

ADSORPTION OF PHENOLS ONTO MACRORETICULAR RESIN PARTICLES

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Abstract – Experimental uptake curves were collected by a shallow bed technique at 298.2 K. Adsorbent particles employed were macroreticular (MR) resins and adsorbates were phenol and its derivatives. From the uptake curves and equilibrium data obtained by the so-called, batch bottle technique, equilibrium and kinetic parameters were determined and the effects of functional groups within both adsorbate molecules and adsorbent particles on those parameters are discussed. From the results, it became clear that physical and chemical properties, surface area of adsorbent functional group, and solubility of adsorbates affected adsorption equilibria. Also, nitro-functional groups seemed to hinder adsorption equilibria and kinetics. Results can be explained by the resonance effects of functional groups.

Key words: Adsorption, Interparticle Mass Transfer, Phenols Removal, Macroreticular Resin Particles, Shallow Bed Technique

INTRODUCTION

Liquid-phase adsorption has been used to remove impurities dissolved in water and also has been applied to the separation of bioproducts, i.e. physiologically active materials and enzymes.

To design adsorbents optimized for removal of given adsorbate species, it is necessary to have interaction on the effects of adsorbate structure and/or surface structure of the adsorbents. Of course, it is well known that both the isotherm parameters and intraparticle diffusivities are dependent on the adsorption system and temperature, and also that the amount adsorbed is strongly affected by the fluid concentration. For liquid-phase adsorption, interaction forces take place between adsorbate-adsorbent, adsorbate-solvent, and solvent-adsorbent, however, only the affinity of adsorbate molecules for the adsorbent surface is usually considered.

In the case where the adsorbate and solvent molecules and adsorbent surface have particular functional groups, not only London dispersion but also classical electrostatic forces need to be considered [Weber, 1985]. The effects of functional groups can be evaluated by experimental data obtained from adsorption systems containing a series of compounds with various functional groups.

Synthetic resins are attractive because their structures are clearly defined and controllable. Since the internal networks of styrene-divinylbenzene copolymer resins are generally well known, they have been studied by investigators [Komiya and Smith, 1974; Furuya et al., 1989].

In this paper, macroreticular (MR) resin particles were synthesized and their physical and chemical properties were slight-

ly different from each other. For the solids-phenols systems, equilibrium and kinetic parameters were experimentally determined and the effects of functional groups within both the adsorbate molecules and the MR resin particles on those parameters were discussed.

EXPERIMENTALS

The resin particles used have similar chemical structures of styrene-divinylbenzene but different physical properties.

The resin particles were prepared by successive washing with iso-propanol, methanol, and distilled water.

They were then stored in a sealed glass bottle at 278 K. Some of their physical properties are listed in Table 1. Phenols of reagent grade were employed as adsorbates.

Their structure and properties are listed in Table 2.

Uptake data were collected by the following method:

(1) The resin particles were packed in a glass column. Both ends of the shallow resin bed were held by a Teflon screen

Table 1. Physical properties of MR resins

Resin	Surface area [m ² /g]	Pore diameter [Å]	Resin	Surface area [m ² /g]	Pore diameter [Å]
A	300	85	J	680	106
B	630	47	K	700	54
C	800	45	L	780	74
E	580	29	M	920	72
F	590	29	N	910	84
G	590	38	O	810	34
H	590	45	Z	810	86
I	640	76			

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Table 2. Structure and properties of adsorbates

Solubility			Solubility		
Adsorbate	in water	Structure	Adsorbate	in water	Structure
	[mol/l]			[mol/l]	
phenol (PH)	0.638		o-nitrophenol (ONP)	0.0189	
o-chlorophenol (OCP)	0.204		m-nitrophenol (MNP)	0.141	
p-chlorophenol (PCP)	0.187		p-nitrophenol (PNP)	0.103	
di-chlorophenol (DCP)	0.0276		di-nitrophenol (DNP)	0.00265	
tri-chlorophenol (TCP)	0.00435		tri-nitrophenol (TNP)	0.0531	

with dimensions of 8×10^{-3} m diameter and 1×10^{-2} m height.

(2) The solution of known concentration was fed upward through the column for a predetermined time interval.

(3) The solution held in the bed void spacings was removed with a small volume of distilled water. Then, the solute within particles was extracted to determine the amount adsorbed. The concentration of the extracts was determined by ultra-violet absorbance.

(4) This procedure was repeated for different contact times, in order to determine the relationship between the degree of saturation and contact time (uptake curve). The details of the adsorption equipment and the procedure are described elsewhere [Noll et al., 1984].

Equilibrium data were obtained from the saturated amount adsorbed as demonstrated by a constant uptake value after an adequate solid-liquid contact time. The adsorption isotherm was determined as the amounts adsorbed were plotted against equilibrium liquid concentrations.

Apparent intraparticle diffusivities were determined as experimental uptake data were compared with theoretical curves.

Because a large linear flow rate of the solution (0.13 - 0.14 ms^{-1}) and a small bed length were employed, the inlet and outlet concentration were essentially the same and the effect of the fluid-to-solid film diffusion resistance on the apparent diffusivities could be eliminated. The details are shown in the previous paper [Furuya et al., 1989].

FUNDAMENTAL EQUATIONS

Under the experimental conditions of isothermal operation and negligible fluid film resistance, the rate equation within the spherical adsorbent particles and initial and boundary conditions can be expressed as follows provided the fluid concentration difference is the main driving force for intraparticle mass transfer.

$$\rho_s \frac{\partial q}{\partial t} = \frac{1}{r^2} \left\{ D_e \frac{1}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \right\} \quad (1)$$

$$c=0 \quad \text{at } t=0 \quad (2)$$

$$\partial c / \partial r = 0 \quad \text{at } r=0 \quad (3)$$

$$c=c_e \quad \text{at } r=r_p \quad (4)$$

In the case of a non-linear isotherm, Eq. (1) with Eqs. (2), (3) and (4) can not be solved analytically, but can be solved numerically by use of orthogonal collocation method [Finlayson, 1980] with the equilibrium relationship. Prior to solving the equations, dimensionless variables are usually introduced as follows:

$$C = c/c_e \quad (5)$$

$$Q = q/q_e \quad (6)$$

$$T = D_e' t c_e / q_e \rho_s r_p^2 \quad (7)$$

$$R = r/r_p \quad (8)$$

$$\frac{\partial Q}{\partial T} = \frac{1}{R^2} \frac{1}{\partial R} \left(R^2 \frac{\partial C}{\partial R} \right) \quad (9)$$

$$C=0 \quad \text{at } T=0 \quad (10)$$

$$\partial C / \partial R = 0 \quad \text{at } R=0 \quad (11)$$

$$C=1 \quad \text{at } R=1 \quad (12)$$

With the aid of the orthogonal collocation method one can obtain simultaneous ordinary differential equations from the partial Eq. (9) with Eq. (11) as follows:

$$\frac{dQ_i}{dT} = \sum_{j=1}^{NS} B_{ij} C_j \quad (i=1,2,3, \dots, NS) \quad (13)$$

where B_{ij} denotes orthogonal coefficients for the second-order differential, which is automatically determined by choosing the collocation number, NS. Subscripts i and j show the collection points, in this case, so $C_{NS} = C_e$ from Eq. (12). Measurable value of the amount adsorbed, q_e , can be obtained by use of the orthogonal weighting coefficient, W . This value is automatically determined when the number of the collocation points are chosen. Therefore, the value of Q_i can be determined from evaluated values of Q_e . In this paper, seven collocation points and a Freundlich-type equilibrium relationship were employed.

$$\frac{q_i}{q_e} = Q_i = \sum_{j=1}^{NS} W_j Q_j \quad (14)$$

RESULTS AND DISCUSSIONS

The equilibrium relationship could be expressed by Freundlich-type equation and the experimental amounts adsorbed onto each resin were dependent on the adsorbates as shown in Fig. 1. The equilibrium parameters are summarized in Table 3. To reduce the effects of adsorbate solubility, a new parameter, c/c_e ,

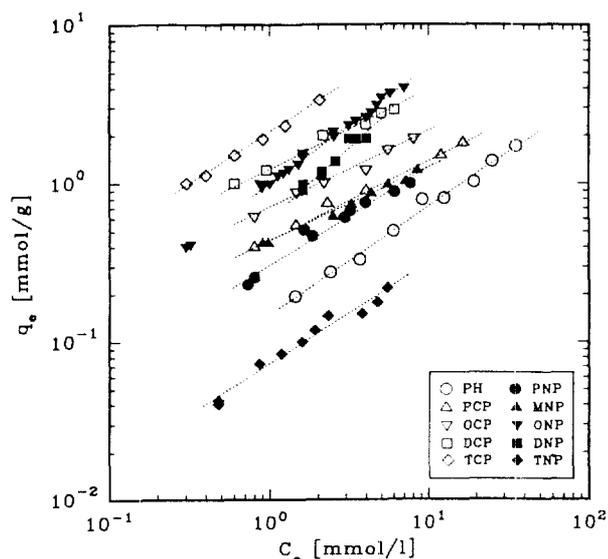


Fig. 1. Adsorption isotherms for resin-B-phenols systems.

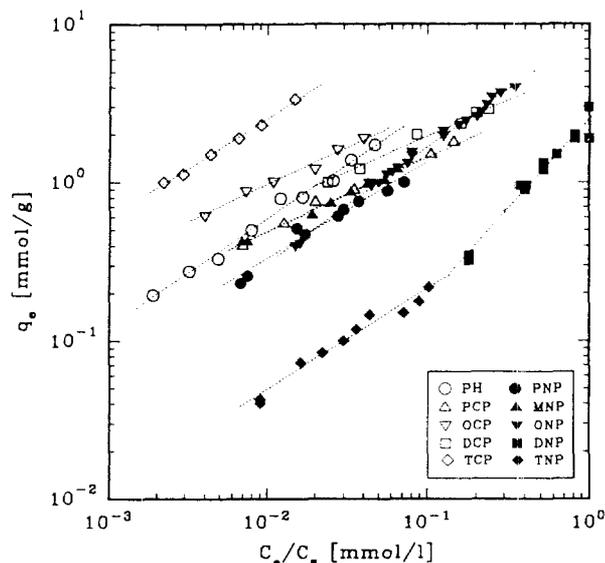


Fig. 2. Influence of solubility to adsorption equilibrium for resin-B-phenols systems.

was introduced instead of c , where c denotes equilibrium fluid concentration and c_s is saturated concentration in Fig. 2.

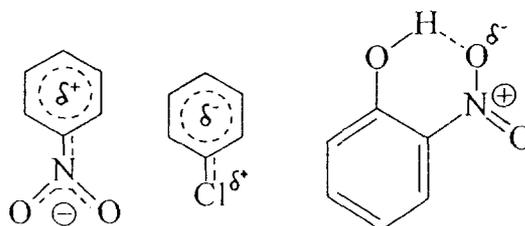
In this figure, however, tri-chlorophenol shows larger amounts adsorbed and tri- and di-nitrophenols indicate lower isotherms.

As well known, benzene rings have π -electrons and the ring exhibits inductive and resonance effects, provided the ring has functional group(s). All of the OH-, NO₂- and Cl-groups cause the negative inductive effect. Both the OH- and Cl-groups have the positive resonance effect at the ortho- and para-positions, while the NO₂-group shows the negative resonance effect at the two positions [Hansch and Leo, 1979].

Therefore, the benzene ring of chlorophenol has more negative charge than benzene, while the benzene ring of nitrophenols has more positive charge than benzene as shown in Scheme I. It is consistent with the nitrophenol being less adsorptive due to hydrogen bond between solvent and nitrogroup

Table 3. Equilibrium parameters of Freundlich equation, $q = KC^{1/n}$, for resin-B systems

Adsorbate	n [-]	k [mmol/g]	Adsorbate	n [-]	k [mmol/g]
PH	1.74	1.33	PNP	1.96	1.44
PCP	2.33	7.78	MNP	1.45	3.96
OCP	2.21	7.86	ONP	1.82	5.96
DCP	2.68	17.5	DNP	1.27	1.93
TCP	1.60	7.39	TNP	1.44	0.39



Scheme I.

Scheme II.

than chlorophenol. On the other hand, adsorbate with nitro-group at ortho-position can make chelate with OH- and nitro-group in the molecule and it is more adsorptive than adsorbate with nitrogroup at meta- or para- position (Scheme II).

Because only water is employed as a solvent in this study, interactions between solvents and adsorbents can not be evaluated.

As a result based on adsorption equilibria, the main factors causing the interactions were conjectured to be electron affinity and solubility.

To study the effects of surface area of the adsorbents, experiments were performed with p-chlorophenol in various resin systems. As shown in Fig. 3, isotherms were dependent on the adsorbent properties.

By normalizing the data (amount adsorbed/surface area), however, all data could be reduced to a single line as shown in Fig. 4. For the phenol-resin systems, then, the adsorption equilibria could be roughly estimated by use of two parameters (1) amount adsorbed/surface area and (2) fluid concentration /saturated fluid concentration.

The values of the apparent intraparticle diffusivities are also thought to be affected by the adsorption and desorption rate of adsorbate molecules at the edge of the microparticles and/or the surface diffusion, since parallel diffusion due to surface and pore diffusion takes place within MR resin particles. By use of the adsorbates listed in Table 2, intraparticle diffusivities onto resin-B were determined 298.2 K by comparisons of experimental uptake curves with theoretical ones for the corresponding values of the Freundlich exponent, $1/n$. The effective intraparticle diffusivity, D_e' , was obtained from the dimensional contact time, t , which corresponds to the dimensionless time, $T = D_e' t c_s / q_p r_p^2 = 1$, as shown elsewhere [Suzuki and Kawazoe, 1975].

As shown in Fig. 5, it becomes clear that the values of D_e'/D_{AB} are independent of the amount adsorbed, where D_{AB} denotes the molecular diffusivity estimated from the equation proposed by Wilke and Chang [Reid et al., 1989]. However, it is

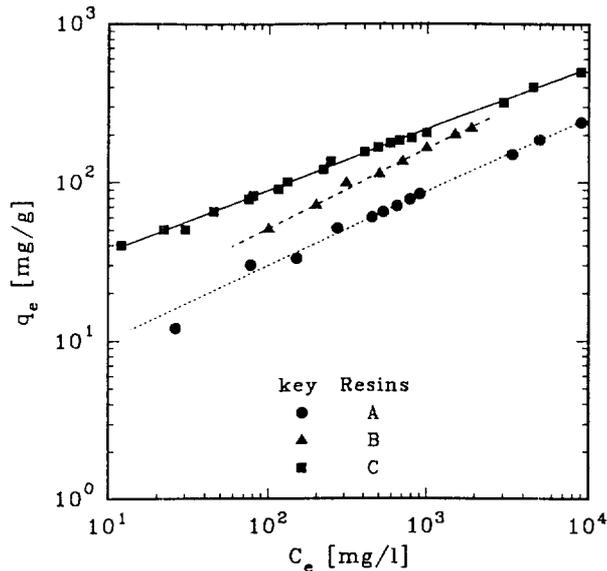


Fig. 3. Dependency of adsorbents on isotherms for p-nitrophenol systems.

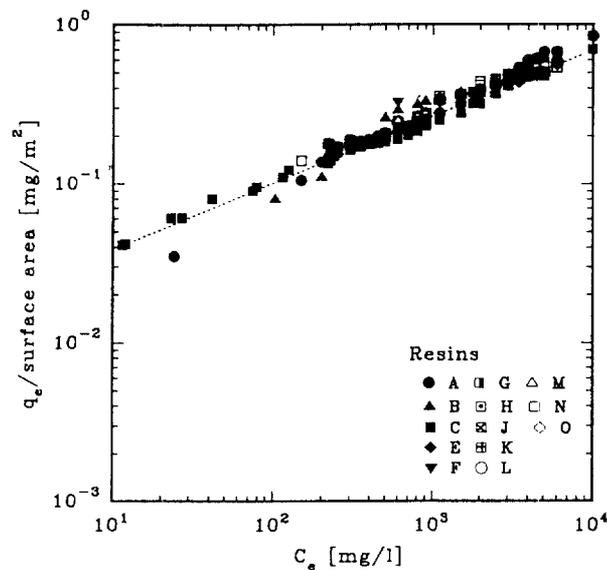


Fig. 4. Reduced isotherm for resin-p-nitrophenol systems.

clear that the values of D_r/D_{AB} increased with Cl- substituent, while the values decreased with increasing NO_2 -groups, and both Cl- and NO_2 -groups at the ortho position accelerated the intraparticle diffusion. The results are similar to those with respect to amount adsorbed.

Since ortho-substituted phenols can be made by intramolecular rearrangement, the apparent diffusivities seem to be enlarged by the chelate effect. On the other hands, Snoeyink and Weber reported that surface adsorption sites changed to another type when the sites were saturated by p-nitrophenol molecules [Snoeyink and Weber, 1965].

Because surface diffusion within MR resin particles contributes overall intraparticle mass transfer as mentioned above, the hindrance and acceleration seem to be the reason for the Cl- and NO_2 -groups dependency on apparent intraparticle diffusivi-

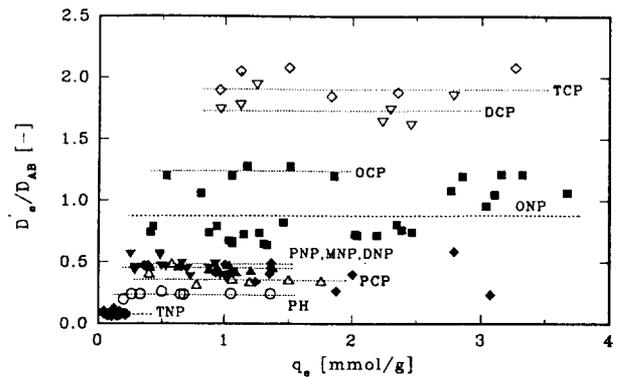


Fig. 5. Relationship of D_r/D_{AB} with q_e for resin-B-phenols systems.

ties.

However, more studies are needed, because the values of D_r/D_{AB} should be a function of amount adsorbed when the contribution due to surface diffusion is relatively larger.

CONCLUSION

Uptake curves of phenols onto macro-reticular (MR) resin particles were collected by a shallow bed technique at 298.2 K. From the curves and equilibrium experimental data obtained by the batch bottle technique, equilibrium and kinetic parameters were determined and effects of functional groups of both the adsorbate molecules and the adsorbent particles on those parameters were evaluated. The results showed physical and chemical properties, surface area of the adsorbents, functional group on the solid surface, and solubility of the adsorbates all affected adsorption equilibria.

Also, nitro-functional groups seems to hinder adsorption equilibria and kinetics.

This result could be explained by the resonance effects of functional groups. Existence of functional groups at ortho position enhanced adsorption capacity and accelerated intraparticle mass transfer.

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NOMENCLATURE

- C : dimensionless fluid concentration c/c_s , [-]
- c : concentration in bulk phase [kg m^{-3}]
- C_e : fluid concentration through shallow bed [kg m^{-3}]
- C_s : saturated concentration of adsorbate dissolved in solvent [kg m^{-3}]

- B : orthogonal coefficient for second-order differential [-]
 D_{AB} : molecular diffusivity [$m^2 s^{-1}$]
 D_e' : effective intraparticle diffusivity based on difference of liquid concentration [$m^2 s^{-1}$]
 Q : dimensionless amount adsorbed q/q_e [-]
 q : amount adsorbed [$kg kg^{-1}$]
 q_e : amount adsorbed in equilibrium with c_e [$kg kg^{-1}$]
 q_t : amount adsorbed at time t [$kg kg^{-1}$]
 R : dimensionless radial length r/r_p [-]
 r : radial length within adsorbent particles [m]
 r_p : mean particle radius [m]
 T : dimensionless time $D_e' t c_e / q_e \rho_s r_p^2$ [-]
 t : contact time [s]
 W : orthogonal weighting coefficient [-]
 ρ_s : solid density [$kg m^{-3}$]

REFERENCES

- Finlayson, B. A. and Alan, B., "Nonlinear Analysis in Chemical Engineering", McGraw-Hill Inc., 1980.
- Furuya, E., Takeuchi, Y. and Noll, K. E., "Interparticle Diffusion of Phenols with Bidispersed Macroreticular Resin Particles", *J. Chem. Eng. Japan*, **22**, 670 (1989).
- Hansch, C. and Leo, A., "Substituent Constants for Correlation Analysis in Chemistry and Biology", A Wiley-Interscience Publication, 1979.
- Noll, K. E., Hass, C. N., Menez, J. P., Aquwa, A. A., Sakoh, M., Belalia, A. and Bartholomew, P. S., "Direct Differential Reactor Studies on Adsorption from Concentrated Liquid and Gaseous Solution", *Fundamentals of Adsorption* (Eds. A. L. Myers and G. Belfort), Engineering Foundation, 411 (1984).
- Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids", McGraw-Hill Book Company, 1989.
- Snoeyink, V. L., Weber Jr., W. J. and Harry, B. Mark Jr., "Sorption of Phenol and Nitrophenol by Active Carbon", *Env. Sci. Tech.*, **3**, 918 (1969).
- Suzuki, M. and Kawazoe, K., "Effective Surface Diffusion Coefficients of Volatile Organics on Activated Carbon during Adsorption from Aqueous Solution", *J. Chem. Eng. Japan*, **8**, 379 (1975).
- Weber W. J., "Modeling of Adsorption and Mass Transport Processes in Fixed-Bed Adsorbers", *Adsorption Technology* (Ed. F. L. Slejiko), Marcel Dekker, Inc., 1985.