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Removal of Phenols from Aqueous Solutions by Purolite A-510 Resin

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ABSTRACT

Experiments on the removal of various phenols from aqueous solution by Purolite A-510 resin, a strongly basic anion polystyrene–divinylbenzene resin with quaternary ammonium group, were carried out under different operating conditions in batch reactors. The phenols studied in this research include 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 2,4-dinitrophenol, 2-methylphenol, and 2,4-dimethylphenol. The experimental observations indicate that the removal of various phenols by Purolite A-510 resin could be described by either Langmuir or Freundlich models. The removals of phenols by Purolite A-510 resin for solutions of different pH varied significantly and can be explained by the species distribution of phenols in aqueous solutions. Phenols were

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adsorbed by Purolite A-510 resin at acidic conditions where the presence of molecular phenol species dominates. The removal increased sharply for alkaline solutions where the negatively charged ionic phenol species is exchanged with chloride ion on the resin. The removal of phenols by Purolite A-510 resin in alkaline/neutral solutions was interfered in the presence of chloride ions. The proposed equilibrium model adequately describes the sorption behavior of phenols by Purolite A-510 resin. The removals of phenols were found to correlate with the octanol/water partition coefficients of various phenol compounds.

Key Words: Phenols; Adsorption; Resin; Aqueous solution; Partition coefficients.

INTRODUCTION

Phenols are pollutants of high-priority concern because of their toxicity and possible accumulation in the environment. The ion-exchange process is considered one of the possible techniques for treating synthetic organic compounds, especially phenols. Refractory organic compounds could also be concentrated and removed from aqueous solution via ion exchange by macroreticular resins with ion-exchange functional groups. That is, the ions held by electrostatic forces to charged functional groups on the surface of resin are exchanged for ionic species of phenols in the aqueous solutions. Several researchers have reported on the removal of phenols in aqueous solutions by various ion-exchange resins.[1,2] The removal of phenols by various technologies[3−7] was reported to be highly dependent on the solution pH because the species distribution of phenol compounds varies at different pH levels. The type and number of functional groups on the benzene ring were also found to be important in the removal of phenol compounds.[8,9] A conceptual model is established based on the elemental balances and equilibrium equations to describe the ion-exchange behavior and differentiate the extent of removal of various phenol species by Purolite A-510 resin under different experimental conditions.

EXPERIMENTAL

Purolite A-510, a strongly basic anion polymeric resin composed of polystyrene chains cross-linked with divinylbenzene with quaternary ammonium group, was used for studying the removal of various phenols in aqueous solution. The medium size of the resin is 35–40 mesh. Several surface characteristics of the resin were measured using a Micromeritics

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ASAP 2000 BET analyzer (Australia). The specific surface area, average pore volume, and average pore diameter were determined to be 35 m^3/g, 0.28 cm^2/g, and 163 Å, respectively. The stock solutions used in this investigation were prepared with reagent-grade chemicals and reverse osmosis (RO)-deionized water. Standard acid and base solutions (H_2SO_4 and NaOH) were prepared weekly for pH adjustment. The phenols studied in this research included phenol, 2-chiorophenol, 2,4-dichlorophenol, 2,4,6-tricholrophenol, 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 2-methylphenol, and 2,4-dimethyiphenol.

For the equilibrium experiments, predetermined amounts of Purolite A-510 resin were introduced into 100-mL reactors filled with aqueous solutions of known concentrations of phenol and the reaction setups were maintained at 25°C ± 1°C by containing in a shaker water bath. The solution pH was adjusted to desired level (between 3 and 11) by adding acidic or alkaline solutions to the reactor prior to the addition of resin. The ionic strength of solution was kept constant with 0.5 N $NaNO_3$. After 72 hr of contact time for resin and phenol-containing solution, the solution pH was recorded and the resin was allowed to settle for about 5 min before the supernatant was withdrawn and filtered. The solution pH was recorded and the concentrations of various phenols in the filtered samples were determined by detecting the absorption of specific wavelength with a Shimaszu model UV-160A UV/visible spectrophotometer (Japan).

RESULTS AND DISCUSSION

Results for experiments conducted under various solution pH conditions showed that most phenols studied in this research were removed very effectively by Purolite A-510 resin for alkaline solutions; the removals of phenols reduced sharply for acidic solutions. For instance, the removal of 2-nitrophenol by Purolite A-510 resin at different solution pH values is shown in Fig. 1; the removals were kept constantly high for solution pH above 8.0 and the removals reduced significantly for pH less than 6.5. Almost no removals were found for solutions of pH 5.0 and less.

The effect of solution pH on the removal of various phenols from aqueous solutions by adsorption can be discussed by considering the theoretical distribution of various phenol species in aqueous solutions. Since most phenols act like weak acids in aqueous solution, the dissociation of hydrogen ion from the phenol molecules strongly depends on the pH level of solution. The distribution of POH and PO species can be calculated as a function of solution pH if the dissociation constant of phenols is available. The molecular species, POH, is predominant in acidic solutions, whereas the ionic species, PO, predominates in alkaline solutions. The removals of phenols by Purolite

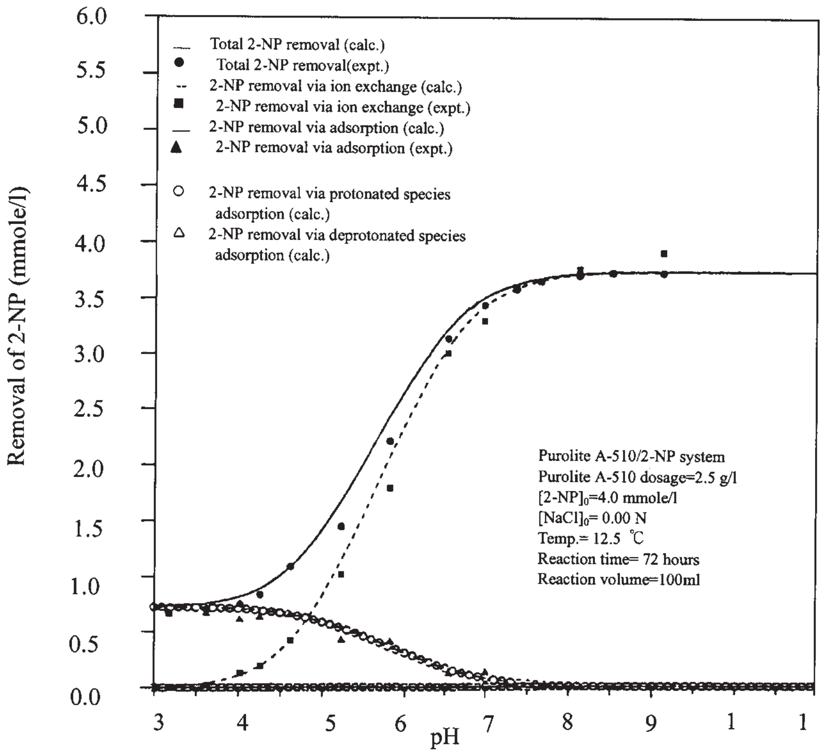

Figure 1. The effect of solution pH on the removal of 2-nitrophenol by A-510 resin.

A-510 resin for acidic solutions may involve the adsorption of molecular phenolic species. However, the ion exchange between ionic phenolic species in aqueous solution and chloride on the Purolite A-510 resin surface dominates for alkaline solutions. The simplified overall scheme for the removal of phenols by Purolite A-510 resin can be expressed by following equations:

Adsorption:

$$\mathrm{POH} \xleftrightarrow{K_a} \mathrm{PO^-} + \mathrm{H^+}$$

$$\mathrm{POH} + \mathrm{RCl} \xleftrightarrow{K_{ad1}} (\mathrm{ClRPOH})_{ad}$$

$$\mathrm{PO^-} + \mathrm{RCL} \xleftrightarrow{K_{ad2}} (\mathrm{ClRPO^-})_{ad}$$

Ion exchange:

$$\mathrm{POH} \xleftrightarrow{K_a} \mathrm{PO^-} + \mathrm{H^+}$$

$$\mathrm{PO^-} + \mathrm{RCl} \xleftrightarrow{K_{ion}} (\mathrm{POR})_{ion} + \mathrm{Cl^-}$$

where $(\mathrm{ClRPOH})_{ad}$ and $(\mathrm{ClRPO^-})_{ad}$ are the molecular and ionic phenol species adsorbed by Purolite A-510 resin, respectively, and $(\mathrm{POR})_{ion}$ is the amount of ionic phenol removed by ion exchange. In order to establish the site balance, the concentrations of the resin sites, either vacant or occupied by the various phenol species, RCl, $(\mathrm{ClRPOH})_{ad}$, $(\mathrm{ClRPO^-})_{ad}$, and $(\mathrm{POR})_{ion}$, are defined as the ratio of the equivalent amount of sorption sites to the volume of reaction solution. The equilibrium constants for the molecular and ionic phenol species, K_{ad1}, K_{ad2}, and K_{ion}, are defined as followed:

$$K_{ad1} = \frac{(\mathrm{ClRPOH})_{ad}}{[(\mathrm{POH}) + (\mathrm{PO^-})][1/((\mathrm{H^+})/K_a)][(\mathrm{RCl})_{ad}]} \tag{1}$$

$$K_{ad2} = \frac{(\mathrm{ClRPO^-})_{ad}}{[(\mathrm{POH}) + (\mathrm{PO^-})][1/((\mathrm{H^+})/K_a)][(\mathrm{RCl})_{ad}]} \tag{2}$$

$$K_{ad3} = \frac{(\mathrm{PRO})_{ion}(\mathrm{Cl^-})}{[(\mathrm{POH}) + (\mathrm{PO^-})][1/((\mathrm{H^+})/K_a)][(\mathrm{RCl})_{ion}]} \tag{3}$$

If the values of K_{ad1}, K_{ad2}, K_{ion}, and K_a are known, the individual contributions of the adsorption of the molecular and ionic phenol species by Purolite A-510, $(\mathrm{RPOH})_{ad}$ and $(\mathrm{RPO})_{ad}$, can be calculated instantaneously from the mass balance and equilibrium expressions shown in Eqs. (1)–(3), by using nonlinear Newton's method.[10] For highly acidic conditions (pH less than 4 in this research) where the presence of ionic phenol species is considered negligible, the phenol removed is assumed to be totally in the form of molecular phenol species, thus the values of K_{ad1} can be calculated. Because the removal of ionic phenol species at alkaline conditions is assumed to be predominantly contributed by ion exchange rather than by adsorption, it is difficult to determine the minimal contribution by the adsorption of ionic phenol species. Therefore, the adsorption constant for ionic phenol species, K_{ad2}, is determined by adopting the results reported previously for similar experiments conducted with a nonionic resin, Amberlite XAD-4.[11] The K_{ion} values for Purolite A-510 resin can be determined from the experimental results obtained for alkaline conditions (pH greater than 10 in this research) where the adsorption of ionic phenol species is considered negligible. With the determined equilibrium constants (K_{ad1}, K_{ad2}, and K_{ion}) for the removal of various phenols by Purolite A-510 resin as summarized in Table 1, the

Table 1. The calculated equilibrium constants for various phenols.

	K_p	K_{ad1}, (1/mmol)	K_{ad2}, (1/mmol)	K_{ion}
Phenol	0.077	0.015	0.00048	4
2-Chlorophenol	0.34	0.070	0.0033	16
2,4-Dichlorophenol	0.68	0.19	0.0059	100
2,4,6-Trichlorophenol	3.12	0.22	0.011	275
2-Nitrophenol	0.14	0.036	0.00029	32
2,4-Dinitrophenol	0.10	0.022	0.00077	470
2-Methylphenol	0.30	0.073	0.0067	4.28
2,4-Dimethylphenol	0.19	0.039	0.0038	3.77

established equilibrium equations expressed below can adequately describe the adsorption behavior of phenols by Purolite A-510 resin.

$$K_{ad1} = \frac{(\mathrm{ClRPOH})_{ad}}{[(\mathrm{P})_0 + (\mathrm{ClRPOH})_{ad} + (\mathrm{ClRPO}^-)_{ad} + (\mathrm{POR})_{ion}]} \times \frac{1}{[1/(1 + K_a/(\mathrm{H}^+))][(\mathrm{RCl})_{0,ad} - (\mathrm{ClRPOH})_{ad} + (\mathrm{ClRPO}^-)_{ad}]} \tag{4}$$

$$K_{ad2} = \frac{(\mathrm{ClRPO})_{ad}}{[(\mathrm{P})_0 + (\mathrm{ClRPOH})_{ad} + (\mathrm{ClRPO}^-)_{ad} + (\mathrm{POR})_{ion}]} \times \frac{1}{[1/(1 + K_a/(\mathrm{H}^+))][(\mathrm{RCl})_{0,ad} - (\mathrm{ClRPOH})_{ad} + (\mathrm{ClRPO}^-)_{ad}]} \tag{5}$$

$$K_{ion} = \frac{(\mathrm{POR})_{ion}(\mathrm{Cl}^-)}{[(\mathrm{P})_0 + (\mathrm{ClRPOH})_{ad} + (\mathrm{ClRPO}^-)_{ad} + (\mathrm{POR})_{ion}]} \times \frac{1}{[1/(1 + K_a/(\mathrm{H}^+))][(\mathrm{RCl})_{0,ion} - (\mathrm{POR})_{ion}]} \tag{6}$$

The effect of chloride ions on the removal of various phenols by Purolite A-510 resin was studied under different solution pH conditions. The results for experiments conducted for acidic solutions indicate that the removal of molecular phenol species is less influenced by the presence of chloride ion. However, removals of ionic phenol species are severely inhibited by the presence of chloride ion for alkaline solutions. Experimental results for the removal of 2-nitrophenol by Purolite A-510 resin are shown in Fig. 2. Similar results are observed for experiments conducted with other phenolic compounds. As indicated by the simplified reaction scheme, the presence of

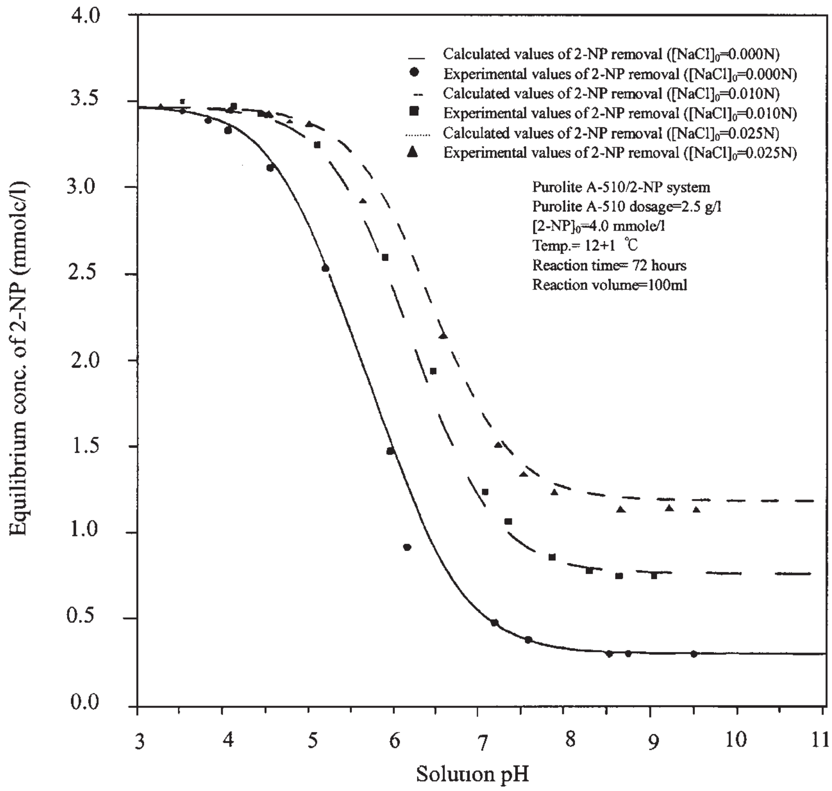

Figure 2. The effect of solution pH on the adsorption of 2-nitrophenol by A-510 resin in presence of chloride ion.

chloride ion interferes with the removal of ionic phenol species by Purolite A-510 resin according to Le Chatelier's principle.

For experiments conducted at same solution pH, the removal of 2-nitrophenol by Purolite A-510 resin slightly decreased with increasing solution temperature for acidic solutions, comparing the results shown in Figs. 1, 3, and 4 indicating the adsorption is endothermic. The adsorption heat for the adsorption of 2-nitrophenol by Purolite A-510 resin at various solution pH values was calculated by correlating the equilibrium constants with solution temperature via the Van't Hoff equation and determined to be about $-5.7\,\mathrm{kcal/mol}$ at pH 3. The results for experiments conducted for alkaline solutions indicate that the solution temperature does not influence the removal of ionic phenol species.

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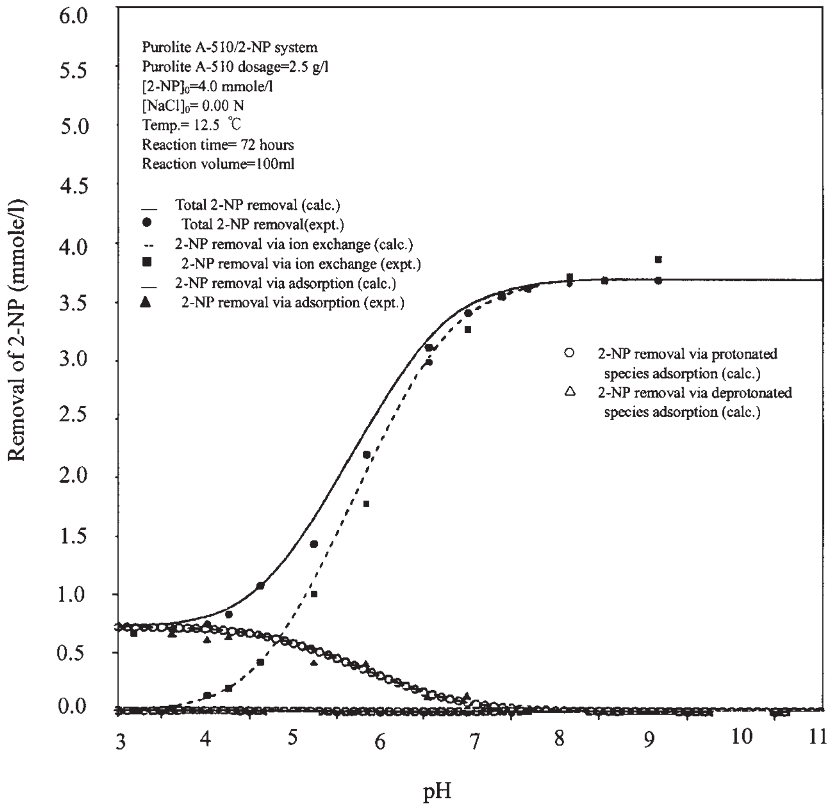

Figure 3. The effect of solution pH on the removal of 2-nitrophenol by A-510 resin at 12.5°C.

The effect of initial concentration on the removal of 2-nitrophenol by Purolite A-510 resin was studied at 25°C in order to establish the adsorption isotherm. The Langmuir and Freundlich models were used to correlate the experimental equilibrium data. The values of Langmuir and Freundlich parameters are summarized in Table 2 with relatively good applicability. The fitted results also indicate that adsorption of 2-nitrophenol in aqueous solutions was considered to be unfavorable for both acidic and alkaline conditions.

In order to further identify the effect of solution condition on the removal of various phenols, a partition constant, K_p, defined as the ratio of the amount of a specific phenol species removed by Purolite A-510 resin to the total

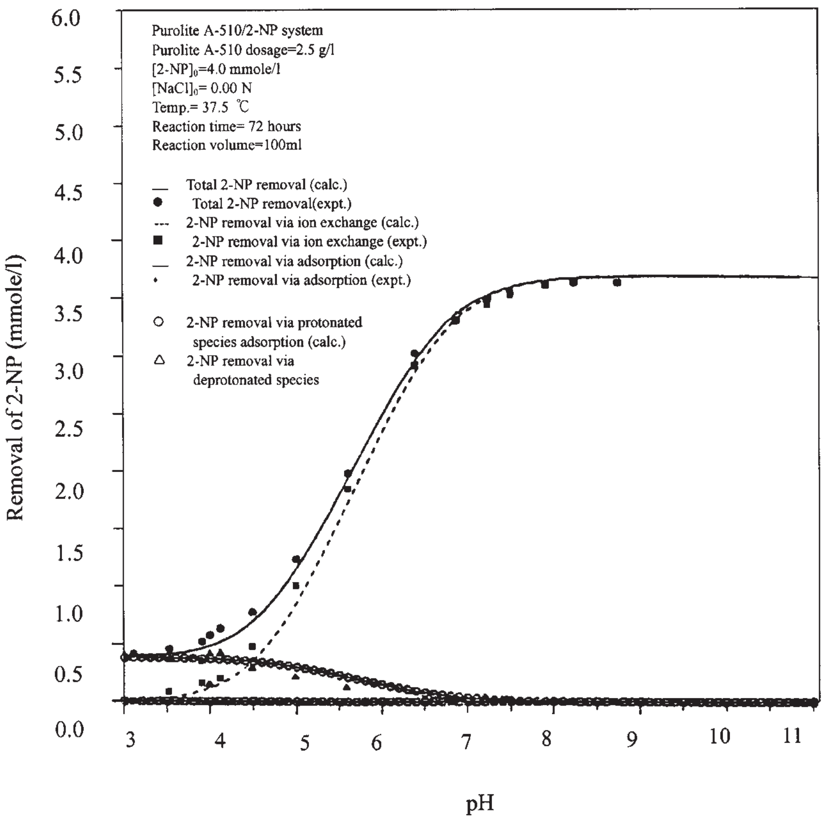

Figure 4. The effect of solution pH on the removal of 2-nitrophenol by A-510 resin at 37.5°C.

amount of phenol in aqueous solution, is introduced. For instance, K_p for the removal of molecular phenol species by Purolite A-510 resin can be expressed as:

$$K_p = \frac{\{(RPOH)_{ad}\}}{\{POH\}} \tag{7}$$

Several previous researches reported that the adsorption behavior of phenol compounds by natural adsorbents is highly influenced by hydrophobic interaction. In most cases, the affinity between a sorbent and a hydrophobic

Table 2. The correlated parameters of Freudlich and Langmuir isotherms for the adsorption of 2-nitrophenol by Purolite A-510 resin.

Solution pH	3.0	11.3
Freundlich isotherm	$\log(x) = 0.42\log(C_e) + 0.93$ ($r^2 = 0.95$)	$\log(x) = 1.26\log(C_e) - 0.67$ ($r^2 = 0.97$)
K	13.51	0.21
n	2.01	0.79
Langmuir isotherm	$(1/X) = 0.0376(1/C_e) + 0.0746$ ($r^2 = 0.98$)	$(1/X) = 4.082(1/C_e) - 0.15$ ($r^2 = 0.97$)
X_m	6.70	—
B	2.38	—

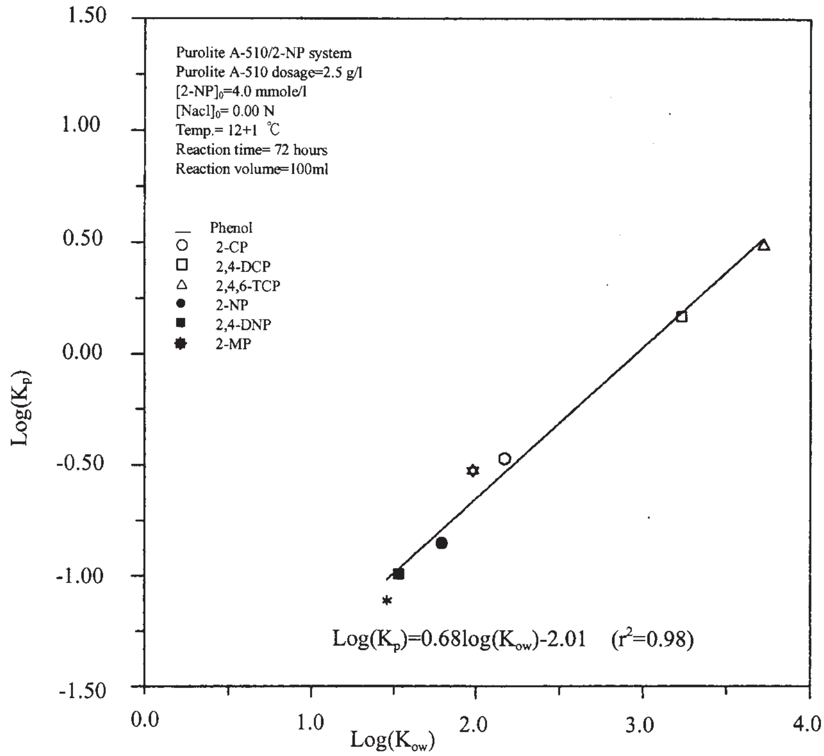

Figure 5. Correlation between K_p and K_{ow} for the removal of various phenols by Purolite A-510 resin.

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solute can be linearly corrected with the organic carbon content of the sorbent,[12,13] as shown by the following equation:

$$K_{xp} = (b)(\text{foc})(K_{ow})^{a} \tag{8}$$

The K_{ow} (octanol/water partition constant) value of different phenols usually varied with the type and number of functional groups on the benzene ring. As shown in Fig. 5, the experimental results in this research indicate that the partition constant (K_{ad1}) of various molecular phenols increased linearly with the K_{ow} value for phenols adsorbed by Purolite A-510 resin in acidic solutions. On the contrary, the partition constant of various ionic phenols (K_{ion}) decreased linearly with the dissociation constant (K_a) for phenols removed by Purolite A-510 resin in alkaline solutions, as shown in Fig. 6. Thus, the equilibrium and partition constants of phenols removed by Purolite

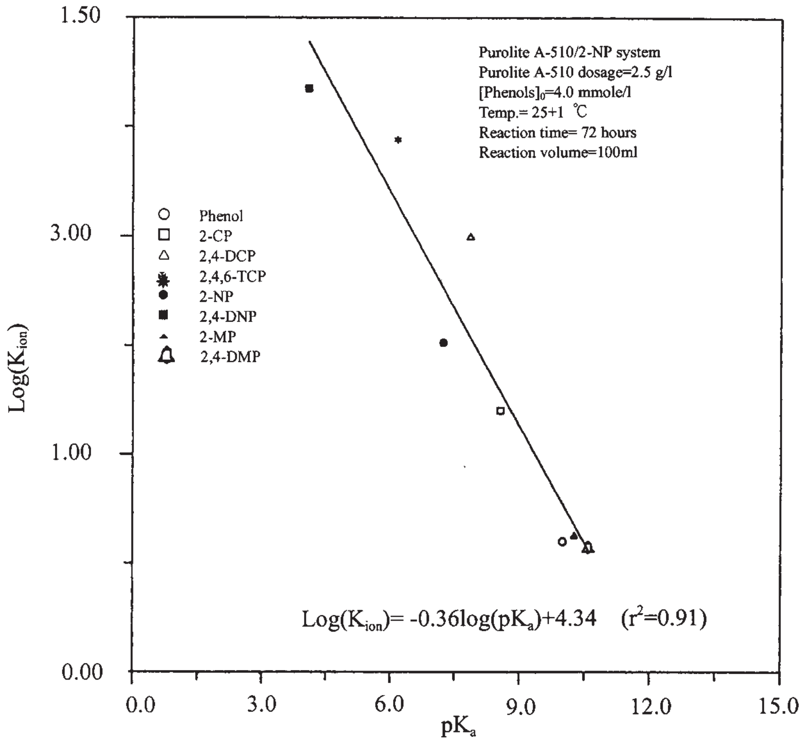

Figure 6. Correlation between K_{ion} and pK_a for the removal of various phenols by Purolite A-510 resin.

A-510 resin under acidic conditions can be roughly estimated from the octanol/water partition coefficient of the phenol compounds by using Eq. (8).

CONCLUSION

The removal of phenols by Purolite A-510 resin was found to be feasible for alkaline conditions but decreased significantly with decreasing solution pH levels. The effect of solution pH on the removal of phenols can be discussed by considering the predominant phenol species present in the solution. Experimental results indicated that adsorption equilibrium behavior of various phenols by Purolite A-510 resin can be described by either the Langmuir or Freundlich models. The extent of phenol removal by Purolite A-510 resin was found to decrease with increasing solution temperature for acidic conditions but kept constant for alkaline solutions. The equilibrium model based on species distribution and mass balance considerations is capable of describing the removal behavior of phenolic compounds at different solution pH conditions and calculating the individual removals of various phenol species presented in the reacting systems. Despite the different type and number of functional groups on the benzene ring, the equilibrium constants of various phenol species by Purolite A-510 resin were found to correlate well with the octanol/water partition coefficients of the phenols.

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