Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Choung, Jae-Hoon , Lee, Young-Whan , Choi, Dae-Ki and Kim, Sung-Hyun(2003) 'Adsorption Dynamics of Toluene in a Packed Bed Charged with the Polymeric Adsorbent', Separation Science and Technology, 38: 1, 77 — 91

To link to this Article: DOI: 10.1081/SS-120016699

URL: http://dx.doi.org/10.1081/SS-120016699

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 1, pp. 77–91, 2003

Adsorption Dynamics of Toluene in a Packed Bed Charged with the Polymeric Adsorbent

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ABSTRACT

Experimental and theoretical studies were made on the adsorption of toluene by polymeric adsorbent in an isothermal condition of 298K. A mathematical model was developed to simulate the column dynamics of a pure adsorption system. To represent the mass-transfer rate inside the adsorbent particle, the linear driving-force approximation model was applied. By optimizing the breakthrough curve data with a dynamic model, an empirical correlation was proposed to represent the overall mass-transfer rate for the toluene-polymeric adsorbent system. The result with this correlation, which is a function of the partial pressures for adsorbate and interstitial bulk fluid velocities, showed that the prediction agreed well with the experimental data of breakthrough curves.

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DOI: 10.1081/SS-120016699 0149-6395 (Print); 1520-5754 (Online)

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INTRODUCTION

Volatile Organic Compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are among the main sources of photochemical reaction in the atmosphere leading to various environmental hazards. However, VOCs have good commercial value. Increasing environmental awareness has led to stringent regulations to control the VOCs emissions. In these circumstances, it becomes mandatory for each VOCs emitting industry or facility to opt for proper VOCs control measures. There are many techniques available to control VOCs emission (destruction-based and recovery-based) with many advantages and limitations.[1]

Adsorption is the most effective method of controlling VOCs emission. The design of adsorptive separation and purification processes requires primarily the knowledge of thermodynamic data and kinetic characteristic on the adsorption equilibrium for the adsorption system of interest. This information is used to calculate the operation time of a specific concentration level and to derive optimum size of adsorbers and operating conditions. The kinetic information, such as transport properties in the apparatus and intraparticle diffusion mechanisms, can be extracted from the column experiments with the changeable operating variables (fluid velocity, concentrations, and temperature).[2] In this regards, several efforts have been made to measure adsorption kinetic information simultaneously by analyzing the breakthrough curve data.[3–5]

Recently, some interest has focused on the potential application of polymeric adsorbents for separation and purification problems. One clear advantage of polymers is the ability to control their pore structure and internal surface area by varying the polymerization conditions. Moreover, one of the main advantages of polymeric adsorbents is that the adsorption can occur by weak adsorption affinity in opposition to other well-known adsorbents such as activated carbons. Therefore, it is expected that the polymeric adsorbents are useful for treating solvent vapors by pressure swing adsorption.[6]

In this study, toluene was considered as an adsorbate. As potential adsorbent for VOCs treatment, the polymeric adsorbent was selected: Dowex Optipore V493.

In the previous study, we investigated the adsorption equilibria of toluene on Dowex Optipore V493 by a static volumetric technique. The experimental equilibrium data were obtained and correlated by the Dubinin–Astakhov equation.[7]

In the present study, we focused our attention on investigating the kinetic information on the adsorption system of toluene with Dowex Optipore V493 at 298K. By optimizing the breakthrough curve data with a mathematical model, the effective overall mass-transfer coefficient with changeable operating variables was obtained and represented by an empirical correlation. This correlation is a function of the partial pressures of adsorbate and interstitial bulk fluid velocities and yields reasonable predictions compared with the experimental data of breakthrough curve.

MATHEMATICAL MODELING OF ISOTHERMAL FIXED BED

A mathematical model was developed to analyze the experimental results of the isothermal fixed adsorption bed dynamics. We considered an isothermal and axial dispersed plug-flow system, in which variation in the fluid velocity along the bed length was negligible. The adsorption equilibrium relationship was represented by the Dubinin–Astakhov equation as discussed in a previous investigation.[7] The mass-transfer rate inside the adsorbent particle was approximated by a linear driving force (LDF) rate expression. The linear driving force model approximates the solution of Fickian diffusion inside a spherical particle. This expression assumes that the mass-transfer rate of adsorption is proportional to the differences between the equilibrium concentration and the bulk concentration of the component.[8–10] Since the solution of the LDF model is much easier and faster than the solution of a diffusion model, we employed this model in the present study.

The assumptions made in developing the model equation are:

1. The ideal gas law applies.
2. The velocity of the gas is constant through the bed.
3. Radial temperature, concentrations, and velocity gradients within the bed are negligible.
4. The mass transfer rate is represented by a linear driving force expression.
5. The axial dispersion is negligible.

Because Dowex Optipore V493 polymeric adsorbent is supplied as 20 to 50 mesh spherical beads, pressure drop due to fluid flow through a bed is an important design consideration. For the velocity of the gas through a packed bed with Dowex Optipore V493 adsorbent, pressure drop was shown graphically in Fig. 1.

Applying the above assumptions to the mass balance of the gas phase through a packed bed, the following equation is obtained:

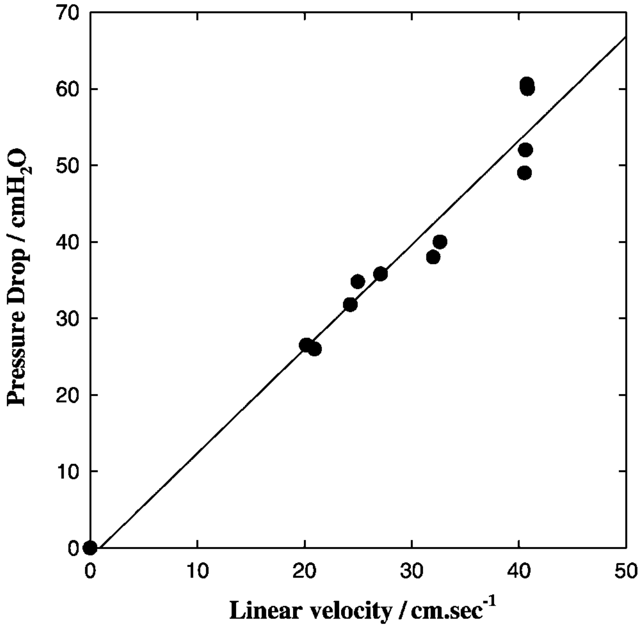


Figure 1. Pressure drop due to fluid flow through a bed of Dowex Optipore V493.

Mass-balance for component:

$$u\frac{\partial y}{\partial z}+\frac{\partial y}{\partial t}+\frac{RT}{P}\frac{1-\varepsilon}{\varepsilon}\rho_P\frac{\partial n}{\partial t}=0 \tag{1}$$

Mass-transfer rate:

$$\frac{\partial n}{\partial t}=k(n^*-n) \tag{2}$$

Adsorption equilibrium:

$$n=m\exp\left[-\left(\frac{e}{\beta E^0}\right)^r\right] \tag{3}$$

where m, e, βE^0, and r are isotherm parameters.

Boundary conditions at $z=L$, and for $t>0$:

$$\left.\frac{\partial y}{\partial z}\right|_{z=L}=0 \tag{4}$$

Initial condition for $0 < z < L$:

$$y(z,0) = 0; n(z,0) = 0 \tag{5}$$

By introducing approximate dimensionless variables, the above equations are written as follows:

$$\frac{\partial Y}{\partial \tau} = -\frac{\partial Y}{\partial X} - \phi\frac{\partial Q}{\partial \tau} \tag{6}$$

$$\frac{\partial Q}{\partial \tau} = \alpha(Q^* - Q) \tag{7}$$

Boundary conditions at $X = 1$, and for $\tau > 0$:

$$\left.\frac{\partial Y}{\partial X}\right|_{X=1} = 0 \tag{8}$$

Initial conditions, for $0 < z < L$:

$$Y(X,0) = 0; Q(X,0) = 0 \tag{9}$$

In the above equations, the dimensionless variables are defined as follows:

$$Y = y/y_0,\ \ Q = n/n_0,\ \ Q^* = n^*/n_0,\ \ \tau = ut/L,\ \ X = z/L,$$

$$\phi = \frac{RT}{Py_0}\frac{1-\varepsilon}{\varepsilon}n_0\rho_P,\ \ \alpha = k\frac{L}{u}.$$

Numerical Technique

The mathematical model developed in this study is an isothermal fixed-bed model. In the model, there are two partial differential equations (PDEs) for mass balances within the packed bed. The PDE representing the packed bed dynamics were solved by the numerical method of lines (MOL) technique. The partial differential equations of Eqs. (1) and (2) were reduced to a set of ordinary differential equations (ODEs) by the method of lines technique. The resulting set of ordinary differential equations (ODEs) was solved by using the subroutine DIVPAG of the International Mathematical and Statistical Library (IMSL). The DIVPAG program employs Gear's method with variable order and step size.

EXPERIMENTAL STUDIES

A laboratory scale fixed-bed adsorption unit was used to study isothermal adsorption of toluene on polymeric adsorbent. Dowex Optipore V493 was chosen as an adsorbent and supplied by Dow Chemical Co. The physical properties of adsorbent and the packing characteristic of adsorption column are tabulated in Table 1.

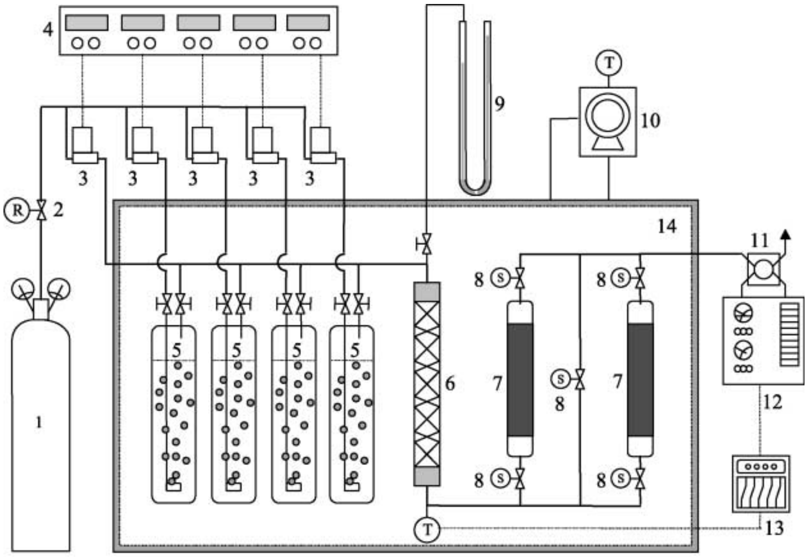
In this study, a schematic representation of the equipment is shown in Fig. 2. The nitrogen gas line was divided into five branches. One was for pure nitrogen gas as a carrier and the others were connected to four branched solvent saturators. In the method, a part of nitrogen gas was fed to a saturator to load objective solvent and was mixed with the pure nitrogen gas stream. In order to ensure homogeneous mixing of solvent vapors with pure nitrogen gas stream, a static in-line mixer was installed at the inlet section of the adsorption column. At a fixed concentration, a flow rate, and constant temperature, the solvents-laden gas stream was fed to a fixed-bed adsorption column.

The system pressure was monitored by a pressure manometer. All the gas flow rates were metered and adjusted by five mass flow controllers (Brooks type 5850E) with a readout power supply (Rich Field type MGF-4C). Temperature was maintained by circulating water bath with an accuracy of ± 0.02°C at 298K. To check the system temperature, a K-type thermocouple was used. All the experiments were carried out at 298K and the temperature of the system was monitored by chart recorder (Yokogawa type 4179).

During the adsorption, the concentration history at the exit of the adsorption bed was monitored by a gas chromatograph (Hewlett Packard type

Table 1. The physical properties of adsorbent and the packing characteristic of adsorption column.

Polymeric adsorbents	Dowex Optipore V493
Physical form	Orange, spheres
Mean particle diameter, mm	0.56
BET surface area, m^2/g	1100
Total pore volume, cc/g	1.16
Particle porosity (ε_p)	0.55
Bed packing density, g/cc	0.34
Bed void fraction (ε)	0.28
Packing length, cm	9.2
Packing amount, g	8.14
Column I.D., cm	1.82



1. Nitrogen Gas
2. Inlet Pressure Regulation Valve
3. Mass Flow Meter
4. Control Box
5. Solvent Evaporator
6. Inline Static Mixer
7. Adsorption Column
8. Solenoid Ball Valve
9. Manometer
10. Refrigerating/Heating Water Circulator
11. Auto Injection Valve
12. Gas Chromatograph (FID)
13. Recorder
14. Constant Temperature Water Bath

Figure 2. Schematic diagram of experimental apparatus.

5890 series II) equipped with a flame ionization detector and helium as the carrier gas. A packed column (Supelco type Bentone 34) was used to separate BTX in a nitrogen flow. The retention times of the chromatograms under conditions of interest were approximately 2 min for toluene.

To analyze the concentration of effluent gas streams with a constant time interval, an automatic 6-port infection valve (Valco Co.) with a digital timer (Autonics type FX4) was used. After each adsorption experiment (i.e., after

Table 2. Fixed-bed adsorption runs for toluene-Dowex Optipore V493 system.

		Feed C (ppm)
Run no.	u (cm s^{-1})	Toluene
Run #1	21.9	2586
Run #2	32.0	2654
Run #3	40.6	2647
Run #4	51.2	2571
Run #5	20.9	3344
Run #6	32.6	3324
Run #7	41.3	3228
Run #8	51.6	3249
Run #9	20.9	4492
Run #10	32.2	4495
Run #11	40.7	4548
Run #12	51.2	4422

the adsorption column was saturated with the feed concentration), a saturated adsorption column was regenerated for the next experimental run by admitting pure nitrogen at 393K for 12 h.

In all experimental runs, the inlet concentrations of solvent-laden gas were set at 2600, 3300 and 4500 ppm for toluene. The linear velocity to gas stream varied between 0.2 and 0.5 m/s, which is same condition as for a commercial solvent recovery system. All experimental conditions were tabulated in Table 2.

RESULT AND DISCUSSIONS

Equilibrium Isotherm

In general, thermodynamic information on adsorption equilibrium can be obtained by the conventional measurement techniques such as the static volumetric and the static gravimetric methods.[11] Besides, the kinetic information, such as transport properties in the apparatus and intraparticle diffusion mechanisms, can be extracted from the column experiments with the changeable operating variables (fluid velocity, concentrations, and temperatures).

In the present study, experimental and theoretical works have been made on adsorption of toluene by polymeric adsorbent fixed bed in an isothermal condition of 298K.

If the adsorbable species exist at the trace level and the flow rate and temperature are constant during the experiment, one can calculate the amount adsorbed at a specific equilibrium concentration (inlet concentration) as follows:

$$N = \frac{FC_0}{w}\left[t_s - \int_0^{t_s} \frac{C}{C_0}dt\right] \tag{10}$$

where t_s is saturation time, which is the elapsed time when all C reach C_0 at the exit of the column.

In a previous study, we obtained pure adsorption equilibrium isotherm for toluene on Dowex Optipore V493 by the static volumetric method.[7] In Fig. 3, we compared the data obtained by static volumetric method with the data obtained from the breakthrough data analysis. In this figure, the closed symbols indicate the data obtained by the static volumetric method, the open

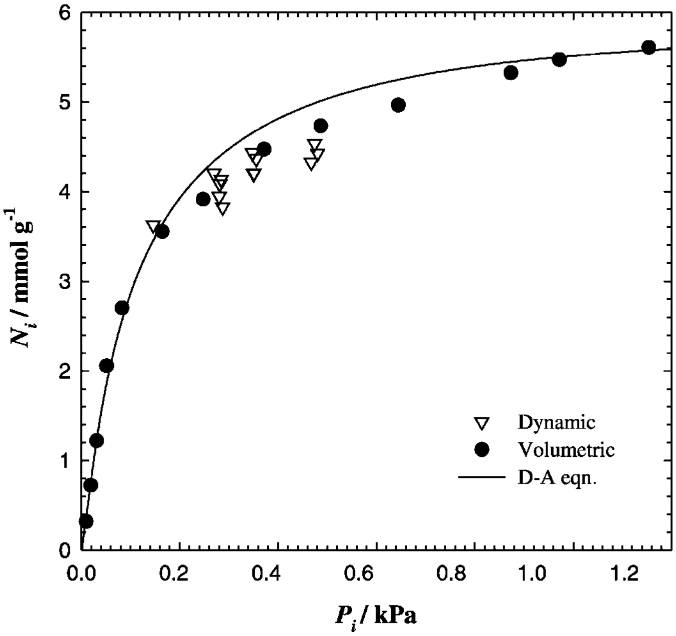


Figure 3. Equilibrium isotherm of toluene on Dowex Optipore V493 at 298K.

Table 3. Dubinin–Astakhov equation parameters for toluene on Dowex Optipore V493.

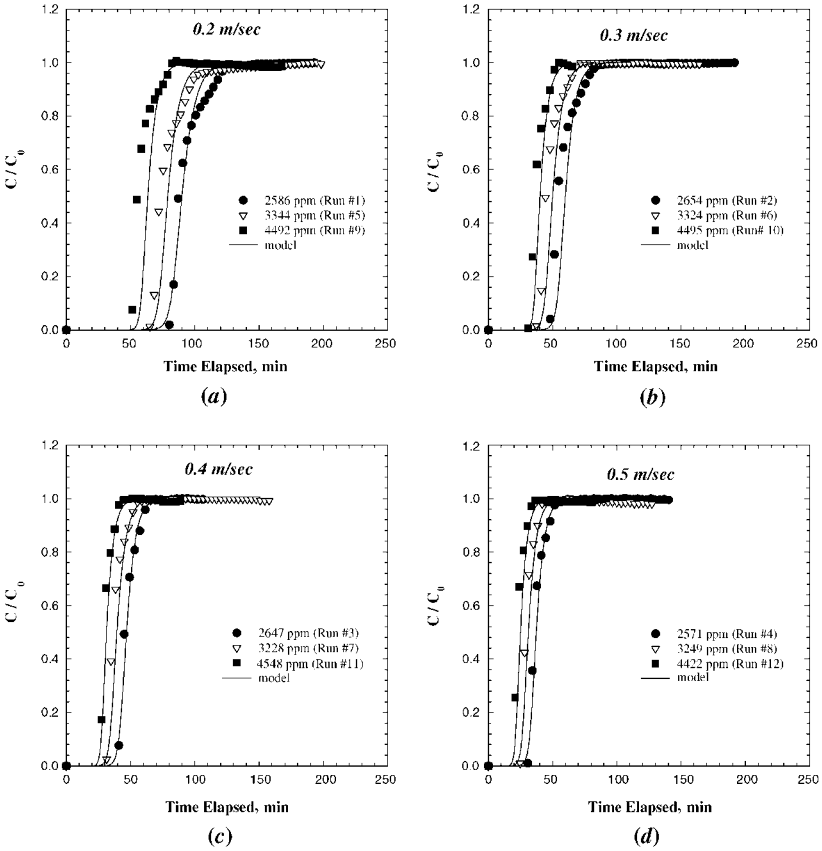
Adsorbent	T (K)	M (mol kg^{-1})	E^0 (kJ mol^{-1})	r	B
Dowex Optipore V493	298.15	5.73	10.225	2.866	1.190

symbols indicate the data obtained from the breakthrough data analysis, and the prediction result using the D–A equation is represented by the solid line, respectively. As can be seen in Fig. 3, the qualitative agreements of two different experimental techniques are found in the data. The experimental isotherm was fitted with the D–A equation and the isotherm parameters used are given in Table 3.

Column Dynamics

A mathematical fixed-bed model was used to simulate the column dynamics of adsorption of pure toluene. As mentioned early, for isothermal adsorption, the mass transfer mechanism includes fluid film transfer pore diffusion, adhesion on surface, and surface diffusion. In order to make quantitative prediction of the dynamic behavior of adsorber, complete solution for each step must be required. However, it is not easy to compute the adsorption dynamics using a complete model, because of mathematical difficulties and a lot of computation time. In this regard, the linear driving force (LDF) approximation model for overall mass transfer has been widely applied for dynamic modeling. Strictly speaking, the overall LDF mass-transfer coefficient is an effective lumped-resistance coefficient. Therefore it is important to investigate the effects of control variables on adsorption behaviors. In this study, the effects of two control variables such as the bulk fluid velocity and the concentrations (or partial pressures) for toluene were investigated.

Typical adsorption breakthrough curves for toluene are illustrated in Figs. 4 and 5. As can be found in Fig. 4, the dynamic behaviors were affected by the feed concentrations. It is obvious that high feed concentration makes abrupt breakthrough more than low feed concentration. This is because of a fact that higher bulk concentration can make greater concentration driving force between bulk and solid phases. Besides, when the feed concentration is lower, a very long time is required for reaching the bed saturation. This is due to the fact that the equilibrium amount of toluene on polymeric adsorbent is very high even at low concentration. In addition, the fluid velocity can also



(*a*) (*b*) (*c*) (*d*)

Figure 4. Effect of feed concentration under constant velocity.

play a role in column dynamics as shown in Fig. 5. As can be found in this figure, lower fluid velocity makes the breakthrough curves more broad. This is because the external film diffusion resistance is related with the fluid velocity. Generally, the external film diffusion resistance can be reduced as the fluid velocity is increased.

In the present study, our consideration on adsorption kinetics in an isothermal fixed bed was devoted to investigating the effect of feed concentration and the fluid velocity. By using a mathematical model to optimize the breakthrough data of toluene with the prediction results, the values of the overall linear driving force mass-transfer coefficients were obtained for various experimental conditions. By adapting a non linear

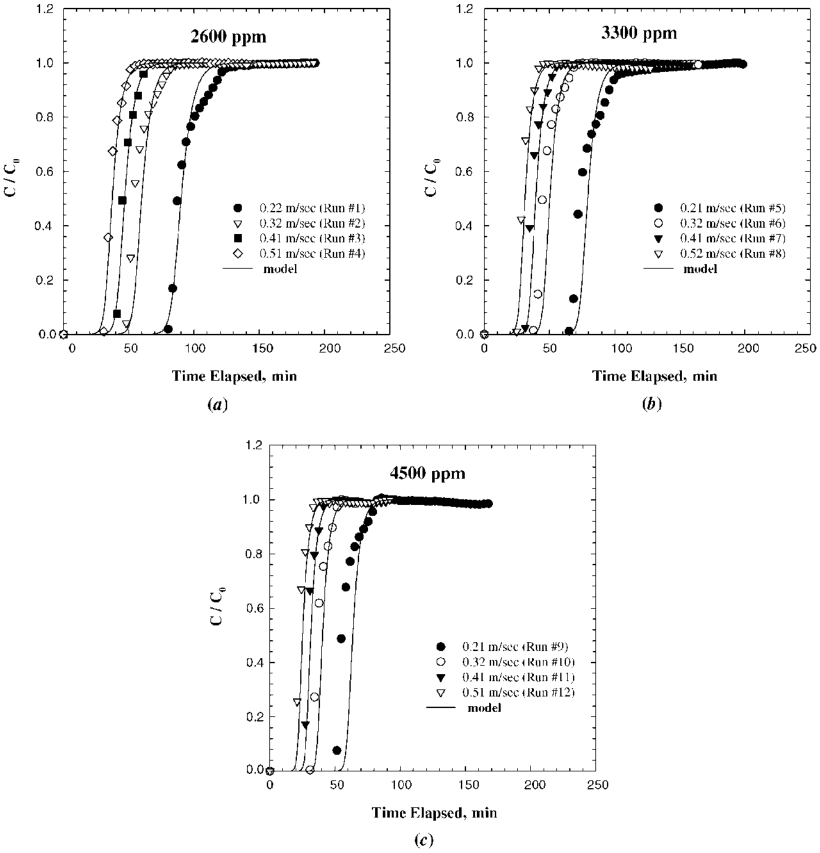


Figure 5. Effect of bulk fluid velocity under constant concentration.

regression technique, the results were correlated with the following relationship[8]:

$$k = 0.00465 \times [P]^{0.46}[u]^{0.96} \tag{11}$$

In Eq. (11), k is overall mass-transfer rate coefficient, P is partial pressure (in kPa), and u is interstitial bulk fluid velocity (in m/s) in a packed bed. Because of the lack of experimental data, the correlation cannot give a sufficiently useable range (i.e., can only be available in the experimental range). The possible range is the partial pressure of 0.2 to 0.5 kPa and the interstitial bulk

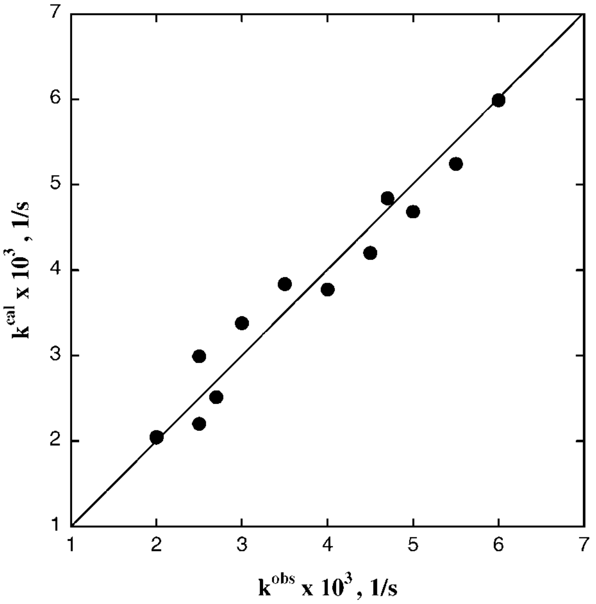


Figure 6. Comparisons between measured overall mass-transfer coefficients and values calculated by Eq. (11).

fluid velocity of 0.2 to 0.5 m/s. A comparison between the observed values of *k* and the values calculated from Eq. (11) is shown in Fig. 6.

It must be noted that the correlation for representing the adsorption mass-transfer rates limits the extension to different operating conditions. This is due to the dearth of experimental data. Therefore, it could be only available in our experimental range as described in above. Although the correlation cannot provide sufficient useable range, it can be satisfactorily used to design the VOC recovery equipment since the adsorption-based VOC treatment facilities are usually operated in pressure range of 0.2–0.5 kPa and in linear velocity range of 0.2–0.5 m/s.

CONCLUSIONS

In this study, experimental and theoretical studies were made on the adsorption of toluene by polymeric adsorbent in an isothermal condition of 298K. For the adsorption equilibrium isotherm, the isotherm measured by breakthrough analysis was compared with that by the static volumetric method. The result of the two different experimental techniques agreed well with each other qualitatively. In adsorption dynamics, by using our dynamic model to analyze the breakthrough data, an empirical correlation was suggested to the overall mass-transfer rate of toluene in a fixed bed that is charged with polymeric adsorbent. The correlation agreed with the experiment, relatively. The experimental and theoretical results will contribute to our future work on the removal of toluene from air by the cyclic operation of vacuum swing adsorption (VSA).

NOMENCLATURE

a_s	particle external surface area to volume ratio, l/cm
C_0	inlet concentration of adsorbate, mmol/l
C	exit concentration of adsorbate, mmol/l
F	volume flow rate, l/min
k	overall LDF mass-transfer coefficient, 1/s
L	bed length, cm
m	limiting moles adsorbed, mmol/g
N^*	moles adsorbed at equilibrium with y^*, mmol/g
N	equilibrium moles adsorbed, mmol/g
P	total pressure, kPa
Pe	Peclet number, uL/D_L
Q	dimensionless adsorbate concentration in solid phase, n/n_0
R	gas constant
R_P	particle radius, cm
t	time, min
t_s	saturation time, min
T	temperature, K
u	interstitial velocity, m/s
w	mass of adsorbent, g
X	dimensionless axial distance, z/L
y	mole fraction of adsorbate in gas phase
Y	dimensionless mole fraction of adsorbate in gas phase
z	axial distance coordinate, cm
Greek letters	
α	kL/u
ε	bed voil fraction
τ	dimensionless time, ut/L

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Received July 2001
Revised March 2002