Korean J. Chem. Eng., **18**(5), 755-760 (2001)

Effect of pH on Adsorption of 2,4-Dinitrophenol onto an Activated Carbon

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(*Received 13 March 2001 • accepted 5 June 2001*)

Abstract−The adsorption characteristics of 2,4-dinitrophenol from water onto a granular activated carbon, F-400, were studied at pH 4.3, 7 and 10. Adsorption equilibria of 2,4-dinitrophenol on GAC could be represented by Sips equation. Equilibrium capacity increased with decreasing pH. The differences in the rates of adsorption are primarily attributable to the differences in the equilibrium at the various pHs. Intraparticle diffusion was explained by surface diffusion mechanism. An adsorption model based on the linear driving force approximation (LDFA) was used for simulating the adsorption behavior of 2,4-dinitrophenol in a fixed bed adsorber.

Key words: Adsorption, 2,4-Dinitrophenol, Activated Carbon, Fixed Bed, pH

INTRODUCTION

Agrochemical products are vitally important in agriculture to protect fiber corps and food from weeds, insect pests and diseases. To feed the growing world population today, large amounts of agrochemical products have to be used to produce enough food; thus the removal and disposal of pesticides and other chemicals is still one of the important problems since the environment is exposed to the harmful effects of these chemicals and pesticides [Mehmit et al., 2000]. Increasing concerns over surface water pollution by pesticides has been voiced recently. Major sources contributing to this pollution include surface run-off from agricultural land, direct application, domestic usage, industrial waste and large scale of weed control operations on industrial sites, railways and road verges [Kamel and Tahar, 1998]. 2,4-dinitrophenol is used in making dyes, wood preservatives, explosives, insect control substances, and photographic developer, and released into the air, water and soil. It may also be released into the environment from landfill leaks and accidental spills. The ingestion of 2,4-dinitrophenols causes harmful effects on human beings. Increased basal metabolic rate and sweating, feeling of warmth, weight loss, and increased breathing rate and body temperature have been observed from those who have swallowed as little as 1 mg/kg/day for short or long periods.

Adsorption is one of the key processes that protect the environment from organic pollutants [Teng and Hsieh, 1998]. Activated carbon possesses a large capacity for adsorption of organic matters due to its large surface area. Pore structure, in terms of surface area and pore volume, is an important property of activated carbon products, which determines the performance of the carbon during adsorption. In this work, the effect of pH on the equilibrium adsorption and adsorption dynamics is studied in a fixed bed adsorber to remove 2,4-dinitrophenol from the aqueous solution.

THEORETICAL APPROACH

It is assumed that adsorption occurs instantaneously and equilibrium is established between adsorbates in the fluid and on the surface. The driving force is the concentration gradient of the adsorbate between liquid bulk and pore walls. The adsorbed species then diffuses into the pores in the adsorbed state. Provided that surface diffusion is dominant, the following equation can be expressed to describe the rate of adsorption for a spherical particle as

$$\frac{\partial q}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_s\frac{\partial q}{\partial r}\right) \tag{1}$$

with the initial and boundary conditions

$$\frac{\partial q}{\partial t}=0 \qquad \text{at } r=0 \tag{2}$$

$$q=0 \qquad \text{at } t=0 \tag{3}$$

$$k_f(C-C_s)=D_s\rho_p\frac{\partial q}{\partial r_p} \qquad \text{at } r=R_p \tag{4}$$

The mass balance equation in the column and the relevant initial and boundary conditions are

$$-D_L\frac{\partial^2 C_i}{\partial Z^2}+\frac{\partial vC_i}{\partial Z}+\frac{\partial C_i}{\partial t}+\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t}=0 \tag{5}$$

$$C_i(z, t=0)=0 \tag{6}$$

$$D_L\left.\frac{\partial C_i}{\partial z}\right|_{z=0}=-v(C_i|_{z=0}-C_i|_{z=0}) \tag{7}$$

$$\left.\frac{\partial C_i}{\partial z}\right|_{z=L}=0 \tag{8}$$

EXPERIMENTAL

The concentration of 2,4-dinitrophenol was determined by using a spectrophotometer [Shimadzu 1601]. The wavelength, corresponding to a maximum absorbance of 2,4-dinitrophenol, was found to be 350 nm with an accuracy of ±0.3 nm. HCl and NaOH solutions

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‡Presented at the Int'l Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

Table 1. Physical properties of an activated carbon

	Activated carbon
Supplier	Calgon (F-400)
Particle diameter (mm)	0.37-0.54
BET surface area (m^2/g)	1050
Micropore distribution (1 nm) (%)	45.16
Porosity	0.48

were used to adjust solution pH. The adsorbent used in this study was an activated carbon, Filtrasorb-400, manufactured by Calgon Co. (USA). The particle size of the activated carbon was 0.37-0.54 mm in diameter, and the properties of this sorbent measured are listed in Table 1. All sorbent particles were dried in vacuum oven to remove impurities prior to use. Equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of 2,4-dinitrophenol, 0.54 mol/m^3. The solution was kept in the shaking batch at 25 °C for one week after a given amount of sorbent was introduced. Batch adsorption experiments were conducted in a Carberry-type batch adsorber. All the experiments were carried out at approximately 400 rpm, since the film mass transfer coefficient, k_f, is practically constant at this condition. Single-specie adsorption was carried out in a fixed bed adsorber that was made of a glass column of 1.54 cm diameter and 30 cm length. The column was lined with a water jacket, and all experiments were performed at 25 °C. The flow rate was regulated with a flow meter. To enhance uniform distribution of the solution radially, small glass beads were packed in the top and bottom ends of the column. Experimental conditions used are listed in Table 2. The samples were withdrawn from the effluent line and analyzed with a UV spectrophotometer.

Table 2. Experimental conditions for a fixed bed adsorption

Variables	Range	Unit
Bed length	0.06-0.14	m
Flow rate	0.66×10^{-2}-1.31×10^{-2}	m/s
Bed porosity	0.271	-
Packing density	741.3	kg/m^3
Bath temperature	298	K

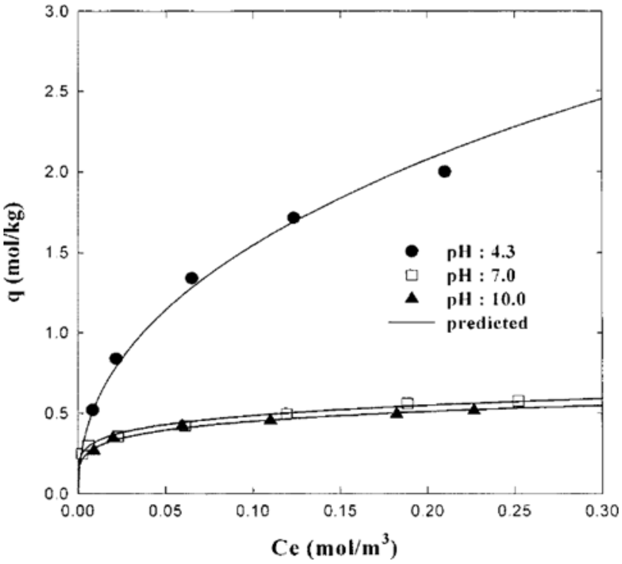

Fig. 1. Single-species isotherms of 2,4-dinitrophenol on GAC for various pH at 25 °C.

RESULT AND DISCUSSION

1. Adsorption Equilibrium

Since the adsorption of this study is mainly driven by physical force between the adsorbate and the adsorbent, the adsorption capacity depends on the structure of the adsorbate, temperature and pH of the solution. Figs. 1 and 2 show the adsorption capacity of 2,4-dinitrophenol in terms of pH and temperature of the solution. The adsorption amounts decreased with increasing temperature and pH of the solution. As shown in Figs. 1 and 2, pH effect was greater than that of temperature on the adsorption capacity of 2,4-dinitrophenol on activated carbon. This suggests that effective separation could be achieved by the adjustment of pH rather than temperature. Single-specie isotherm data were correlated by the well-known Lang-

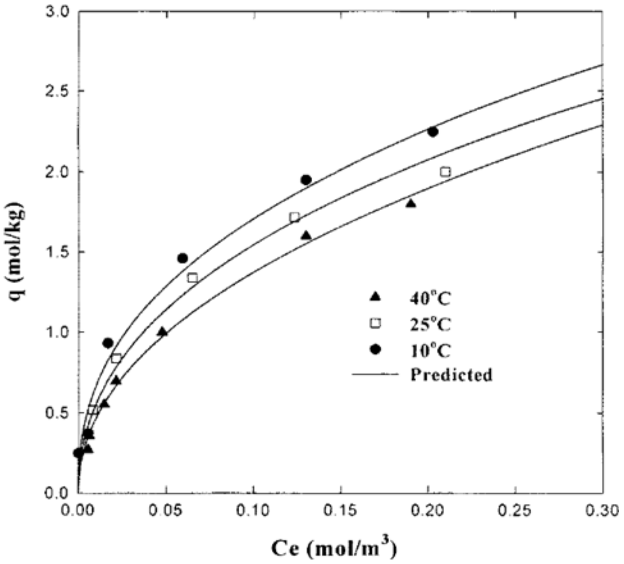

Fig. 2. Single-species isotherms of 2,4-dinitrophenol on GAC for various temperatures at pH 4.3.

Table 3. Adsorption equilibrium constants of 2,4-dinitrophenol on an activated carbon at 25 °C

Isotherm	Parameters	pH 4.3	pH 7	pH 10
Langmuir	qm	2.09	0.59	0.53
	b	32.97	80.9	77.1
	Error (%)	6.39	9.10	6.21
Freundlich	k	4.44	0.72	0.69
	n	2.25	5.69	5.21
	Error (%)	2.32	2.49	2.98
Sips	qm	17.9	2.32	2.00
	b	0.28	0.67	0.50
	n	2.12	5.69	4.21
	Error (%)	1.89	2.49	2.65

muir, Freundlich and Sips equations. The parameters of each isotherm were obtained by least square fitting with experimental data. These parameters and the average percent differences between measured and calculated values are given in Table 3. As shown in the table, the Sips equation gives the best fit of our data among the three. From this result, we believe that the Sips equation is suitable for predicting single-component adsorption of 2,4-dinitrophenol on activated carbon.

2. Batch Adsorption

For the modeling of the adsorption kinetics, one has to pay attention to two problems: (i) the pore structure of adsorbents and (ii) the mass transfer resistance involved in the adsorption. The adsorption on a solid surface takes place in several steps, such as external diffusion, internal diffusion, and actual adsorption. In general, the actual adsorption process is relatively fast compared to the previous two steps. Intraparticle diffusion has been usually considered as the rate-controlling step in liquid-phase adsorption. However, it is important to estimate the order of magnitude of the mass transfer coefficient. There are several correlations for estimating the film mass transfer coefficient, k_f, in a batch system. In this work, we estimated k_f from the initiation concentration decay curve when the diffusion resistance does not prevail. The transfer rate of any species to the external surface of the adsorbent, N_A, can be expressed by

$$N_A=k_fA_s(C-C_s) \tag{9}$$

By rearrangement and approximation for batch system with adsorption time of less than 300 seconds [Misic et al., 1982].

$$\ln(C/Co)=-\frac{k_fA_st}{V} \tag{10}$$

where V is the volume of solution and A_s is the effective external surface area of adsorbent particles,

$$A_s=\frac{3M}{\rho_pR_p} \tag{11}$$

M is the total mass of adsorbent particles loaded and ρ_p is the particle density. Fig. 3 is a typical plot to estimate k_f from the initial concentration data of 2,4-dinitrophenol at pH 4.3. The value of k_f obtained from Fig. 3 is 4.29×10^{-5} m/s. In this study, the pore diffusion coefficient, D_p, and surface diffusion coefficient, D_s, are estimated by pore diffusion model (PDM) and surface diffusion model (SDM) [Moon, 1983, 1987]. The estimated values of k_f, D_p and D_s for 2,4-dinitrophenol are listed in Table 4. Table 4 shows that when the film mass transfer coefficient is dominant, the effective diffusion coefficients are a very small. This implies that the diffusion inside a particle is a rate-controlling step.

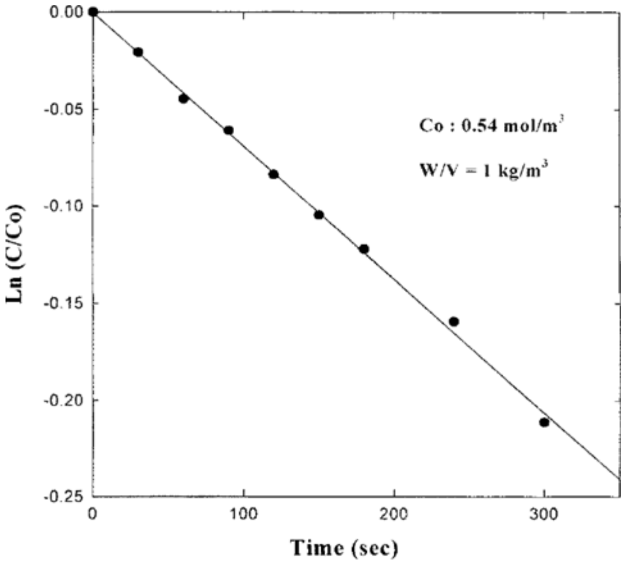

Fig. 3. Determination of k_f from an initial concentration decay plot (T: 25 °C, pH 4.3).

Table 4. Kinetic parameters in a batch adsorber

Adsorbate	pH	$k_f\times10^5$ [m/s]	$D_p\times10^{10}$ [m^2/s]	$D_s\times10^{14}$ [m^2/s]
2,4-Dinitrophenol	4.30	4.29	74.85	47.92
	7.00	2.79	3.93	2.82
	10.0	2.51	4.36	4.50

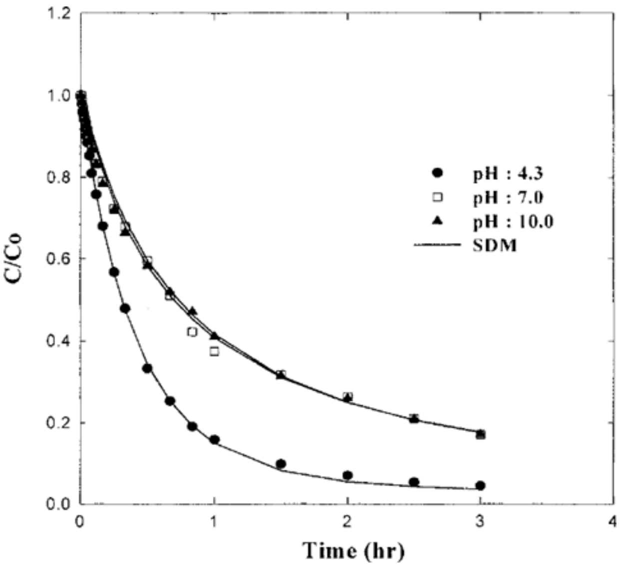

Fig. 4. Single-species batch adsorption of 2,4-dinitrophenol on GAC for various pH at 25 °C.

Fig. 4 represents the experimental data and model prediction for the adsorption of 2,4-dinitrophenol for three pH values in a batch adsorber. The surface diffusion model (SDM) shows satisfactory prediction of concentration decay curves. The effect of mixing rate on k_f was studied experimentally, and the results are shown in Table 5. As can be seen in this table, the diffusion coefficient increased practically linearly below the rpm of 200, but the film mass transfer coefficient was constant above the rpm of 400.

3. Bed Adsorption

For a packed bed adsorber, the main parameters for mass transfer are the axial dispersion coefficient and the external film mass transfer coefficient. Axial dispersion contributes to the broadening

Table 5. Film mass transfer coefficient (pH: 4.3, 25 °C)

rpm	0	50	200	400	500
$k_f\times10^6$ [m/s]	1.36	4.37	13.0	42.9	43.0

of the adsorption front axially due to flow in the interparticle void spaces. Usually it comes from the contribution of molecular diffusion and the dispersion caused by fluid flow. In this study, the axial dispersion coefficient, D_L, for the fixed bed adsorber was estimated by Wakao and Funazkri [1978].

$$\frac{D_L}{2vR_p}=\frac{20}{\varepsilon}\left(\frac{D_m}{2vR_p}\right)+\frac{1}{2}=\left(\frac{20}{\mathrm{Re\ Sc}}+\frac{1}{2}\right) \tag{12}$$

External film mass transfer is that by diffusion of the adsorbate molecules from the bulk fluid phase through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid. The external film mass transfer coefficient, k_f, in a fixed bed adsorber can be estimated by the Ranz and Marshall equation [Ruthven, 1984].

$$\frac{2k_fR_p}{D_m}=2.0+0.6S_c^{1/3}R_e^{1/2} \tag{13}$$

where S_c and R_e are Schmidt and Reynolds numbers, respectively. In Eqs. (12) and (13), molecular diffusion coefficients, D_m, of 2,4-dinitrophenol can be calculated by the Wilke-Chang equation [Reid, 1994]. The estimated values of axial dispersion coefficient, external film mass transfer coefficient, and molecular diffusion in a fixed bed are listed in Table 6.

The breakthrough curves of all species, in general, depend on adsorption equilibrium, intraparticle mass transfer, and the hydrodynamic conditions in the column. Therefore, it is reasonable to consider adsorption equilibrium and mass transport simultaneously in simulating the adsorption behavior in the fixed bed adsorber. On the other hand, the operational factors such as input concentration, pH, flow rate and bed height are important in column design and optimization. In this work, breakthrough curves were obtained under various experimental conditions mentioned above. The experimental conditions are summarized in Table 2.

Table 6. Bed dynamic parameters for model simulation

Parameter	Symbol (unit)	Values
Axial dispersion coefficient	D_L (m^2/s)	1.28×10^{-5}
Film mass transfer coefficient	k_f (m/s)	8.08×10^{-4}
Molecular diffusion coefficient	D_m (m^2/s)	9.18×10^{-8}

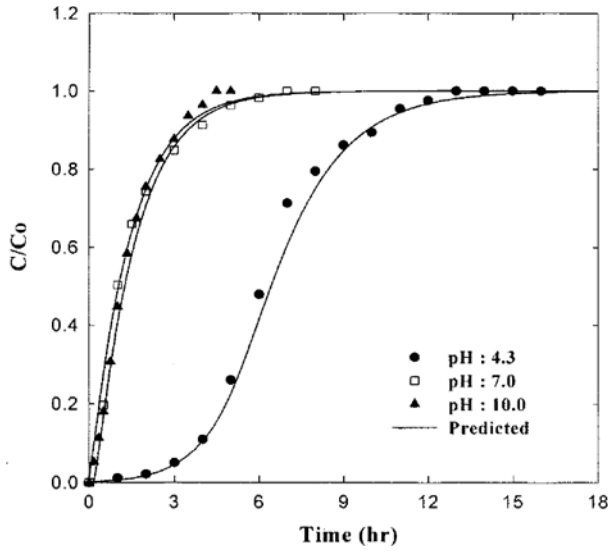

Fig. 5. Effect of pH on the experimental results and model predictions of adsorption breakthrough curves (T: 25 °C, Vs: 0.665×10^{-2} m/s, Co: 0.54 mol/m^3, L: 0.1 m).

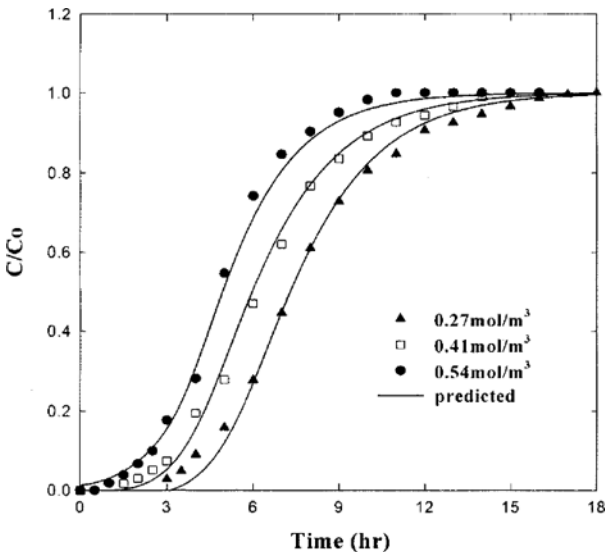

Fig. 6. Effect of concentration on the experimental results and model predictions of adsorption breakthrough curves (T: 25 °C, pH: 4.3, Vs: 0.965×10^{-2} m/s, L: 0.1 m).

In order to demonstrate the effect of the pH on the breakthrough curves of 2,4-dinitrophenol, breakthrough curves under different pH values are shown in Fig. 5. The breakthrough time was decreasing with increasing of pH value, since the hydrogen ion concentration (pH) has a major effect on the degree of ionization of the phenolic sorbate and the surface properties of the adsorbents. These in turn lead to shift in the sorption capacity of the equilibrium sorption process. Anions are favorably adsorbed on the surface of adsorbents at low pH. The dependence of diffusion on adsorbate concentration is important both in process modeling and in understanding the mechanism of the diffusion process. Adsorption also depends on adsorbate and adsorbent as well as adsorption conditions such as temperature and concentration. Fig. 6 illustrates the effect of input concentration on experimental breakthrough curves. The breakthrough time decreases with the increase of input concentration. The result can be explained by the concept of the mass transfer zone (MTZ) velocity [Ruthven, 1984]. Velocity of MTZ is a function of interstitial velocity, particle density, bed porosity and slope of the equilibrium isotherm. For a linear isotherm adsorption system, the velocity of the MTZ is constant. Therefore, the breakthrough time is not affected by input concentrations at constant MTZ velocity. However, the adsorption isotherm of 2,4-dinitrophenol on GAC is very favorable as shown in Fig. 1. As the input concentration increases, the value of slope of the equilibrium isotherm decreases and the zone velocity increases. Therefore, the breakthrough time becomes shorter under this circumstance.

Fig. 7 shows the effect of bed length on adsorption of 2,4-dinitrophenol on GAC. The experimental data of our study show shorter breakthrough times and sharper breakthrough curve for a shallow bed compared to those for a deeper bed, which is typical in fixed

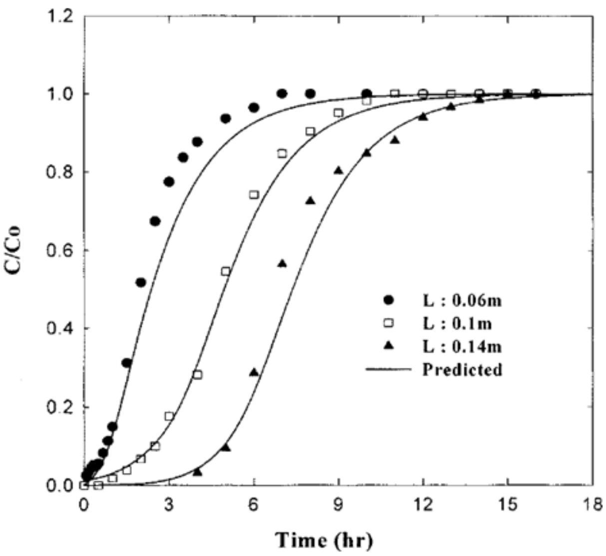

Fig. 7. Effect of bed length on the experimental results and model predictions of adsorption breakthrough curves (T: 25 °C, pH: 4.3, Vs: 0.965×10^{-2} m/s, Co: 0.54 mol/m^3).

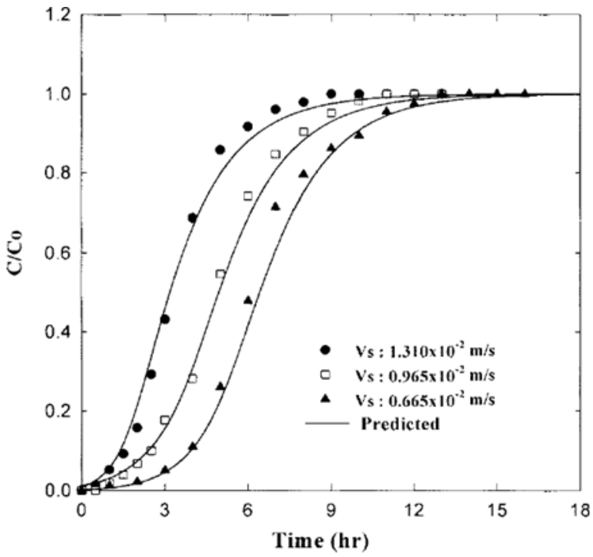

Fig. 8. Effect of flow rate on the experimental results and model predictions of adsorption breakthrough curves (T: 25 °C, pH: 4.3, Co: 0.54 mol/m^3, L: 0.1 m).

bed adsober. Since the flow rate is a very important factor in fixed bed design, the effect of flow rate is studied and the results are shown in Fig. 8. This figure shows that the breakthrough time is decreased with increasing flow rate, and the breakthrough curves are steeper for higher flow rates. In general, the breakthrough curves become steeper with increasing flow rate and decreasing bed height. Since the intraparticle diffusivity is usually independent of flow rate, this behavior is due to the external film mass transfer resistance. This resistance is weaker when flow rate is higher, so that the length of the mass transfer zone is reduced, and sharper breakthrough curve is generated.

CONCLUSIONS

1. Sips isotherm was suitable for single component systems among the various isotherms, and the equilibrium adsorption capacity of GAC for 2,4-dinitrophenol decreased with increasing pH.
2. Adsorption of 2,4-dinitrophenol on GAC was found to be physical adsorption.
3. The differences in the rate of adsorption are primarily attributable to the differences in the equilibrium at the various pHs, and the surface diffusion model simulated our data satisfactorily.
4. Adsorption dynamics of 2,4-dinitrophenol in a fixed-bed could be simulated by LDFA (linear driving force approximation).

ACKNOWLEDGEMENT

This research was financially supported by the Korea Science and Engineering Foundation (No. 98-1111-2066-2).

NOMENCLATURE

A_s	: surface area of the sorbent particles [m^2]
c	: concentration in the fluid phase [mol/m^3]
c_i	: initial concentration of bulk fluid [mol/m^3]
c_s	: concentration on the surface of adsorbent [mol/m^3]
D_L	: axial dispersion coefficient [m^2/sec]
D_m	: molecular diffusion coefficient [m^2/sec]
D_p	: effective pore diffusion coefficient [m^2/sec]
D_s	: effective surface diffusion coefficient [m^2/sec]
L	: bed length [m]
k_f	: film mass transfer coefficient [m/sec]
M	: total mass of sorbent particle
N_A	: rate of mass transfer of adsorbates to the external surface of the adsorbent [mol/sec]
q	: equilibrium amount adsorbed on the adsorbent [mol/kg]
r	: radial distance [m]
R_p	: particle radius [m]
t	: time [sec, hr]
V	: volume of solution [m^3]
v	: interstitial velocity [m/sec]
v_s	: superficial velocity [m/sec]
z	: axial distance [m]

Greek Letters

ε_b	: bed porosity [-]
ρ_p	: particle density [kg/m^3]

Abbreviation

GAC	: granular activated carbon
MTZ	: mass transfer zone
PDM	: pore diffusion model
Re	: Reynolds number
Sc	: Schmidt number
SDM	: surface diffusion model

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