ADSORPTION OF PHENOLS ONTO A POLYMERIC SORBENT

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Abstract – Adsorption of phenols from aqueous solutions onto a polymeric sorbent, SP206, was carried out in a finite batch adsorber. Multicomponent adsorption equilibrium data were experimentally measured and compared with those predicted by the ideal adsorbed solution theory (IAST) based on the Langmuir equation as single species isotherms. Intraparticle diffusion during adsorption was assumed to be expressed by the pore diffusion and the surface diffusion mechanisms and the effective diffusion coefficient of each species was determined by comparing experimental and predicted concentration histories. The surface diffusion model incorporated with the IAST successfully simulated the adsorption behaviour of a phenols-polymeric sorbent system up to three-species mixtures. The regeneration of spent sorbents was also investigated to get information for a cyclic adsorption process.

INTRODUCTION

The adsorption of organic substances from aqueous solutions is of considerable practical interest in developing a technical process for the purification of domestic and industrial effluents because it is more energy efficient than most competing technologies [1]. In recent days the contamination of Korean rivers with phenolic species was reported to be a serious environmental problem. This comes from industrial wastewater containing untreated organic substances. Organic substances can impart an objectionable taste or odor but a more serious problem is that those substances and their derivatives, which are formed by chemical reactions between substances, are potentially carcinogenic and mutagenic [2].

The removal of organic substances including phenols has been dealt with by activated carbon adsorption in batch or fixed-bed adsorbers because activated carbon has energetically heterogeneous surfaces and can adsorb most organic substances effectively even from relatively dilute and complex aqueous solutions [3-5]. However, it has been pointed out that the regeneration of spent carbon is not easy because of considerable irreversible adsorption [6]. Since an adsorption process consists of three main steps: loading (adsorption), regeneration (desorption) and washing, regeneration efficiency in particular is a critical factor for the economy of the overall process. Recently, some workers have been interested in using polymeric sorbents which are available on the market as an alternative to activated carbon for the removal of organic substances from aqueous solutions [6-11]. The regeneration of such sorbents can be easily accomplished by leaching with a proper solvent or alkaline solutions [6, 7, 12]. Furthermore, polymeric sorbents can be made to have highly specific surfaces for a certain species by changing surface functional groups.

Adsorption calculations for the design of a cyclic process in general require information on adsorption equilibria, intraparticle transport of adsorbates and regeneration. For single-species adsorptions, determining adsorption isotherms presents no serious problems. On the other hand, multicomponent equilibrium data are time-consuming and tedious to obtain experimentally. Thus, a lot of efforts were, as a practical matter, made to predict multicomponent equilibrium data based on only single-species isotherm data [13-15]. Among them, the ideal adsorbed solution theory (IAST) invokes the assumption that adsorbates in the adsorbed phase form an ideal solution, particularly on homogeneous sorbents. Intraparticle diffusion within porous sorbents depends on the mechanism of adsorbate transport such as pore diffusion, surface diffusion and others. However, it is often handicapped by the fact that the mechanism of adsorbate transport can not be completely understood because of its complicated character. To circumvent this difficulty, a number of workers have chosen one major mechanism as a matter of convenience and subsequently the effective

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diffusion coefficient may be determined by comparing experimental data with those predicted by the model [4, 16]

The present work is concerned with the adsorption of phenolic species such as phenol, p-chlorophenol (PCP) and p-nitrophenol (PNP) onto a nonfunctional macroreticular polymeric sorbent, SP206, based on a polystyrene matrix crosslinked with divinylbenzene. The regeneration of SP206 loaded with phenols is also carried out by using a sodium hydroxide solution as a regenerant. The major emphasis of this study is placed on the acquisition of valuable information on a cyclic adsorption process for phenol removal by using polymeric sorbents.

THEORETICAL

1. Adsorption Isotherms

The single-species isotherm may be assumed to be the Langmuir-type when the sorbent has energetically homogeneous surfaces [17].

$$\mathbf{Q}_i = \mathbf{Q}_{mi} \mathbf{b}_i \mathbf{C}_i / (1 + \mathbf{b}_i \mathbf{C}_i) \tag{1}$$

where Q_{mi} is the saturation amount of adsorption and b_i is the Langmuir constant of species i. Assuming that adsorbates on the surface form an ideal solution, multicomponent adsorption equilibrium data can be estimated by the IAST. This assumption, together with the Langmuir equation as a single-species isotherm, provides a set of equations for multicomponent adsorption calculations. According to the IAST, Q_i and C_i are related by the following set of equations:

$$C_i = C_i^{\nu}(\pi) Z_i \tag{2}$$

$$\mathbf{Q}_T = \{ \mathbf{\Sigma} \; \mathbf{Z}_i / \mathbf{Q}_i^p \}^{-1} \tag{3}$$

$$\mathbf{Z}_i = \mathbf{Q}_i / \mathbf{Q}_T \tag{4}$$

$$\Sigma Z_t = 1 \tag{5}$$

$$\pi_1 = \pi_2 = \cdot \cdot = \pi_N = \pi \tag{6}$$

where C_t^n and Q_t^n are the liquid-phase concentration and the amount of adsorption in single-species adsorption, which gives the spreading pressure, π for the adsorbed mixture [14]. Q_T is the total amount of adsorption and Z_t is the mole fraction of species i in the adsorbed phase. According to the Gibbs isotherm [18], the spreading pressure may be calculated by

$$\Pi_{i} = \frac{\pi_{i}A}{RT} = \int_{0}^{C_{i}''} (\mathbf{Q}_{i}''/C_{i}'') \ \mathrm{d}C_{i}''$$
(7)

If single-species isotherm is given by the Langmuir equation, Π_i and C_i^o are related by the expression

$$\Pi_{i} = Q_{mi} \ln(1 + b_{i} C_{i}^{o}) \tag{8}$$

Once the spreading pressure is evaluated at a given condition, it completes the adsorption calculation [14, 17].

2. Intraparticle Diffusion Model

The following assumptions are usually made in developing the surface diffusion model [4, 16]: The concentrations of adsorbates are uniform in the batch. The adsorbents are spherical particles with identical radius and their physical properties are homogeneous. Since diffusion occurs much more slowly than mass transfer through external film, local equilibrium is established at the external surface of particles.

According to the assumptions above, adsorption occurs at the outer surface of the particle, which can be described by a multicomponent isotherm, followed by the surface diffusion into the particle. The governing equations for this model are written in the following dimensionless forms. The material balance of species i in the finite batch adsorber is given by

$$\xi = 1 - \alpha_i \underline{\Psi}_i \tag{9}$$

$$\underline{\Psi}_{i} = 3 \int_{0}^{1} \Psi_{i} x^{2} dx \qquad (10)$$

where $\underline{\Psi}_i$ is the volume-average amount of adsorption and α_i is defined as

$$\alpha_i = WQ_{i0}/VC_{i0} \tag{11}$$

The material balance in the particle is given by

$$\frac{\partial \Psi_i}{\partial \tau} = \gamma_i \left(\frac{\partial^2 \Psi_i}{\partial x^2} + \frac{2}{x} \frac{\partial \Psi_i}{\partial x} \right)$$
(12)

$$\Psi_{r} = 0$$
 at $\tau = 0, \ 0 < x < 1$ (13)

$$\frac{\partial \Psi_{i}}{\partial x} = 0 \qquad \text{at } x = 0, \ \tau > 0 \tag{14}$$

$$\frac{\partial \Psi_{i}}{\partial x} = \lambda_{i} (\xi_{i} - \xi_{s}) \quad \text{at } x = 1, \ \tau > 0 \tag{15}$$

Here, the dimensionless variables are defined as follows:

$$\boldsymbol{\xi}_i = \boldsymbol{C}_i / \boldsymbol{C}_{i0} \tag{16}$$

$$\Psi_i = \mathbf{Q}_i / \mathbf{Q}_{i0} \tag{17}$$

$$\mathbf{x} = \mathbf{r}/\mathbf{R} \tag{18}$$

$$\tau = D_{s1} t/R^2 \tag{19}$$

 λ_r represents the Biot number for species i and γ_r and λ_r are dimensionless groups which are dependent on process variables of the adsorption system.

$$\gamma_i = \mathbf{D}_{si} / \mathbf{D}_{s1} \tag{20}$$

$$\lambda_i = \mathbf{k}_{fi} \mathbf{R} \mathbf{C}_{i0} / \rho_p \mathbf{D}_{si} \mathbf{Q}_{i0} \tag{21}$$

Eqs. (9) and (12) are related with the boundary condition of Eq. (15) at the external surface of the particle.

The surface adsorbate concentration, ξ_{si} , in Eq. (15) is calculated from the amount of adsorbates adsorbed at a previous time by using a multicomponent adsorption isotherm. For multicomponent adsorptions, the IAST which is thermodynamically consistent is applied. A great advantage of this theory is that it requires only single-species isotherm data in predicting multicomponent adsorption equilibrium data. The incorporation of the IAS theory into the model equation is given elsewhere [5, 19]. The concentration history in the batch adsorber can be found by solving the above set of equations using an algorithm depicted by Moon and Tien [19].

EXPERIMENTAL

The sorbent used in this study was a nonfunctional macroreticular polymeric sorbent, SP206, manufactured by Mitsubishi Chemical Ind. Co., Japan. The properties of this sorbent measured and obtained from the manufactures' specifications are listed in Table 1. The average particle diameter of the sorbent particles was estimated to be 0.50×10-3 m from microscopic measurement. All sorbent particles were leached with methanol to remove impurities and to wet internal pores prior to use. Sorbent particles were loaded in a 0.01 m ID glass column and a ten-bed volume of methanol was passed through the column at a flow rate of 1×10^{-6} m³/min. After leaching with methanol, a twenty-bed volume of distilled and deionized water (Sigma LC grade) was passed at the same flow rate in order to remove methanol. It was confimed that methanol at the column effluent after passing a tenbed volume of water was no longer detected by a flame ionization detector.

The adsorbates were phenol, p-chlorophenol (PCP), and p-nitrophenol (PNP) which are common industrial contaminants. Stock solutions of each species were made up by dissolving the reagent-grade chemicals supplied by Sigma Chemical Co. into distilled and deionized water. Binary and ternary solutions were prepared by adding stock solutions. The concentration of each species in the solution was determined by using UV spectrometry. Wavelengthes used were 270, 280 and 318 nm for phenol, PCP and PNP, respectively. The concentrations of individual species in mixture were obtained by solving the corresponding Beer-

roperty		onac
Particle size*	250/1000	μm
Particle density	640	kg/m ³
Packing porosity	0.44	
Moisture content*	50	%
Surface area*	556	m²/g
Average pore diameter*	70	Α

*from the manufactures' specifications

**measured based on dry basis

Lambert equation with calibration constants.

Equilibrium data were taken by introducing a given amount of sorbent into a mixed solution of 2×10^{-4} m³, shaking in a constant temperature incubator at 20° for a week and measuring the adsorbate concentrations remained in the solution. A week was enough for the system to reach equilibrium. The dry-base weight of sorbent was measured by weighting after drying for 10 hours in a vaccum oven at 90°C.

Adsorption experiments were conducted in a Carberry-type batch adsorber of 2×10^{-3} m³ used in previous studies [4, 21]. Sorbent particles were loaded into four cages made of 80 mesh stainless-steel screen and the cages were affixed to the rotating shaft to permit good contact with solution. All the experiments were carried out at approximately 500 rpm so that the film mass transfer coefficient, k_f , would be nearly constant.

RESULTS AND DISCUSSION

1. Adsorption Equilibrium Data

There are various single-species isotherms reported in literatures [18]. In this study, single-species equilibrium data were correlated by the two-parameter Freundlich equation and the three-parameter Sips equation [25] as well as the Langmuir equation.

Freundlich	equation:	Q = k	C ^{1/n}	(22)
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Sips equation: $Q = Q_m b C^{1/n} / (1 + b C^{1/n})$ (23)

In principle, one can obtain the values of the isotherm parameters by minimizing the mean percent deviation between experimental and predicted values of Q defined as

$$E(\%) = \frac{100}{N} \sum_{k=1}^{N} \left[(\mathbf{Q}_{xxp} - \mathbf{Q}_{pm}) / \mathbf{Q}_{xp} \right]_{k}$$
(24)

The parameters of adsorption isotherms were determined by fitting experimental data to Eqs. (1), (22) and (23) and the results of the parameter search are sum-

Species	k	n	E(%)
Phenol	0.329	1.710	4.62
PCP	0.655	2.660	8.95
(B) Langmuir	0.688 Equation	2.290	2.17
PNP (B) Langmuir Species	0.688 Equation Q _m	2.290 b	2.17
PNP (B) Langmuir Species Phenol	0.688 Equation Q _m 0.626	2.290 b 1.136	2.17 E(%) 2.52
PNP (B) Langmuir Species Phenol PCP	0.688 Equation Q _m 0.626 0.736	2.290 b 1.136 6.074	2.17 E(%) 2.52 1.03

Table 2. Single-species isotherms of phenols on SP206

Species Q_m b E(%) n Phenol 1.187 2.6000.7591.51 PCP 5.275 7.4220.945 0.82PNP 1.218 0.821 1.5821.66



Fig. 1. Single-species isotherms of phenols on SP206 at 20°C.

marized in Table 2. Among three equations, the Sips equation gives the best fit but it is likely to be an inevitable result since this equation contains three adjustable parameters. However, it should be noted that the Langmuir equation gives better fit than the Freundlich equation. This is contrary to the result of phenol adsorption onto activated carbon [4]. Considering the fact that the Langmuir equation is adquate in representing single species isotherms, one may conjecture that the polymeric sorbent used here has energetically

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0.249 0.191 0.353 0.172 0.341 (0.182		
0.212 0.107 0.382 0.099 0.350 (0.121		

Table 3. Binary adsorption equilibrium data of phenols on

SP206 at 20°C

homogeneous surfaces. This fact is also confirmed by the value of n in the Freundlich equation or the Sips equation ranging from 0.759 to 2.660 because the value of n is an indirect measure of surface heterogeneity [4, 21]. In this study, the Langmuir equation, as a matter of convenience, was adopted as a single species isotherm. All the species are favorable on SP206 as shown in Fig. 1 and the adsorption amount of phenols on SP206 is in the order of phenol <PNP<PCP. However, the adsorption amounts of PCP and PNP have reversed at higher concentrations. This comes from the mutual interaction between the sorbent and the functional group of adsorbate. On the other hand, one may also guess that the surface of SP206 is relatively hydrophobic from the fact that the adsorption amount of phenol, which is more soluble in water than PCP and PNP, is quite low [4].

Multicomponent adsorption equilibrium data, in this work, were predicted by the ideal adsorbed solution theory. The background to this choice is that the surface of SP206 seems to be energetically homogeneous like mentioned above. Experimental binary and ternary data are listed in Tables 3 and 4 as well as those predicted from the IAST by using relevant parameters listed in Table 2. One can find that the predictions are in reasonably good agreement with the experimental data. It should also be emphasized that the IAST can be incorporated with the adsorption model for

Adsorption	Experimental data					Predicted by the IAST		IAST	
system	C ₁	C ₂	C ₃	Q_1	Qz	Q_3	Q ₁	Q_2	Q_3
Phenol(1)/	0.155	0.177	0.275	0.008	0.240	0.271	0.029	0.239	0.258
PCP(2)	0.304	0.096	0.099	0.063	0.187	0.137	0.088	0.189	0.132
PNP(3)	0.186	0.265	0.166	0.0*	0.370	0.144	0.033	0.344	0.150
	0.045	0.220	0.323	0.0*	0.313	0.258	0.008	0.269	0.276
	0.209	0.096	0.034	0.046	0.269	0.058	0.073	0.223	0.053

Table 4. Ternary adsorption equilibrium data of phenols on SP206 at 20°C

*: trace concentrations

batch or fixed-bed adsorbers and subsequently makes the adsorption calculation much easier [5, 19].

2. Estimation of Film Mass Transfer Coefficients

In most of the adsorption processes where highly porous sorbents are used, the solution-particle mass transfer resistance may be neglected when comparing it with that of intraparticle diffusion. However, it is important to estimate the order of magnitude. There are some correlations for estimating the film mass transfer coefficient, k_f , in a batch system [22, 23]. In this work, we estimated k_f from the initial concentration history in which the diffusional resistance does not significantly prevail. The initial concentration history may be approximated by Eq. (25) when the adsorption time is less than 300 seconds [23].

$$\ln(C/C_0) = -k_f A t/V \tag{25}$$

where V is the volume of solution and A is the effective external surface area of sorbent particles which is given by

$$A = 3W/\rho_{p}R \tag{26}$$

W is the weight of sorbent particles loaded and ρ_p is the particle density. Fig. 2 represents a typical plot to estimate k_f from the initial concentration history of phenol with $C_0=0.911$ mol/m³ and W/V=0.846 kg/m³. The value of k_f obtained from Fig. 2 is 3.9×10^{-5} m/sec. Since the phenols used have a similar kinetic diameter, the values of k_f may be assumed to be constant [21]. In this work, $k_f=4 \times 10^{-5}$ m/sec was used in predicting all concentration histories regardless of the adsorbate and its concentration.

3. Effective Diffusion Coefficients

Since intraparticle diffusion is usually the rate-controlling step in most adsorption processes, the determination of diffusion coefficients is an important task. There are various methods for determining the diffusion coefficient in the literatures [4, 16]. The most general method for this is to compare the experimental concentration history and the predicted one by



Fig. 2. Determination of k_f from an initial concentration history.

using the specified diffusion model. Since the diffusion coefficient, which is obtained by this method, reflects all kinds of mass transfer resistances inside a particle, it has been called the effective diffusion coefficient. In this work, two diffusion models, the pore diffusion model and the surface diffusion model, were employed and the effective diffusion coefficients obtained are listed in Table 5. The values of D_p is in the range of $0.77 - 2.79 \times 10^{-9}$ m²/sec and those of D_s, $2 - 7.5 \times 10^{-12}$. It should be noted that the effective pore diffusion coefficients of phenols are similar to and higher than the molecular diffusion coefficients, $D_m \cong 0.9 \times 10^{-9} \text{ m}^2$ /sec, in water [21]. From the point of physics, the above is hard to conceive since the transport rate inside particles cannot exceed that in free-liquid solutions. This implies that the intraparticle diffusion may be controlled not only by pore diffusion but by other mechanisms. However, pore and surface diffusion mod-

	C ₀	W/V	Q*	$D_s \times 10^{12}$	$D_p \times 10^9$
Species	mol/m ³	kg/m ³	mol/kg	m ² /sec	m²/sec
Phenol	0.940	0.950	0.273	6.83	1.39
	1.440	1.170	0.339	4.81	0.77
	2.063	1.148	0.404	7.48	0.96
	1.190	0.960	0.314	4.77	0.88
PCP	1.168	1.298	0.543	2.84	1.31
	2.709	1.855	0.662	5.44	0.85
	1.461	0.726	0.631	3.28	0.93
	1.052	0.993	0.554	3.77	2.00
PNP	0.976	0.868	0.499	1.96	0.91
	0.507	1.105	0.303	3.00	2.79
	0.887	0.950	0.487	2.84	1.54
	2.051	1.400	0.653	3.73	0.91

Table 5. Effective diffusion coefficients determined



Fig. 3. Comparison of pore and surface diffusion models.

els predict an almost identical concentration history as shown in Fig. 3. Accordingly, it is not a critical matter which diffusion model one choose in predicting only the concentration history. In this work, we employed the surface diffusion model. Fig. 4 shows the effect of D_s on the concentration history of PCP at $C_0=1$ mol/m³ and W/V=1 kg/m³.

4. Multicomponent Concentration Histories

In order to verify the applicability of the model, two- and three-species concentration histories were predicted by the proposed adsorption model above. Fig. 5 shows the effective diffusion coefficients obtained in terms of the equilibrium amount of adsorption, Q^* . Although the surface diffusion coefficient has been known to be concentration dependent [4, 21], the result shown in Fig. 8 does not imply any specific rela-



Fig. 4. Effect of D, on the concentration history of PCP at $C_0 = 1.0 \text{ mol/m}^3$ and $W/V = 1 \text{ kg/m}^3$ with $k_f = 4 \times 10^{-5} \text{ m/sec}$.



Fig. 5. Variation of D_s of phenols within SP206.

tionship between D_s and Q^* . Therefore, the arithmetic average values of D_s were used in predicting multicomponent concentration histories as follows:

$$\begin{split} D_{s, phenol} &= 6.0 \times 10^{-12} \text{ m}^2/\text{sec} \\ D_{s, PCP} &= 3.8 \times 10^{-12} \text{ m}^2/\text{sec} \\ D_{s, PNP} &= 2.9 \times 10^{-12} \text{ m}^2/\text{sec} \end{split}$$

Figs. 6-8 show two-species concentration histories and the solid lines represent the prediction by the adsorption model which is incorporated with the IAST. In Predicted

Phenol

PCP





Fig. 7. Binary batch adsorption of phenol(1) and PNP(2) (C_{10} =0.497, C_{20} =0.465 mol/m³ and W/V=0.926 kg/m³).

these calculations, the isotherm parameters of the single-species listed in Table 2 and the effective diffusion coefficients given above are used without any adjustment. A three-species concentration history is shown in Fig. 9. One can see that the adsorption model used here simulates satisfactorily the adsorption behavior of phenolic mixtures on SP206.

5. Regeneration of Spent SP206

One of objectives of this study is to investigate the possibility of using polymeric sorbents as an alterna-



Fig. 8. Binary batch adsorption of PCP(1) and PNP(2) (C_{10} =0.685, C_{20} =0.461 mol/m³ and W/V=0.927 kg/m³).

Table 6. Regeneration results of SP206 loaded with phenols

	$W \times 10^3$	Total moles	Moles	Regeneration
Species	kg	adsorbed(WQ)	leached	efficiency(%)
Phenol	2.233	0.310	0.304	98.1
PCP	1.840	0.505	0.459	90.9
PNP	2.281	0.516	0.453	87.8

All experiments were conducted in a 2L batch adsorber and 0.05 N NaOH solution was used as a regenerant.

tive to activated carbon which cannot be easily regenerated. The regeneration of spent sorbent particles was also investigated by leaching with 0.05 N sodium hydroxide solution. A typical result is shown in Fig. 10. Phenol adsorbed on a polymeric sorbent has been known to be desorbed by the following reaction [7].

 $C_6H_5OH + OH^- = C_6H_5O^- + H_2O$

It has been also known that an increase in pH enhances the formation of the phenate species which is not retained by the sorbent. The concentration means the total amount of phenol plus phenate in the solution but at the concentration of NaOH used the phenate species is dominant [7]. All the regeneration results are summarized in Table 6. As shown in Fig. 10, most phenols retained by SP206 can be desorbed very quickly within a few minutes. At present, we do not know why the desorption occurs so fast, a possible reason is that polymeric sorbent particles shrink in the alkaline solution [24]. One more feature of regeneration is that PCP and PNP desorb slowly compared

1.0

0.8

0.6

0.4

0.2

C,/C,0



Fig. 9. Ternary batch adsorption of phenol(1), PCP(2) and PNP(3)(C_{10} =0.202, C_{20} =0.598, C_{30} =0.227 mol /m³ and W/V=1.014 kg/m³).



Fig. 10. Regeneration of SP206 loaded with phenol.

to phenol. This can be explained by the adsorbate-sorbent interaction, that is, the surface of sorbent may interact with -Cl and $-NO_2$ of phenols. Anyway, the result of regeneration is quite positive and the cyclic operation for phenol removal by polymeric sorbents is likely to be possible. However, it is highly recommended that more work on this subject should be conducted in the near future.

CONCLUDING REMARKS

As a removal method for phenols dissolved in aqueous solutions, batch adsorption experiments were

carried out using a nonfunctional polymeric sorbent, SP206. Single-species isotherms were represented by the Langmuir equation and multicomponent equilibrium data were predicted by the ideal adsorbed solution theory based on the Langmuir equation as singlespecies isotherms. The IAST predicted satisfactorily multicomponent adsorption equilibrium data up to a three-species mixture. Intraparticle diffusion was assumed to be represented by the pore and the surface diffusion mechanisms and the effective diffusion coefficients were determined from experimental concentration histories. The adsorption model which employs the surface diffusion mechanism incorporated with the IAST successfully simulates the adsorption behavior of phenols on SP206 up to a three-species mixture. It was also confirmed that phenols retained by SP206 were desorbed very quickly by a 0.05 N sodium hydroxide solution within a few minutes and the extent of regeneration was over 87% even in the finite batch operation.

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NOMENCLATURE

Α	: surface area of sorbent particles
b	: Langmuir constant
С	: concentration in the liquid phase [mol/m ³]
D_m	: molecular diffusivity [m²/sec]
D_{p}	: effective pore diffusion coefficient [m ² /sec]
D_s	: effective surface diffusion coefficient $[m^2/s]$
Е	: mean percent deviation defined in Eq. (24)
\mathbf{k}_{f}	: film mass transfer coefficient [m/s]
k	: Freundlich coefficients in Eq. (22)
m	: number of species
Ν	: number of data points
n	: exponent in Eqs. (22) and (23)
Q	: amount adsorbed [mol/kg]
\mathbf{Q}_m	\vdots amount adsorbed for monolayer formation
	[mol/kg]
R	; gas constant and radius of particle [m]
r	: radial distance [m]
Т	: temperature
t	time [s or hr]
V	: volume of solution [m ³]
W	; weight of sorbents [kg]

- X : dimensionless radial distance (=r/R)
- Z : mole fraction in the adsorbed phase

Greek Letters

- α : dimensionless group defined in Eq. (11)
- γ_i : dimensionless group defined in Eq. (20)
- ε_{p} : particle porosity
- λ_r : dimensionless group defined in Eq. (21)
- ξ_i : normalized concentration (= C_i/C_{i0})
- ρ_p : apparent particle density, kg/m³
- π : spreading pressure
- Π : modified spreading pressure defined in Eq. (7)
- τ : dimensionless time (= $D_{s1}t/R^2$)
- Ψ_i : dimensionless amount adsorbed (= Q_i/Q_{i0})

Abbreviations

exp	: measured value
pre	: calculated value
IAST	: ideal adsorbed solution theory
PCP	: p-chlorophenol
PNP	: p-nitrophenol

Subscripts and superscripts

- 0 : initial value
- i, j : subscripts for species
- o : single-species state
- p : particle
- s : surface
- T : total
- − ∶average
- * : equilibrium

REFERENCES

- 1. Jain, J. S. and Snoeyink, V. L.: J. WPCF, 45, 2463 (1973).
- Keith, L. H. and Telliard, W.: Environ. Sci. Tech., 13, 416 (1979).
- Fritz, W., Merk, W. and Schlünder, E. U.: Chem. Eng. Sci., 36, 731 (1981).

- Moon, H. and Lee, W. K.: J. Colloid Interface Sci., 96, 162 (1983).
- Moon, H. and Lee, W. K.: Chem. Eng. Sci., 41, 1995 (1986).
- 6. Costa, C. and Rodrigues, A.: AIChE J., 31, 1645 (1985).
- 7. Costa, C. and Rodrigues, A.: AIChE J., 31, 1655 (1985).
- Hasanain, M. A. and Hines, A. L.: Ind. Eng. Chem. Process Des. Dev., 20, 621 (1981).
- 9. Garcia, A. A. and King, C. J.: Ind. Eng. Chem. Res., 28, 204 (1989).
- 10. Rixey, W.G. and King, C.J.: *AIChE J.*, **35**, 69 (1989).
- 11. Huang, T. and Cho, L.: J. Chem. Eng. Japan, 21, 498 (1988).
- 12. Saunders, M. S., Vierow, J. B. and Carta, G.: *AI-ChE J.*, **35**, 53 (1989).
- Reich, R., Ziegler, W. T. and Rogers, K. A.: Ind. Eng. Chem. Proc. Des. Dev., 19, 336 (1980).
- 14. Myers, A. L. and Prausnitz, J. M.: *AIChE J.*, 11, 121 (1965).
- Suwanayuen, S. and Danner, R. P.: AIChE J., 26, 68 (1980).
- Ditl, P., Coughlin, R. W. and Jere, E. H.: J. Colloid Interface Sci., 63, 410 (1978).
- 17. Moon, H. and Tien, C.: Chem. Eng. Sci., 43, 2967 (1988).
- Ruthven, D. M.: "Principles of Adsorption and Adsorption Processes", John Wiley and Sons, New York, 1984.
- Moon, H. and Tien, C.: Chem. Eng. Sci., 43, 1269 (1988).
- Moon, H. and Tien, C.: Ind. Eng. Chem. Res., 26, 2042 (1987).
- 21. Moon, H., Park, H. C. and Lee, W. K.: Korean J. Chem. Eng., 7, 250 (1990).
- Teshima, H. and Ohashi, Y.: J. Chem. Eng. Japan, 10, 70 (1977).
- Misic, D. M., Sudo, Y., Suzuki, M. and Kawazoe, K.: J. Chem. Eng. Japan, 15, 67 (1982).
- 24. Tsou, H. S. and Graham, E. E.: AIChE J., 31, 1959 (1985).
- 25. Sips, R.: J. Chem. Phys., 16, 490 (1948).