

고정층에서 활성탄 흡착에 의한 톨루엔의 파과곡선 분석

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Breakthrough Analysis of Adsorption of Toluene Vapor in a Fixed-Bed of Granular Activated Carbon

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Introduction

Granular activated carbon (GAC) has long been used to treat effectively industrial gas streams containing volatile organic compounds (VOCs) for the adsorption of VOCs onto solids. Various contacting devices are available for adsorption systems, such as batch adsorbers and fixed bed adsorbers. This study aims to obtain breakthrough curves of toluene vapor (VOC) on GAC with the changing adsorption temperature, inlet concentrations of VOC, flow rate of carrier gas (N₂), and amount of GAC. The deactivation model (DM) [Yasyerli, 1996], whose kinetics is first-order with respect to GAC and activity of the adsorbate, respectively, is used to describe the adsorption breakthrough curves in addition to adsorption isotherms.

Theory**Breakthrough Analysis for the Deactivation Model**

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

$$-Q_o \frac{dC_A}{dS} - k_o C_A \alpha = 0 \quad (1)$$

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

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

$$-\frac{d\alpha}{dt} = k_d C_A^n \alpha^m \quad (2)$$

where t is the adsorption time and k_d , the deactivation rate constant. The zeroth solution [Suyadal et al., 2000] of the deactivation models is obtained by taking $n=0$, $m=1$, and the initial activity of the solid as unity.

$$a = \exp[-k_o \tau \exp(-k_d t)] \quad (3)$$

where a is the dimensionless concentration of VOC defined as C_A/C_{A1} , and C_{A1} , the inlet concentration of VOC. Analogous to the weight-time and volume-time given by Levenspiel[1999] for a batch of catalyst particles undergoing first-order deactivation with a plug constant flow of fluid, the ratio of S_o to Q_o may be called the surface-time(τ) in Eq. (3).

To obtain the analytical solution of Eq. (1) and (2) by taking $n=m=1$, an iterative procedure was applied. The procedure used here is similar to the procedure proposed by Dogu[1986] for the

approximate solution of nonlinear equations. In this procedure, 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.

$$a = \exp \left[\frac{[1 - \exp(k_0 \tau (1 - \exp(-k_d t)))]}{1 - \exp(-k_d t)} \exp(-k_d t) \right] \quad (4)$$

The breakthrough curve for the deactivation model with two parameters ($k_0 \tau$ 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 (5). VOC was carried out 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 chromatography. The flow rate of gas mixture of VOC and nitrogen were within the range of 80-150 cm³/min. The amount of adsorbent was in the range of 2-4 g. The sparger temperature was in the range of 20-30°C. Experiments were repeated over a temperature range between 25 and 50°C. A gas chromatography (detector: thermal conductivity detector; column: SE-30(15%)(10 feet by 1/8 inch of stainless steel; detector temperature: 190°C; feed temperature: 190°C; flow rate of He: 25.7 cm³/min; retention time of N₂, VOC, : 1.065, 1.535 min, respectively.) connected to the exit stream of the adsorber allowed for on-line analysis of VOC and N₂. The experimental procedure used to obtain the breakthrough curve of VOC was the same as that reported in detail previously [Park et al., 2006].

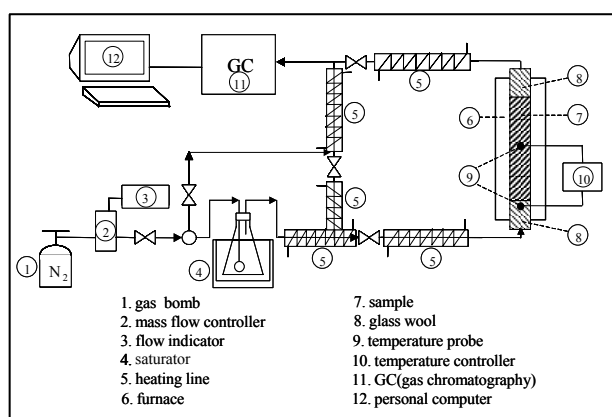


Figure 1. Schematic diagram of a fixed bed apparatus.

Results and discussion

Kinetics of VOC adsorption on GAC

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

To investigate the effect of adsorption temperature on the breakthrough curves, 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. 2 under the experimental conditions such as 100 m³/min of N₂, 3 g of GAC, and T_s of 25°C. The results in Fig. 2, which indicated a shift in breakthrough curves toward the right with decreased temperature, which may be attributed to an increase in the amount of adsorbed toluene and is the same result of the breakthrough curves of trichloroethylene vapor on GAC [Suyadal et al., 2000]. Arrhenius plots of the dimensionless adsorption rate constant ($k_0 \tau$) and

deactivation rate constant (k_d) are shown in Fig. 3, and the activation energy for the adsorption (E_a) was 2.6 kcal/mole. This is as almost same as 4.2 kcal/mole in adsorption of trichloroethylene on GAC [Orbey et al., 1982], but Ed (4.6kcal/mole) was much smaller than that (33.9 kcal/mole) given in the literature mentioned above [Orbey et al., 1982]. The kind of VOC and properties of GAC may cause the different values of the activation energy.

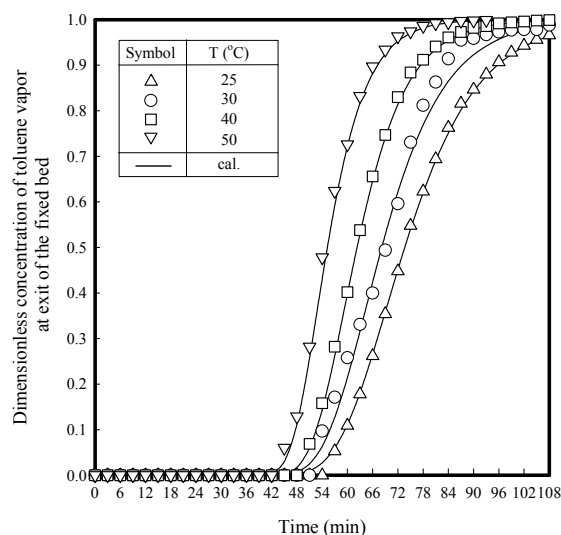


Figure 2. Breakthrough curves of toluene vapor for various flow rates of N_2 . ($W_f = 3$ g; $T = 30$ °C; $T_S = 25$ °C)

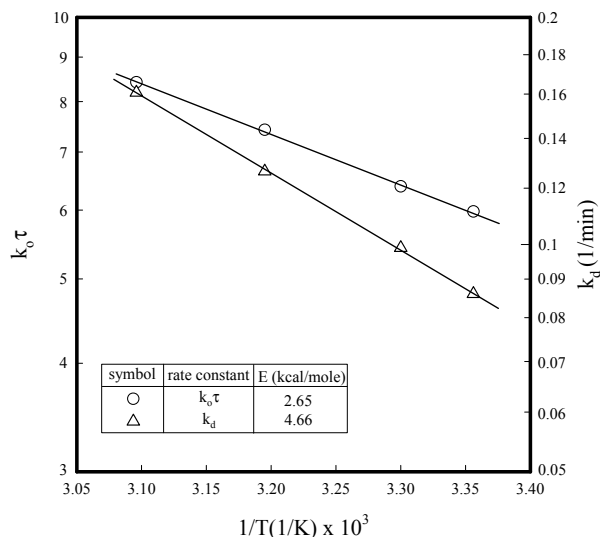


Figure 3. Breakthrough curves of toluene vapor for various amount of AC. ($Q_0 = 100$ cm³/min; $T = 30$ °C; $T_S = 25$ °C)

Table 1. 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
Brunauer-Emmett-Teller	$y = \frac{x}{(1-x)(a+bx)}$	$\frac{x}{y(1-x)} = a + bx$	$a = -62.4$ $b = 734.4$ $r^2 = 1.7988$
Freundlich	$y = ax^b$	$\ln(y) = \ln(a) + b \ln(x)$	$a = 1.2164$ $b = 0.1510$ $r^2 = 0.9645$
Langmuir	$y = \frac{ax}{(1+bx)}$	$\frac{1}{y} = \frac{1}{ax} + \frac{b}{a}$	$a = 230.81$ $b = 160.33$ $r^2 = 0.8906$
Dubinin-Radshkevich-Kagener	$y = a \exp[-b/n^2(x)]$	$\ln(y) = \ln(a) - b \ln^2(x)$	$a = 1.1453$ $b = 0.0256$ $r^2 = 0.6496$
Deactivation model (this study)	x, y according to Eq. (5)		$k_s\tau = 6.39$ $k_d = 0.099$ $r^2 = 0.9999$

Comparison of the Proposed Models

To compare DM with the others, which are so-called adsorption isotherms encountered frequently in the literature [Ruthven, 1984]. In Fig. 4, the dimensionless concentration of VOC in the gas phase (x) and solid phase (y) were determined according to Eq. (5) and the fitted to the models of the equilibriums for single-solute sorption given in the literature [Suzuki, 1990] are frequently presented as dimensionless concentration isotherms. As can be seen from Table 1 and Fig. 4, the proposed DM

fitted the data with the highest correlation coefficient (r^2) of 0.9999, and the adsorption of toluene vapor on GAC may be favorable isotherms due to the separation factor less than unity.

$$x = \frac{\int_0^t \text{adt}}{\int_0^\infty \text{adt}}, \quad y = \frac{t - x \int_0^\infty \text{adt}}{\int_0^\infty \text{dt} - \int_0^\infty \text{adt}} \quad (5)$$

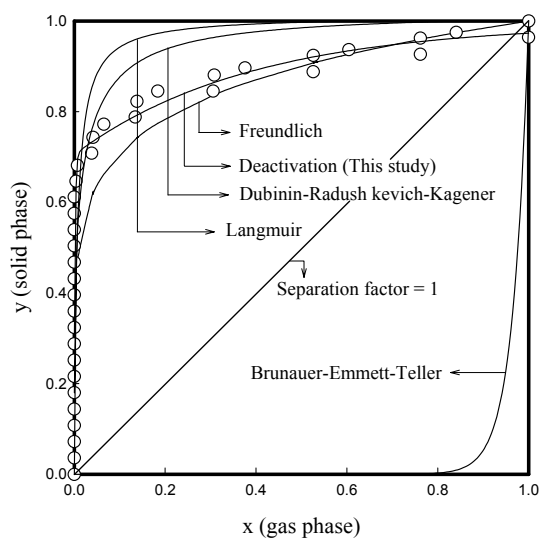


Figure 4. Comparison of the models in describing the experimental breakthrough curves of toluene vapor according to Table 1.

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 observed values of the adsorption rate constant and the deactivation rate constant in the adsorption kinetics of the first-order with respect to the concentration of toluene vapor and the activity of the adsorbent, respectively, were evaluated through analysis of the experimental breakthrough data using a nonlinear least squares technique. A good agreement of the deactivation model was obtained with the experimental breakthrough data more accurately compared to the conventional adsorption isotherms in the literature.

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