Korean J. of Chem. Eng., 9(4), 225-232 (1992)

ADSORPTION OF PHENOLS IN A FIXED-BED ADSORBER CHARGED WITH POLYMERIC SORBENTS

Hee Moon*, Jae Wook Lee and Heung Chul Park

Department of Chemical Technology, Chonnam National University, Kwangju 500-757, Korea

(*Received 30 September 1992 • accepted 16 November 1992*)

Abstract—Adsorption of phenols onto a polymeric sorbent, SP206, was carried out in a fixed-bed adsorber and the saturated bed was regenerated by using 0.05 N sodium hydroxide solution to get information for a cyclic adsorption process as an alternative for the activated carbon process. Furthermore, a simple dynamic model for simulating the dynamic behavior of multicomponent adsorption systems was proposed based on both the ideal adsorbed solution theory (IAST) for multicomponent equilibria and the linear driving force approximation (LDFA) for intraparticle mass transport. In spite of its simplicity, the proposed dynamic model successfully simulated breakthrough curves up to a three-species mixture.

INTRODUCTION

The adsorption process has been known to be a more efficient technology than most competing processes to remove organic substances from aqueous streams. For this reason, activated carbon adsorption has been rigorously applied for the last several decades. Since activated carbon has a well-developed pore structure and energetically heterogeneous surfaces [1], it can adsorb most organic substances including phenolic species, even from relatively dilute and complex aqueous streams [2, 3]. However, a weak point of the activated carbon process is that activated carbons have a considerable amount of irreversible adsorption. Consequently the regeneration of spent carbon is not easy and, even if possible, a very expensive process. From the environmental point of view, the disposal of spent carbon causes secondary environmental pollution. For this reason, some investigators [4, 5] have been interested in using polymeric sorbents as an alternative to activated carbon. The regeneration of polymeric sorbents can be easily accomplished by using organic solvents, bases or acids, and steam etc. In the case of phenol-saturated sorbents, regeneration can be easily performed by using either methanol or sodium hydroxide solution [4, 5].

In general, fixed-bed adsorbers have been used for wastewater treatments. In this case, a mathematical model is required to obtain design and optimal operating conditions. There are some available models in the literature [4-7]. Although they are powerful for predicting the performance of fixed-bed adsorption, it is sometimes time- and effort-consuming to implement those models into multicomponent calculations. Therefore, the development of a simple model has been an interesting subject in this field [8, 9].

The development of an adsorption model requires information on adsorption equilibria in addition to interparticle and intraparticle transport phenomena. The success of modelling in general depends on how to incorporate the adsorption equilibrium relationship and the transport mechanism with mass balance equations. In order to develop a simplified model, one has to find reasonable methods for incorporation. Whenever the adsorption system contains more than one component, it is very tedious to get multicomponent equilibrium data experimentally. In this case, one needs a theoretical approach to predict multicomponent adsorption equilibria such as the ideal adsorbed solution theory (IAST) [10]. On the other hand, the linear driving force approximation (LDFA) may be accepted in simply describing the intraparticle surface diffusion [8, 9]. Therefore in this study, a simple but practical model will be proposed based on the two major simplifications mentioned above.

The present work also represents the author's continuing effort to investigate the use of nonfunctional polymeric sorbent as an alternative of activated carbon

---

*To whom all correspondence should be addressed.

for removing organic substances from contaminated aqueous streams, after previous work [11] on the adsorption of phenols in a finite batch adsorber. Our major concern is to get valuable information on the adsorption and desorption of phenols in a cyclic fixed-bed adsorber.

THEORETICAL

1. Model Formulation

For fixed-bed adsorptions of N adsorbable species from aqueous streams, the mass balance equation for each component is written by assuming that the axial dispersion is negligible as follows:

$$U\frac{\partial C_i}{\partial z}+\varepsilon_b\frac{\partial C_i}{\partial t}+\rho_b\frac{\partial Q_i}{\partial t}=0 \qquad (1)$$

the initial and boundary conditions are

$$C_i=0 \text{ and } Q_i=0 \qquad \text{at } t=0,\ 0<z<L \qquad (2)$$

$$C_i=C_{i0} \qquad \text{at } z=0,\ t>0 \qquad (3)$$

The dependent variables are the concentration in the solution phase, C_i and the average adsorbed amount in the adsorbed phase, Q_i. The independent variables are the axial distance, z and the time, t. U, ε_b and ρ_b are superficial flow rate, bed porosity and packing density, respectively. Eq. (2) implies that the sorbent is initially sorbate-free.

If the effect of intraparticle diffusion can be lumped into a solid-phase mass transfer coefficient based on the LDFA [12], one can considerably reduce computational expences for predicting multicomponent breakthrough curves. Such a manipulation yields the following simple rate equations instead of a set of partial differential equations.

$$\frac{\partial Q_i}{\partial t}=\frac{3k_{fi}}{R\rho_p}(C_i-C_{si})=k_{si}(Q_{si}-Q_i) \qquad (4)$$

where R is the radius of the sorbent particle, ρ_p is the particle density, and C_{si} and Q_{si} are the interface concentration at the exterior surface of the sorbents. According to Eq. (4), two mass transfer coefficients, k_{fi} and k_{si}, control the interphase and intraparticle transport, that is, there are two mass transfer resistances during the adsorption process.

Eqs. (1)-(4) can be written into the following dimensionless form, by introducing the corrected time, θ, defined as $t-\varepsilon_b z/U$

$$\frac{\partial Y_i}{\partial S}+\frac{\partial \psi_i}{\partial \tau}=0 \qquad (5)$$

$$Y_i=\psi_i=0 \qquad \text{at } \tau=0,\ 0<S<1 \qquad (6)$$

$$Y_i=1.0 \qquad \text{at } S=0,\ \tau\geq 0 \qquad (7)$$

$$\frac{\partial \psi_i}{\partial \tau}=\lambda_{fi}(Y_i-Y_{si})=\lambda_{si}(\psi_{si}-\psi_i) \qquad (8)$$

Here, the dimensionless variables are

$$Y_i=C_i/C_0 \qquad (9)$$

$$\psi_i=Q_i/Q_0 \qquad (10)$$

$$S=z/L \qquad (11)$$

$$\tau=UC_0\theta/L\rho_bQ_0 \qquad (12)$$

$$\lambda_{fi}=3L\rho_bk_{fi}/R\rho_pU \qquad (13)$$

$$\lambda_{si}=L\rho_bk_{si}Q_0/UC_0 \qquad (14)$$

where L is the bed height and C_0 and Q_0 are the reference concentrations which have a magnitude of unity.

2. Multicomponent Adsorption Equilibria

In addition to the set of equations above, an equilibrium relationship is required to complete the model. Two interface concentrations, C_{si} and Q_{si} in Eq. (4) [or y_{si} and ψ_{si} in Eq. (8)] should be incorporated with the multicomponent adsorption equilibrium relationship [8, 9]. In the case of polymeric sorbents, the Langmuir equation has been known to be suitable in describing the single-species isotherm [4, 5, 11]. Since the polymeric sorbent has energetically homogeneous surfaces, it is quite possible to assume that sorbates on the surface form an ideal adsorbed solution.

The IAST based on the Langmuir equation as a single-species isotherm gives the following set of equations [3, 13].

$$C_i=C_i^o(\pi)Z_i \qquad (15)$$

$$Q_T=\{\Sigma(Z_i/Q_i^o)\}^{-1} \qquad (16)$$

$$Z_i=Q_i/Q_T \qquad (17)$$

$$\Sigma Z_i=1.0 \qquad (18)$$

$$\pi_1=\pi_2=\cdots=\pi_N=\pi \qquad (19)$$

where $C_i^o(\pi)$ and Q_i^o are the single-species fluid phase concentration which gives the spreading pressure, π, for adsorbed mixture. Z_i is the mole fraction of the i-th species in the adsorbed phase and Q_T is the total amount of adsorption from the mixture. The Gibbs isotherm yields the spreading pressure as follows

$$\pi_i=(R_gT/A)\ \{Q_{mi}\ln(1+bC_i^o)\} \qquad (20)$$

when the single species isotherm is

Table 1. Properties of a polymeric sorbent, SP206

Property		Unit
Particle diameter	250/1000	μm
Particle density	640	kg/m^3
Packing porosity	0.44	–
Moisture content	50	%
Surface area	556	m^2/g
Average pore diameter	70	Å

Table 2. Langmuir constants of phenols on SP206 at 20 °C

Species	Q_m	b	E(%)*
Phenol	0.626	1.136	2.52
PCP	0.736	6.074	1.03
PNP	0.815	3.556	2.58

*average percent error

$$Q_i'' = Q_{mi} b_i C_i''/(1+bC_i'') \tag{21}$$

3. Adsorption Calculation

Dimensionless equations, Eqs. (5)-(8), were solved by a numerical algorithm used in previous works [8, 9]. The interface concentrations were calculated by incorporating Eqs. (15)-(20) into Eq. (8).

$$Y_{si} + (\lambda_{si}/\lambda_{ni})\psi_{si} = Y_i + (\lambda_{si}/\lambda_{ni})\underline{\psi}_i \tag{22}$$

or $Y_{si} + A_i\psi_{si} = B_i$ (23)

where $A_i = \lambda_{si}/\lambda_{ri}$ (24)

$$B_i = Y_i + (\lambda_{si}/\lambda_{ni})\underline{\psi}_i \tag{25}$$

Here A_i and B_i are considered as constants at a given time step.

EXPERIMENTAL

1. Sorbent and Sorbates

The nonfunctional polymeric sorbent used in this study was a reticular-type spherical polystyrene resin cross-linked with DVB (divinylbenzene), SP206, which was manufactured by Mitsubishi Co. (Japan). Prior to experiments, the sorbent was pretreated with methanol and 0.05 N NaOH solution to remove impurities. The properties of the sorbent are listed in Table 1. Sorbates are phenol, PCP (p-chlorophenol), and PNP (p-nitrophenol) which have been known as typical pollutants. Adsorption isotherms were obtained from batch experiments and the Langmuir parameters for phenols on SP206 are listed in Table 2.

2. Fixed-Bed Adsorber

Single-species and multicomponent adsorptions were carried out in a fixed-bed adsorber which was made of a glass column of 1 cm diameter and 20 cm length. The column was lined with a water jacket to maintain the uniform column temperature and all experiments were performed at 20℃. The flow rate was regulated by a precision needle valve and a flowmeter. The solution was introduced downward into the column. To prevent channeling and to enhance distribution of the solution through the column, small glass beads were packed in the top and bottom region of the column. Experimental conditions used here are listed in Table 3.

Table 3. Experimental conditions for fixed bed adsorptions

Variables	Range	Unit
Bed length (L)	0.06-0.1	m
Flow rate (U)	0.0849-2.123×10^{-2}	m/sec
Bed porocity (ε_b)	0.44	–
Packing density (ρ_b)	368	kg/m^3
Temperature (T)	20	℃
Concentration (C_0)	0.532-2.00	mol/m^3

The samples were withdrawn from the effluent line and analyzed by using UV spectrometry. Wavelengthes used were 270, 280, and 318 nm for phenol, PCP, and PNP, respectively. However, the concentrations of phenate-type phenols were measured at 285, 300 and 400 nm because their maximum peaks are shifted.

RESULTS AND DISCUSSION

1. Estimation of Model Parameters

There are two major model parameters, k_f and k_s, in Eq. (4) which should be incorporated with equilibrium relations to get interface concentrations. These parameters may be estimated from proper correlations. For spherical particles, the external film mass transfer coefficient can be estimated from the Ranz and Marshall equation [1].

$$2k_f R/D_m = 2.0 + 0.6\ Sc^{1/3}\ Re^{0.5} \tag{26}$$

where Sc and Re are Schmidt and Reynolds numbers, respectively and D_m is the molecular diffusion coefficient. Molecular diffusion coefficients of phenols in water were estimated by the Wilke-Chang equation [14]. Under the experimental conditions used here, the estimated k_f for phenol is 0.35×10^{-4} m/sec when the flow rate is 0.2×10^{-2} m/sec.

The solid-phase mass transfer coefficient may be estimated from the surface diffusion coefficient when-

Table 4. D_s and k_s for phenols within SP206 at 20°C

Species	$D_s\times10^{12}$ (m^2/sec)	$k_s\times10^3$ (1/sec)
Phenol	6.80	1.63
PCP	3.80	0.91
PNP	2.90	0.70

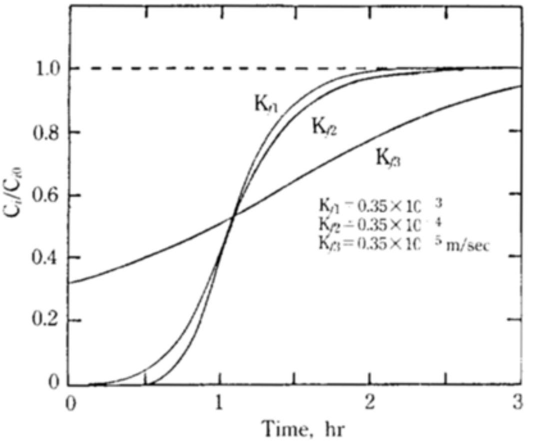

Fig. 1. Sensitivity of k_f on breakthrough curves of phenol.
($C_0=2.0$ mol/m^3, U=0.002 m/sec, $k_s=1.6\times10^{-3}$ sec^{-1} and L=0.1m)

ever the LDFA or the parabolic profile of sorbate concentration in the particle is assumed [12].

$$k_s=15\,D_s/R^2 \tag{27}$$

The surface diffusion coefficients and the solid-phase mass transfer coefficients are listed in Table 4.

Prior to simulating single-species breakthrough curves, the sensitivities of major parameters were tested. Figs. 1 and 2 show the sensitivities of k_f and k_s on the breakthrough curve of phenol. As the value of the mass transfer coefficients increases, the breakthrough curve becomes a sharp sigmoid shape. This implies that the adsorption equilibrium controls the breakthrough when the mass transfer resistance disappears.

2. Single-species Breakthrough Curves

In commercial equipment for adsorption separation, a fixed-bed adsorber has been used since it gives a sharp breakthrough by means of the difference in affinity to the sorbent particle. The breakthrough curve of any species in general depends on adsorption equilibrium, interparticle and intraparticle mass transfer, and hydrodynamic conditions in the column. In the special case that the column is long enough and the flow rate is sufficiently slow, the equilibrium solution can predict the breakthrough curves [15]. However, it is quite reasonable to consider adsorption equilibrium and mass transport simultaneously in simulating the adsorption and desorption behavior in the fixed-bed adsorber.

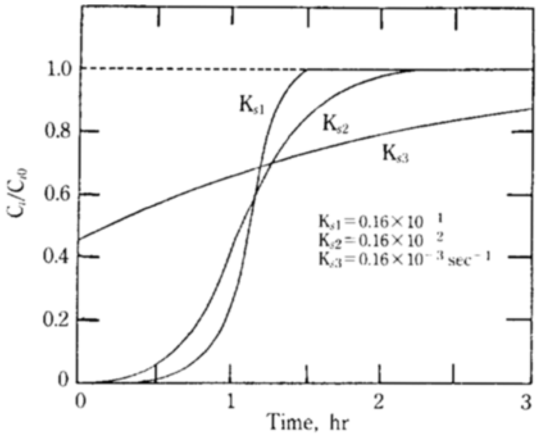

Fig. 2. Sensitivity of k_s on breakthrough curves of phenol.
($C_0=2.0$ mol/m^3, U=0.002 m/sec, $k_f=3.5\times10^{-5}$ m·sec^{-1} and L=0.1m)

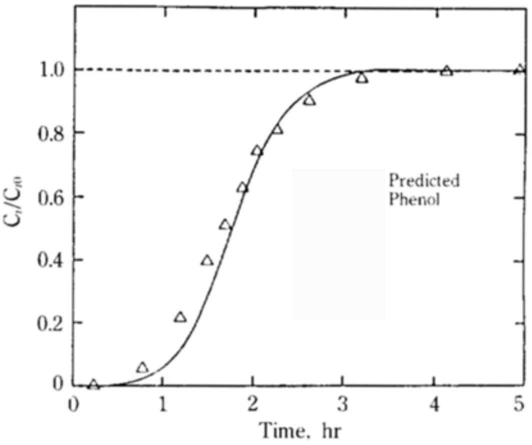

Fig. 3. Experimental and predicted breakthrough curve of phenol.
($C_0=1.527$ mol/m^3, U=0.00148 m/sec and L=0.1 m)

Figs. 3 and 4 show the experimental and predicted breakthrough curves of phenol and PCP, respectively. The predicted breakthrough curve was obtained by using the model, without any manipulation of the model parameters which were estimated from the correlations given in the previous section.

3. Regeneration of Spent Sorbent

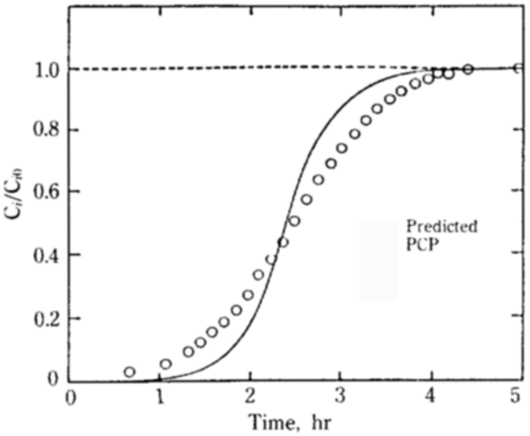

Fig. 4. Experimental and predicted breakthrough curve of PCP.
(C_0 = 1.287 mol/m^3, U = 0.00213 m/sec and L = 0.1 m)

One of major advantages for the use of polymeric sorbents is that the spent sorbent can be easily regenerated, that is, the sorbent can be used repeatedly by using a cyclic process. The spent sorbent was regenerated by NaOH solutions of different concentrations and it was found that a concentration of 0.05 N is proper. As known from batch experiments, the phenols retained on SP206 are removed quickly. This can be explained as follows: sodium hydroxide, which diffuses into the pores of the sorbent, reacts with phenol and the phenate-type phenol formed diffuses out very quickly because of the Donnan effect [4, 5].

The adsorption and desorption breakthrough curves of phenol after 5, 10 and 15 times repeated regeneration are shown in Fig. 5. Regardless of repeated regeneration, the sorbent has almost the same adsorption capacity as the fresh sorbent. For the case of PCP and PNP, the regeneration of spent sorbents were easily performed. This result is different from that of the finite batch adsorber in which the degree of regeneration was 88-91% [11]. In the fixed-bed adsorber, the degree of regeneration is high because fresh solvent is supplied continuously.

4. Multicomponent Adsorptions

When two or more components flows through the bed, the adsorption behavior becomes quite different from that of a single-species case. In this case, a competitive adsorption between sorbates appears because the affinity of each species to the sorbent is different from the others. The competitive effect of each component can only be described by adsorption equilibrium relationships when simulating for multicomponent adsorptions. Consequently, the accuracy of the simulation is mainly influenced by equilibrium data [9].

Figs. 6, 7 and 8 show typical binary breakthrough curves for phenol/PCP, phenol/PNP, and PCP/PNP systems. The solid lines in these figures are results simulated by using the dynamic model. As expected, the binary breakthrough curves show an over shoot behavior, namely, excess concentration over the inlet value for a species having lower affinity. The excess concentration reaches an ultimate value when the column is sufficiently long. This value called "maximum excess concentration" does not vary with the mass transfer coefficient but with the equilibrium relation-

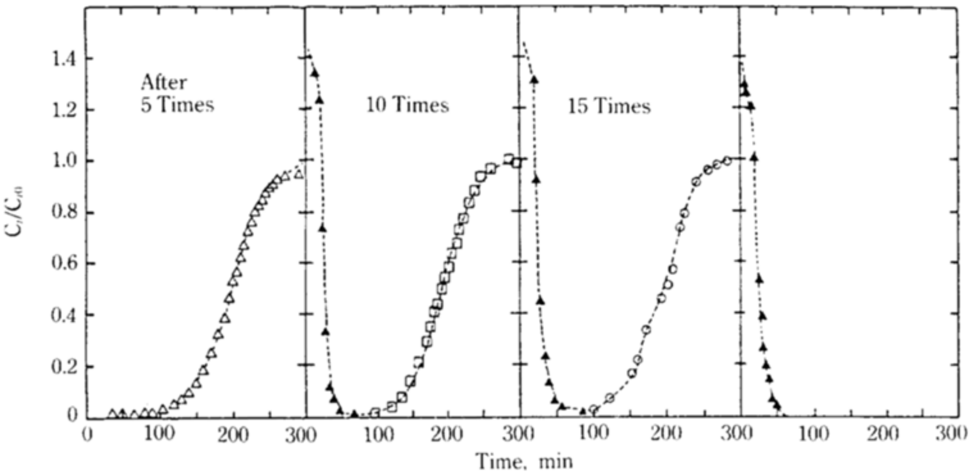

Fig. 5. Repeated adsorption and desorption of phenol.
(C_0 = 2.0 mol/m^3, U = 0.00085 m/sec and L = 0.06m)

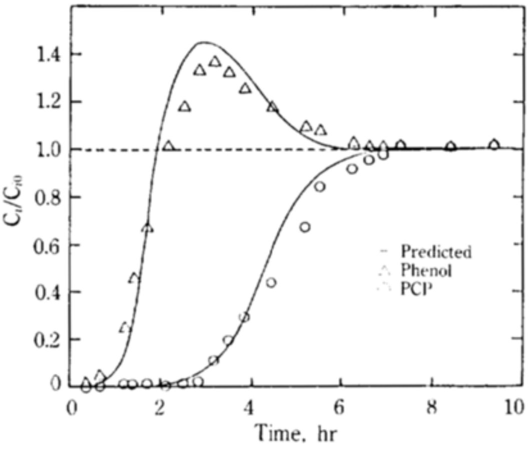

Fig. 6. Binary breakthrough curves of phenol(1)/PCP(2) system.
($C_{10}=1.000$, $C_{20}=0.868$ mol/m^3, $U=0.00149$ m/sec and $L=0.1$m)

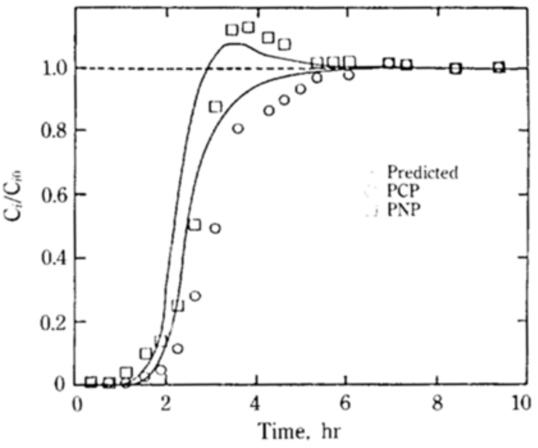

Fig. 8. Binary breakthrough curves of PCP(2)/PNP(3) system.
($C_{20}=1.112$, $C_{30}=0.884$ mol/m^3, $U=0.00149$ m/sec and $L=0.1$m)

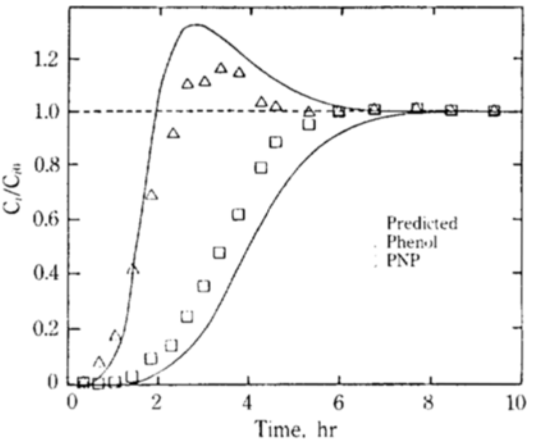

Fig. 7. Binary breakthrough curves of phenol(1)/PNP(3) system.
($C_{10}=1.053$, $C_{30}=0.838$ mol/m^3, $U=0.00170$ m/sec and $L=0.1$m)

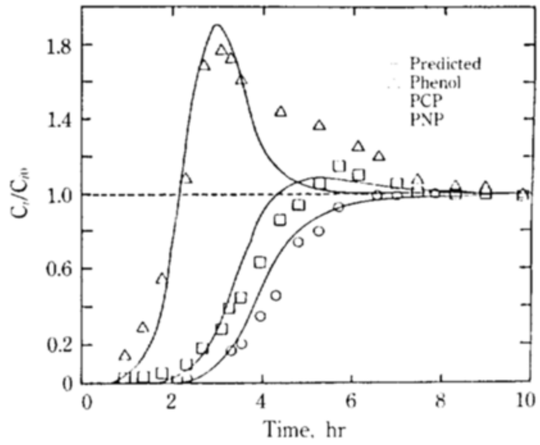

Fig. 9. Ternary breakthrough curves of phenol(1)/PCP(2) /PNP(3) system.
($C_{10}=0.528$, $C_{20}=0.760$, $C_{30}=0.621$ mol/m^3, $U=0.00128$ m/sec and $L=0.1$m)

ship [8, 9]. In this study, the adsorption equilibrium has been represented by the IAST based on the Langmuir equation as single-species isotherms. It is also interesting to see binary breakthrough curves for PCP/PNP as shown in Fig. 8, which are quite different from other binary systems. These two components have very similar affinities to SP206 and the relative adsorption amounts are reversed at about 1.5 mol/m^3 of sorbate concentration(see Fig. 1 of Moon et al. [11]). According to Fig. 8, the affinity of PCP is higher than that of PNP as expected from the results for single-species isotherms. The breakthrough curves will be changed according to the range of concentration taken.

Fig. 9 shows some typical breakthrough curves of a ternary system, phenol/PNP/PCP. As mentioned above, sorbates having a lower adsorption affinity have over shoot behavior. Although there are discrepancies between experimental and predicted results, the model simulates the adsorption behavior very well up to three-species systems. Although the LDFA model incorporated with the IAST is a simplified model in

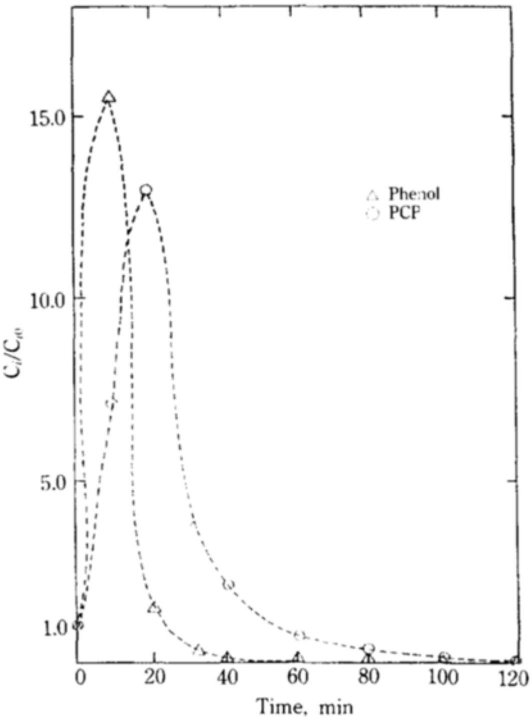

Fig. 10. Typical binary desorption curves of phenol(1)/PCP(2) by using 0.05 N NaOH solution.
(after Fig. 6)

which the intraparticle mass transfer is approximated by a single mass transfer coefficient, it has proved to be applicable in simulating general features of fixed-bed adsorption systems within experimental error.

The regeneration of spent sorbents used in a binary adsorption was also performed by means of 0.05 N sodium hydroxide solution and the result is shown in Fig. 10. Desorption breakthrough curves of each species are obtained by allowing the desorbent to flow after satuation of the bed. In multicomponent cases, the species having the lowest affinity desorbs first. It is also shown in Fig. 10 that the concentration of sorbates when desorbing is 13-14 times that of the inlet concentration. This phenomenon can be explained in the same way as for single-species systems. The phenols adsorbed on SP206 are changed into phenate-types and desorbed very fast by the Donnan effect. The model proposed here does not cover the case of desorption because of its limitation for the transition of phenols into their phenate-types and the Donnan effect. The development of a practical model for a complete cyclic adsorption still remains as a continuing work which should be studied in the future.

CONCLUSIONS

As a relevant technology for removing dissolved phenols in aqueous solutions, the adsorption and desorption of phenols onto a nonfunctional polymeric sorbent, SP206, was carried out in a fixed-bed adsorber. A simple but practical model was also proposed for predicting breakthrough curves of single- and multi-species adsorptions. The formulated model is based on the linear driving force approximation for intraparticle mass transfer and the ideal adsorbed solution theory for multicomponent adsorption equilibria. The model is simple and easy in implementing into most multicomponent adsorption calculations. In spite of its simplification, it successfully simulated general features of the adsorption behavior within experimental error. The phenols adsorbed on SP206 were desorbed very quickly by 0.05 N sodium hydroxide solution in a fixed-bed adsorber and the sorbent had nearly the same adsorption capacity as the fresh one even after repeated regenerations. This result confirms that porous polymeric resins such as SP206 are promising sorbents for removal of organic pollutants such as phenols from aqueous streams by means of a cyclic adsorption process.

ACKNOWLEDGEMENT

This research was supported by Korea Science and Engineering Foundation under grant No. 901-1001-028-2. The authors gratefully acknowledge the support of Samyang Co. for supplying the polymeric sorbents.

NOMENCLATURE

A : surface area of sorbent particles
A_i : constant defined in Eq. (24)
b : Langmuir constant
B_i : constant defined in Eq. (25)
C : concentration in the fluid phase [mol/m^3]
D_m : molecular diffusion coefficient [m^2/sec]
D_s : effective surface diffusion coefficient [m^2/sec]
k_f : film mass transfer coefficient [m/sec]
k_s : solid-phase mass transfer coefficient [1/sec]
L : bed height [m]
Q : amount adsorbed [mol/kg]
Q_m : amount adsorbed for monolayer formation [mol/kg]
R : radius of particle [m]
R_g : gas constant
S : dimensionless bed height (=z/L)
T : temperature [℃]

t : time [sec or hr]
U : superficial flow rate [m/sec]
Y : dimensionless concentration ($=C/C_0$)
Z : mole fraction in the adsorbed phase
z : axial distance [m]

Greek Letters

ε_b : bed porosity
ε_p : particle porosity
λ_f : dimensionless group defined in Eq. (13)
λ_s : dimensionless group defined in Eq. (14)
ρ_b : packing density [kg/m^3]
ρ_p : apparent particle density [kg/m^3]
π : spreading pressure
τ : dimensionless time defined in Eq. (12)
θ : corrected time
ψ_i : dimensionless amount adsorbed ($=Q_i/Q_0$)

Subscripts and Superscripts

0 : initial value
i, j : species
o : single-species state
s : interface
T : total
$-$: average

Abbreviations

IAST : ideal adsorbed solution theory
LDFA : linear driving force approximation
PCP : p-chlorophenol
PNP : p-nitrophenol
Re : Reynolds number
Sc : Schmidt number

REFERENCES

1. Ruthven, D. M.: "Principles of Adsorption and Adsorption Processes", John Wiley and Sons, New York, 1984.
2. Fritz, W., Merk, W. and Schlünder, E. U.: *Chem. Eng. Sci.*, **36**, 731 (1981).
3. Kim, H. J., Moon, H. and Park, H. C.: *Korean J. Chem. Eng.*, **2**, 181 (1985).
4. Costa, C. and Rodrigues, A.: "Fundamentals of Adsorption", edited by Myers, A. and Belfort, G., 153 (1984).
5. Costa, C. and Rodrigues, A.: *AIChE J.*, **31**, 1645 & 1655 (1985).
6. Mansour, A., von Rosenberg, D. U. and Sylvester, N. D.: *AIChE J.*, **28**, 765 (1982).
7. Morbidelli, M., Servida, A., Storti, G. and Carra, S.: *Ind. Eng. Chem. Fundam.*, **21**, 123 (1982).
8. Moon, H. and Lee, W. K.: *Chem. Eng. Sci.*, **41**, 1995 (1986).
9. Moon, H. and Tien, C.: *Chem. Eng. Sci.*, **43**, 1269 (1988).
10. Radke, C. J. and Prausnitz, J. M.: *AIChE J.*, **18**, 761 (1972).
11. Moon, H., Kook, S. K. and Park, H. C.: *Korean J. Chem. Eng.*, **8**, 168 (1991).
12. Huang, T. and Cho, L.: *J. Chem. Eng. Japan*, **21**, 498 (1988).
13. Moon, H., Park, H. C. and Lee, W. K.: *Korean J. Chem. Eng.*, **7**, 250 (1990).
14. Moon, H. and Lee, W. K.: *J. Colloid Interface Sci.*, **96**, 162 (1983).
15. Moon, H., Park, H. C. and Tien, C.: *Chem. Eng. Sci.*, **46**, 23 (1991).