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# Removal of chlorophenols from aqueous solution by fly ash

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## Abstract

Fly ash from coal-fired thermal power plants can be used for the removal of 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) with enthalpy changes of about  $-3$  kcal/mol. The amounts of 2-CP and 2,4-DCP removed are affected by the pH value of the solution. The efficiency of removal improves when the pH value is less than the  $pK_a$  values of 2-CP and 2,4-DCP, respectively. The adsorbed amount of chlorophenol by fly ash is also affected by particle diameter, carbon content, and the specific surface area of the ash used in this study. As expected, more adsorption takes place with fly ash of higher carbon content and larger specific surface area. Moreover, the adsorbed amount of chlorophenol is not influenced by the matrix in the wastewater, as shown by studying the removal of 2-CP and 2,4-DCP in wastewater from a synthetic fiber plant. Chlorophenols in the wastewater were also removed efficiently through a fly ash column, with breakthrough times being inversely proportional to flow rates. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Adsorption; Chlorophenol; Fly ash; Wastewater

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## 1. Introduction

More than 75% of fly ash in Taiwan has been used as an additive in cement, concrete, construction materials, and road pavements. In addition, fly ash also may be used to remove organic compounds from aqueous solution. For example, Akgerman and

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Zardkoohi [1] and Kumar et al. [2] found that phenol could be removed successfully from industrial wastewater by fly ash. Mott and Weber [3] also showed that low molecular weight organic compounds in aqueous solution are adsorbed by fly ash. Finally, others have reported the adsorption of dyestuff from aqueous solution [4,5].

The purpose of the present investigation is to evaluate the use of fly ash as an adsorbent for the removal of chlorophenols in aqueous solution. The physicochemical properties of fly ash, including carbon content, specific surface area (SSA), etc., on the removal of chlorophenols from wastewater were also studied by batch and column tests. Also, the removal efficiencies of 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) spiked to wastewater from a synthetic fiber plant were determined. The relationship of flow rate and breakthrough time was established from the column test results.

## 2. Experimental

### 2.1. Chemicals and materials

The 2-CP and 2,4-DCP used in this study were analytical grade reagents of 99.5% purity from Riedel-de-Haën. These reagents were used to prepare the stock solution with a concentration of 4000 mg/l, which was kept in sealed ground-glass-stoppered brown bottles that were stored in a refrigerator at 4°C for the shelf life of 1 month. The stock solution was diluted with pure water to achieve the desired concentrations to be used in the tests. The properties of 2-CP and 2,4-DCP are given in Table 1. The pH values of the solutions were adjusted using a  $\text{KH}_2\text{PO}_4\text{--K}_2\text{HPO}_4$  (Merck) buffer with a total phosphate concentration of 0.01 M. Zogorski and Faust [6] reported that the adsorption of undissociated DCP is unaffected by the presence of 0.05 M phosphates, while the equilibrium capacity of dissociated DCP was enhanced by about 10–20%. Due to the sensitivity of adsorption to pH fluctuations in the region near the  $\text{p}K_a$  of the chlorophenols, the use of the buffer to prevent pH change was felt to be more important than the shift in adsorption capacity at a given pH due to the presence of the buffer.

Two batches of dry-type fly ash from a scrubber were supplied by Taichung Thermal Power Plant, Taiwan, and labeled as fly ashes A and B. The sampling dates for fly ashes

Table 1  
Physicochemical properties of 2-CP and 2,4-DCP

	2-CP	2,4-DCP
MW (g/mol)	128.6	163
m.p. (°C)	9	45
b.p. (°C)	176	210
$\text{p}K_a$ at 25°C	8.52	7.85
Solubility in water (g/l) at 20°C	28.5	4.5
$K_{ow}^a$	145	794

<sup>a</sup> $K_{ow}$ : Octanol–water partition coefficient.

A and B were January 1996 and September 1997, respectively. The ash was passed through 53-, 90-, and 212- $\mu\text{m}$  stainless-steel sieves with standard sieve shakers. The sieved materials were dried at  $105 \pm 5^\circ\text{C}$  overnight, and then bottled and stored inside a dry box.

Wastewater samples were taken from the mixing pond of the Taiwan Chemical Fiber Plant, in Changhua, Taiwan. The major pollutants in these samples were cellulose and its derivatives with chemical oxygen demand (COD) of about 200 mg/l. To maintain the stability of the samples, the wastewater was filtered through a 0.45- $\mu\text{m}$  membrane to remove suspended particles, and the filtered wastewater was subsequently kept at  $4^\circ\text{C}$ . Since 2-CP and 2,4-DCP were not found in this wastewater, the samples were spiked with 100 mg/l each of 2-CP and 2,4-DCP prior to testing. Isothermal adsorption experiments were performed with control samples for comparison.

## 2.2. Equipment

Equipment used in the present study included an orbital shaker incubator, with temperature control and rotation speed of 200 rpm, and a Hitachi spectrophotometer model UV-2001 equipped with quartz cuvette of 1-cm light path which was used to determine 2-CP or 2,4-DCP in pure water samples. The absorption wavelengths of 273 nm for 2-CP and 284 nm for 2,4-DCP were selected to obtain maximum absorbance. All samples were filtered with a 0.45- $\mu\text{m}$  membrane before analysis. High-performance liquid chromatography (HPLC) using a Hitachi instrument equipped with a Merck Lichrospher 100 RP-18 column [4 mm (inner diameter)  $\times$  150-mm (length)] was performed to separate and determine 2-CP and 2,4-DCP from wastewater samples. Eluent was made from a methanol:water (70:30, v:v) mixture. A laser particle-size analyzer

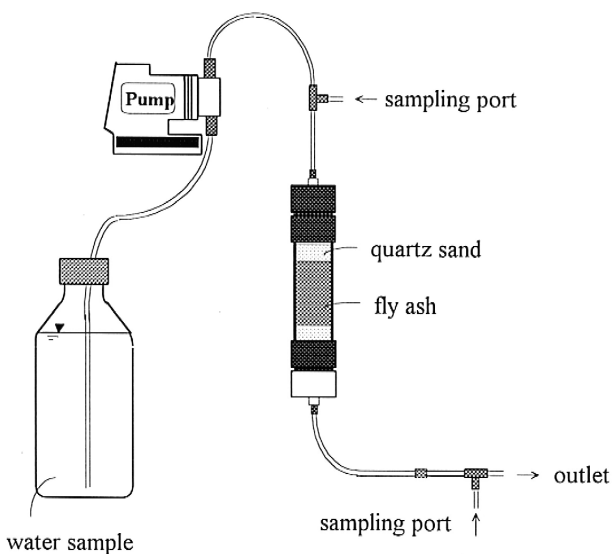


Fig. 1. Schematic diagram of fly ash adsorption column.

(Malven, type 2600) equipped with 30 helium–neon laser beams, was used to analyze the particle sizes in the range of 5–500  $\mu\text{m}$ .

### 2.3. Procedures

#### 2.3.1. Batch tests

Sufficient amounts of fly ash ranging from 5 to 200 g/l were placed in Erlenmyer flasks with addition of 2-CP or 2,4-DCP solutions, respectively. The flasks were shaken in the orbital shaker incubator at 20°C or under controlled temperature as specified for isothermal adsorption for specified times. The filtered solutions consequently were analyzed for chlorophenols.

#### 2.3.2. Column tests

Packed columns, as shown in Fig. 1, were used. About 10 g of fly ash was packed in a 2.5-cm diameter glass column to fill to a height of 6 cm with a packing density of 0.34 g/cm<sup>3</sup>, and both ends were covered by a layer of 3 cm each of quartz sand to ensure uniform flow. Wastewater containing either 100 mg/l of just 2-CP or 100 mg/l of both 2-CP and 2,4-DCP were eluted downward at fixed flow rates of 3.75, 4.50, 5.58, and 7.10 ml/min.

## 3. Results and discussion

### 3.1. Basic properties of fly ash

The sieved ashes are coded as A(1)–A(4) and B(1)–B(4). The particle sizes and their percent weight ratio are shown in Table 2. As indicated in Table 2, the fine particles of size less than 53  $\mu\text{m}$  are most abundant, particularly in fly ash B, followed by around 34% of medium range (53–212  $\mu\text{m}$ ) sizes for both A and B. Fly ash A has a higher percentage of larger particles (i.e., > 212  $\mu\text{m}$ ) than fly ash B.

The SSAs of sieved and unsieved samples of fly ash also given in Table 2 were analyzed by the BET method at the Industrial Technology Research Institute, Hsinchu, Taiwan. In contrast to the results of Kumar et al. [2] and Gupta et al. [5] that indicated SSAs ranging from 3 to 17 m<sup>2</sup>/g, the SSAs in this study range from 5 to 42 m<sup>2</sup>/g. In general, the finer the particles, the greater the SSA. However, observation of the fly ash using a scanning electron microscope (SEM) revealed that the fly ash consisted of small nonporous spheres and larger particles with high porosity. The apparent inhomogeneous nature of the fly ash evaluated in this study as well as the porous nature of the larger particles probably is the reason that the larger particles have larger SSA.

The residual carbon content (RCC) also is included in Table 2. The RCC is higher for the larger particle sizes, being similar to that of Schure et al. [7]. For particles larger than 212  $\mu\text{m}$ , the carbon content could be greater than 50%.

The exact chemical composition of fly ash is dictated by the characteristics of the parent coal material and the combustion temperature. The chemical composition of the fly ashes used in this study based on acid digestion and inductively coupled plasma-mass

Table 2  
Characteristics of fly ash

Fly ash type	Particle size ( $\mu\text{m}$ )	Particle ratio (wt.%)	SiO <sub>2</sub> (wt.%)	Al <sub>2</sub> O <sub>3</sub> (wt.%)	Fe <sub>2</sub> O <sub>3</sub> (wt.%)	CaO (wt.%)	Carbon (wt.%)	SSA (m <sup>2</sup> /g)
A		100	45.0	24.0	4.0	0.5	12.0	11.0
A(1)	< 53	49	–	–	–	–	4.0	5.1
A(2)	53–90	12	–	–	–	–	8.0	–
A(3)	90–212	22	–	–	–	–	38.4	–
A(4)	> 212	17	–	–	–	–	57.6	40.3
B		100	52.9	23.6	5.0	3.2	8.2	9.0
B(1)	< 53	59	–	–	–	–	2.9	5.4
B(2)	53–90	13	–	–	–	–	9.5	–
B(3)	90–212	21	–	–	–	–	49.2	–
B(4)	> 212	7	–	–	–	–	75.2	42.0

(–): Not measured.

spectrometry (ICP-MS) determination for fly ash A and X-ray fluorescence (XRF) for fly ash B indicated that major elements composing the fly ash are Si, Al, and Fe. Based on the assumption that these elements are in the form of oxides (i.e., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>), their weight percentages plus that of CaO are shown in Table 2. Since the resulting combined weight ratios of Si, Al, and Fe oxides exceed 70%, the fly ashes are classified as class F according to ASTM C618.

### 3.2. Effect of adsorption time and amount of fly ash for chlorophenols removal

The effect of shaking time on the adsorption of chlorophenols is shown in Fig. 2. For both fly ashes, rapid adsorption occurred with 90% of maximum removal of chlorophe-

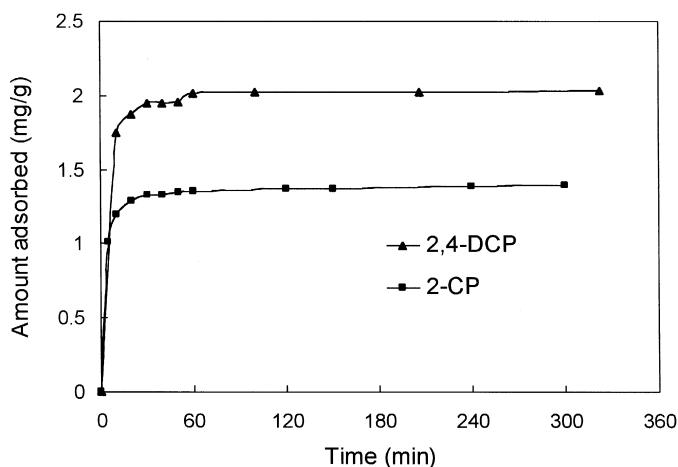


Fig. 2. The effect of time to adsorption amount.

nols within 1 h. These results are similar to those of Gupta et al. [4] for the adsorption of dyes by fly ash in which equilibrium was attained within 2 h. As a result, the batch shaking time used in this study was set for 5 h to ensure attainment of adsorption equilibrium conditions.

Isothermal adsorption experiments also were performed to determine the amount of adsorption of chlorophenols by fly ash. The initial concentration of 2-CP was 100 mg/l, the temperature was controlled at 20°C, and the initial pH was 2.9 (final pH of 4 to 5). The amount of fly ash added was altered, and the resulting amounts of 2-CP adsorbed are shown in Fig. 3a.

For fly ashes A and B in amounts up to 40 and 60 g/l, respectively, the percent removal efficiency was proportional to the amount of fly ash. Beyond these respective fly ash contents, the percent removal increased slowly. Furthermore, whereas 140 g of fly ash A is sufficient to remove 100 mg 2-CP completely in 1-l solution, only around 90% removal was attained for up to 160 g/l of fly ash B. Similar results were obtained for 2,4-DCP as shown in Fig. 3b.

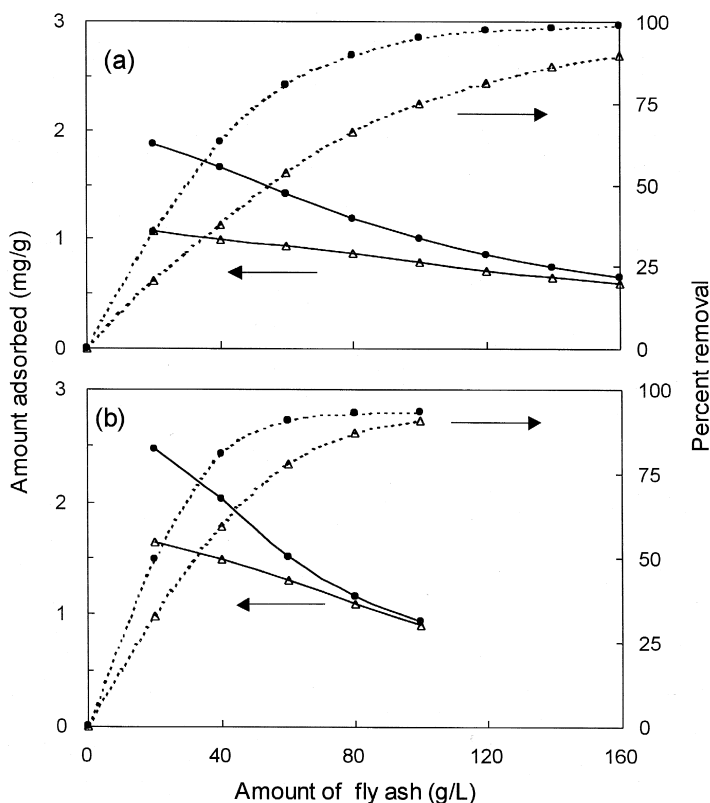


Fig. 3. Adsorption curve of chlorophenols by fly ash A (●) and fly ash B (Δ). (a) 2-CP; (b) 2,4-DCP.

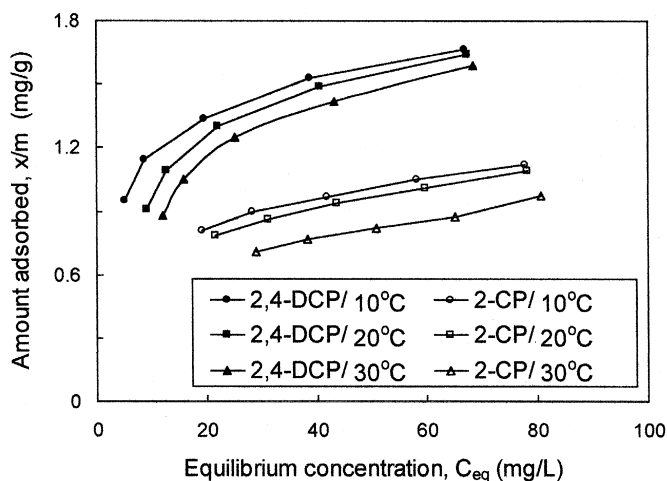


Fig. 4. Adsorption of chlorophenols by fly ash A at different temperatures.

### 3.3. Effect of temperature on fly ash adsorption

The results of a series of isothermal adsorption experiments performed at 10°C, 20°C and 30°C are shown in Fig. 4. Greater adsorption for both phenols is apparent for lower temperatures. The data also were evaluated in accordance with the Freundlich adsorption equation, or

$$x/m = kC_{eq}^{1/n} \quad (1)$$

where  $x$  = amount of adsorbate adsorbed (mg);  $m$  = amount of adsorbent (g);  $C_{eq}$  = concentration of residual amount of adsorbate at equilibrium (mg/l); and  $k$  and  $n$  = Freundlich fitting parameters. The resulting fitting parameters, given in Table 3, were determined by substituting the experimental results into the Freundlich equation for a given temperature. The values of  $k$  for both 2-CP and 2,4-DCP decrease slightly as the temperature increases. These results are similar to the results for the removal of ketones

Table 3  
Freundlich parameters and enthalpy change ( $\Delta H$ ) for 2-CP and 2,4-DCP

	Temperature (°C)	Freundlich adsorption parameters		$\Delta H$ (kcal/mol)
		$k$	$1/n$	
2-CP	10	5.46	0.0054	-3.22
	20	4.89	0.0053	
	30	3.76	0.0048	
2,4-DCP	10	10.70	0.0106	-3.40
	20	8.63	0.0115	
	30	7.20	0.0115	

and alcohols by fly ash obtained by Banerjee et al. [8], being found to be favorable at lower temperatures.

Based on Van't Hoff–Arrhenius equation, or

$$\ln(k) = -\Delta H/RT + C \quad (2)$$

where  $\Delta H$  = the enthalpy change of the reaction (cal/mol);  $R$  = ideal gas constant (1.987 cal/mol), and  $C$  = constant, the values of  $\Delta H$  for 2-CP and 2,4-DCP were found to be around  $-3$  kcal/mol, as shown in Table 3. The negative  $\Delta H$  values imply that the adsorption of chlorophenols by fly ash is exothermic.

### 3.4. Effect of pH in aqueous solutions on chlorophenols adsorption

The value of pH has a pronounced influence on the adsorption of 2-CP and 2,4-DCP to the fly ashes, as shown in Fig. 5. When the pH is less than the  $pK_a$ , both 2-CP and 2,4-DCP primarily exist in their molecular forms, and the amount of adsorption remained almost constant. When the pH value is higher than the  $pK_a$ , the dissociation of chlorophenols to anions increases and the amount of adsorption decreases. Pandey et al. [9] indicated that the accumulation of negative charges on the adsorbent surface

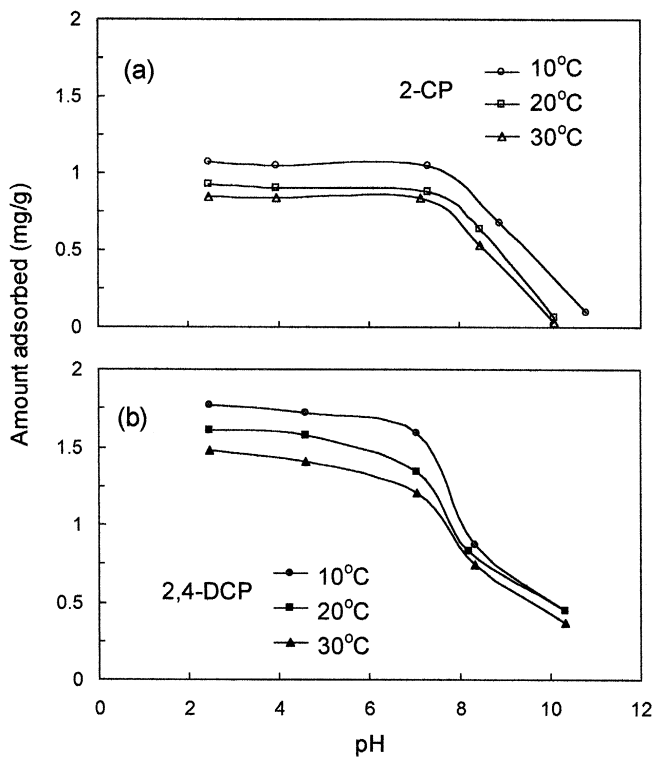


Fig. 5. Effect of pH and temperature on the adsorption of (a) 2-CP, (b) 2,4-DCP.



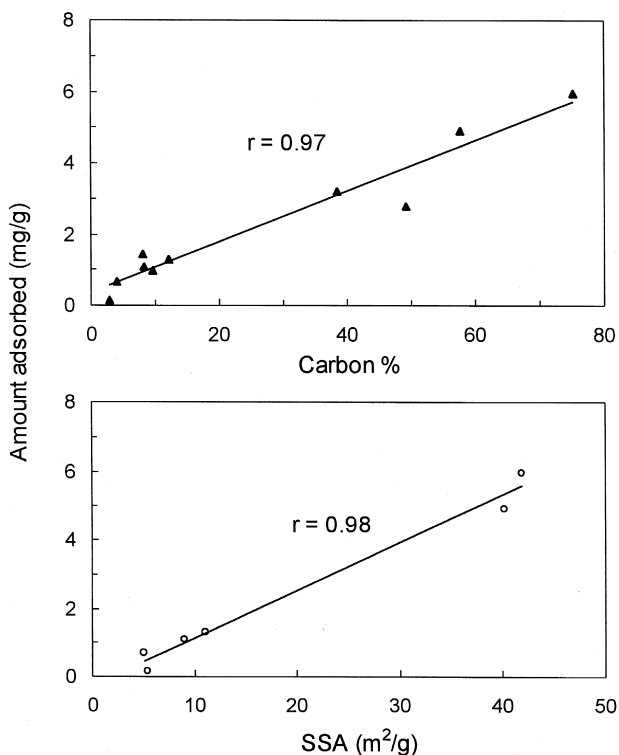


Fig. 6. Relationship of 2-CP adsorption amount with (a) carbon content and (b) SSA of fly ash.

increases as the  $OH^-$  ion concentration on the surface of fly ash increases. Thus, an increase in pH also promotes an increase in the negative charge on the surface of the fly ash particles and a reduction in the amount of adsorption of the chlorophenols that exist as anions.

### 3.5. The relationship of particle size of fly ash with carbon content, SSA and amount of adsorption

Generally, coarse particles have lower adsorption capacity than small particles [5]. However, opposite results were observed in this study. This phenomenon can be seen by comparing the SSA and carbon content between coarse and small fly ash particles.

For example, consider the data shown in Fig. 6. In Fig. 6a, the maximum amount of 2-CP adsorbed ( $Y$ , mg/g), derived from fitting the Langmuir adsorption equation to the measured adsorption data, is plotted vs. the carbon content ( $X$ , %), whereas  $Y$  is plotted as a function of the SSA content ( $Z$ ,  $m^2/g$ ) in Fig. 6b. The resulting data in Fig. 6a indicate a linear relationship of the following form:

$$Y = 0.0712 X + 0.3536; \quad (r = 0.97) \quad (3)$$

whereas the data in Fig. 6b indicate another linear relationship of the following form:

$$Y = 0.1166Z + 0.1811; \quad (r = 0.98) \quad (4)$$

Both regressions show that the amount of adsorption is greater for coarse particles with higher carbon content and SSA. For these two batches of fly ash, the carbon content is also proportional to SSA ( $r = 0.99$ ).

Banerjee et al. [8] and Mott and Weber [3] also found that the carbon content of fly ash plays a significant role during the sorption of organic compounds by fly ash. However, Yenkie and Natarajan [10] suggested that the chemical nature of the surface is considered secondary in significance relative to the magnitude of the surface area. In this study, the individual contribution of SSA and carbon content to the maximum amount of 2-CP adsorbed cannot be evaluated since the ashes which have higher SSA also show higher carbon content.

### 3.6. Adsorption of chlorophenols in wastewater by fly ash

As shown in Fig. 7, the removal of 2-CP from the wastewater that was spiked only with 2-CP generally is greater for a given fly ash content than the removal of 2-CP from the wastewater spiked with both 2-CP and 2,4-DCP, regardless of the type of fly ash used in the experiment. Thus, the presence of the co-pollutant, 2,4-DCP, obviously affected the removal of 2-CP. The effect may be attributed to a combination of relative hydrophobicity of the two chlorophenols and the equilibrium pH.

For example, 2,4-DCP has higher  $K_{ow}$  and lower solubility in water than 2-CP (Table 1). In addition, the initial pH of wastewater after adding fly ash was about 3.5, whereas the final pH after equilibrium was about 5. The pH values at the zero point of charge,  $pH_{ZPC}$ , for  $SiO_2$ ,  $Fe_2O_3$ , and  $Al_2O_3$  are 2, 6.7 and 9.1, respectively [11]. Thus, at pH 5,

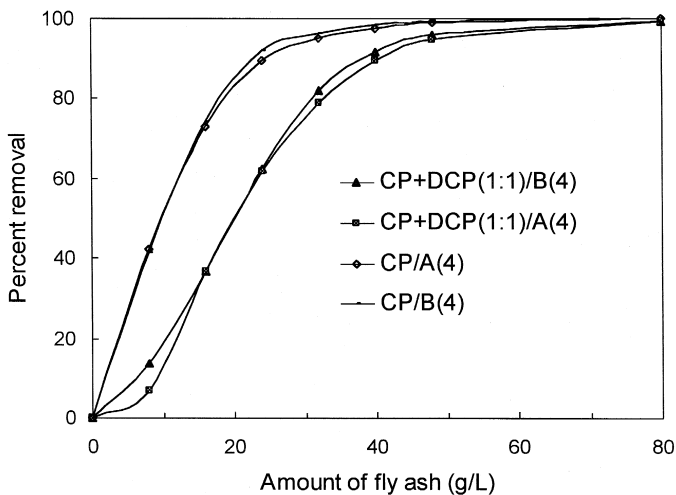


Fig. 7. Adsorption curve of 2-CP in wastewater from a synthetic fiber plant.

the net surface charge is negative for  $\text{SiO}_2$  but positive for both  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . However, both 2-CP and 2,4-DCP exist predominately as neutral molecules at this pH. Therefore, the interaction between fly ash and chlorophenols is considered mainly as a nonpolar interaction between residual carbon in fly ash and chlorophenols. The removal efficiency of 2-CP as affected by 2,4-DCP also is caused by the stronger nonpolar interaction between fly ash and 2,4-DCP.

Ehrlich and Huang [12] studied the adsorption of chlorophenols by kaolin and suggested that the adsorption is related to the hydrophobic nature of chlorophenols when the pH is less than  $\text{p}K_a$ . The more hydrophobic the chlorophenol, the easier the adsorption of the chlorophenol by kaolin. Mott and Weber [3] also found that the correlation of Freundlich sorption capacity parameters with the respective  $K_{ow}$  and the aqueous solubility of the organic contaminants were highly significant. Snoeyink and Murin [13] explained that, in the presence of several chlorophenols in solution, the competition occurred between neutral species and anionic species (affected by pH), and the adsorption was influenced by respective concentrations, degrees of dissociation, and hydrophobic behaviors.

### 3.7. Column test of chlorophenols from wastewater

Fly ash B(4) was used in the column study to evaluate removal of chlorophenols from wastewater. As previously noted, both 2-CP and 2,4-DCP compete for the adsorption sites on fly ash, and fly ash has a stronger adsorption power for 2,4-DCP than for 2-CP. Therefore, breakthrough of 2,4-DCP should take longer than breakthrough of 2-CP.

As shown in Fig. 8, the ratio of concentration of each chlorophenol at the exit end of the column to that at the entrance to the column,  $R (C_{out}/C_{in})$ , is shown as a function of time at a flow rate of 4.5 ml/min. At the beginning of the test, all of the chlorophenol flowing into the column is adsorbed by the fly ash, and the effluent concentrations of the

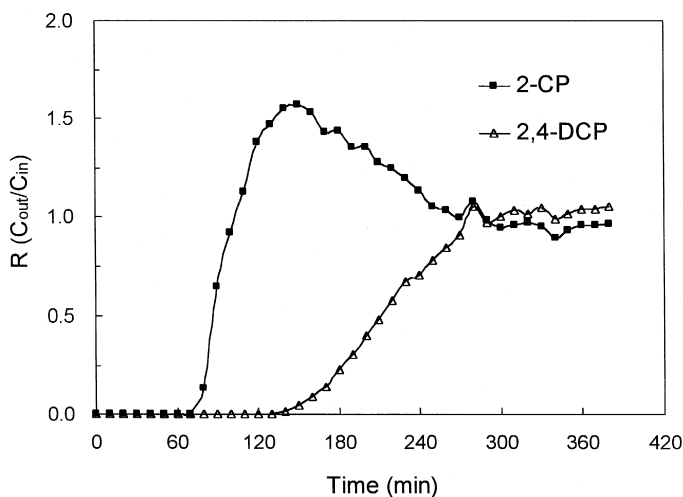


Fig. 8. Removal of 2-CP and 2,4-DCP by fly ash packed column.

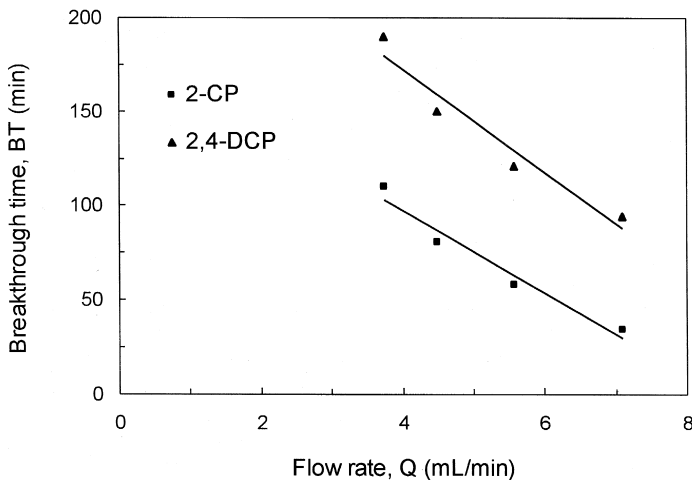


Fig. 9. Effect of flow rate on column breakthrough time.

chlorophenols were zero. The initial breakthrough of the 2-CP in the effluent occurred first at around 75 min, and the concentration ratio,  $R$ , values for 2-CP began to rise. At approximately 120 min,  $R$  for 2-CP reached a maximum value of 1.6. The increase in  $R$  value for 2-CP to values greater than unity is believed to be due to the preferential adsorption of 2,4-DCP within this period resulting in desorption of 2-CP. Subsequently, the  $R$  values for 2-CP start to decline after 120 min as the 2-CP is flushed from the column, and the  $R$  values for 2,4-DCP started to rise. The  $R$  values for both chlorophenols approached the value of unity after approximately 280 min, indicating that the column is saturated with 2,4-DCP.

The effect of the flow rate,  $Q$  (ml/min), on breakthrough time (BT, min) was determined from the results of the column tests performed at different flow rates. As shown in Fig. 9, an inverse linear trend between flow rate and breakthrough time existed for both chlorophenols as expected. As a result, a linear regression analysis was performed on the data shown in Fig. 9 with the following results:

$$2\text{-CP:BT} = -21.76Q + 184.4; \quad (r = 0.96) \quad (5)$$

and

$$2,4\text{-DCP:BT} = -27.43Q + 282.3; \quad (r = 0.94) \quad (6)$$

The data in Fig. 9 also show that the breakthrough time for 2-CP is always shorter than that for 2,4-DCP at a given flow rate. This trend is consistent with the preferential adsorption of 2,4-DCP as previously discussed.

#### 4. Conclusions

The removal of the two chlorophenols, 2-CP and 2,4-DCP, in aqueous solution by fly ash is affected by the pH of the solution, and both the carbon content and SSA of the fly

ash. The two chlorophenols are present predominately in their molecular form at pH less than their  $pK_a$ s. The higher carbon content of fly ash correlates to the higher amount of chlorophenols absorbed at that pH. The preferred adsorption of 2,4-DCP relative to 2-CP by fly ash correlates with its higher  $K_{ow}$  and lower solubility in water. Therefore, the main interaction between chlorophenols and fly ash is consistent with a nonpolar interaction.

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