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Sang-Wook Park[a]; Byoung-Sik Choi[a]; Jae-Wook Lee[b]
[a] Division of Chemical Engineering, Pusan National University, Busan, Korea [b] Department of Chemical Engineering, Sogang University, Seoul, Korea

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Sang-Wook Park and Byoung-Sik Choi
Division of Chemical Engineering, Pusan National University,
Busan, Korea

Jae-Wook Lee
Department of Chemical Engineering, Sogang University, Seoul, Korea

Abstract: Toluene vapor was adsorbed in a laboratory-scale packed-bed adsorber using granular activated carbon (GAC) at constant pressure (101.3 kPa). The adsorber was operated batchwise with the charge of GAC in the range of 2–4 g to obtain the breakthrough curves of toluene vapor. Experiments were carried out at different adsorption temperatures (25–50°C), sparger temperatures (20–30°C), and the flow rates of nitrogen (80–150 cm^3/min) to investigate the effects of these experimental variables on the breakthrough curves. The deactivation model was tested for these curves by combining the adsorption of toluene vapor and the deactivation of adsorbent particles. The observed values of the adsorption rate constant and the deactivation rate constant were evaluated through analysis of the experimental breakthrough data using a nonlinear least squares technique. The experimental breakthrough data were fitted very well to the deactivation model than the adsorption isotherm models in the literature.

Keywords: Toluene vapor, activated carbon, breakthrough curve, deactivation model

INTRODUCTION

Granular activated carbon (GAC) (1) has long been used to treat effectively industrial gas streams containing volatile organic compounds (VOCs) for the

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Address correspondence to Sang-Wook Park, Division of Chemical Engineering, Pusan National University, Busan 609-735, Korea. E-mail: swpark@pusan.ac.kr

adsorption of VOCs onto solids. Various contacting devices are available for adsorption systems, such as batch adsorbers and fixed bed adsorbers. The accurate design of the adsorber is achieved by developing a mass transfer model, which adequately describes the kinetics and mechanisms of the adsorption process. A plug-flow heterogeneous surface diffusion model (2) has been developed for representing the axial dispersed plug-flow, the external mass transfer, the adsorption equilibrium on the fluid-particle interface, and intraparticle diffusion for a fixed-bed adsorption column. It is difficult and tedious to obtain the physicochemical properties, such as diffusivities (3) of a solute, which are required to analyze the adsorption breakthrough curve using the conventional isotherm models, such as Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), and Dubinin-Radushkevich-Kagener (DRK) model, and prepare the experimental values of the adsorption isotherm. On the other hand, the deactivation model (DM) (4, 5) as a simplified model was used to predict the breakthrough curve assuming that the formation of a dense product layer over the surface of the adsorbent changed the number of active sites and the possible variations in the adsorption of active sites to cause a drop in the adsorption rate. In DM, the effects of all of these factors on the diminishing rate of the adsorbate capture were combined in a deactivation rate term.

Although it may seem reasonable to model the adsorption process based on the adsorption isotherms (6), such as Langmuir, Freundlich, BET, and DRK model, the good description of adsorption of trichloroethylene vapor on GAC in the paper of Suyadal et al. (1) and breakthrough curves by DM made that model more appropriate to the adsorption of the vapor. They assumed that the adsorption kinetics of DM was first-order with respect to vapor and zeroth order with respect to activity of GAC, respectively, but, not first-order with respect to activity of GAC. Park et al. (7) recently applied DM for the carbonation of sodium carbonate with CO_2 successfully and indicated also that DM described gas-solid non-catalytic reactions more accurately than the unreacted core and volume reaction models using the deactivation kinetics with first-order with respect to the solid carbonate and the CO_2 concentration, respectively.

This study aimed to obtain breakthrough data of toluene vapor (VOC) adsorbed on GAC according to the changes of adsorption temperature, inlet concentrations of VOC, the flow rate of carrier N_2, and the amount of GAC. The DM with adsorption kinetics of first-order with respect to VOC and activity of GAC, respectively, is used to describe the adsorption breakthrough data in addition to the adsorption isotherms.

THEORY

Breakthrough Analysis for the Deactivation Model

The formation of a dense product layer over the solid adsorbent creates an additional diffusion resistance and is expected to cause a drop in the adsorption rate. One would also expect it to cause significant changes in the accessible pore volume, the active surface area, and activity per unit area of the solid adsorbent with respect to the extent of the adsorption. All of these changes cause a decrease of vacant surface area of the adsorbent with time. In DM, the effects of all of these factors on the diminishing rate of VOC capture are combined in a deactivation rate term.

With assumptions (7) of the pseudo-steady state and the isothermal species conservation equation for VOC in the fixed bed is

$$-\mathrm{Q_o}\frac{\mathrm{dC_A}}{\mathrm{dS}} - \mathrm{k_oC_A}\alpha = 0 \tag{1}$$

where $\mathrm{Q_o}$, $\mathrm{C_A}$, S, $\mathrm{k_o}$, and α are the volumetric flow rate of the gaseous mixture, the concentration of toluene vapor in a gaseous stream, the vacant surface area of the adsorbent, the adsorption rate constant, and the activity of the solid adsorbent, respectively.

In writing this equation, the axial dispersion in the fixed bed and any mass transfer resistances are assumed to be negligible. According to the proposed DM, the rate of change of the activity of the solid adsorbent is expressed as

$$-\frac{\mathrm{d}\alpha}{\mathrm{dt}} = \mathrm{k_dC_A^n}\alpha^{\mathrm{m}} \tag{2}$$

where t is the adsorption time and $\mathrm{k_d}$, the deactivation rate constant. The zeroth solution of the deactivation models is obtained by taking $\mathrm{n} = 0$, $\mathrm{m} = 1$, and the initial activity of the solid as unity.

$$\mathrm{a} = \exp[-\mathrm{k_o}\tau\exp(-\mathrm{k_dt})] \tag{3}$$

where a is the dimensionless concentration of VOC defined as $\mathrm{C_A/C_{A1}}$. $\mathrm{C_{A1}}$ is the inlet concentration of VOC and τ, the surface-time defined as ratio of $\mathrm{S_o}$ (initial vacant surface area of the adsorbent) to $\mathrm{Q_o}$.

Eq. (3) is identical to the breakthrough equation proposed by Suyadal et al. (1) and assumes a fluid phase concentration that is independent of deactivation processes along the adsorber. More realistically, one would expect the deactivation rate to be concentration-dependent and, accordingly, axial-position-dependent in the fixed bed.

To obtain the analytical solution of Eq. (1) and 2 by taking $\mathrm{n} = \mathrm{m} = 1$, an iterative procedure is applied. The procedure used here is similar to the paper proposed by Dogu (8) for the approximate solution of nonlinear equations. In this paper, the zeroth solution Eq. (3) is substituted into Eq. (2), and the first correction for the activity is obtained by the integration of this equation. Then, the corrected activity expression is substituted into Eq. (1), and integration of this equation gives the first corrected solution for the breakthrough curve.

$$\mathrm{a} = \exp\left[\frac{[1 - \exp(\mathrm{k}_o\tau(1 - \exp(-\mathrm{k}_d t)))]}{1 - \exp(-\mathrm{k}_d t)}\exp(-\mathrm{k}_d t)\right] \tag{4}$$

This iterative procedure can be repeated for further improvement of the solution. In this procedure, higher-order terms in the series solutions of the integrals are neglected. The breakthrough curve for the deactivation model with two parameters ($k_o\tau$ and k_d) is calculated from the concentration profiles by Eq. (4).

EXPERIMENTAL

An Apparatus for VOC Capture and its Operation

In this study, adsorption experiment (Fig. 1) was carried out in the presence of VOC with GAC adsorbent in a fixed bed pyrex glass reactor with internal diameter of 2 cm (8). VOC was carried by nitrogen gas through a sparger. The concentration of VOC in the nitrogen stream at the outlet of the sparger was measured by a gas chromatograph. The flow rate of gas mixture of VOC and nitrogen were within the range of 80–150 cm^3/min (measured at 25°C). The amount of adsorbent, the sparger temperature, and the adsorption temperature were in the range of 2–4 g, 20–30°C, and 25–50°C, respectively. Experiments were repeated 3 times to obtain the average value for each type of experiment. A gas chromatograph (detector: thermal conductivity detector; column: SE-30 (10 feet by 1/8 inch of stainless steel; detector temperature: 190°C; feed temperature: 190°C; the flow rate of He: 25.7 cm^3/min; retention time of N_2, VOC,: 1.065, 1.535 min, respectively.) connected to the exit stream of the adsorber allowed for on-line analysis of VOC and N_2.

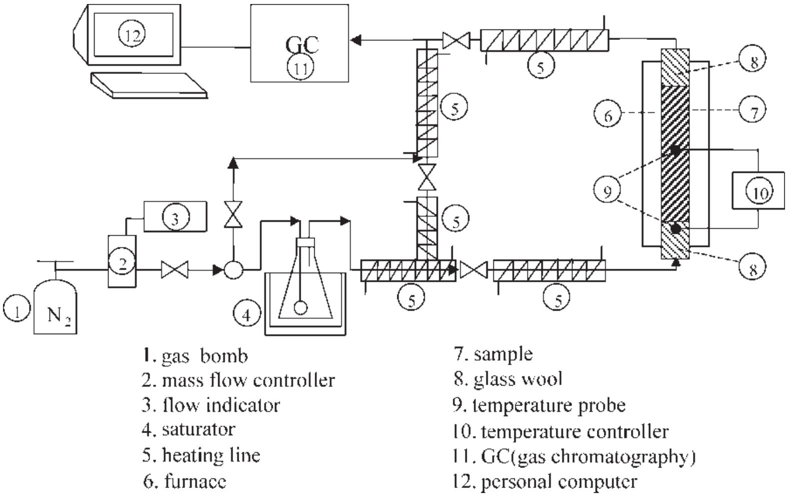

Figure 1. Schematic diagram of a fixed bed apparatus.

GAC particles were supported by glass wool from both sides. The adsorber was placed into a tubular furnace equipped with a temperature controller. The length of the fixed adsorbent section of the bed was 5 cm of the adsorber. Temperature profiles were not observed within this section. All of the flow lines between the adsorber and the gas analyzer were heated to eliminate any condensation. Three-way valves placed before and after the adsorber allowed for flow of the gaseous mixture through the bypass line during flow rate adjustments. The composition of the inlet stream was checked by the analysis of the stream flowing through the bypass line at the start experiments. The experimental procedure used to obtain the breakthrough curve of VOC was the same as that reported in detail previously (7).

Materials

GAC of Samchully Activated Carbon Ltd., Korea, and toluene of Aldrich Chemicals were used in the adsorption experiments. The average size of the adsorbent particle (3.51 mm) was measured in the range of 0.575–5.6 mm using a sieve analyzer; its bulk density (485 kg/m^3), by a conventional method using a mass cylinder. Specific surface area, total pore volume, and the average pore diameter were measured using the BET technique (Micromeritics; ASAP 2000), and their values were 804.59 m^2/g, 0.4734 cm^3/g, 23.54 Å, respectively.

RESULTS AND DISCUSSION

Kinetics of VOC Adsorption on GAC

To investigate the adsorption kinetics of VOC on GAC using two parameters of DM, the breakthrough curves of VOC were measured according to changes of the experimental variables such as the flow rate of the carrier gas, the amount of adsorbent, the adsorption temperature (T), and the sparger temperature (T_S).

Effect of Flow Rate of VOC-rich Gas

To investigate the effect of flow rate of the gaseous mixtures of VOC and N_2 on the kinetics, the breakthrough curves of VOC were measured in the range of flow rate of N_2 from 80–150 cm^3/min (measured at 25°C). The measured outlet concentrations of VOC were typically plotted against the adsorption time for the various flow rates of N_2 indicated as various symbols in Fig. 2 under the typical experimental conditions such as 3 g of GAC, T of 30°C, and T_S of 25°C. As shown in Fig. 2, a shift of breakthrough curves to

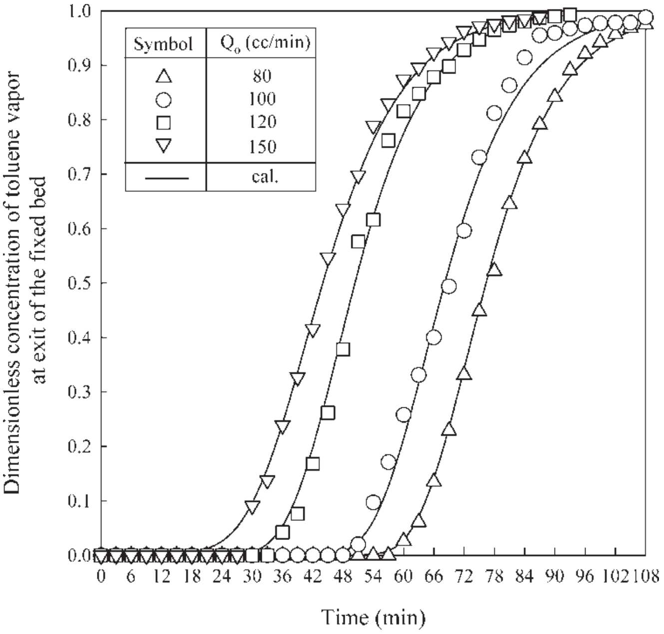

Figure 2. Breakthrough curves of toluene vapor for various flow rates of N_2. ($W_o = 3$ g; $T = 30°C$; $T_S = 25°C$).

shorter times was observed at a greater flow rate of the gaseous mixture with a decrease in the amount of VOC that the bed can hold up to a certain breakthrough level. This result means that the adsorbed amount of VOC decreases as the space time of the gaseous mixtures in the fixed bed decreases. The breakthrough curve was evaluated by analysis of the experimental breakthrough data using a nonlinear least squares technique with two parameters of $k_o\tau$ and k_d (tabulated in Table 1), and drawn as a solid line in Fig. 2. As shown in Fig. 2, the regression analysis of the experimental breakthrough data gave very good agreement with the breakthrough equation Eq. (4) with regression coefficient more than 0.9983. As shown in Table 1, the values of $k_o\tau$ decreased with increasing Q_o whereas the k_d's were almost same.

Effect of Amount of GAC

A set of experiments was performed to investigate the effect of the mass of GAC in the range from 2 to 4 g on the VOC breakthrough curves. As shown in Fig. 3, a good description of data was obtained by using Eq. (4) for each set of amount of GAC at temperature (30°C), flow rate of N_2 (100 cm^3/min), and sparger temperature of 25°C.

Table 1. Rate parameters for various experimental conditions

T_S (C)	T (C)	W_o (g)	Q_g (cm^3/min)	$k_o\tau$ (−)	k_d (1/min)	r^2 (correlation)
25	30	3	80	7.349	0.101	0.9998
25	30	3	100	6.390	0.099	0.9983
25	30	3	120	4.946	0.105	0.9995
25	30	3	150	3.919	0.096	0.9993
25	30	2	100	4.052	0.102	0.9986
25	30	3	100	6.390	0.099	0.9983
25	30	4	100	8.293	0.105	0.9998
20	30	3	100	6.333	0.096	0.9992
25	30	3	100	6.390	0.099	0.9983
30	30	3	100	6.009	0.105	0.9994
25	25	3	100	5.978	0.086	0.9993
25	30	3	100	6.390	0.099	0.9983
25	40	3	100	7.423	0.125	0.9991
25	50	3	100	8.419	0.159	0.9995

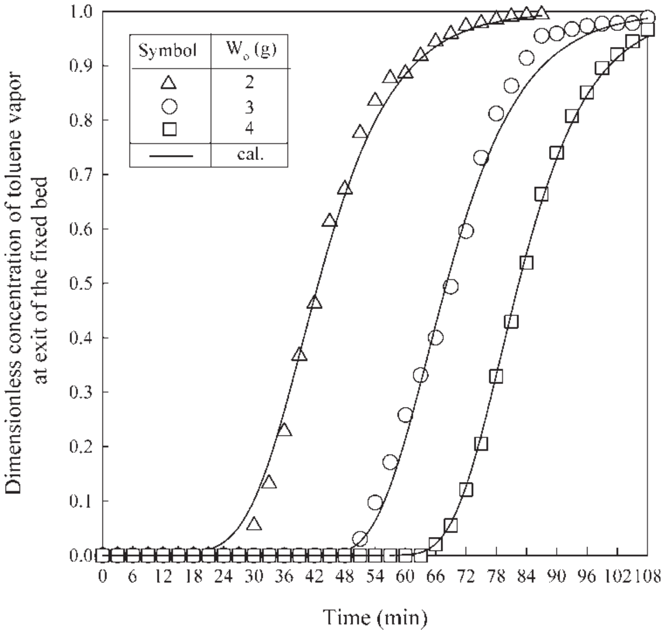

Figure 3. Breakthrough curves of toluene vapor for various amount of AC. ($Q_o = 100\ cm^3/min$; $T = 30°C$; $T_S = 25°C$).

Also, the adsorbed amount of VOC increased with increasing the amount of GAC. The model parameters ($k_o\tau$ and k_d) determined from the analysis of the experimental breakthrough data are tabulated in Table 1. As shown in Table 1, the values of $k_o\tau$ increase with increasing W_o whereas the k_d's are almost the same.

Effect of Feedstock Concentration of VOC

To determine the dependence of the adsorption parameters on the feedstock concentration of VOC, the breakthrough curves of VOC were measured in the sparger temperature range between 20 and 30°C at flow rate of N_2 of 100 cm^3/min, temperature of 30°C, and GAS of 3 g. The feedstock concentrations of VOC at the sparger temperature of 20, 25, and 30°C, which were measured at the inlet of the adsorber by GC, were 28740, 37440, 48250 ppm, respectively. A good fitting of DM predictions to experimental data could be seen by inserting the corresponding values of $k_o\tau$ and k_d tabulated in Table 2 into Eq. (4) and was shown in Fig. 4. As shown in Fig. 4, the acceleration of the toluene breakthrough was observed with an increased feedstock concentration of VOC. This behavior indicated a much quicker saturation of the adsorbent, because the GAC used in this study was relatively coarse-grained, so that internal diffusion might have been a rate-limiting step in the kinetics of physical VOC adsorption.

Table 2. Selected adsorption isotherms to fit the toluene vapor breakthrough data for comparison with the deactivation model

Adsorption isotherms	Mathematical representation of adsorption isotherms	Linearized forms	Parameters and correlation coefficient
Langmuir	$y = ax/(1+bx)$	$1/y = (1/ax + b/a)$	$a = 230.81$ $b = 160.33$ $r^2 = 0.8906$
Freundlich	$y = ax^b$	$\ln(y) = \ln(a) + b\ln(x)$	$a = 1.2164$ $b = 0.1510$ $r^2 = 0.9645$
Brunauer-Emmett-Teller	$y = x/(1 - x)(a + bx)$	$x/y(1-x) = a + bx$	$a = -62.4$ $b = 734.4$ $r^2 = 1.7988$
Dubinin-Radshkevich-Kagener	$y = a \exp[-b\ln^2(x)]$	$\ln(y) = \ln(a) - b\ln^2(x)$	$a = 1.1453$ $b = 0.0256$ $r^2 = 0.6496$
Deactivation model (this study)	x according to Eq. (5) y according to Eq. (6)		$k_S\tau = 6.39$ $k_d = 0.099$ $r^2 = 0.9999$

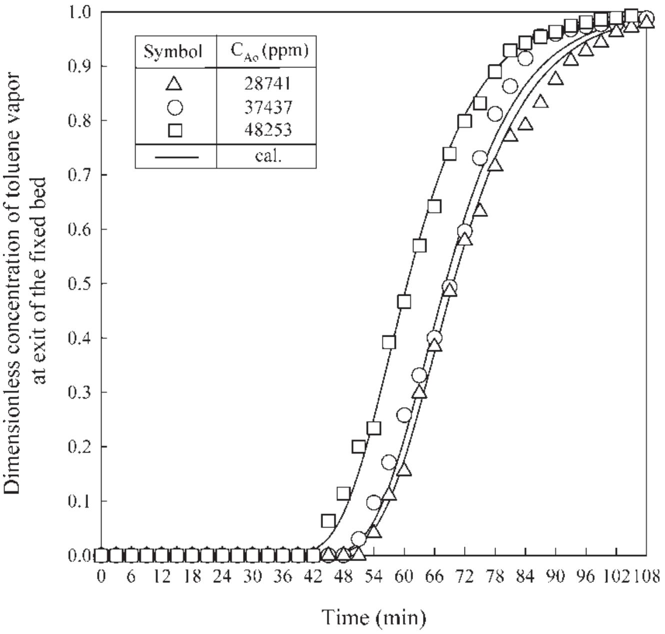

Figure 4. Breakthrough curves of toluene vapor for various feedstock concentration of toluene vapor. ($Q_o = 100\ cm^3/min$; $T = 30°C$; $W_o = 3\ g$).

Effect of Adsorption Temperature

To investigate the effect of the adsorption temperature on the adsorption kinetics, the breakthrough curves of VOC were measured in the range of temperature from 25–50°C. The measured outlet concentrations of VOC were typically plotted against the adsorption time for the various temperatures indicated as various symbols in Fig. 5 under the typical experimental conditions such as 100 m^3/min of N_2 (measured at 25°C), 3 g of GAC, and T_S of 25°C. The model parameters ($k_o\tau$ and k_d) were evaluated by analysis of the experimental breakthrough data using a nonlinear least squares technique and were tabulated in Table 1. The results in Fig. 5 indicated a shift in breakthrough curves toward the right with decreased temperature, which might be attributed to an increase in the amount of adsorbed toluene and was the same result of the breakthrough curves of trichloroethylene vapor on GAC (1). The value of $k_o\tau$ increased as the adsorption temperature increased, as shown in Table 1, but τ decreased because Q_o increased according to the increase of the temperature. This means that k_o may be more sensitive on temperature rather than τ on temperature. Arrhenius plots of the dimensionless adsorption rate constant ($k_o\tau$) and deactivation rate constant (k_d) were shown in Fig. 6, and the value of the activation energy for the adsorption(Ea) was 2.6 kcal/mole. This was almost the same as

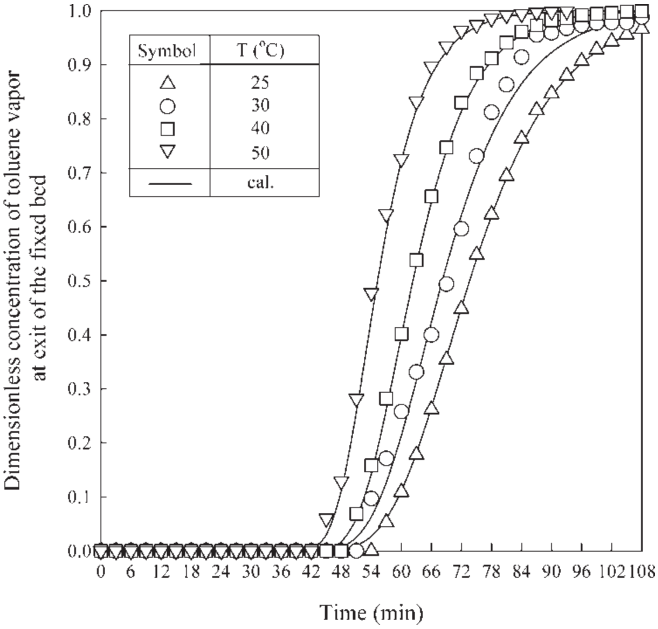

Figure 5. Breakthrough curves of toluene vapor for various temperature. ($Q_o = 100\ cm^3/min$; $W_o = 3\ g$; $T_S = 25°C$).

4.2 kcal/mole in adsorption of trichloroethylene on GAC(1), but Ed (4.6 kcal/mole) was much smaller than that (33.9 kcal/mole) given in the literature mentioned above (1). The kind of VOC and physical properties of GAC may cause the different values of activation and deactivation energies.

Comparison of the Proposed Models

Several equilibrium models (6), which have been developed to describe adsorption isotherm relationships, are useful for describing the adsorption capacity and theoretical evaluation of thermodynamic parameters, such as heats of adsorption. But, sometimes the experimental procedure to prepare the adsorption isotherm relationships is very tedious and takes too much time. The equilibrium concentrations between two phases, which are used to describe adsorption isotherm relationships, can be obtained by Eq. 5 and 6, where a(t), x and y are the dimensionless concentrations of VOC in the breakthrough data, in the gas phase and the solid phase, respectively. As shown in Eq. (5) and (6), the ranges of x and y are between 0 and 1, respectively. The equilibriums for single-solute sorption given in the literature (6) are frequently presented as dimensionless concentration isotherms. To compare the deactivation model with the equilibrium isotherm models, models

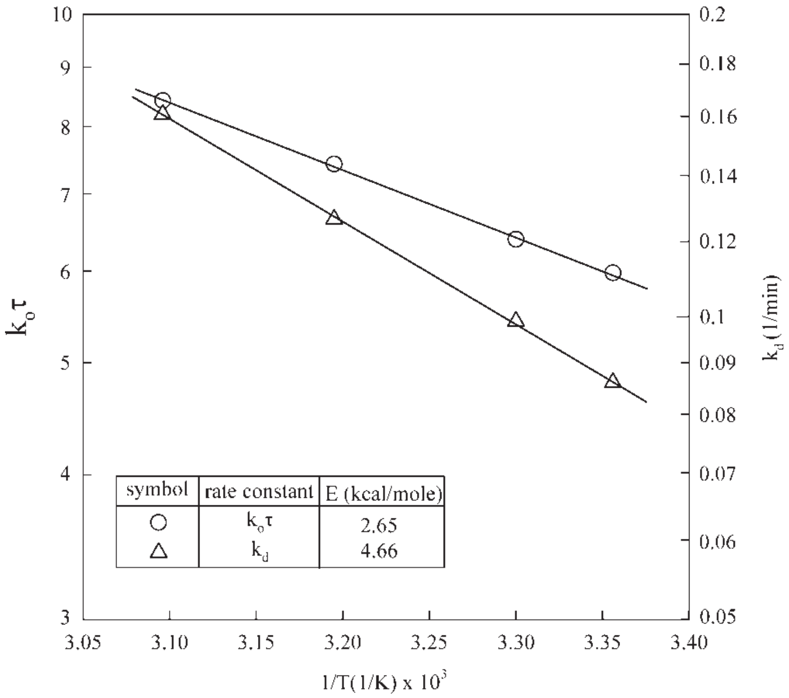

Figure 6. Effect of temperature on dimensionless absorption rate constant and deactivation rate constant.

selected by Suyadal et al. (1) were used as follows; Langmuir, Freundlich, BET, and DRK model, whose formulae were listed in Table 2. The typical experimental conditions indicated as circle in Fig. 2 are used, i.e., flow rate of 100 $\mathrm{cm^3/min}$, amounts of GAC, 3 g, sparger temperature, 25°C, and adsorption temperature, 30°C. Using a(t) obtained from the experimental parameters, the values of x and y obtained from Eq. (5) and (6), were shown in Fig. 7 and used to obtain to give the constants of a and b in each model. As shown in Table 2 and Fig. 7, the proposed deactivation model fitted the data with the highest correlation (r^2) of 0.9999, and the adsorption of toluene vapor on GAC might be favorable isotherms due to the separation factor less than to the unity. The BET model is an extended model of the Langmuir model and includes multi-layer adsorption phenomena. BET has assumptions that any given layer need not be completed before subsequent layers can form, that the first layer of molecules adheres to the surface with a comparable energy to the heat of adsorption for monolayer attachment, and that subsequent layers are essentially condensation reactions (5). The failure of the BET model in the fitting with the experimental data in Fig. 7 may be explained by the practical adsorption situation between the toluene

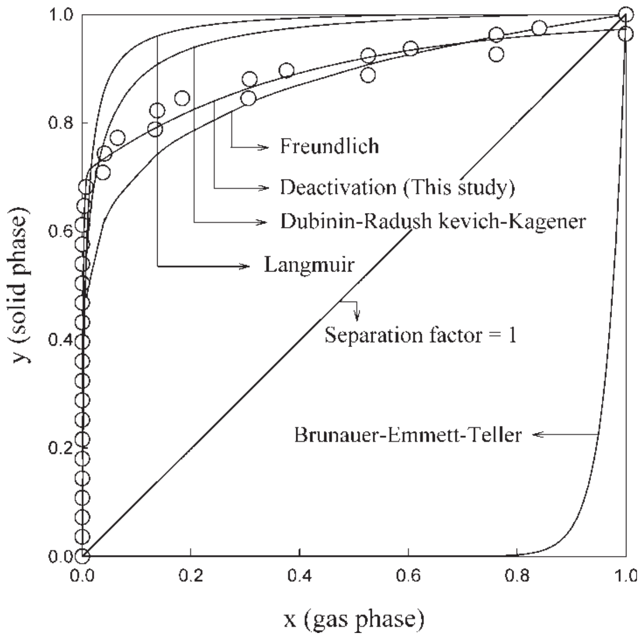

Figure 7. Comparison of the models in describing to the experimental breakthrough curves of toluene vapor according to Table 2.

vapor and GAC used in this study may be different from that of the BET model and the multi-layer adsorption phenomena do not occur in our study.

$$x = \frac{\int_o^t a(t)dt}{\int_o^\infty a(t)dt} \tag{5}$$

$$y = \frac{t - x\int_o^\infty a(t)dt}{\int_o^\infty dt - \int_o^\infty a(t)dt} \tag{6}$$

CONCLUSIONS

Granular activated carbon was used as an adsorbent to capture toluene vapor and the breakthrough data were measured in a fixed bed to observe the adsorption kinetics. The adsorption kinetics was assumed to be the first-order with respect to the concentration of toluene vapor and the activity of the adsorbent, respectively. The adsorption and deactivation rate constant were evaluated by the deactivation model through analysis of the experimental breakthrough data using a nonlinear least squares technique. The experimental breakthrough data were fitted very well to the deactivation model than the adsorption isotherm models in the literature.

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