

## Dynamic determination of the concentration of volatile alcohols in a fixed bed of zeolite 13X by FT-IR

Cheng-Yuan Wu<sup>a</sup>, Tsair-Wang Chung<sup>a,\*</sup>, Thomas C.K. Yang<sup>b</sup>, Mai-Tzu Chen<sup>c</sup>

<sup>a</sup> Department of Chemical Engineering, Chung-Yuan University/Membrane Technology R&D Center, Chungli, Taiwan 320, ROC

<sup>b</sup> Department of Chemical Engineering, National Taipei University of Technology, Taipei 106, ROC

<sup>c</sup> Chang Gung Memorial Hospital, Linko, Taiwan, ROC

Received 20 June 2005; received in revised form 2 March 2006; accepted 4 March 2006

Available online 5 April 2006

### Abstract

A series of dynamic adsorptions of volatile methanol, ethanol, and *iso*-propanol (IPA) onto zeolite 13X were studied. Instead of traditional gas chromatography (GC), a gas-phase Fourier Transformation-IR (FT-IR) spectrometer was used to measure the evolution of concentrations of these volatile alcohols due to its quick response to the instantaneous changes of the gas concentration. Even though it has rarely been used in dynamic adsorption experiments in the literature, an FT-IR equipped with a constant-temperature gas cell was shown to be adequate to obtain breakthrough curves. In this study, the experiments were carried out at different gas flow rates and feed concentrations for each type of alcohol. Significant influences of the operating conditions on the breakthrough time, the shape of the breakthrough curve, and the uptake of each alcohol were found. A simple mathematical model proposed by Yoon and Nelson was applied to fit the experimental data. Good consistency between the experimental data and the regressed breakthrough curves was observed.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption; Breakthrough curve; Zeolite 13X; Alcohols; IPA; FT-IR

### 1. Introduction

Poor indoor air quality is considered to be responsible for a number of health problems, which result in increased absenteeism from work and rising medical costs [1]. Zeolites, silica gels, and activated carbons are used primarily as sorbents to remove pollutants because of their good surface characteristics [2–4]. Up to the present, the use of zeolites for the removal of pollutants has not been fully explored. There are many natural and synthetic zeolites with good surface properties, such as large surface area and more active sites on the surface to adsorb pollutants. Compared with the existing zeolites, the zeolite 13X is known to have a better surface property to remove VOCs (volatile organic compounds) because its pore diameter is larger than most of the organic compounds found indoors [5]. In addition, zeolite 13X has been found to have significant adsorption capacities for VOCs

such as aldehydes [6], aromatics [7], and chlorinated hydrocarbons [8]. However, dynamic adsorption studies of alcohols onto zeolite 13X are rare in the literature. Therefore, the objective of this work is to obtain the breakthrough curves of volatile alcohols in a fixed bed of zeolite 13X. The breakthrough curves obtained in this study will provide a useful design rule for the construction of an adsorber for removal of VOCs.

The zeolite 13X has been considered as a favorable adsorbent for VOCs. Hines et al. [8] used zeolite 13X to adsorb aromatics and aldehydes compounds. Results showed that the 13X adsorbed a large amount of aromatics and aldehydes even at low concentration levels. They suggested that 13X could adsorb most VOCs in the same manner. Studies of VOC adsorption by zeolite 13X are prevalent. However, similar studies in a dense environment are rare. Lee [9] used a mixing adsorbent (silica gel, active carbon and zeolite 13X) to adsorb toluene, 1,1,1-trichloroethane, and CO<sub>2</sub>. The results showed that the 1,1,1-trichloroethane was a polar compound and a stronger adsorbate than others. Furthermore, the impact of moisture on gas adsorption processes is a critical factor in practical applications. However, studies on

\* Corresponding author. Tel.: +886 3 2654125; fax: +886 3 2654199.  
E-mail address: twchung@cycu.edu.tw (T.-W. Chung).

### Nomenclature

$C$	concentration of gas mixture (a specific alcohol and nitrogen) (g adsorbate/g gas mixture)
$C_0$	initial concentration of gas mixture (a specific alcohol and nitrogen) (g adsorbate/g gas mixture)
$F$	flow rate of gas mixture (L/min)
$k$	proportionally constant
$k'$	rate constant ( $\text{min}^{-1}$ )
$P$	probability of adsorbate breakthrough
$q$	uptake (g adsorbate/g adsorbent)
$Q$	probability of adsorbate adsorption on the adsorbent
$t$	time (min)
$t_b$	time required for the solute in the effluent concentration to reach the breakpoint concentration (min)
$W$	adsorbent weight (g)
$W_c$	weight of adsorbent (g)
$W_e$	total adsorption capacity (g)

### Greek letters

$\rho_a$	density of gas mixture (g/L)
$\tau$	time required for 50% contaminant breakthrough (min)

### Subscripts

A	component A
0	initial condition

VOC adsorption in the presence of water vapor are also rare in the literature.

It is noted that the temperature kinetic plot, the thermal wave scheme [10], or the method of the breakthrough curve [11] are applicable to interpretation of the dynamic adsorption behavior of VOCs in an adsorption bed. The information obtained from thermal wave experiments only reveals the amount of heat released and the adsorptive behavior as a function of time. Compared to the thermal wave method, the method of the breakthrough curve provides both information on the mass transfer zone and dynamic adsorption data [12], which are useful for designing an adsorber [13–15]. Therefore, the method of breakthrough curve was adapted in this study and used to evaluate the adsorption performance of alcohols onto zeolite 13X under different gas flow rates and feed concentrations. The results can further understanding of the mechanisms of adsorption behavior on the adsorbent and its capabilities in alcohol adsorption under various operating conditions.

An empirical model for column adsorption was developed by Yoon and Nelson [16,17]. It is a simple model and can simulate the breakthrough curves well. Hung et al. [18] used modified activated carbon cloth to adsorb VOCs and found a good fitting with Yoon and Nelson's model. In this study, Yoon and Nelson's model was examined in a system using the sorbent zeolite 13X.

## 2. Theory

Yoon and Nelson [16,17] assumed that some gas molecules are adsorbed onto activated sites and others pass through the activated sites when a gas stream flows through a stationary bed of activated carbon. Yoon and Nelson further proposed that the decreasing rate of the probability of adsorption for each molecule is proportional to the probability of adsorbate adsorption,  $Q$ , and probability of adsorbate breakthrough,  $P$ . It can be written as

$$-\frac{dQ}{dt} \propto QP \quad (1)$$

From experimental evidence, the rate of decrease in the probability of adsorption is directly proportional to the contaminant concentration ( $C$ ) and the flow rate of the gas stream ( $F$ ), and inversely proportional to the weight of the adsorbent ( $W_c$ ). Thus

$$-\frac{dQ}{dt} \propto \frac{CF}{W_c} QP \quad (2)$$

The number of activated sites is proportional to the weight of the adsorbent ( $W_c$ ) and the adsorption capacity of the adsorbent ( $W_e$ ). Given a proportionality constant,  $k$ , Eq. (2) becomes

$$-\frac{dQ}{dt} = k \frac{CF}{W_e} QP \quad (3)$$

Since  $Q = 1 - P$ , Eq. (3) can be rewritten as

$$\frac{dP}{dt} = k'(1 - P)P \quad (4)$$

where  $k' = kCF/W_e$ . Integrate Eq. (4), and we obtain

$$\ln \frac{P}{1 - P} = k'(t - \tau) \quad (5)$$

where  $\tau$  is the time required to obtain 50% breakthrough. Rearranging Eq. (5), the breakthrough time can be written as

$$t = \tau + \frac{1}{k'} \ln \frac{P}{1 - P} \quad (6)$$

Since  $P = C/C_0$ , Eq. (6) becomes

$$t = \tau + \frac{1}{k'} \ln \frac{C}{C_0 - C} \quad (7)$$

The constant parameters  $\tau$  and  $k'$  are determined from experimental data.

## 3. Experimental

### 3.1. Materials

The adsorbent selected for this study was zeolite 13X (Lancaster Co.) with an average grain size of 1.5 mm. Its surface properties were measured with a BET sorptometer (ASAP2000). The pore volume of the zeolite 13X is  $0.117 \text{ cm}^3/\text{g}$ , the surface area is  $441.34 \text{ m}^2/\text{g}$ , and the average pore diameter is 9.93 nm. The organic solvents (methanol, purity 99.90%; ethanol, purity 99.50%; *iso*-propanol, purity 99.96%) treated as the sources of VOCs were procured from Aldrich Co.

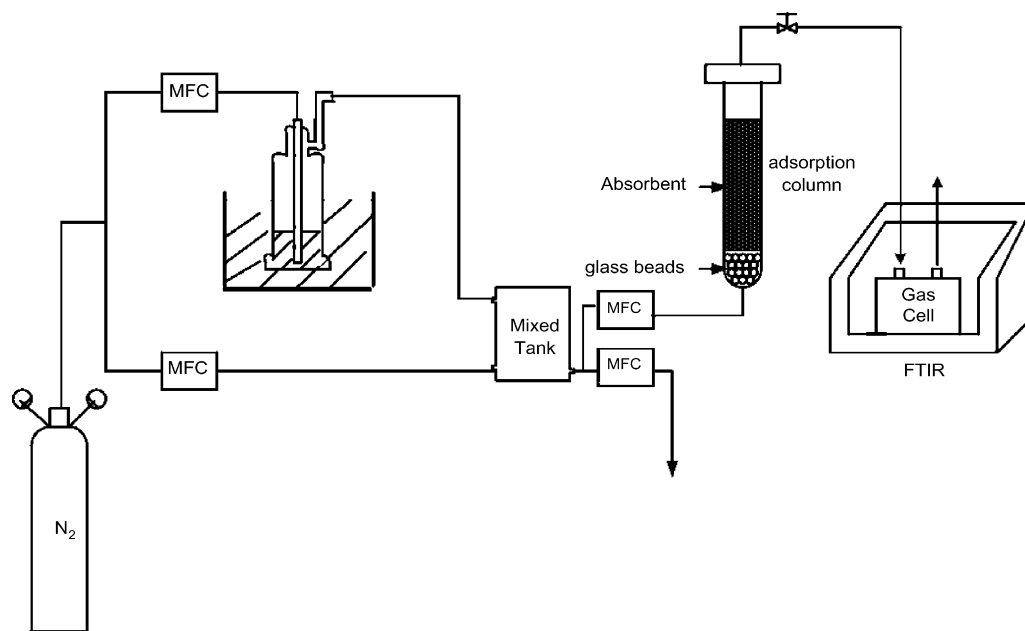


Fig. 1. The flow diagram of this dynamic adsorption system.

### 3.2. Dynamic adsorption process

The schematic diagram of the dynamic adsorption process is shown in Fig. 1. The main system consists of a VOC generator and a packed adsorber. Dried and pure  $N_2$  carrier gases are divided into two flow streams before entering the main system. One stream is connected to an impinger containing the alcohols, and the other is merged to a mixed tank to regulate the initial concentration of alcohols. The impinger is placed in a constant-temperature ( $20^\circ\text{C}$ ) water bath to prevent temperature perturbation. The flow rates of two gas streams are controlled by mass flow controllers (Brooks Co.) and then merged into a mixed tank to be the inlet gas stream. The stainless-steel packed adsorber is 2.9 cm in diameter and 15 cm in length. The adsorber is first filled with 25 g of glass beads for uniform distribution of the gas stream and then 2 g of zeolite 13X on the top. The adsorption is operated at room temperature. The VOC outlet concentrations are continuously monitored by an FT-IR (Spectrum One C59080, Perkin-Elmer Company) equipped with a constant-temperature gas cell. The 100 mm long stainless steel cell is designed for collecting gas spectra at the elevated temperatures, decomposition studies, and measurements of gas evolving from heated samples. The light path of the gas cell is 100 mm long sealed by two 38 mm IR windows. Gas is introduced into the cell through a high precision stainless-steel valve, and the cell chamber was made to withstand pressures up to 100 psi. The cell features a stainless steel body resistant to most gaseous samples. A deuterated triglycine surface detector (DTGS) at a resolution of  $4\text{ cm}^{-1}$  is used, and each spectrum is obtained from 16 scans at a 1 min interval time. The time-dependent gas concentrations are continuously monitored until the concentration does not change. To eliminate the fluctuation of IR absorbance due to the variation of environmental temperature, the gas cell, as well as all of the pipelines, are thermally insulated. The absorbance of IR

peak height is supposed to be linearly proportional to the concentration of the VOC according to Beer's law [19]. As a result, the breakthrough curve can be obtained by plotting the peak absorbance with respect to time.

Before each experimental run, dry and pure  $N_2$  was purged through the adsorption column as well as the IR gas cell to drive off the residual VOCs and water vapor. Zeolites, regenerated at  $120^\circ\text{C}$  for 10 h under vacuum, were sequentially packed into the column with glass beads. A constant inlet concentration of VOC was regulated by the volumetric flow rate of the dry  $N_2$  (0.2–0.6 L/min) as well as the saturated vapor pressure of the VOC in the liquid impinger. As the various concentrations of stream flowed through the gas cell, time-evolution FT-IR spectra were continuously monitored until the adsorption reached equilibrium (i.e. optical absorbance became constant).

### 4. Results and discussion

In this work, the granular zeolite 13X was loaded into a vertical cell tower. Process air was purged through the tower, giving up its pollutant to the adsorbent. The concentrations of the process air were measured by a gas-phase FT-IR spectrometer. The breakthrough curves with the gas flow rate of 0.6 L/min for methanol, ethanol and *iso*-propanol at various initial concentrations are shown in Fig. 2. The mass transfer zone of the methanol system is narrower than those of the ethanol and *iso*-propanol systems, as shown in Fig. 3. Therefore, the mass transfer resistance for methanol is smaller than that of ethanol or *iso*-propanol, which indicates that the adsorption performance of methanol on zeolite 13X is better than that of ethanol or *iso*-propanol under the same operating conditions.

The alcohols uptakes were obtained by subtracting the weight of adsorbent before and after each adsorption run. In addition, the integrated area under the breakthrough curve was another

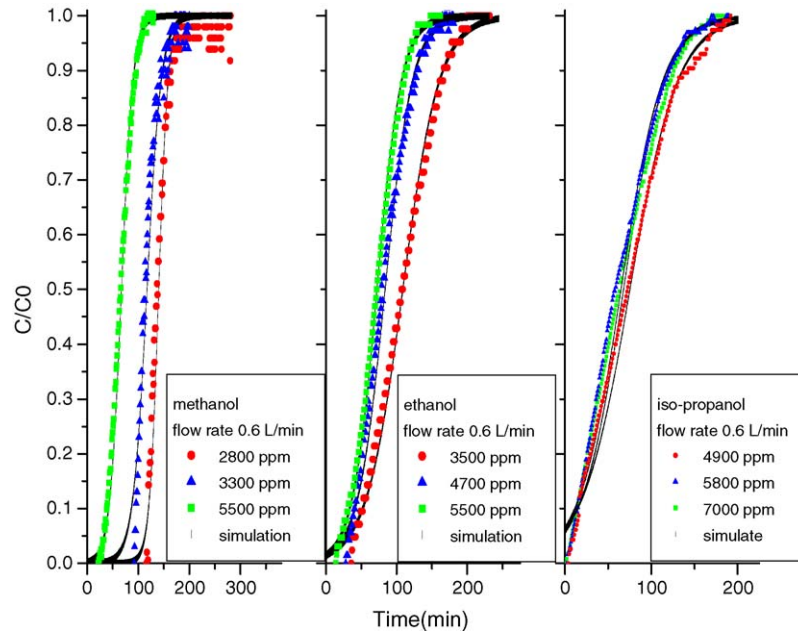


Fig. 2. Influence of the initial concentration on the breakthrough curve.

mean with which to investigate the uptake quantity of alcohols based on the mass conservative concept, which suggested [20]:

$$q = \frac{F \times \rho_a \times C_0}{W} \int_0^\infty \left(1 - \frac{C}{C_0}\right) dt \quad (8)$$

where  $F$  is the gas flow rate,  $\rho_a$  the gas density,  $C_0$  the initial concentration,  $C$  the effluent concentration, and  $W$  is the adsorbent weight.

The product of  $q \times W$  is the adsorptive amount of alcohols by zeolite 13X and can be measured directly from its weight. Once the value of  $q \times W$  is known, the feed concentration,  $C_0$ , is available from Eq. (8). As a consequence, the combination of  $C_0$ ,  $F$ , and the integral area of the adsorptive alcohols gives the uptake amount of each alcohol. However, the integral area is strongly dependent on the breakthrough time, which is usually affected by the operating conditions. As shown in Fig. 2, the breakthrough

time is short, yet the corresponded initial concentration,  $C_0$ , is large. Therefore, the uptake of methanol adsorption onto zeolite 13X is not always higher than those of the other two alcohols. It depends on both the breakthrough time and the initial concentration. Table 1 shows the uptakes of methanol, ethanol, and *iso*-propanol by the zeolite 13X under different initial concentrations.

The breakthrough curves under the selected gas flow rates for methanol, ethanol and *iso*-propanol at concentrations of 7300 or 5500 ppm are shown in Fig. 4. Since the mass transfer resistance is smaller in the methanol system, a narrower mass transfer zone is observed. In addition, the breakthrough time is short when the gas flow rate,  $F$ , is large. The uptakes of the alcohols by the zeolite 13X at different flow rates are listed in Table 2. Results

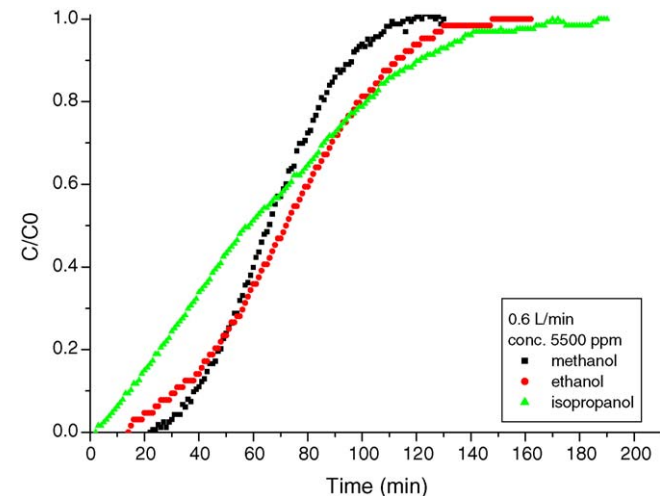


Fig. 3. Comparison of the breakthrough curves for different alcohols.

Table 1  
The uptakes of alcohols at different operating conditions

Pollutants	Flow rate (L/min)	Concentration (ppm)	Uptake (g/g zeolite)
Methanol	0.2	5500	0.138
	0.4	5500	0.134
	0.6	5500	0.149
	0.6	3300	0.137
	0.6	2800	0.140
Ethanol	0.2	5500	0.135
	0.4	5500	0.149
	0.6	5500	0.140
	0.6	4700	0.139
	0.6	3500	0.136
<i>Iso</i> -propanol	0.2	7300	0.153
	0.4	7300	0.150
	0.6	7300	0.154
	0.6	5800	0.133
	0.6	4900	0.130

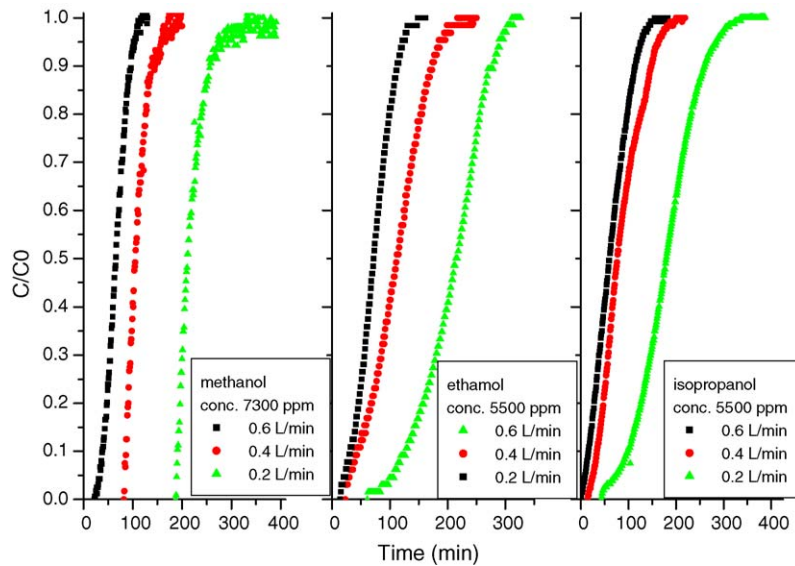


Fig. 4. Influence of the gas flow rate on the breakthrough curve.

Table 2  
Experimental and calculated values of  $\tau$ ,  $t_b$  for alcohols at various concentrations

Pollutants	Concentration (ppm)	$\tau$ (min)		$t_b$ ( $C/C_0 = 0.1$ ) (min)	
		Experimental	Calculated	Experimental	Calculated
Methanol	5500	66	67.1	39	42
	3300	113.5	117.1	96	86.6
	2800	137	140.1	120	120.1
Ethanol	5500	72	72.1	32	33.8
	4700	80.5	83.7	41	40.9
	3500	108.9	108.9	52.5	52
Iso-propanol	7300	63.5	63.2	14	14.6
	5800	58.5	64.9	15	11.6
	4900	73	75.3	16.5	14.4

show that the uptake quantity is dependent on the breakthrough time, initial concentration, and gas flow rate.

The Yoon and Nelson's model fit the experimental data well, as shown in Fig. 2. The simulation curves are a little higher than those of the experimental data. The deviation of  $\tau$  is 0–3.9% and break-time,  $t_b$ , is 0.2–11% except for the case of iso-propanol adsorption at the 5800 ppm initial concentration and the 0.6 L/min flow rate. All deviations are ranged within the

acceptable allowance for engineering applications. The experimental and calculated values of  $\tau$  and  $t_b$  are listed in Table 2. The values of  $k'$  at different feed concentrations are shown in Table 3.

## 5. Conclusions

A dynamic adsorption experimental system was built in this study. The VOC outlet concentrations were continuously monitored by a gas-phase FT-IR equipped with a constant-temperature gas cell. This on-line monitoring method is rare in the open literature and was tested successfully in this study. Based on the results, the gas flow rate and initial concentration have an influence on the breakthrough time and the uptake of alcohols adsorption onto zeolite 13X. The adsorption of methanol onto zeolite 13X has a narrower mass transfer zone. The measurement of dynamic breakthrough curves for VOCs with a gas-phase FT-IR instead of the traditional GC can provide faster responses. It provides a simple and fast way to get the experimental breakthrough curves for the adsorption of various pollutants. Although the selected adsorbent is zeolite 13X, the

Table 3  
Values of  $k'$  at different concentrations

Pollutants	Concentration (ppm)	$k'$ ( $\text{min}^{-1}$ )
Methanol	5500	0.0879
	3300	0.0731
	2800	0.0819
Ethanol	5500	0.0573
	4700	0.0514
	3500	0.0386
Iso-propanol	7000	0.0479
	5800	0.0403
	4900	0.0351

Yoon and Nelson model provides a fair consistency with experimental data, and their deviations are within the acceptable range. Moreover, engineers who are working on the improvement of air quality should also pay attention to the impact of moisture on the adsorbent's performance through the variation of humidity in the atmospheric or working environments. These co-adsorption experiments will be conducted in future studies.

### Acknowledgements

This work was partly supported by the National Science Council under the grant NSC92-2214-E-033-007. The authors wish to express gratitude to Dr. C.K. Liao of Yuan-Ze University for his technical support on the FT-IR.

### References

- [1] T.-W. Chung, T.K. Ghosh, A.L. Hines, D. Novosel, *Sep. Sci. Technol.* 30 (1995) 1807.
- [2] J.A.C. Silva, V.G. Mata, M.M. Dias, J.C.B. Lopes, A.E. Rodrigues, *Ind. Eng. Chem. Res.* 39 (2000) 1030.
- [3] E. Jolimaitre, K. Ragil, M. Tayakout-Fayolle, C. Jallut, *AIChE* 48 (2002) 1927.
- [4] Z.-H. Huang, F. Kang, K.-M. Liang, J. Hao, *J. Hazard. Mater. B* 98 (2003) 107.
- [5] D.W. Breck, *Molecular Sieve Zeolites*, Wiley, New York, 1984.
- [6] T.K. Ghosh, A.L. Hines, *Sep. Sci. Technol.* 26 (1991) 931.
- [7] T.L. Thomas, R.L. Mays, in: W.G. Berl (Ed.), *Physical Method in Chemical Analysis*, Academic Press, New York, 1961.
- [8] A.L. Hines, T.K. Ghosh, S.K. Loyalka, R.C. Warder Jr., *Indoor Air Quality and Control*, Prentice-Hall, Englewood Cliffs, New Jersey, 1993.
- [9] S.Y. Lee, *Adsorption of moisture and indoor pollutants on a mixed-adsorbent*, MS Thesis, University of Missouri Columbia, Missouri, 1997.
- [10] F. Delage, P. Pre, P.L. Cloirec, *J. Environ. Eng.* 125 (1999) 1160.
- [11] T.-W. Chung, C.-C. Chung, *Chem. Eng. Sci.* 54 (1999) 1803.
- [12] A.L. Hines, R.N. Maddox, *Mass Transfer Fundamentals and Applications*, Prentice-Hall, Englewood Cliffs, New Jersey, 1985.
- [13] G.O. Wood, *Carbon* 40 (2002) 1883.
- [14] C.-L. Chuang, P.-C. Chiang, E.-E. Chang, *Chemosphere* 53 (2003) 17.
- [15] T. Cheng, Y. Jiang, Y. Zhang, S. Liu, *Carbon* 42 (2004) 3081.
- [16] Y.H. Yoon, J.H. Nelson, *Am. Ind. Hyg. Assoc. J.* 45 (1984) 509.
- [17] Y.H. Yoon, J.H. Nelson, *Am. Ind. Hyg. Assoc. J.* 45 (1984) 517.
- [18] C.-C. Huang, Y.-C. Lin, F.-C. Lu, *Sep. Sci. Technol.* 34 (1999) 555.
- [19] D.A. Skoog, J.J. Leary, *Principles of Instrumental Analysis*, 4th ed., Saunders College Publishing, New York, 1992.
- [20] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York, 1984.