Adsorption 11: 437–441, 2005

Adsorption Dynamics of Water Vapor on Activated Carbon

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Abstract. The effect of relative humidity on the adsorption of trichloroethylene (TCE) as a representative VOC, was investigated under the practical relative humidity (RH) range of 40–80%. Adsorption equilibria of water and TCE vapors were measured at 293.15, 303.15, and 313.15 K using gravimetric technique. Dubinin-Astakov (DA) and Sips isotherms correlated the measured adsorption data well over the whole pressure range. To investigate the effect of competitive adsorption between water and TCE vapors on hydrophobic activated carbon, adsorption and desorption breakthrough curves were conducted under various humidity conditions in a fixed-bed column. It was found that, under the experimental conditions studied, water vapor in the TCE stream had little effect on the adsorption capacity of TCE up to 80% RH.

Keywords: adsorption, desorption, trichloroethylene, humidity, activated carbon

1. Introduction

Activated carbon has been mainly used for the removal of pollutant vapors from the air. Its capacity and kinetics depend on the nature of adsorbed molecules. In general, non-polar vapors are held within the micropores by dispersion interactions, whereas the adsorption of polar compounds involves oxygen species present at the surface (Cossarutto et al., 2001; Stoeckli et al., 1994). Since the carbon surface is hydrophobic in nature, the dispersion forces have a predominant effect. Water vapor is frequently present at high levels in the atmosphere and may influence the adsorption properties of activated carbon. Loss of adsorption capacity due to high humidity is well known for volatile organic compounds. The influence of water in porous carbon is very complex compared to that of non-polar gases, due to the hydrophobic nature of the carbon surface and the hydrogen-bonded nature of bulk water (Do and Do, 2000). There have been many studies on the adsorption isotherms of water vapor on activated carbon. Contrary to equilibrium studies, however, investigations on the adsorption kinetics and column dynamics of water vapor are very limited, but are very important in assessing the performance of activated carbon column for the adsorption of pollutants (Marban and Fuertes, 2004).

The goal of this study is to understand the competitive adsorption between organic and water vapor mixtures on porous hydrophobic activated carbon. For this purpose, binary adsorption and desorption breakthrough curves of water and trichloroethylene (TCE) vapor mixtures were obtained, under various humidity conditions. Since TCE is widely used in many industries and has the capacity to cause damage to the central nervous system on exposure at high concentration, it was chosen as a representative organic adsorbate for our study.

2. Theoretical Approach

In order to simulate the competitive adsorption behavior of TCE and water vapor mixtures in a fixed-bed,

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Table 1. Mathematical model for a fixed-bed column.

1. Material balance	2. Linear driving force approximation (LDFA) model
$-D_L \frac{\partial^2 c}{\partial z^2} + v\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{1-\varepsilon_B}{\varepsilon_B}\rho_s \frac{\partial q}{\partial t} = 0$	$\frac{\partial q}{\partial t} = k_s \cdot (q^* - q)$
3. Pure component adsorption isotherms	
$W = W_0\left[\exp\left(-\frac{A}{\beta \cdot E_0}\right)^n\right]$ (DA)	$q = \frac{q_m b P^n}{1 + bP^n}$ (Sips)

a simple dynamic model was developed. The governing model equations are listed in Table 1. The adsorption model was solved numerically by applying the orthogonal collocation method to discretize the equations (Lee et al., 2004a; Shim et al., 2003b, 2004). The discretization of the spatial variable, resulted in a set of ordinary differential equations with the adsorbate concentrations as the dependant variable. These equations are solved on a personal computer using a FORTRAN Compiler in double precision and using LSODI of the international Mathematics and Science Library (IMSL).

3. Experimental

An activated carbon (DY-GAC, Korea) was used as the adsorbent material in this study. The surface area of the activated carbon used was 1170 m^2/g. The pore size (0.32 nm) and pore volume (0.45 cm^3/g) were determined by nitrogen desorption data. Prior to use, the samples were kept in a drying vacuum oven at 423 K for more than 24 h to remove impurities. Adsorption equilibrium data were measured using gravimetric technique with a quartz spring balance as shown in Fig. 1 (Lee et al., 2003; Shim et al., 2003a). The vapor of water and TCE was generated in a small chamber that was maintained at a constant temperature. The adsorption amount was measured by a quartz spring balance, which was placed in a closed glass system. Adsorbent amount of 0.1 g was placed on the dish, which was attached to the end of the quartz spring. Adsorbent samples were weighed with an accuracy of $\pm 10\ \mu g$. The variation of mass was measured by a digital voltmeter that was connected to the spring sensor. Prior to adsorption, all adsorbents were evacuated to 1×10^{-3} Pa for 15 h at 523.15 K. The high vacuum system composed of a turbomolecular pump (Edward type EXT70) and a rotary vacuum pump (Edward model RV5). Pirani and Penning vacuum gauges (Edwards Series 1000) were used for the measurement of vacuum. The pressure was measured using a Baratron absolute pressure transducer (MKS instruments type 127), allowing measurements from 0 to 133 kPa with the reading accuracy of ±0.15% and a power supply read out instrument (MKS type PDR-C-1C). During adsorption, the adsorption cell was placed in a temperature controlled water bath with a circulator at a constant temperature (variation of ±0.02 K). Adsorption isotherms were obtained by admitting successive increments of sample gas to the adsorbent sample. The adsorption equilibrium was usually attained within 30–50 min. Adsorption amounts of TCE and water on activated carbon were measured at temperatures of 293.15, 303.15, and 313.15 K.

On the other hand, adsorption and desorption breakthrough curves for pure and binary components were

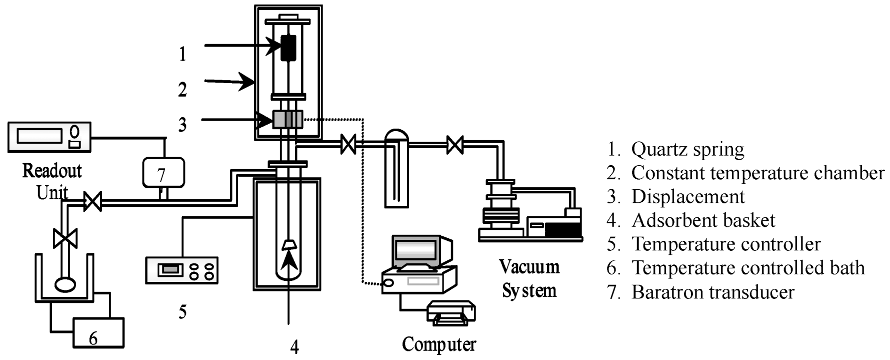

Figure 1. Schematic diagram of equilibrium apparatus.

obtained in a fixed-bed column charged with activated carbon. The concentration of TCE was determined using a gas chromatography (Shimadzu GC-14B, Japan), equipped with a hydrogen flame ionization detector. The concentration of water vapor was determined using hygrometer (TCEPCL-332, Taiwan).

4. Results and Discussion

Isotherms play a crucial role in model prediction and design of adsorption and desorption processes (Lee et al., 2004a; Lee et al., 2004b; Oh et al., 2003; Do and Do, 2000). The adsorption equilibrium data of TCE and water vapor on activated carbon were obtained at 293.15, 303.15 and 313.15 K. The adsorption isotherms of water and TCE were found to be Type V and Type I, respectively, according to the IUPAC classification. Figure 2 shows a unique temperature-independent characteristic curve of water and TCE. The Nelder-Mead simplex method was used for the determination of isotherm parameters based on minimizing the sum of the square of the residues (SOR) (Lee et al., 2004b). The determined DA isotherm parameters are listed in Table 2.

The adsorption and desorption kinetics under various humidity conditions were examined. The kinetics of water vapor at lower relative humidity was faster, while it was found to be slower at higher ranges (40–70%). This difference in the kinetic pattern results from the different adsorption mechanism with respect to the relative humidity. These results are not shown here for brevity.

Table 2. Estimated DA isotherm parameters of TCE and water on activated carbon as a function of temperature.

	Temperature	W_0	E_0		
Adsobate	K	mmol g^{-1}	kJ mol^{-1}	n	SOR
TCE	293.15	4.794	9.800	2.65	6.44×10^{-1}
	303.15	4.271	10.699	3.43	5.70×10^{-2}
	313.15	3.686	11.798	4.37	2.93×10^{-2}
Water	293.15	13.405	8.792	2.98	1.01
	303.15	13.457	7.407	3.21	3.76
	313.15	13.319	3.023	2.49	4.89

The regeneration of activated carbon columns pre-adsorbed with water (Fig. 3(a)) and TCE (Fig. 3(b)) was examined by the adsorption of TCE and water vapor, respectively. Prior to regeneration, the column was saturated with water by passing a feed stream at 45% RH through the column, until the RH of the effluent stream was also 45% (Fig. 3(a)). Then, a feed stream containing TCE (1 kPa) was introduced. Results indicated that water desorption could be easily achieved by TCE adsorption (Fig. 3(a)), and also TCE was easily replaced by water adsorption at relatively low RH 45% (Fig. 3(b)). Adsorption breakthrough curve of TCE had a typical pattern (S-shape), while that of water was unusual, due to the different adsorption isotherm patterns of TCE (Type I) and water (Type V). The solid lines in Fig. 3 are the predicted results of adsorption and desorption breakthrough curves by the proposed dynamic model. A good agreement between experimental and predicted results can be observed.

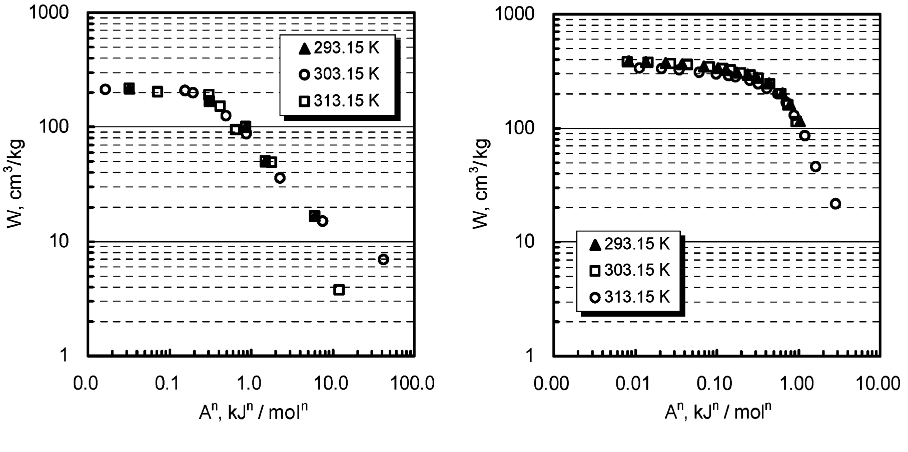

Figure 2. Characteristic curves of water (left) and TCE (right) vapors.

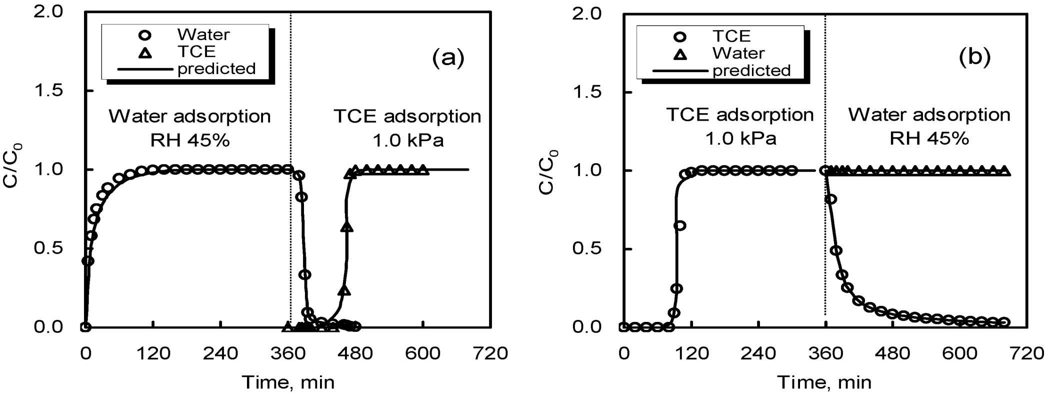

Figure 3. Adsorption and desorption breakthrough curves of water and TCE vapor on activated carbon.

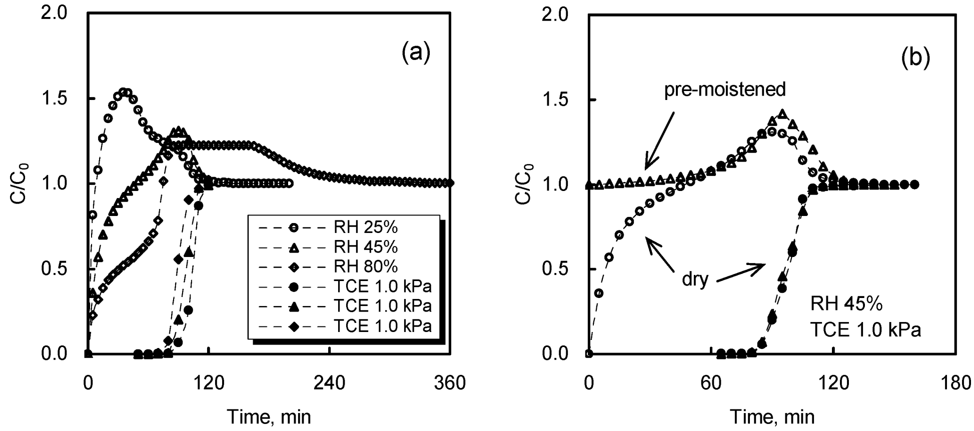

Figure 4. Binary adsorption breakthrough curves of water and TCE vapor mixtures on dry and pre-moistened activated carbon.

Figure 4 shows the adsorption and desorption breakthrough curves of TCE and water vapor mixtures on dry and pre-moistened activated carbon. In order to examine the influence of RH on the adsorption capacity of TCE, breakthrough curves were obtained on dry activated carbon for three different conditions of RH (25, 45, 80%) containing the same amount of TCE concentration (1 kPa) as shown in Fig. 4(a). Results showed that adsorption capacity of TCE was almost independent of RH up to the investigated RH of 80%. However, breakthrough patterns of water were quite unusual with increasing RH. Figure 4(b) compares the binary adsorption breakthrough curves of TCE (1 kPa) and water vapor (RH 45%) mixtures both on dry and on pre-moistened (RH 45%) activated carbon. Adsorption capacity of TCE was almost equal regardless of whether the activated carbon was pre-moistened or dry.

Figure 5(a) displays binary adsorption and desorption breakthrough curves of water and TCE vapors. Coadsorption of TCE-water mixtures consisting of a constant RH containing different TCE feed concentrations (0.5, 1, 2 kPa) was examined in pre-moistened (45% RH) activated carbon column. It was found that the breakthrough time for water vapor was shortened and the rate of adsorption clearly increased with TCE concentration. On the other hand, activated carbon column saturated with different TCE concentration was easily regenerated using water adsorption (45% RH), regardless of TCE loading, even though the regeneration time was longer. To further understand the influence of the extent of pre-moistened activated carbon on the competitive adsorption of TCE-water vapor mixtures, binary adsorption and desorption breakthrough curves were obtained (Fig. 5b). Prior to adsorption, activated carbon was pre-moistened with different amounts of water vapor (25, 45, 55% RH). Then, water-TCE mixtures consisting of different RH (25, 45, 55%) and constant TCE concentration (1 kPa) were evaluated. The

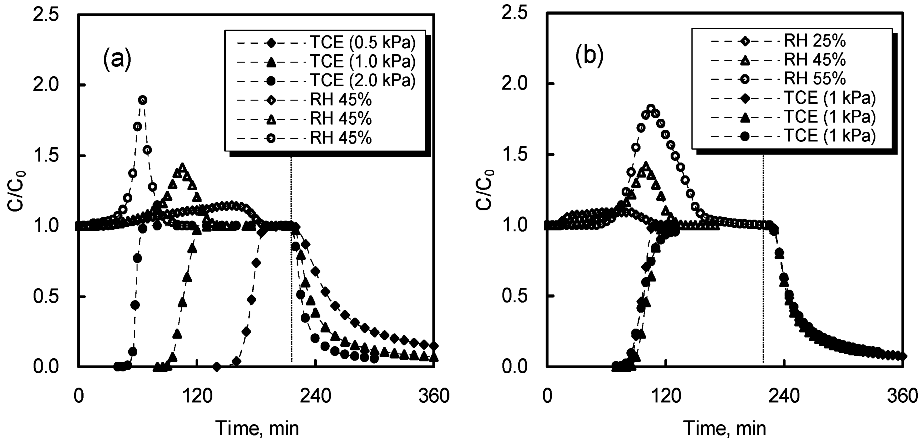

Figure 5. Binary adsorption and desorption breakthrough curves of water and TCE vapor mixtures on pre-moistened activated carbon (open symbols (water); closed symbols (TCE)).

shape of roll-up curves corresponding to desorption rate of water was steeper with increasing RH. Desorption rate was almost similar for RH 45 and 55%, whereas it was quite different at RH 25% without changing of TCE loading. Regardless of pre-moistened conditions investigated here, TCE adsorption capacity was almost equal and activated carbon loaded with TCE could be easily regenerated by water adsorption at relatively low RH of 45%.

5. Conclusion

Pure component equilibrium data of water and TCE shows Type V and Type I isotherms, respectively. The adsorption data were well fitted with DA equation. The kinetics of water vapor at lower relative humidity was faster, while at higher ranges (40–70%), it was found to be slower. This difference in the kinetic pattern results from the different adsorption mechanism with respect to the relative humidity. Experimental results of competitive adsorption of water and TCE indicated that adsorption capacity of TCE was almost equal, regardless of whether activated carbon was dry or pre-moistened up to 80% RH. Especially, activated carbon loaded with TCE could be easily regenerated by water adsorption at low RH of 45%.

Acknowledgment

This work was supported by grant No (R-01-2001-000-00414-0 (2003)) from the Korea Science & Engineering Foundation.

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