**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
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Kuen-Chyr Lee[a]; Young Ku[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY, TAIPEI, TAIWAN, REPUBLIC OF CHINA

**To cite this Article** Lee, Kuen-Chyr and Ku, Young(1996) 'Removal of Chlorophenols from Aqueous Solution by Anion-Exchange Resins', Separation Science and Technology, 31: 18, 2557 — 2577
**To link to this Article: DOI:** 10.1080/01496399608001065
**URL:** http://dx.doi.org/10.1080/01496399608001065

SEPARATION SCIENCE AND TECHNOLOGY, **31**(18), pp. 2557–2577, 1996

# Removal of Chlorophenols from Aqueous Solution by Anion-Exchange Resins

KUEN-CHYR LEE and YOUNG KU*
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TAIWAN INSTITUTE OF TECHNOLOGY
TAIPEI, TAIWAN, REPUBLIC OF CHINA

## ABSTRACT

The effects of pH value and chloride ion concentration on the removal of chlorophenols from aqueous solutions by Purolite A-510 resin [macroreticular polystyrene–divinylbenzene resin with $R(CH_3)_2(C_2H_4OH)N^+$ group] are discussed by the species distributions of chlorophenols. Those chlorophenols include phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. The investigations showed that the chlorophenols could be removed effectively at alkaline conditions where the ion-exchange reaction was dominant. Also, the removal of chlorophenols increased with the number of chlorine atoms on the chlorophenols. The removal of chlorophenols via the ion-exchange reaction was hindered by the presence of chloride ions. The effect of chloride ions, however, was diminished in acidic solutions where the adsorption reaction was dominant. The proposed equilibrium model, which considers both adsorption and ion-exchange reactions, adequately describes the sorption behavior of chlorophenols. The partition constants of the protonated chlorophenols can be estimated from the octanol/water partition coefficients of the phenolic compounds.

*Key Words.* Chlorophenols removal; Anion-exchange resin; Partition constant

## INTRODUCTION

Phenol and phenolic compounds exist in wastewater at levels of parts of ten thousands or less from oil refineries, coke plants, and phenolic resin

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* To whom correspondence should be addressed.

plants. Phenols are pollutants of priority concern because of their toxicity and possible accumulation in the environment (1, 2). Vigorous research activities have been devoted toward the development of various treatment technologies, such as sorption and mineralization processes for phenols removal from water and wastewater. The treatment of chlorophenols by anion-exchange resins is generally recognized as an effective method to remove pollutants from dilute aqueous solutions (3). According to earlier research reports (4, 5), the mechanism of removing humic acids by anion-exchange resins might include ion-exchange and adsorption reactions simultaneously. The sorption of phenols from aqueous solutions by quaternary ammonium anion-exchange resins is favorable due to the ion-exchange reaction involving the replacement of counterions on the resin. The removal of phenols was especially increased with the ratio of the deprotonated phenol species to the protonated species (6). Aromatics could also be removed from aqueous solution via adsorption by macroreticular resins without ion-exchange functional groups, i.e., the attachment of the nonionic portion of the solute to the internal surface of the resin. The sorption behavior could be described by the Freundlich isotherm or a three parameter adsorption model (7, 8). This article reports the sorption equilibrium behavior of chlorophenols by the use of anion-exchange resins. A conceptual model is also established based on elemental balances and equilibrium equations for distinguishing the contributions of the sorption species on the removal of chlorophenols.

## THEORETICAL CONSIDERATION

Since a chlorophenol in aqueous solution is a weak acid, the dissociation of the chlorophenol strongly depends on the pH value of the solution and can be expressed as

$$\mathrm{CPOH} \xrightleftharpoons{K_a} \mathrm{CPO^-} + \mathrm{H^+},\ K_a = \frac{\{\mathrm{CPO^-}\}\{\mathrm{H^+}\}}{\{\mathrm{CPOH}\}} \qquad (1)$$

where {CPOH} and {CPO$^-$} represent the activity of the protonated and the deprotonated species, respectively, and $K_a$ is the dissociation constant. The values of $K_a$ at 25°C for phenol, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) are listed in Table 1 (9). Figure 1 illustrates the theoretical species distributions for these four chlorophenols as a function of solution pH values. The protonated species CPOH is predominant in acidic solutions, whereas the deprotonated species CPO$^-$ predominates in alkaline solutions. The removal of chlorophenols by Purolite A-510 resin may involve the adsorption reactions of protonated and deprotonated chlorophenols, and the ion-

TABLE 1
Properties of Chlorophenols

| | Phenol | 2-Chlorophenol | 2,4-Dichlorophenol | 2,4,6-Trichlorophenol |
|---|---|---|---|---|
| $K_a$[a] | $10^{-9.99}$ | $10^{-8.55}$ | $10^{-7.85}$ | $10^{-6.15}$ |
| log $K_{ow}$ | 1.46[b] | 2.17[b] | 3.23[c] | 3.72[c] |

[a] Dean (9).
[b] Leo, Hansch, and Elkins (16).
[c] Schellenberg, Leuenberger, and Schwarzenbach (13).

exchange reaction of deprotonated chlorophenols. This dual functionality is mainly attributed to the structure of the resin, which contains both the hydrophobic group of polystyrene–divinylbenzene and quaternary amino segments of $R(CH_3)_2(C_2H_4OH)N^+$. The overall reaction scheme can be expressed as follows

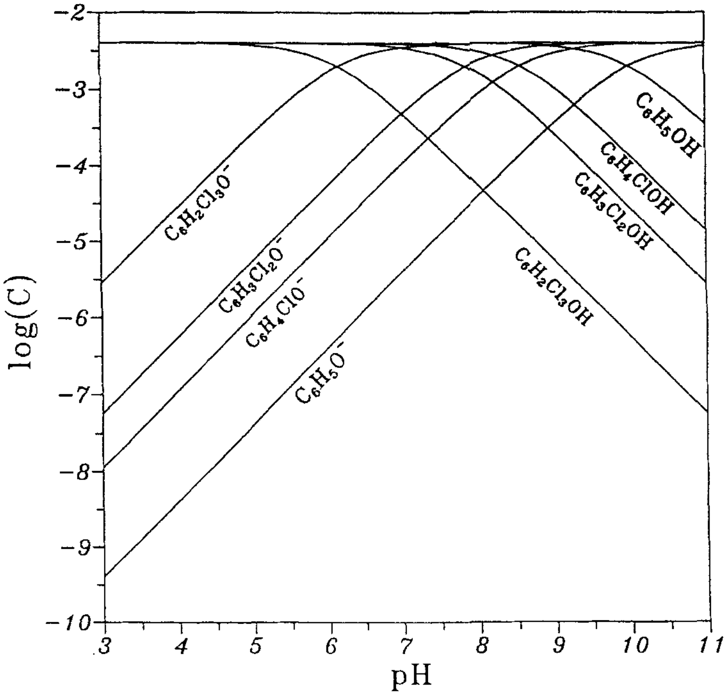


FIG. 1 The species concentrations of chlorophenols with pH values as [chlorophenols] = $4.00 \times 10^{-3}$ M.

Adsorption reaction:

$$\begin{array}{l} \mathrm{CPOH} + (\mathrm{RCl})_{\mathrm{ad}} \xrightleftharpoons{K_{\mathrm{ad1}}} (\mathrm{ClRCPOH})_{\mathrm{ad}} \qquad (2) \\ K_{\mathrm{a}} \upharpoonleft\downharpoonright \; - \mathrm{H}^+ \\ \mathrm{CPO}^- + (\mathrm{RCl})_{\mathrm{ad}} \xrightleftharpoons{K_{\mathrm{ad2}}} (\mathrm{ClRCPO}^-)_{\mathrm{ad}} \qquad (3) \end{array}$$

Ion-exchange reaction:

$$\begin{array}{c} \mathrm{CPOH} \\ K_{\mathrm{a}} \upharpoonleft\downharpoonright \; - \mathrm{H}^+ \\ \mathrm{CPO}^- + (\mathrm{RCl})_{\mathrm{ion}} \xrightleftharpoons{K_{\mathrm{ion}}} (\mathrm{CPOR})_{\mathrm{ion}} + \mathrm{Cl}^- \qquad (4) \end{array}$$

where $(\mathrm{RCl})_{\mathrm{ad}}$ and $(\mathrm{RCl})_{\mathrm{ion}}$ are the adsorption sites and ion-exchange sites on the Purolite A-510 resin, and $(\mathrm{ClRCPOH})_{\mathrm{ad}}$ and $(\mathrm{ClRCPO}^-)_{\mathrm{ad}}$ are the protonated species removal and deprotonated species removal via adsorption reaction. $(\mathrm{CPOR})_{\mathrm{ion}}$ represent deprotonated species removal via ion-exchange reaction. In order to evaluate the effect of solution conditions on the removal and establishment of the elemental balances, $(\mathrm{RCl})_{\mathrm{ad}}$, $(\mathrm{RCl})_{\mathrm{ion}}$, $(\mathrm{ClRCPOH})_{\mathrm{ad}}$, $(\mathrm{ClRCPO}^-)_{\mathrm{ad}}$, and $(\mathrm{CPOR})_{\mathrm{ion}}$ are defined as the ratio of the equivalent amount of sorption sites to the volume of reaction solution. The equilibrium constants of adsorption for the protonated and the deprotonated chlorophenols, and the ion-exchange reactions for the deprotonated chlorophenols ($K_{\mathrm{ad1}}$, $K_{\mathrm{ad2}}$, and $K_{\mathrm{ion}}$) are defined, respectively, as follows:

$$K_{\mathrm{ad1}} = \frac{\{(\mathrm{ClRCPOH})_{\mathrm{ad}}\}}{(\{\mathrm{CPOH}\} + \{\mathrm{CPO}^-\})(1/(1 + (K_{\mathrm{a}}/\{\mathrm{H}^+\})))\{(\mathrm{RCl})_{\mathrm{ad}}\}} \tag{5}$$

$$K_{\mathrm{ad2}} = \frac{\{(\mathrm{ClRCPO}^-)_{\mathrm{ad}}\}}{(\{\mathrm{CPOH}\} + \{\mathrm{CPO}^-\})(1/(1 + (\{\mathrm{H}^+\}/K_{\mathrm{a}})))\{(\mathrm{RCl})_{\mathrm{ad}}\}} \tag{6}$$

$$K_{\mathrm{ion}} = \frac{\{(\mathrm{CPOR})_{\mathrm{ion}}\}\{\mathrm{Cl}^-\}}{(\{\mathrm{CPOH}\} + \{\mathrm{CPO}^-\})(1/(1 + (\{\mathrm{H}^+\}/K_{\mathrm{a}})))\{(\mathrm{RCl})_{\mathrm{ion}}\}} \tag{7}$$

where the unit of $K_{\mathrm{ad1}}$ and $K_{\mathrm{ad2}}$ is l/mmol, and $K_{\mathrm{ion}}$ is dimensionless. All activity coefficients of the solid species, including $(\mathrm{RCl})_{\mathrm{ad}}$, $(\mathrm{RCl})_{\mathrm{ion}}$, $(\mathrm{ClRCPOH})_{\mathrm{ad}}$, $(\mathrm{ClRCPO}^-)_{\mathrm{ad}}$, and $(\mathrm{CPOR})_{\mathrm{ion}}$, are set to unity. The values of $K_{\mathrm{ad1}}$, $K_{\mathrm{ad2}}$, and $K_{\mathrm{ion}}$ are corrected to zero ionic strength in the aqueous phase, and the activity coefficient of an ionic species is calculated from the Debye–Huckel limiting law if the ionic strength is lower than 0.005 M. Otherwise, the Davies equation is applied (10). These two models are given by Eqs. (8) and (9), respectively.

$$\log \gamma_i = -0.5z^2I^{0.5} \qquad (8)$$

$$= -0.5z^2((I^{0.5}/(1 + I^{0.5})) - 0.3I) \qquad (9)$$

where $\log \gamma_i$ is the common logarithm of the activity coefficient of species $i$, $z$ is the charge of species $i$, and $I$ is the ionic strength. If the values of $K_{ad1}$, $K_{ad2}$, and $K_{ion}$ are known, the removal of chlorophenols by the adsorption, $(ClRCPOH)_{ad}$ and $(ClRCPO^-)_{ad}$, and the ion-exchange reaction, $(CPOR)_{ion}$, can be calculated from the mass balances and equilibrium equations, simultaneously, by a nonlinear Newton's method (11). The equilibrium equations are expressed as

$$K_{ad1} = \frac{\{(ClRCPOH)_{ad}\}}{\begin{array}{c}(\{(CP)_0\} - (\{(ClRCPOH)_{ad} + \{(ClRCPO^-)_{ad}\} + \{(CPOR)_{ion}\})) \\ \cdot(1/(1 + (K_a/\{H^+\})))*(\{(RCl)_{0,\,ad}\} - (\{(ClRCPOH)_{ad}\} + \{(ClRCPO^-)_{ad}\}))\end{array}} \qquad (10)$$

$$K_{ad2} = \frac{\{(ClRCPO^-)_{ad}\}}{\begin{array}{c}(\{(CP)_0\} - (\{(ClRCPOH)_{ad} + \{(ClRCPO^-)_{ad}\} + \{(CPOR)_{ion}\})) \\ \cdot(1/(1 + (\{H^+\}/K_a)))*(\{(RCl)_{0,\,ad}\} - (\{(ClRCPOH)_{ad}\} + \{(ClRCPO^-)_{ad}\}))\end{array}} \qquad (11)$$

$$K_{ion} = \frac{\{(CPOR)_{ion}\}\{Cl^-\}}{\begin{array}{c}(\{(CP)_0\} - (\{(ClRCPOH)_{ad} + \{(ClRCPO^-)_{ad}\} + \{(CPOR)_{ion}\})) \\ \cdot(1/(1 + (\{H\}/K_a)))*(\{(RCl)_{0,\,ion}\} - \{(CPOR)_{ion}\})\end{array}} \qquad (12)$$

In addition, in order to identify the effect of various solution conditions and different phenolic compounds on chlorophenol removal, a distinction should be made between the distribution constant, $K_d$, and the partition constant, $K_p$. The former is defined for the total species removal of chlorophenols via adsorption and ion-exchange reactions at various solution conditions:

$$K_d = \frac{(\{(ClRCPOH)_{ad}\} + \{(ClRCPO^-)_{ad}\} + \{(CPOR)_{ion}\})}{(\{CPOH\} + \{CPO^-\})} \qquad (13)$$

and the latter is defined for a particular species, the protonated chlorophenols, removal via adsorption in acidic solutions.

$$K_p = \frac{\{(ClRCPOH)_{ad}\}}{\{(CPOH)\}} \qquad (14)$$

For evaluating the relationship between the partition constants and octanol/water partition coefficients of chlorophenols in the presence of Purolite A-510 resin. Earlier research reported that the sorption of phenolic compounds by natural adsorbents is dominated by hydrophobic interactions. In most cases the affinity between an adsorbent and a hydrophobic solute can be reliably correlated with its organic carbon or lipid content (12, 13). Consequently, the partition constant ($K_P$), normalized by the organic carbon content of the sorbent ($f_{oc}$) could be empirically correlated with the octanol/water partition coefficient ($K_{ow}$) of the chemicals involved, i.e.,

$$K_p = (f_{oc})(b)(K_{ow})^a \tag{15}$$

## EXPERIMENTAL

Purolite A-510, a quarternary ammonium anion-exchange resin, with a medium size of 30–35 mesh, was used as the adsorbent for studying the sorption behavior of chlorophenols in aqueous solutions. The resin was treated with 1 N HCl solution for about 72 hours. A slow rinse with double-distilled water followed to insure that the resin was in the chloride form. All experimental solutions were prepared with certified reagent-grade chemicals (purity > 99.9%) and double-distilled water. In the sorption equilibrium experiments, predetermined amounts of the pre-swollen anion-exchange resin and the aqueous solutions of chlorophenols (phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol) were introduced into 100 mL reactors and maintained at 25 ± 1°C in a shaker water bath for 72 hours. When the equilibrium state was reached, the pH value of the solution was recorded. The resin was allowed to settle at least 5 minutes before the supernatant was withdrawn and filtered. The concentrations of the chlorophenols in the filtered sample were determined with a Shimazu model UV-160A UV/visible spectrophotometer. The chloride ion concentration was determined with a Dionex model DX-100 ion chromatograph. The used Purolite A-510 resin could be regenerated by 0.5–2 N NaOH or 0.1–1 N HCl solutions for reuse.

## RESULTS AND DISCUSSIONS

A series of batch tests was carried out to study the sorption behavior of chlorophenols by Purolite A-510 resin under various pH conditions at 25°C. The removal of the chlorophenols increases significantly with pH values as shown in Fig. 2. According to Reactions (2)–(4) above, the removal of chlorophenols via the ion-exchange reaction could be determined by measuring the concentration of chloride ion, and the remaining amounts of chlorophenols removal were assumed to result from the adsorption reactions. The experimental and calculated results are summarized in Tables 2–5 for phenol, 2-chlorophenol, 2,4-dichlorophenol, and

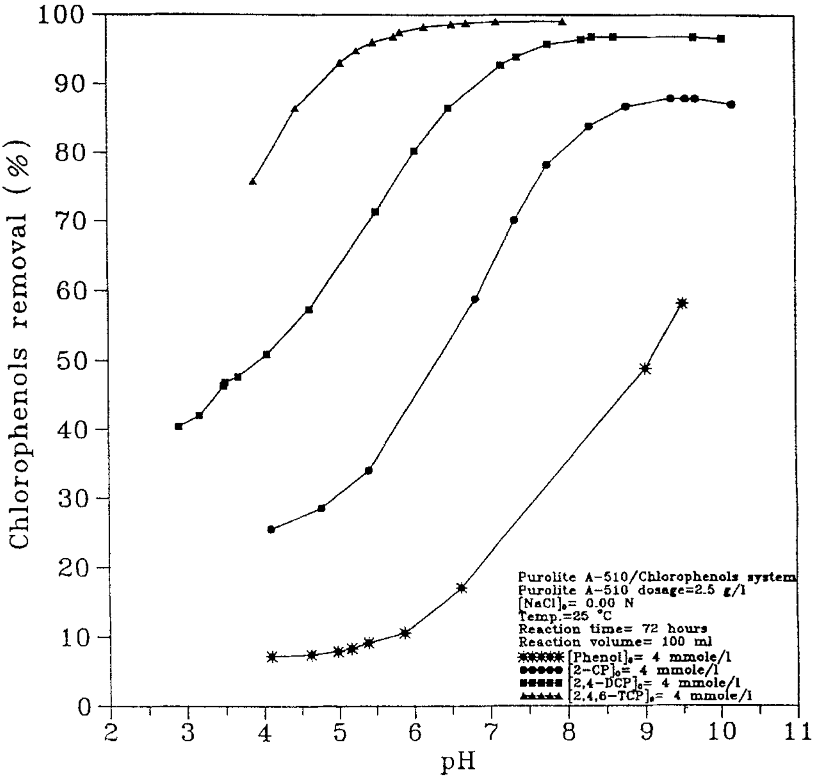


FIG. 2 Removal of chlorophenols by Purolite A-510 resin.

TABLE 2
Equilibrium Experimental Results (initial concentration of phenol = 4.00 mmol/L, amount of anion-exchange resins dosed = 2.50 g/L)

| Solution pH | Total phenol removal | Removal due to ion exchange | Removal due to adsorption | Distribution constant |
|---|---|---|---|---|
| 3.52 | 0.29 | 0 | 0.29 | 0.077 |
| 4.01 | 0.29 | 0 | 0.29 | 0.078 |
| 4.18 | 0.30 | 0 | 0.30 | 0.081 |
| 4.43 | 0.32 | 0.03 | 0.29 | 0.096 |
| 5.10 | 0.34 | 0.06 | 0.28 | 0.092 |
| 5.43 | 0.37 | 0.08 | 0.29 | 0.102 |
| 6.10 | 0.43 | 0.15 | 0.28 | 0.119 |
| 7.14 | 0.69 | 0.41 | 0.28 | 0.207 |
| 8.12 | 1.19 | 0.95 | 0.24 | 0.423 |
| 9.02 | 1.96 | 1.78 | 0.18 | 0.956 |
| 9.51 | 2.33 | 2.19 | 0.14 | 1.398 |

TABLE 3
Equilibrium Experimental Results (initial concentration of 2-CP = 4.00 mmol/L, amount of anion-exchange resins dosed = 2.50 g/L)

| Solution pH | Total 2-CP removal | Removal due to ion exchange | Removal due to adsorption | Distribution constant |
|---|---|---|---|---|
| 4.10 | 1.02 | 0.15 | 0.87 | 0.34 |
| 4.77 | 1.15 | 0.25 | 0.90 | 0.40 |
| 5.41 | 1.37 | 0.46 | 0.91 | 0.52 |
| 6.82 | 2.36 | 1.62 | 0.74 | 1.44 |
| 7.34 | 2.81 | 2.13 | 0.68 | 2.36 |
| 7.76 | 3.13 | 2.66 | 0.47 | 3.60 |
| 8.31 | 3.36 | 2.92 | 0.44 | 5.25 |
| 8.79 | 3.47 | 3.05 | 0.42 | 6.55 |
| 9.37 | 3.52 | 3.43 | 0.09 | 7.33 |

2,4,6-trichlorophenol, respectively. In acidic solutions, most chlorophenols removal was assumed to be due to protonated species adsorption; in alkaline solutions, removal of chlorophenols could be mostly attributed to the ion-exchange reaction of the deprotonated species. The distribution constants of the chlorophenols in alkaline solutions, as shown in Tables 2–5, are significantly higher than those in acidic solutions. A possible

TABLE 4
Equilibrium Experimental Results (initial concentration of 2,4-DCP = 4.00 mmol/L, amount of anion-exchange resins dosed = 2.50 g/L)

| Solution pH | Total 2,4-DCP removal | Removal due to ion exchange | Removal due to adsorption | Distribution constant |
|---|---|---|---|---|
| 2.91 | 1.62 | 0 | 1.62 | 0.68 |
| 3.18 | 1.68 | 0.10 | 1.58 | 0.72 |
| 3.51 | 1.88 | 0.31 | 1.57 | 0.89 |
| 4.06 | 2.04 | 0.50 | 1.54 | 1.04 |
| 4.62 | 2.30 | 0.81 | 1.49 | 1.35 |
| 5.53 | 2.85 | 1.56 | 1.29 | 2.48 |
| 6.49 | 3.46 | 2.52 | 0.94 | 6.18 |
| 7.17 | 3.71 | 3.13 | 0.58 | 12.79 |
| 7.77 | 3.83 | 3.57 | 0.26 | 22.53 |
| 8.21 | 3.86 | 3.71 | 0.15 | 27.57 |
| 8.35 | 3.87 | 3.84 | 0.03 | 29.77 |
| 8.65 | 3.87 | 3.84 | 0.03 | 29.77 |

TABLE 5
Equilibrium Experimental Results (initial concentration of 2,4,6-TCP = 4.00 mmol/L, amount of anion-exchange resins dosed = 2.50 g/l)

| Solution pH | Total 2,4,6-TCP removal | Removal due to ion exchange | Removal due to adsorption | Distribution constant |
|---|---|---|---|---|
| 3.89 | 3.03 | 2.21 | 0.81 | 3.12 |
| 4.46 | 3.46 | 2.93 | 0.53 | 6.41 |
| 5.06 | 3.72 | 3.42 | 0.30 | 13.29 |
| 5.28 | 3.79 | 3.52 | 0.27 | 18.05 |
| 5.50 | 3.84 | 3.66 | 0.18 | 24.00 |
| 5.78 | 3.87 | 3.75 | 0.12 | 29.77 |
| 5.86 | 3.90 | 3.77 | 0.13 | 39.00 |
| 6.17 | 3.93 | 3.81 | 0.12 | 56.14 |
| 6.53 | 3.95 | 3.95 | 0 | 79.00 |
| 6.72 | 3.95 | 3.95 | 0 | 79.00 |
| 7.11 | 3.96 | 3.95 | 0 | 99.00 |

reason is that the deprotonated species possess a stronger affinity with the Purolite A-510 resin through the ion-exchange reaction.

For modeling the sorption behavior of the chlorophenols in the presence of Purolite A-510 resin, the ion-exchange capacity of the Purolite A-510 resin was determined to be about 2.20 meq/L by adding 2 N NaOH solution to elute the chloride ions on the Purolite A-510 resin, slightly higher than that listed by the manufacturer, which is about 1.94 meq/g, similar to the adsorption capacity of Purolite A-510 resin as determined by the Langmuir adsorption isotherm. The values of $K_{ad1}$ can be roughly estimated from Eq. (5) at acidic conditions where the adsorption and ion exchange of the protonated chlorophenols are negligible. Similarly, $K_{ion}$ can be estimated from Eq. (7) at alkaline conditions where the ion-exchange reaction is dominant. However, $K_{ad2}$ can not be determined accurately because the adsorption of deprotonated chlorophenols is very small as shown in Tables 2–5. Experiments were conducted for removal of various chlorophenols by XAD-4 resin which contains hydrophobic polystyrene–divinylbenzene groups, similar to Purolite A-510, but no ion-exchange reaction occurs with this resin (14). The ratio of equilibrium constants of the deprotonated chlorophenols to that of the protonated chlorophenols was determined to be about 0.04 (15). By using this ratio, the $K_{ad2}$ value is assumed to be ($0.04K_{ad1}$) in this study. The optimum values of $K_{ad1}$ and $K_{ion}$ for the chlorophenols were determined by fitting the model to the experimental results with the estimated $K_{ad1}$ and $K_{ion}$ values as the initial numbers. The determined equilibrium constants are reported in Table 6. Figures 3–6

TABLE 6
The values of $K_p$, $K_{ad1}$, $K_{ad2}$, and $K_{ion}$ for Phenol, 2-Chlorophenol, 2,4-Dichlorophenol, and 2,4,6-Trichlorophenol

| | Phenol | 2-Chlorophenol | 2,4-Dichlorophenol | 2,4,6-Trichlorophenol |
|---|---|---|---|---|
| $K_p$ | 0.077 | 0.34 | 0.68 | 3.12 |
| $K_{ad1}$ | 0.015 | 0.070 | 0.19 | 0.22 |
| $K_{ad2}$ | 0.00048 | 0.0033 | 0.0059 | 0.011 |
| $K_{ion}$ | 4 | 16 | 100 | 275 |

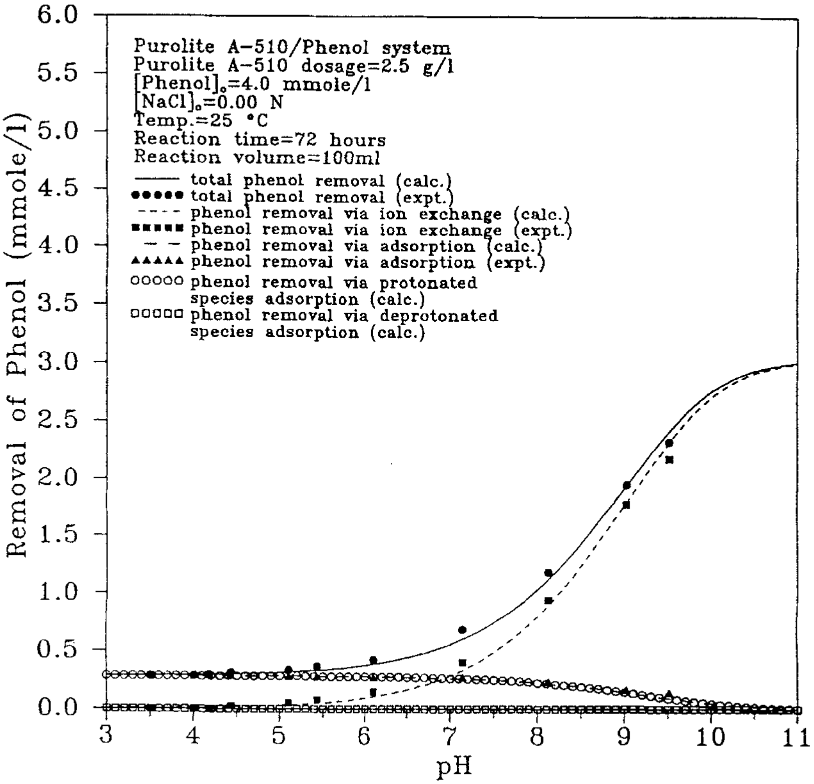


FIG. 3 Sorption of phenol by Purolite A-510 resin at various solution pH values.

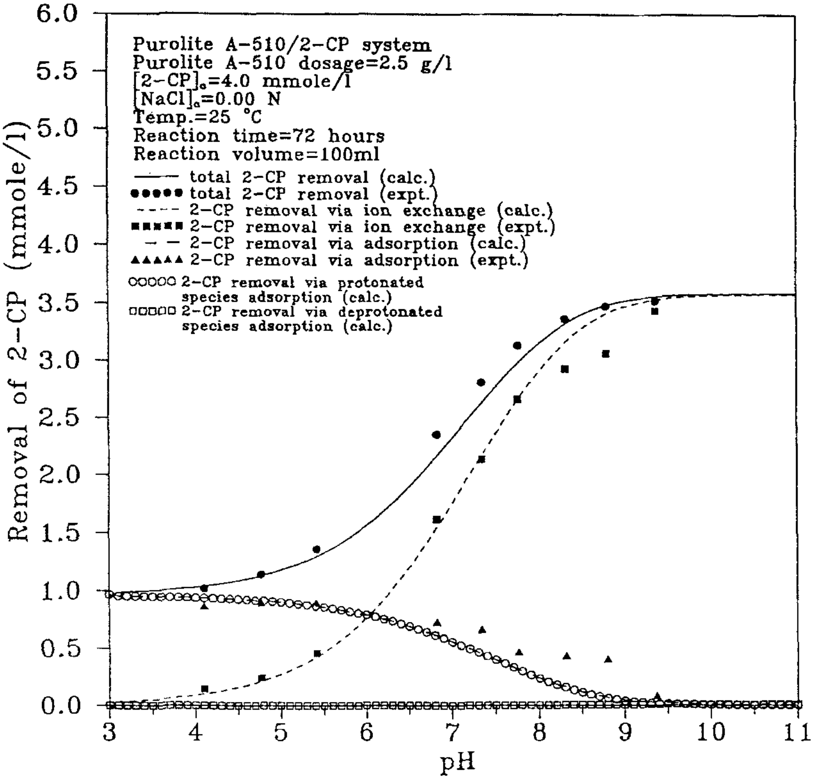


FIG. 4 Sorption of 2-chlorophenol by Purolite A-510 resin at various solution pH values.

show that agreement between the calculated and the experimental values appears to be satisfactory for the removals of phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol over the entire range of investigated conditions. The amounts of chlorophenols removed via deprotonated species adsorption could be neglected, as shown in Figs. 3–6, since the affinity of the deprotonated chlorophenols with Purolite A-510 resin through the ion-exchange reaction is much stronger than that through adsorption in alkaline solutions.

Figure 7 depicts the removal of phenol at different concentrations of chloride ion by Purolite A-510 resin. The equilibrium concentration of phenol increases with the amount of chloride ion added, as predicted

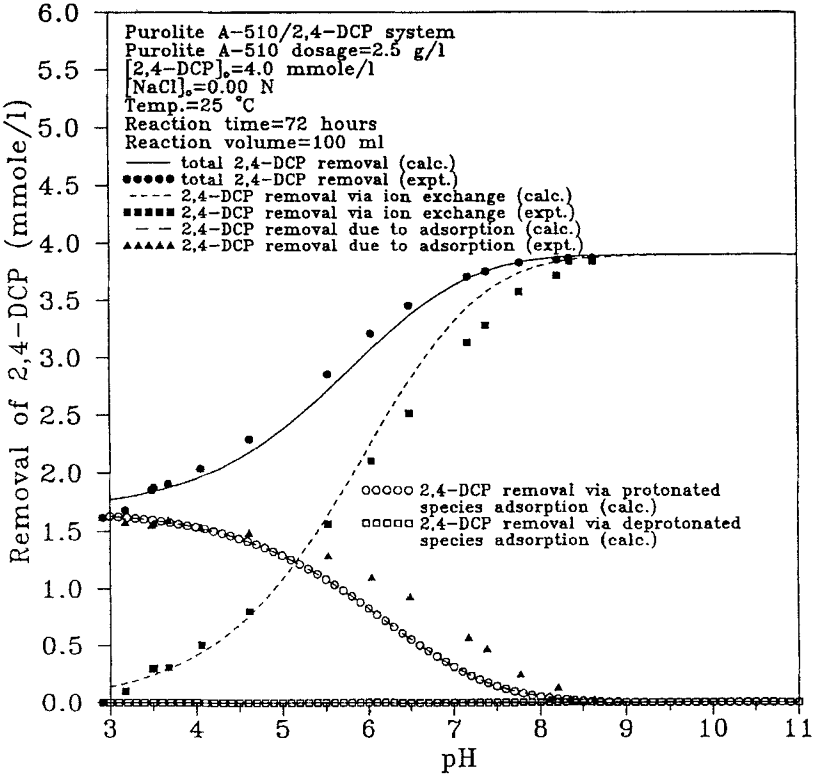


FIG. 5 Sorption of 2,4-dichlorophenol by Purolite A-510 resin at various solution pH values.

according to Reactions (2)–(4). The effect is more significant in alkaline solutions where the ion-exchange reaction is dominant. On the contrary, most phenol is removed by Purolite A-510 resin via adsorption in acidic solutions. The effect of chloride ions is almost negligible in the low pH region, as shown in Fig. 7. The effect of chloride ions on the removal of 2,4,6-trichlorophenol, 2-chlorophenol, and 2,4-dichlorophenol, as shown in Figs. 8–10, is similar to that of phenol. The Davies equation was used in the equilibrium calculation to address the effect of chloride ion on the activity calculation of ionic species at relative high ionic concentrations

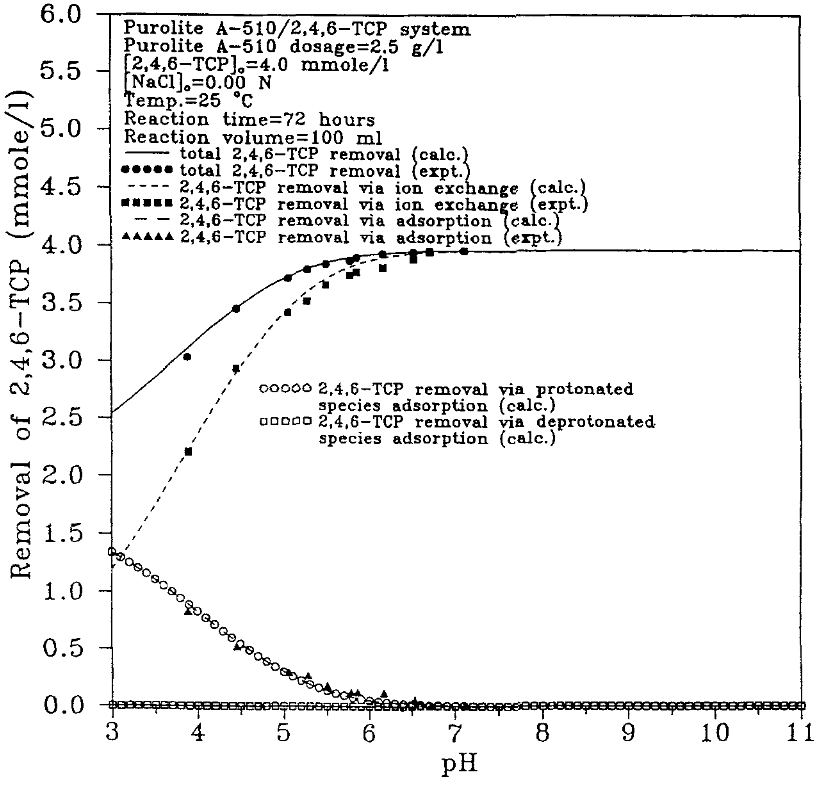


FIG. 6 Sorption of 2,4,6-trichlorophenol by Purolite A-510 resin at various solution pH values.

where the infinite dilute assumption (i.e., Debye–Hückel model) is invalid. The predicted values are comparable to the experimental results for phenol and 2,4,6-trichlorophenol, as shown in Figs. 7 and 8, and the model qualitatively predicts the trend of the chloride ion effect on the equilibrium concentrations of 2-chlorophenol and 2,4-dichlorophenol, as shown in Figs. 9 and 10.

Partition constants of the protonated chlorophenols ($K_p$) in the presence of Purolite A-510 resin, listed in Table 6, were determined according to Eq. (14). The values of $K_p$ tend to increase with the $K_{ow}$ of the protonated

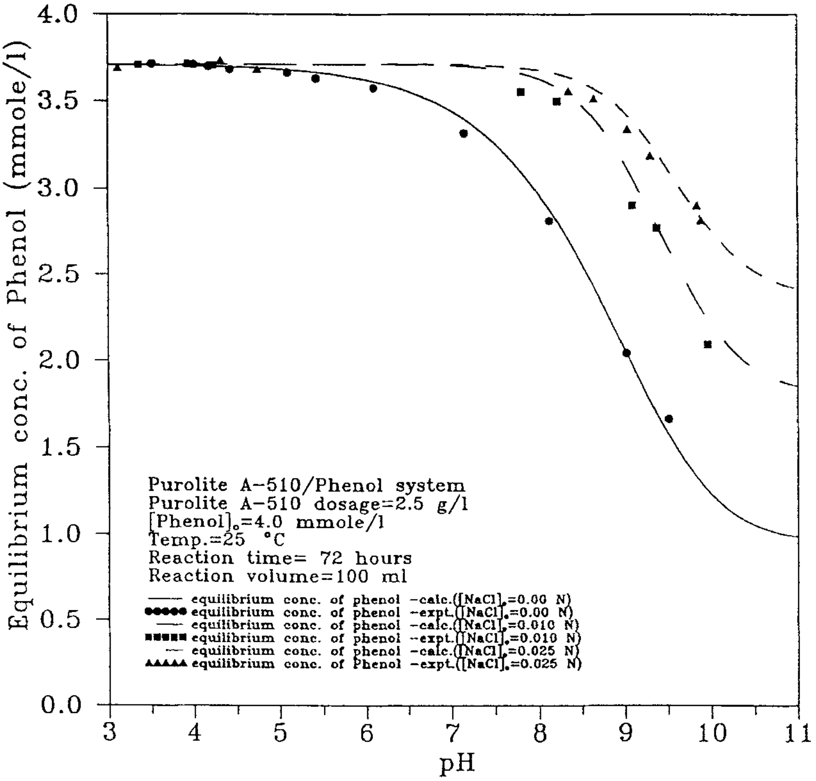


FIG. 7 The effect of chloride ion concentrations on the removal of phenol by Purolite A-510 resin.

chlorophenols. The correlation between $\log(K_p)$ and $\log(K_{ow})$, presented in Fig. 11, can be expressed as

$$\log(K_p) = 0.69 \log(K_{ow}) - 2.06 \qquad (r^2 = 0.99) \qquad (16)$$

A good correlation between $\log(K_p)$ and $\log(K_{ow})$ is shown in Fig. 11. It illustrates that the partition constants of the chlorophenols ($K_p$) in the presence of Purolite A-510 resin could be estimated from the octanol/water partition coefficients by Equation (16).

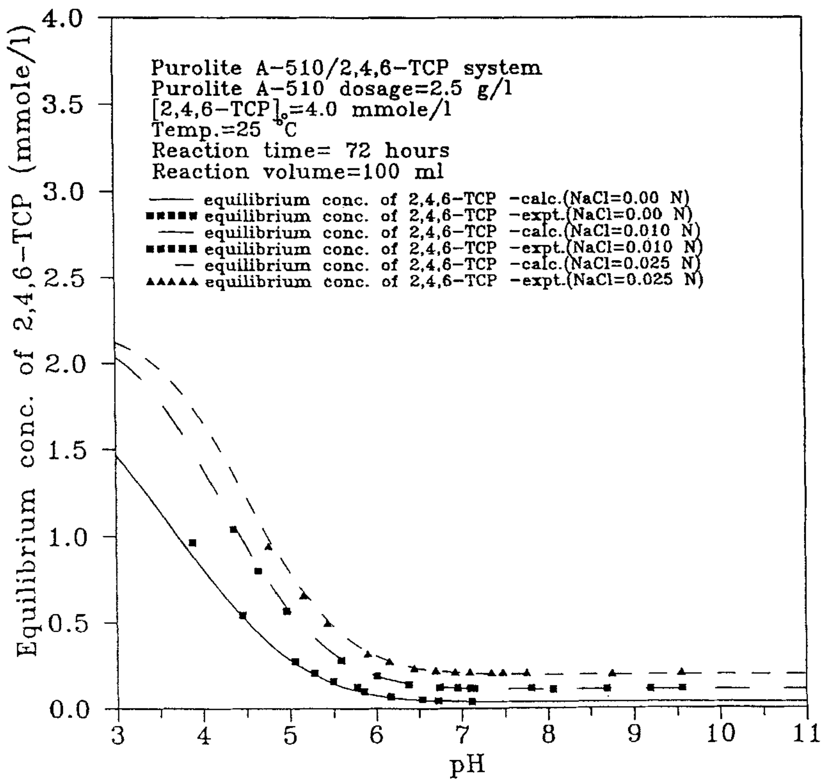


FIG. 8 The effect of chloride ion concentrations on the removal of 2,4,6-trichlorophenol by Purolite A-510 resin.

Table 6 indicates that the magnitudes of $K_{adl}$ for the chlorophenols follow the sequence 2,4,6-TCP > 2,4-DCP > 2-CP > phenol. This may be explained by the hydrophobicity of the chlorophenols increasing with the number of substituted chlorine atoms. As also shown in Table 6, the magnitudes of $K_{ion}$ for the chlorophenols are in the same order as those of $K_{adl}$. A possible explanation is that the substituted chlorine atoms may affect the resonance effect of the chlorophenols on the Purolite A-510 resin to enhance the inductive ability of the $NR_4^+$ group. It has been proven that the substituted fluorine could push electrons into the aromatic ring

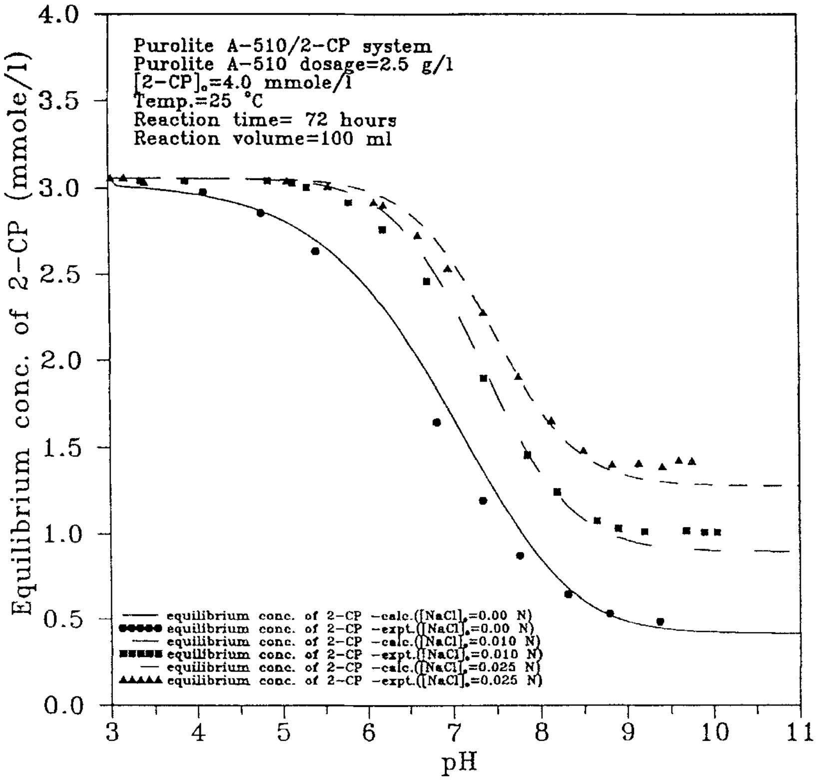
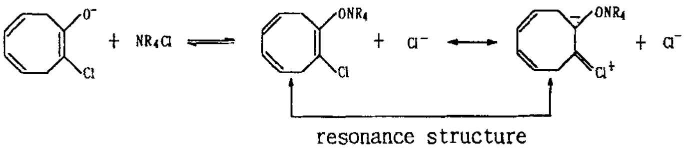


FIG. 9 The effect of chloride ion concentrations on the removal of 2-chlorophenol by Purolite A-510 resin.

for protonated 4-fluorophenol but not for deprotonated 4-fluorophenol (17). This might be attributed to the resonance compound of deprotonated 4-fluorophenol which has two adjacent negative charges, thus resulting in instability, but protonated 4-fluorophenol could increase the stability of the resonance structure by reducing the negative charges by the $H^+$ group in protonated 4-fluorophenol. Furthermore, the ability of electron attraction of the $NR_4^+$ group in Purolite A-510 resin was found to be much greater than that of the $H^+$ group (18). As an example, the reaction scheme of the removal of 2-chlorophenol via the ion-exchange reaction by Purolite A-510 resin as follows:



The induction effect of the $NR_4^+$ group in Purolite A-510 resin could elevated the ability of electron attraction to reduce the negative charge density on the oxygen atom by resonance of the chlorine atom. Moreover, the resonance effect of the chlorine atom increases with the number of

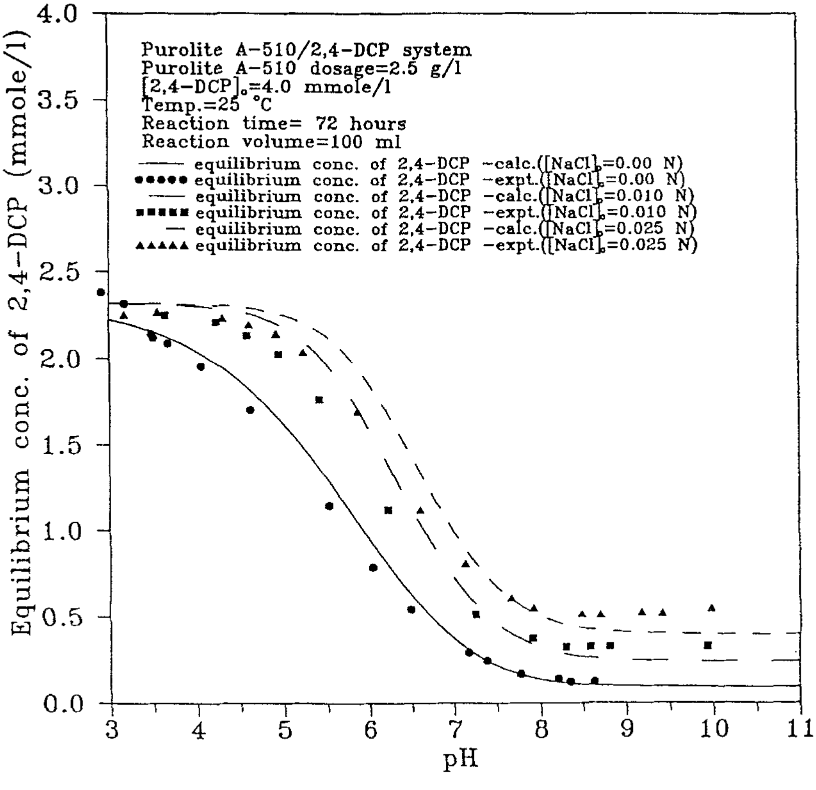


FIG. 10 The effect of chloride ion concentrations on the removal of 2,4-dichlorophenol by Purolite A-510 resin.

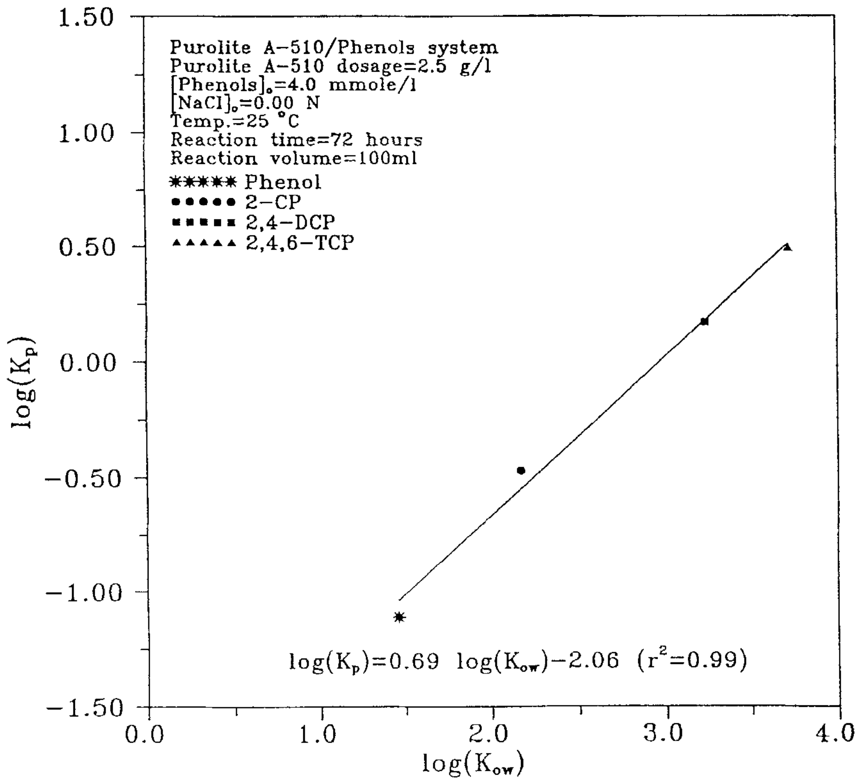


FIG. 11 Correlation of $\log(K_p)$ versus $\log(K_{ow})$ for protonated chlorophenols in the presence of Purolite A-510 resin.

chlorine functional groups. Hence, the values of $K_{ion}$ for those chlorophenols were in the order 2,4,6-TCP > 2,4-DCP > 2-CP > phenol, as we expected.

## CONCLUSION

Removal of chlorophenols by Purolite A-510 resin increases with the pH values of aqueous solutions. Adsorption of deprotonated chlorophenols by Purolite A-510 resin can be neglected in alkaline solutions since the deprotonated species possess a much stronger affinity with Purolite A-510 resin for the ion-exchange reaction to proceed. The equilibrium model developed in this study is capable of describing the sorption behavior of the investigated systems. The adsorption of protonated chlorophenols by Purolite A-510 resin is related to the hydrophobicity of the chlorophenols, which increases with the number of chlorine atoms on the chlorophenols. Therefore, the magnitudes of $K_{ad1}$ for the protonated chlorophenols were in the order 2,4,6-TCP > 2,4-DCP > 2-CP > phenol. Chlorophenol removal by Purolite A-510 resin via the ion-exchange reaction increases with the number of substituted chlorine groups. This might be attributed to enhancement of the resonance effect by the chlorine atoms of the chlorophenols and elevation of the inductive effect by the $NR_4^+$ group on the Purolite A-510 resin.

## ACKNOWLEDGMENT

This research was supported by a grant from the National Science Council, Republic of China, under Contract NSC 82-0410-E011-010.

## NOMENCLATURE

| | |
|---|---|
| $\{CPOH\}$ | the activity of the protonated chlorophenol in solution (mmol/L) |
| $\{CPO^-\}$ | the activity of the deprotonated chlorophenol in solution (mmol/L) |
| $K_a$ | the dissociation constant of chlorophenol in water |
| $(RCl)_{ad}$ | the adsorption sites on the Purolite A-510 resin (mmol/L) |
| $(RCl)_{ion}$ | the ion-exchange sites on the Purolite A-510 resin (mmol/L) |
| $(ClRCPOH)_{ad}$ | the protonated chlorophenol removal via adsorption reaction (mmol/L) |
| $(ClRCPO^-)_{ad}$ | the deprotonated chlorophenol removal via adsorption reaction (mmol/L) |
| $(CPOR)_{ion}$ | the deprotonated chlorophenol removal via ion-exchange reaction (mmol/L) |
| $K_{ad1}$ | the equilibrium constant of adsorption for the protonated chlorophenol in solution (1/mmol) |
| $K_{ad2}$ | the equilibrium constant of adsorption for the deprotonated chlorophenol in solution (1/mmol) |
| $K_{ion}$ | the equilibrium constant of ion-exchange reaction for the deprotonated chlorophenol in solution (dimensionless) |
| $(CP)_0$ | the total amounts of chlorophenol in aqueous solution and solid phase (mmol/L) |

| | |
|---|---|
| $(\mathrm{RCl})_{0,\mathrm{ad}}$ | the total adsorption sites on the Purolite A-510 resin (mmol/L) |
| $(\mathrm{RCl})_{0,\mathrm{ion}}$ | the total ion-exchange sites on the Purolite A-510 resin (mmol/L) |
| $\log \gamma_i$ | the common logarithm of the activity coefficient of species *i* |
| $z$ | the charge of species *i* |
| $I$ | the ionic strength of the aqueous solution |
| $K_\mathrm{d}$ | the distribution constant of chlorophenol (dimensionless) |
| $K_\mathrm{p}$ | the partition constant of chlorophenol (dimensionless) |
| $K_\mathrm{ow}$ | the octanol/water partition coefficient of chlorophenol (dimensionless) |
| $f_\mathrm{oc}$ | the organic carbon content of the sorbent |

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*Received by editor January 17, 1995*
*Revision received September 1, 1995*