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Mineralization of aqueous pentachlorophenolate by anodic contact glow discharge electrolysis

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Abstract

Exhaustive mineralization of pentachlorophenolate ion (PCP) in phosphate buffer was carried out using anodic contact glow discharge electrolysis (CGDE), in which plasma was sustained between the electrolyte and anode. During CGDE, PCP degraded smoothly. The amount of total organic carbon decreased significantly, indicating the eventual conversion of the carbon atoms of benzene nucleus to inorganic carbons. Furthermore, chlorine atoms in PCP were liberated as chloride ions. As a primary intermediate product, 2,3,5,6-tetrachloro-1,4-benzoquinone was detected, and oxalate and formate as byproducts were also found. It was revealed that disappearance of PCP obeyed first-order kinetics. The reaction rate was generally unaffected by both O_2 and inert gases in the cell, although it decreased by raising initial pH of solution. In addition, a plausible reaction pathway involving hydroxyl radical was proposed.

Key words: pentachlorophenol; mineralization; contact glow discharge electrolysis; first-order rate law

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Introduction

In these decades, wastewater containing persistent organic pollutants (POPs) has caused a lot of environmental problems (Marye and Maria, 1993; Ollis and Ekabi, 1993). Pentachlorophenol (PCP), a typical POP, has been widely used as a fungicide, bactericide, and wood preservative. The toxicity of PCP has been well studied even at a low concentration level (Liu et al., 1982), and PCP is listed as a priority pollutant by the U.S. Environmental Protection Agency (Luise et al., 2000). Nevertheless, PCP still continues to contaminate the effluents from several industries such as pulp and paper industry (Verenich et al., 2001). Thus, the efforts to develop advanced oxidation processes (AOPs) for destruction of PCP (Pera-Titus et al., 2004) are in progress. The methods employed are ozone oxidation (Weavers et al., 2000), UV light (Jardim et al., 1997), ultrasound (Weavers et al., 2000), glow discharge (Sharma et al., 2000), TiO_2 photocatalysis (Jardim et al., 1997), Fenton's reagent (Fukushima and Tatsumi, 2001), and the combination of the above (Weavers et al., 2000). In each case, hydroxyl radical has been postulated as a potent oxidizing species.

In recent years, a great interest has been attracted to utilization of plasmas in contact with liquids for the purpose of water purification (Malik et al., 2001). We have paid particular attention to the use of contact glow discharge electrolysis (CGDE), which was extensively studied by several groups of researchers (Hickling and Ingram, 1964; Hickling, 1971; Sen Gupt and Singh, 1991; Gangal et al., 2009). In CGDE, a continuous gaseous plasma can be sustained between the solution and the tip of thin wire anode in contact with the surface when the applied voltage is higher than 430–450 V. The charged species in the gaseous plasma are accelerated due to the steep potential gradient and rush into the solution with a distribution of energy covering the range that high enough to lead the chemical changes in the solution. In the reaction zone, ionized and/or activated water molecules resulting from the collision of bombarding ions would react with other water molecules to produce hydroxyl radicals and, sometimes, hydrogen atoms. Hydrogen peroxide is one of the main products of CGDE in the solution of inert electrolytes and should be formed by the recombination of OH radicals (Hickling, 1971; Mazzocchin et al., 1973; Almubarak and Wood, 1977; Bullock et al., 1980; Sen gupta and Singh, 1994; Sen gupta et al., 1998a, 1998b; Gangal et al., 2010).

Previously we reported a series of studies on degradation of aqueous aromatic compounds by means of CGDE and proposed the scheme for the breakdown of benzene nucleus by the attack of hydroxyl radicals generated in the process (Tezuka and Iwasaki, 1997; Amano and Tezuka, 2006; Tomizawa and Tezuka, 2007). Recently, Yang et al.

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(2009) reported the degradation of monochlorophenols in water by CGDE; Gao et al. (2003) and Wang and Jiang (2008) presented works on the use of CGDE for AOP. In this article, we describe the mechanistic and kinetic aspects of the mineralization of PCP in phosphate solutions.

1 Experimental

The reaction apparatus for CGDE experiment is illustrated in Fig 1. A cylindrical glass cell was employed. The anode was a platinum wire of 0.6 mm diameter sealed into a glass tube introduced into the cell. The cathode was a stainless steel plate (35 × 10 × 2 mm) placed in another glass tube, the lower end of which was plugged by a sintered glass disk of medium porosity, and immersed into 70 mL of an aqueous phosphate solution. For CGDE under an atmosphere of gas other than air, the solution was thoroughly bubbled with the gas to purge air in the cell prior to the run. A voltage of 500 V from a DC power supply was applied between the electrodes. The depth of discharge electrode (anode) into solution was 1 mm and adjusted so as to maintain the average current of 70 mA. The total electricity passed during CGDE was measured by a digital coulomb-meter. In the course of CGDE, the solution was gently stirred with a Teflon-coated magnet bar and the cell was placed in an ice-water bath to hold the temperature of the bulk solution at 20°C.

Sodium pentachlorophenolate (PCP) of reagent grade was used without further purification. As an electrolytic solution, three phosphate solutions were used: 8.7 mmol/L potassium dihydrogenphosphate + 30.4 mmol/L disodium hydrogenphosphate (solution A); 39.1 mmol/L disodium hydrogenphosphate (solution B); 39.1 mmol/L trisodium phosphate (solution C)). pH of solutions A, B, and C were 7.4, 9.7 and 12.5, respectively. The aliquots were sampled out and analyzed by HPLC (Shimadzu LC10A, Japan). The unreacted PCP was quantified on GL Sciences Inertsil ODS-3V column (5 μm, 4.6 × 150 mm) connected with a UV-Vis detector (Shimadzu SPD-M10A, Japan) and the eluent was acetic acid + methanol (1:99). Shodex Ionpak KC-811 column (8 × 300 mm) with the eluents of 0.5 mmol/L perchloric acid and 15 mmol/L perchloric acid + acetonitrile (85:15) was used with a conductivity detector (Shimadzu CDD-6A, Japan) for the analysis of formate and oxalate, respectively. In addition, Shodex Ionpak IC I-524A column with the eluent of 2.5 mmol/L phthalic acid (pH 2.5, flow rate 1.5 mL/min, 40°C) was used with a conductivity detector for the analysis of chloride ion. The amount of total organic carbon (TOC) in the solution was determined by a TOC analyzer (Shimadzu TOC-V_E, Japan). The identification of minor products was based on GC-MS (Shimadzu GC-MS 5050, Japan) measurement.

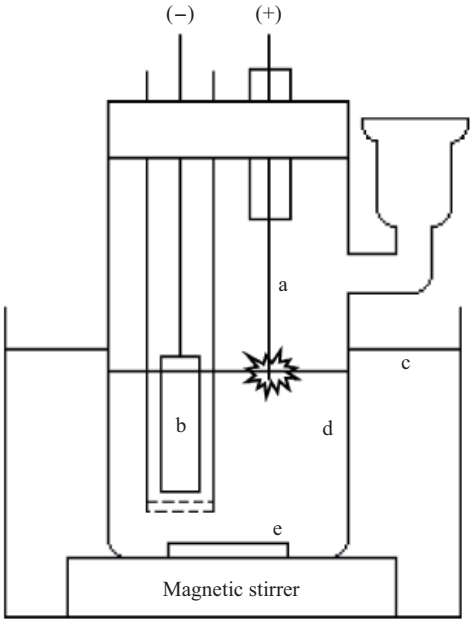

Fig. 1 Apparatus for contact glow discharge electrolysis. a: anode; b: cathode; c: ice-water bath; d: electrolytic solution; e: Teflon-coated magnet bar.

2 Results and discussion

2.1 Mineralization of PCP

While anodic CGDE of an aqueous phosphate solution containing PCP went on, PCP smoothly degraded, and the TOC in water decreased significantly as shown in Fig. 2, where the initial concentration of PCP (2.1 mmol/L) corresponds to 151 mg/L of TOC.

At 240 min, all of PCP and most of TOC disappeared. This implies that carbon atoms of benzene nucleus could be effectively converted to inorganic carbon (IC) which might exist as hydrogencarbonate in the solution and/or carbon dioxide released to the gas phase depending on pH of the solution.

The gap between the decay curves of PCP and TOC suggests the occurrence of organic intermediate products. A diversity of carboxylates were detected but most of them except oxalate and formate have not been well determined yet, owing to their extreme minuteness and lability. Figure 3 shows the variations of the yields of oxalate and formate. The yield of oxalate rose to a maximum at 60 min and fell thereafter. On the other hand, the yield of formate increased slowly up to 180 min, and then remained. It appears that oxalate formed and decomposed faster than formate. However, it should be ruled out that formate might

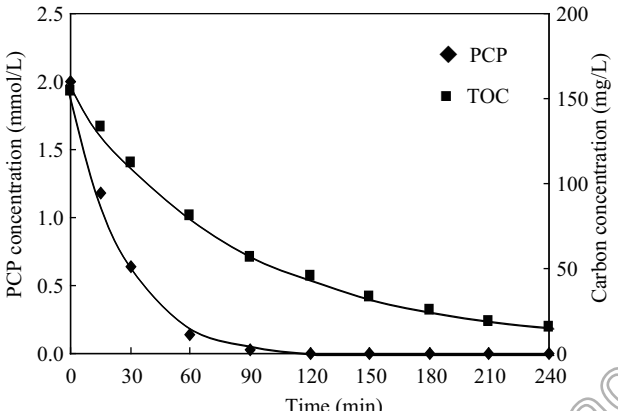

Fig. 2 Decomposition of 2.10 mmol/L PCP in solution A by CGDE.

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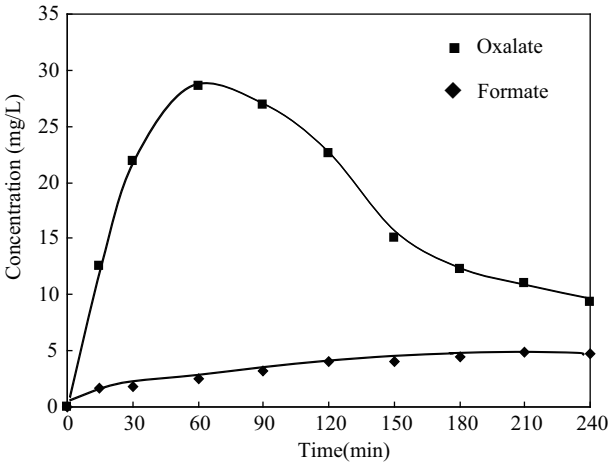

Fig. 3 Oxalate/formate from CGDE of 2.10 mmol/L PCP in solution A.

result from the decomposition of oxalate, because formate was not obtained in CGDE of oxalate (Amano and Tezuka, 2006).

In addition, it was confirmed that chlorine atoms of PCP was quantitatively released as chloride ions. The yields of the products from CGDE of PCP, namely IC, oxalate, formate and Cl^-, as well as the conversion of PCP are summarized in Table 1. The yield is defined as the percentage of moles of a certain element (C or Cl) in each product per moles of that in the initial material. The yields of undetermined intermediates, specified as ND (Table 1). Although the yields of ND were considerable in the earlier stage, they substantially lowered with the progress of CGDE. The yields of Cl^- ion and IC reached 100% and 91%, respectively, at the termination of CGDE.

2.2 Effects of initial conditions

The effects of initial conditions, such as surrounding gases and pH of electrolytic solution, on the rate of PCP degradation were examined. The influence of electrolytic solutions can be seen in Fig. 4. The exponential decay of PCP concentration with the discharge time demonstrates that the first-order kinetics and the rate constant k (min^{-1}) can be evaluated from the slope of the linear plot as the following equation:

$$\ln(C_0/C) = kt$$

Table 1 Elemental yields of products from CGDE of PCP[a]

Time (min)	PCP conversion (%)	Product yield (%)					
		Chlorine			Carbon		
		Cl^-	ND[c]	Formate	Oxalate	IC[b]	ND[c]
15	41	38	3	1	8	14	18
30	68	59	9	1	14	28	25
60	93	86	7	2	18	47	26
90	98	93	6	2	17	63	16
120	100	99	0	3	15	71	11
150	100	100	0	3	10	78	9
180	100	100	0	3	8	83	6
210	100	100	0	3	7	88	2
240	100	100	0	3	6	91	0

[a] C_0: 2.10 mmol/L in solution A; [b] inorganic carbon; [c] not determined.

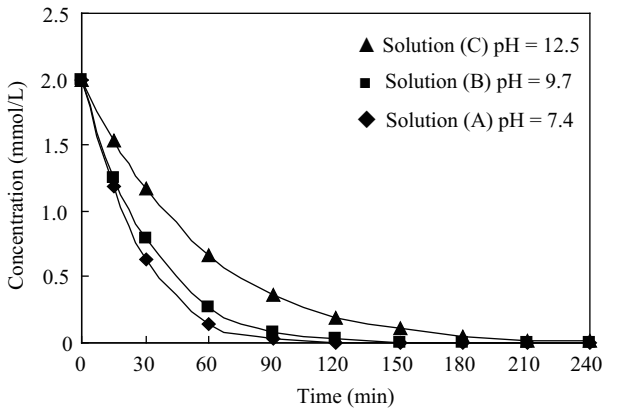

Fig. 4 Influence of solutions on the decay of PCP.

where, C, C_0, k and t denote the concentrations of PCP at time t, that at $t = 0$, the rate constant and reaction time, respectively. The plots for the decay of PCP using three solutions are shown in Fig. 5.

The apparent rate constants for the disappearance of PCP, k, were calculated to be: 4.6×10^{-2} min^{-1} (for solution A, pH = 7.4), 3.6×10^{-2} min^{-1} (for solution B, pH = 9.7), and 2.0×10^{-2} min^{-1} (for solution C, pH = 12.5), which are indicated together with the correlation coefficients in Table 2. With a rise in pH, the rate constant, k, decreases significantly. This result might be interpreted by the concept that the reduction potential of hydroxyl radical would decline with the basicity of solution (Buxton et al., 1988).

Table 2 also exhibits the effect of surrounding gases. Under O_2 and N_2 atmospheres the rate constants for the decay of PCP were quite similar and somewhat lower than those in the cases of air and Ar. The fact that k undergoes no remarkable influence irrespective of the difference in chemical properties of the surrounding gases might seem

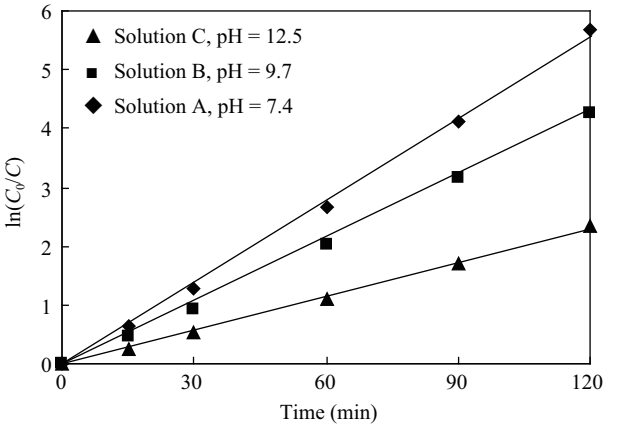

Fig. 5 Kinetical plots for the decay rate of PCP.

Table 2 Effects of initial conditions on the decay rate of PCP

Atmosphere	Solution	k (10^{-2} min^{-1})	R^2
Air	A, pH = 7.4	4.6	0.998
	B, pH = 9.7	3.6	0.996
	C, pH = 12.5	2.0	0.998
N_2	A, pH = 7.4	4.1	0.999
O_2	A, pH = 7.4	4.0	0.999
Ar	A, pH = 7.4	4.5	0.999

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consistent with the idea that the species responsible for organic oxidation by anodic CGDE in aqueous media should be hydroxyl radical generated near the plasma-anolyte interface (Sen Gupta and Singh, 1994; Sen Gupta et al., 1995, 1998a, 1998b; Gangal et al., 2010).

2.3 Mineralization pathway

As an intermediate product, 2,3,5,6-tetrachloro-1,4-benzoquinone (**I**) was detected in the initial stage of CGDE. This may result from the attack of hydroxyl radical that would occur at the position para to the phenolic OH group of PCP on account of the combined effects of the electron-donating character of phenolic OH group and the electrophilicity of OH radical. A possible pathway for the formation of (**I**) is depicted in Scheme1. Subsequently, (**I**) should undergo further oxidation to overall degradation.

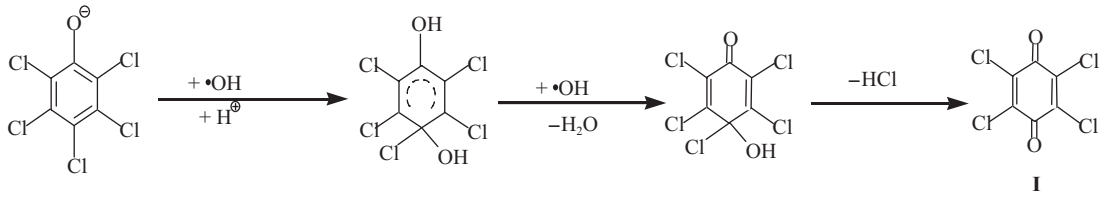
Another route may be triggered by the attack at the position ortho to the phenolic OH group of PCP. A plausible pathway leading to the formation of oxalate/formate is proposed in Scheme 2. Dechlorination of PCP, as seen in Schemes 1 and 2, might proceed through the steps such as: (1) hydrolysis of acid chlorides leaving carboxyl group and (2) elimination of HCl from –CCl(OH)– structures to form a carbonyl group.

2.4 Comparison with other AOPs

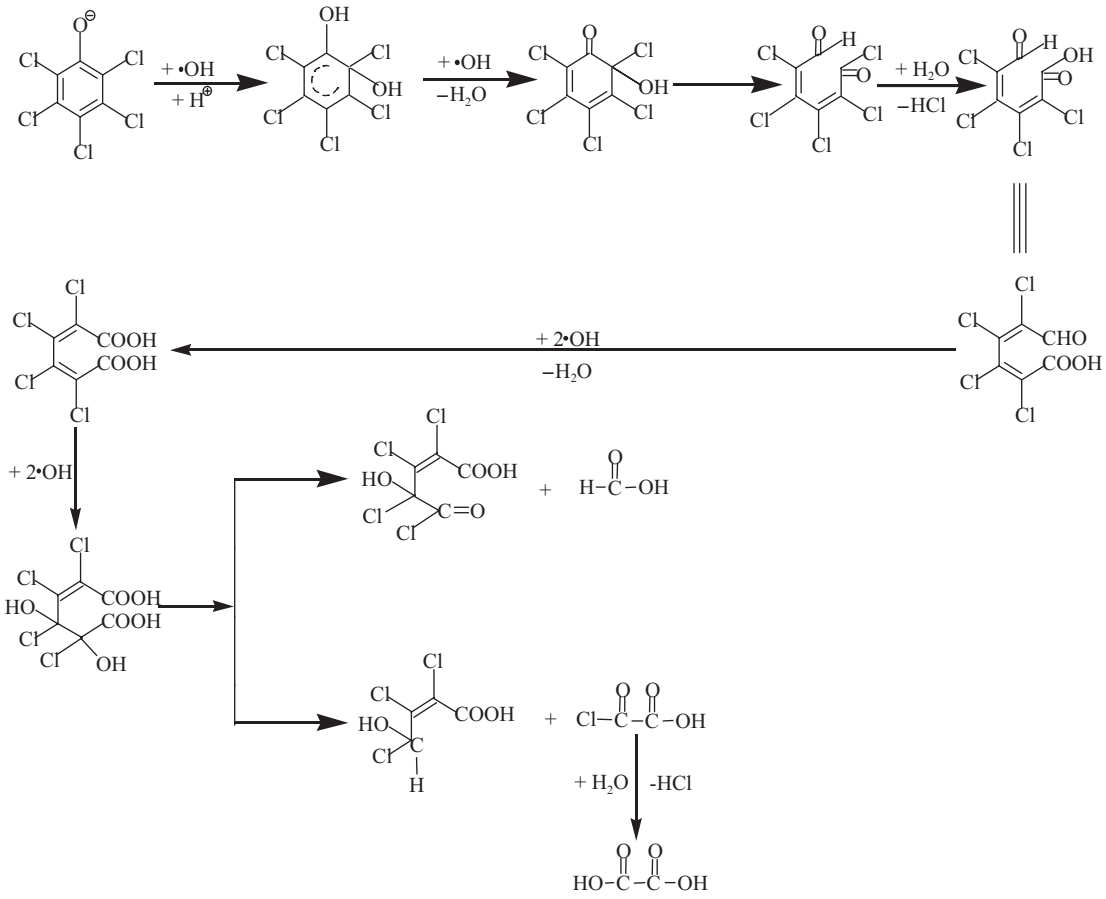
It is worth comparing CGDE with other AOPs in terms of the removal of organic pollutants in water. In Table 3, the performance in the decomposition of PCP by means of glow discharge electrolysis (Sharma et al., 2000), photocatalysis (Jardim et al., 1997), Fenton's reagent (Fukushima and Tatsumi, 2001), sonolytic ozonation (Weavers et al., 2000) and CGDE was collected. On the whole, CGDE seems to have an advantage over other AOPs for exhaustive mineralization of PCP and TOC in relatively concentrated solution as well as dechlorination.

3 Conclusions

The complete mineralization of PCP into inorganic carbon and chloride ions was carried out in aqueous



Scheme 1 A possible pathway for the formation of 2,3,5,6-tetrachloro-1,4-benzoquinone (**I**).



Scheme 2 A plausible pathway for the formation of oxalate/formate.

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Table 3 Comparison of CGDE with other AOPs for mineralization of PCP

C_0 (mmol/L)	Method	pH	PCP removal/ time (%/min)	TOC removal/ time (%/min)	Cl-liberation/ time (%/min)	References
2.1	CGDE 35W	7.4	100/120	90/240	100/150	This work
0.19	Glow discharge	7.0	100/120		70/120	Sharma et al., 2000
0.65	Photocatalytic TiO_2 (0.1 g/L) 125 W high pressure Hg lamp	7.0	97/360	91/360		Jardim et al., 1997
0.005	Fentons reagent	5.0	90/300			Fukushima and Tatsumi, 2001
0.06	Sonolytic Ozonation	7.3	100/210		100/250	Weavers et al., 2000

phosphate buffers. The degradation obeyed first-order kinetics, and proceeded more smoothly at lower pH. But the reaction rate was unaffected even in O_2 atmosphere. It was concluded that the collapse of PCP might cascade as follows: the attack of hydroxyl radical at the para and ortho positions to the phenolic OH group of PCP giving rise to the corresponding benzoquinones or the precursors, the subsequent oxidative ring cleavage to form carboxylates, and final mineralization to inorganic carbon and chloride ion.

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