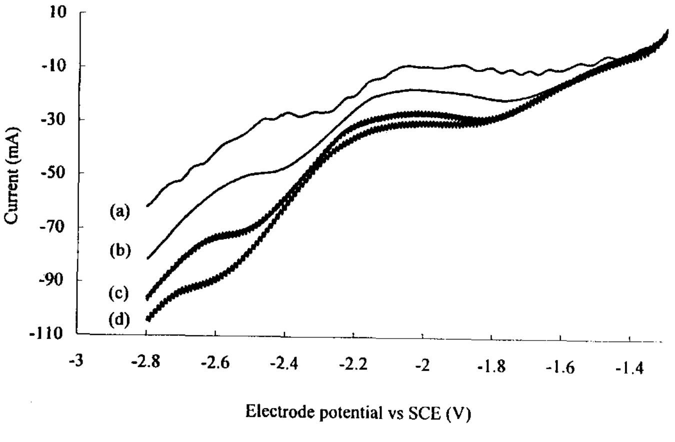


Figure 4. Effect of sweep rate on the cyclic voltammograms recorded for reduction of 20 mM PCP in 0.25 M TEACl/propylene carbonate on a zinc electrode. (a) 5 mV/s (b) 20 mV/s (c) 50 mV/s (d) 100 mV/s.

Table 1. Cyclic voltammetric peak parameters observed on zinc electrode in the presence of 20 mM PCP

Sweep rate (mV/s)	E_p *(V)		I_p* (mA)	
	C_1	C_2	C_1	C_2
5	-1.6	-2.28	-10	-26.1
20	-1.7	-2.43	-25	-48.7
50	-1.9	-2.52	-30	-71.3
100	-1.9	-2.61	-30	-89.3

* I_p is the limiting current and E_p is the potential of limiting current.

Figure 4 shows the effect of sweep rate on the limiting current in the presence of PCP. It was found that the wave heights of C_1 and C_2 increased with the increase of sweep rate. The starting point of limiting current was also slightly shifted to more negative potential with the increase of sweep rate. Table 1 shows the peak parameters obtained on the zinc electrode surface in the presence of 20 mM PCP. E_p increased from –2.28 V to –2.61 V with increasing in sweep rate at C_2, and the limiting current (I_p) also increased obviously from –26.1 mA to –89.3 mA.

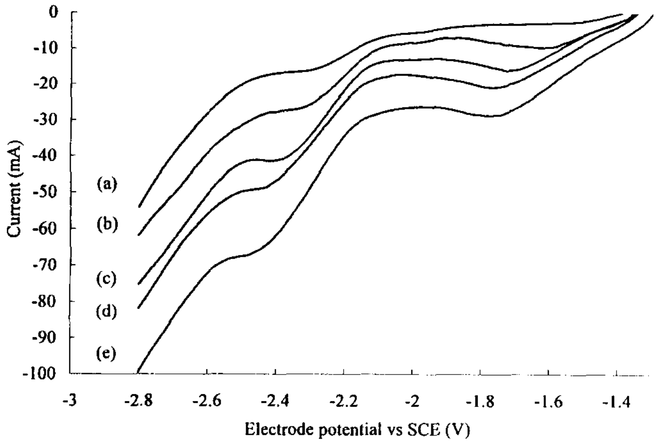


Figure 5. Cyclic voltammograms for the reduction of PCP in propylene carbonate on a zinc electrode at a voltage scan rate 20 mV/s. (a) 5 mM (b) 9.6 mM (c) 15 mM (d) 20 mM (e) 30 mM.

The effects of PCP concentration on limiting current were also studied. Figure 5 shows that the limiting current increased with increase of PCP concentration. In the first reduction, the limiting current increases from 10 mA to 30 mA with increase of PCP concentration from 5 mM to 30 mM. In addition, the limiting current also increases from 15 mA to 66 mA with increase of PCP concentration from 5 mM to 30 mM when the further reduction takes place. Figure 6 shows the plot of the increase of limiting current with respect to the PCP concentration at electrode potential of C_1 and C_2. The limiting current at C_2 was higher than at C_1 in the same concentration of PCP. It was suggested the reaction rate of the second reduction were faster than the first one. The increases of concentration of PCP could enhance the concentration of proton source by the formation of dissociated species. It is the reason for increasing the rate of reductive dechlorination.

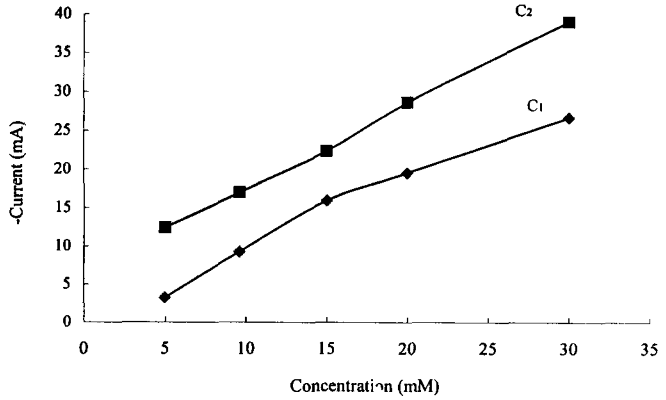


Figure 6. The relationship between limiting current and the concentration of PCP at two irreversible reductions C_1 and C_2.

Controlled potential electrolysis

To determine the mechanism of the reductive dechlorination of PCP that took place at -2.1 V~-2.4 V, electrolysis of controlled potential of –2.3 V was conducted. The product after 7-hrs electrolysis was analyzed and the results are shown in Figure 7. Compared to the retention time of the chlorophneol standards, component (b) was identified as 2,3,4,6-tetrachlorophenol and component (c) and (d) were identified as 2,4,6-trichlorophend and 2,4,5-trichlorophenol, respectively. However, without being able to obtain a suitable standard, product (e) could not be confirmed further. It might be the trichlorophenol or dichlorophenol.

The degradation progress curves of PCP are shown in Figure 8. Sixty percent of the PCP was degraded within 7 hrs. 2,3,4,6-tetrachlorophenol was generated much more quickly and small amounts of trichlorophenols were also detected. Mass balances based on the substrate PCP and the intermediate product 2,3,4,6-tetrachlorophenol showed that the total chlorophenols (CPs) (see Figure 8) within 7 hrs was 22% less than the initial concentration. The poor mass balances suggested that an additioned transformation beyond the observed product. It was possible that other tetrachlorophenols might have been produced and then coeluted with the 2,3,4,6-isomer.

Based upon the HPLC analysis, it was found that the 2,3,5,6-tetrachlorophenol could coelute with the 2,3,4,6-tetrachlorophenol. The coeluted peak was used to calculate total tetrachlorophenols, and mass balances were also taken once more. Well mass balances of total chlorophenols are shown in Figure 8 (described in dash line). It was suggested that 2,3,5,6-tetrachlorophenol might be also one of the intermediates of electrolysis, and it was the reason for the poor mass balances encountered. The similar intermediates were observed in the reductive dechlorination of PCP by vitamin B_{12} [6]. Vitamin B_{12s} could completely transform PCP to a mixture of 2,3,4,6-tetrachlorophenol and 2,3,5,6-tetrachlorophenol. In this study, the electrochemical reduction of PCP preferentially removed chlorine atom meta and para rather than ortho-chlorine removal. It was not the same as the reductive dechlorination of PCP by anaerobic sediment slurries. Anaerobic sediments acclimated to various dichlorophenol showed different regiospecificity in dechlorination of PCP [4], and the order of chlorine removal was ortho > para > meta.

From practical point of view, the target of electrochemical reduction of PCP is to dechlorinate completely and to form an innocuous compound. In this study, tetrachlorophenol and trichlorophenpol were the intermediate products at the controlled potential electrolysis, and further degradation or conversion of PCP to di or mono chlorinated phenol could not occur. In fact, we performed the similar controlled potential to electrolyze 2,4-dichlorophenol and no reduction of 2,4-dichlorophenol was observed after 7hrs on a zinc electrode. The highly negative potential may be necessary for reducing the lower chlorinated phenol. Thus, the reaction potentials for all of chlorophenols must be taken and a gradient potential should be taken if less chlorinated phenols have to be broken down.

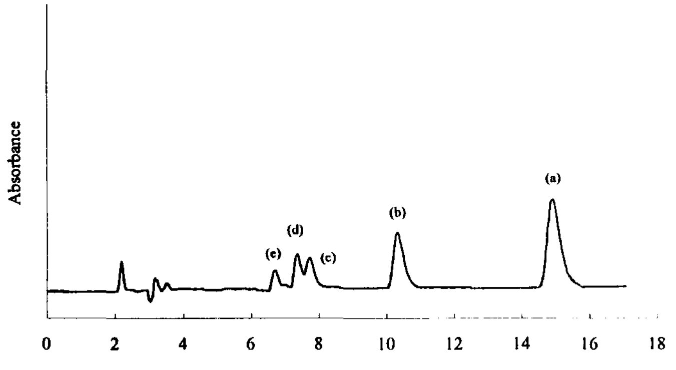


Figure 7. Chromatogram monitoring the electrolysis of PCP on a zinc electrode at -2.3 V. (a) PCP (b) 2,3,4,6-tetrachlorophenol (c) 2,4,6-trichlorophenol (d) 2,4,5-trichlorophenol (e) unknown product.

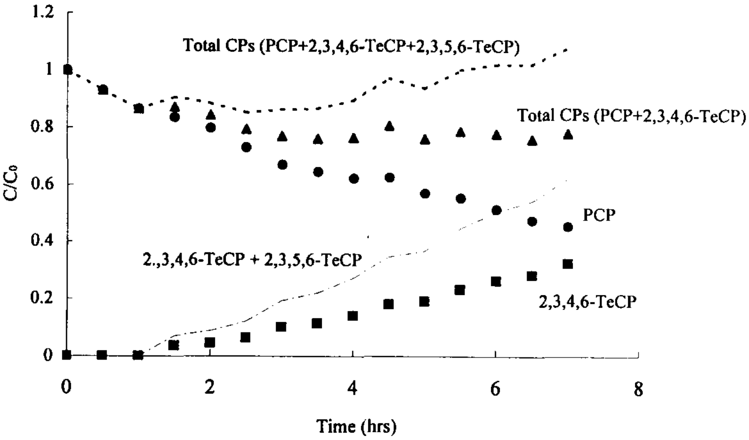


Figure 8. Transient decay of PCP as a function of electrolysis time. Electrode potential: -2.3 V. Initial concentration of PCP is 20 mM. C/C_0, ratio of the concentration of the compound to the initial concentration of PCP (C_0). Dash lines are the concentration of tetrachlorophenols and total chlorophenols that calculated using the coeluted peak.

Mechanism study

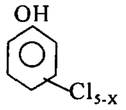
In addition to the identification of product after electrolysis, the evolution of hydrogen was also observed during the electrolysis period. For the formation of hydrogen, two steps could be considered. At first, proton was reduced to atomic hydrogen; then, two atomic hydrogens combined to form H_2. Thus, atomic hydrogen was the intermediate during the electrolysis and adsorbed layer was formed on the surface of electrode that could mediate the reduction of both PCP and partially dechlorinated products. The electrochemical mechanism of dechlorination of PCP at C_2 was tentatively proposed as following :

$$H_2O \rightarrow H^+ + OH^- \qquad (1)$$

$$PCP \rightarrow PCP^- + H^+ \qquad (2)$$

$$H^+ + e^- \rightarrow [H] \qquad (3)$$

PCP+2X[H] →



+HCl (4)

Proton source came from both acidic dissociation of PCP and trace water, presented as an impurity in the solvent and the TEACl electrolyte. The similar mechanism of reductive dechlorination of PCP on a lead cathode had been observed, but the intermediate product was different [14]. 2,3,4,5-tetrachlorophenol was detected while using lead electrode, however, only 2,4,6-trichlorophenol was detected in our study.

Direct electron transfer mechanism was not suggested at C_2 because proton was reduced to hydrogen rapidly at the controlled potential. In addition, the direct reduction mechanism required adsorption of the organic substrate on the metal surface and electron transfer. At the experimental acid-base values (pH≒11), PCP was present predominantly in the ionized form (e.g., PCP^-). According to the Stern double layer principle, PCP with negative charge is against the cathodic surface. It exists mostly in the diffusion layer and can not be adsorbed on the cathode surface. Therefore, direct electron transfer mechanism could not explain the reductive dechlorination of PCP with the controlled potential electrolysis at -2.3 V. This mechanism is not the same as those of alkyl halides. It is suggested that dissociative process results in the formation of a carbon-centered radical for alkyl halides, and the electron is transferred into the lowest unoccupied orbital of the substrate molecule [12]. It was also different from the electroreduction of HCB, in which a single electron is transformed to form a radical anion whose major reaction channel is ejection of Cl^- [15].

Current efficiency

The current efficiency for the electrochemical reduction of PCP on a zinc cathode was also investigated. The removal mole amounts of PCP in practice could be calculated using the following equations :

$$N=-\left(\frac{Vc}{Am}\right)\frac{dC}{dt} \tag{5}$$

where N is the removal mole amounts of PCP (mole/hr cm^2), Vc is the volumes of reaction liquid (L), Am is the surface areas of electrode (cm^2), C is the concentration of PCP (M), t is the electrolysis time (hr).

To calculate the removal mole amounts of PCP in theory, the mechanism of reductive dechlorination proposed in above section was applied. That is, PCP was reduced by hydrogen atom, and reduction of one mole of PCP required two mole hydrogen atoms. Furthermore, the formation of two moles of hydrogen atoms must have to transfer equal moles of electrons. That is, two moles of electrons could reduce one mole of PCP if no extra reaction occurred. Because only a few of trichlorophenol was formed in this study, the electrons of donor were nearly used to reduce PCP. Thus, the removal mole amounts of PCP in theory, No, could be calculated as follow:

$$No=\left(\frac{1}{nFAm}\right)\frac{dQ}{dt}=\left(\frac{1}{nFAm}\right)\frac{dIt}{dt}=\left(\frac{1}{nFAm}\right)\left(I+t\frac{dI}{dt}\right) \tag{6}$$

where n is the electron donor numbers per one molecule of PCP (=2), F is the Faraday constant (26.8Ahr/mole), Q is the electric charge (Ahr) and I is the electrolysis current (A). In this study, current was nearly constant during electrolysis period of 7 hrs, so the dI/dt was negligible. Thus, equation (6) can be rearranged as below:

$$No = \left(\frac{I}{nFAm} \right) \tag{7}$$

The ratio of N to No was defined as the current efficiency (CE) for the reduction of PCP. The instantaneous current efficiency was calculated using the following equation:

$$CE = \frac{N}{No} 100\% = -\frac{\left(\frac{Vc}{Am} \right) \frac{dC}{dt}}{\frac{I}{nFAm}} = -\frac{dC}{dt} . \frac{VcFn}{I} \tag{8}$$

dC/dt could be normalized with initial concentration of PCP (Co), and the equation (8) could be rewritten as follow:

$$CE = -\frac{dP}{dt} \frac{CoVcFn}{I} \tag{9}$$

where P is the ratio of concentration of PCP at any time to initial concentration of PCP (C/Co). An average current efficiency could be then calculated with equation (10)

$$CEavg = \frac{CoVcFn}{I\tau} \int_0^{\tau} -\frac{dP}{dt} dt \tag{10}$$

where τ is the interval of electrolysis times (hr).

Vc, F, Co, I were known, and the task was to find the *-dP/dt* that could be used to calculate the instantaneous current efficiency. From Figure 8, pseudo-first-order rate constant (hr^{-1}) determined by linear regression of the –ln(C/Co) verus time data were 0.1136, and P could be described as below :

$$P = e^{-0.1136t} \tag{11}$$

with differentiating equation (11), we obtain equation (12)

$$-\frac{dP}{dt} = 0.1e^{-0.1136t} \left(\frac{1}{hr} \right) \tag{12}$$

substituting equation (12) into equation (9), (10) and integrating the resulting equation, we obtain CE and CEavg as below:

$$CE = \frac{CoVcFn}{I} - \frac{dP}{dt} = \frac{20 \times 10^{-3}\, M \times 0.25L \times 26.8 \times 2Ahr/mole}{32 \times 10^{-3}\, A} \times 0.1e^{-0.1136t}\ {}^{1}\!/_{hr} \times 100\% \tag{13}$$

$$= 84e^{-0.1136t}\,\%$$

$$CEavg = \frac{CoVcFn}{I\tau} \int_0^\tau - \frac{dP}{dt}dt = \frac{84}{7}\int_0^7 - e^{-0.1136t}\,dt\% = 60\% \tag{14}$$

Figure 9 shows current efficiency calculated using equation (13). Current efficiency exhibited an exponential decay over the electrolysis time. The current efficiency decreased with time during electrolysis and finally reached a value of about 38% after 7hrs, and an average value that calculated by equation (14) was found to be 60%.

There were some reasons for causing lower current efficiency with electrolysis time. From cyclic voltammetric studies, it was known the reaction was limited by the transport of PCP. The concentration of PCP decreased with electrolysis time, and the transfer limitation increased with decrease of the concentration of PCP. Then, adsorbed atomic hydrogen should combined with itself and H_2 was accumulated at metal surface or evolution. H_2 is not a facile reductant and it will not contribute directly to dehalogenation. In fact, excessive H_2 accumulation at the metal surface was known to inhibit the continuation of reduction reactions in organic synthesis [12]. Thus, it is suggested that transport limitation of PCP and the formation of H_2 were the major causes to affect the dehalogenation rate as well as current efficiency. A suitable controlled electrolysis potential of PCP perhaps is necessary to increase the current efficiency and avoid the evolution of hydrogen. In addition, organic mediators [16] such as zinc phthalocyanine may provide better catalysis to solve the problem of transport limitation and can improve the current efficiency.

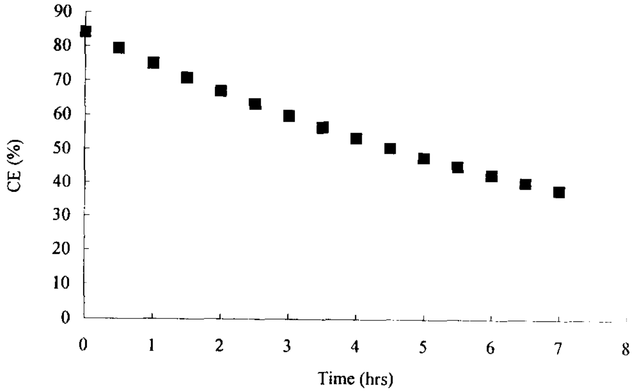


Figure 9. Current efficiency of reductive dechlorination of PCP as a function of time for an electrode potential of -2.3 V.

Reduction of PCP in water on zinc electrode

In contrast to the reduction of PCP in propylene carbonate, the cyclic voltammograms for the reduction in water were investigated. Figure 10 shows that two irreversible reductions were also observed at -1.6 V and -1.95 V, respectively. In earlier report, only one reductive feature was observed on a lead electrode, a peak centred on -1.75 V. The mechanism of the reduction of PCP in water was suggested to be the direct electron transfer reduction [14]. Based on our result, it implied that the reduction of PCP on a zinc cathode was more complex than it was on a lead cathode in water system. Two reaction schemes including reduction by adsorbed layer of hydrogen and direct electron transfer might occur simultaneously in water system with a much higher overpotential zinc cathode.

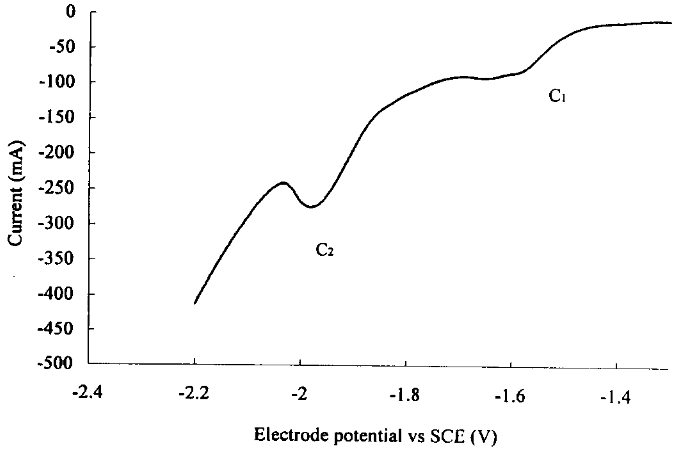


Figure 10. Cyclic voltammogram for reduction of 20 mM PCP in 0.25 M TEACl/water on a zinc electrode at a voltage scan rate 20 mV/s. C_1 and C_2 are irreversible reductions at -1.6 V and -1.95 V.

Conclusion

In this paper, we first used metallic zinc as a cathode to dechlorinate PCP. Two irreversible reductions of PCP on zinc cathode were verified in both solvent and aqueous solutions. The results suggest that zinc metal can be a suitable cathode and is able to dechlorinate PCP even in aqueous solution. Hydrogen atoms act an important catalyst to reduce PCP at the second reduction in the solvent system. The transport limitation of PCP and the formation of H_2 are the main reasons that cause the lower current efficiency.

In this report, higher PCP concentration was taken for cyclic voltammetric studies, because at lower concentration (<5mM) no wave was observed at all. But in contaminated sites, the contaminant of PCP was almost taken place about several hundreds or thousands micro molar concentration. Hence, much further research is needed to devise at the low contaminant concentrations encountered in practical situations. In addition, the sorption of chlorinated phenols by soils and aquifer materials is another concern problem. In earlier report [17], a large amount of PCP was adsorbed in aquifer material, it is difficult to solve such this problem. Some suitable solvent may be chosen to release PCP from sorbents and electrochemically reductive dechlorination of chlorinated phenol is needed in those of solvent system further. We are now investigating this study and will report the result lately.

Acknowledgments

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