활성탄 충전층에서 1,1,2-trichloro-1,2,2-trifluoroethane의
흡착특성에서 상대습도의 영향

<u>김태영</u>*, 정성태, 김용미, 박기민, 김승재[1], 조성용
전남대학교 환경공학과, [1]전남대학교 환경연구소
(tykim001@chonnam.ac.kr*)

The Effect of Relative Humidity on Adsorption Characteristics of 1,1,2-trichloro-1,2,2-trifluoroethane onto Activated Carbon Bed

<u>T.Y.Kim</u>*, S.T.Jeng, Y.M.Kim, G.M.Park, S.J.Kim[1], S.Y.Cho
Department of Environment Engineering, Chonnam Nat'l. University,
[1]Environment Research Institute, Chonnam Nat'l. University
(tykim001@chonnam.ac.kr*)

Introduction

   In recent years, the adsorption process of removing and recovering organic solvents in trace levels from air has attracted special interests as a means of protecting the environment from air pollution. Volatile organic compounds(VOCs) are a family of carbon containing compounds which are emitted or evaporated into the atmosphere where they participate in photochemical reactions. Some VOCs are toxic and carcinogenic. Most VOCs for varying degrees, contribute to the formation of ground level ozone. The VOCs which may cause stratospheric ozone depletion are mostly a chlorine-containing group of compounds known as chloroflourocarbons or CFCs. They release chlorine and other halogens into the stratosphere gradually. These compounds are particularly effective in destroying the ozone even when present in small quantities. VOCs are used as solvents in manufacturing of countless products. Some prominent examples of these products include crystallized organic chemicals, printed materials, paints and coatings and dry-cleaning agents in magnetic tape and semiconductor manufacturing facilities. One consequence of these manufacturing operations is that large amounts of organics are being emitted to the atmosphere. VOCs have been implicated as a major contribution to photochemical smog, which can cause haze, damage to plant and animal life, and eye irritation and respiratory problem. Several technologies can be used for recovering VOCs from gaseous wastes but one of the most important and effective methods for controlling the emission of VOCs is the adsorption process. Temperature swing adsorption using an activated carbon bed is probably the most common adsorption cyclic process for the separation of strongly adsorbed species. It has been widely used in industries for removal and recovery of hydrocarbon and solvent vapors. In this work, the removal of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) was studied theoretically and experimentally.

Mathematical Model

A mathematical model was developed, which takes into account the non-ideality of adsorbable species in the adsorbed phase under equilibrium. Applying the typical assumptions [Hwang, 1994], and taking the mass balance of the gas phase in a packed bed, the following governing equation for isothermal adsorption is obtained:

$$\frac{\partial c_i}{\partial t} = D_L \frac{\partial^2 c_i}{\partial z^2} - v \frac{\partial c_i}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \rho_p \frac{\partial q_i}{\partial t} \tag{1}$$

In Eq. (1), the gas-solid mass transfer rate can be expressed as the following linear driving force (LDF) model for surface diffusion :

$$\frac{\partial q_i}{\partial t} = k_s(q_i^* - q_i) = \frac{3k_f}{r_p \rho_p}(c_i - c_i^*) \tag{2}$$

where

$$k_s = \frac{15D_s}{r_p^2} \tag{3}$$

As denoted by Eqs. (2) and (3), the LDF model is an approximation to the solution of Fickian diffusion inside a spherical particle. The expression assumes that the mass transfer rate of adsorption is proportional to the difference between the equilibrium concentration and the bulk concentration of the component. Since the solution of the LDF model is much simpler than the solution of a diffusion model, we employed this model in the present study. By introducing appropriate dimensionless variables, Eq. (1) can be written as follows:

$$\frac{\partial \zeta_i}{\partial \tau} = \frac{1}{\beta} \frac{\partial^2 \zeta_i}{\partial S^2} - \frac{\partial \zeta_i}{\partial S} + \alpha_i(\zeta_i - \zeta_i^*) \tag{4}$$

and the dimensionless variables are defined as follows:

$$\zeta_i = \frac{c_i}{c_{i0}}, \tau = \frac{vt}{L}, S = \frac{z}{L}, \beta = \frac{vL}{D_L}, \alpha_i = \frac{3k_f L}{r_p v}\left[\frac{1-\varepsilon}{\varepsilon}\right] \tag{5}$$

The associated initial conditions for $0 < z < L$ is

$$\zeta_i(z, 0) = 0 \tag{6}$$

and the boundary conditions at $z = 0$ and $z = L$ for t>0 are:

$$\frac{1}{\beta}\frac{\partial \zeta_i}{\partial S}\Big|_{z=0} = -(\zeta_i|_{z=0^-} - \zeta_i|_{z=0^+}) \tag{7}$$

$$\frac{\partial \zeta_i}{\partial S}\Big|_{z=L} = 0 \tag{8}$$

Result

The gravimetric method is a well established technique for obtaining adsorption equilibria of pure gases and vapors. 0.1g of activated carbon in the quartz basket is ventilated to remove impurities within the activated carbon at 503K for approximately 4hr using a vacuum pump. Adsorption amounts are measured at different temperatures of 303K, 318K, and 333K. The adsorbent used for this experiment is Norit B4 and the adsorbates is CFC-113. The adsorption equilibrium data were obtained using a high-pressure microbalance. Isotherms of CFC-113 onto the activated carbon at three different temperatures are shown in Fig. 1. As Shown in this Figure, The isotherm of CFC-113 was favorable type and adsorption amount increased with decreasing temperature. Single-species isotherm data were correlated by well-known Langmuir,

Freundlich and Sips equations. The parameters of each isotherm were obtained by the least square fitting with experimental data. These parameters and the average percent differences between the measured and calculated values are given in Table 1. Among these isotherms, the Sips equation is more appropriate in predicting our data compared to the Langmuir or Freundlich isotherms.

Fig. 2 illustrates the effect of inlet concentration on experimental breakthrough curves for CFC-113. The breakthrough time decreases with the increase of inlet concentration. The result can be explained by the concept of the mass transfer zone (MTZ) velocity. The velocity of MTZ is a function of interstitial velocity, particle density, bed porosity, and the slope of the equilibrium isotherm. For a linear isotherm adsorption system, the velocity of MTZ is constant. Therefore the breakthrough time is not affected by inlet concentrations at constant MTZ velocity. However, the adsorption isotherm of CFC-113 on activated carbon is favorable as shown in Figure 1. As the inlet concentration increases, the value of slope of the equilibrium isotherm decreases and the MTZ velocity increases. Therefore, the breakthrough time becomes shorter under this circumstance.

Fig. 3 shows the effect of bed height on the CFC-113 adsorption. The breakthrough curves for different bed heights are similar in shape. Since the breakthrough curve retains a constant pattern, it may be interpreted that the adsorption zone has a constant length.

Fig. 4 shows that the breakthrough curves of relative humidity onto activated carbon. As show in this Figure, breakthrough time of CFC-113 onto activated carbon decreased with increasing relative humidity. Since the humidity adsorbed onto activated carbon was occupied adsorption site, so breakthrough curves with humidity faster than that of dry air stream.

Reference

1. Kim, T. Y., Jeng S. J., Kim, J. H., Kim, S. J. and Cho, S. Y., J. Ind. Eng. Chem, **10**, 4, 2004
2. Kim, S. J., Kim, T. Y., Kim, S. J. and Cho, S. Y., Korean J. Chem. Eng., *19*, 6, 2002
3. Kim, T. Y., Kim, S. J. and Cho, S. Y., Korean J. Chem. Eng., *18*, 5, 2001

Table 1. Adsorption equilibrium isotherm parameters of CFC-113 onto Activated carbon

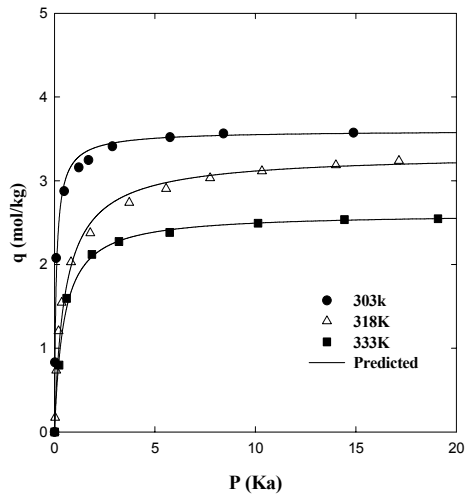| Temp. [K]	Langmuir		Freundlich		Sips		
	q_m	b	k	n	q_m	b	n
303	3.48	5.76	2.64	5.18	3.60	8.79	1.13
Error(%)	3.4		17.9		3.8		
318	3.12	2.59	2.04	5.42	3.33	1.75	1.09
Error(%)	3.8		4.3		3.2		
333	2.69	1.89	1.51	4.38	2.6	2.17	1.01
Error(%)	3.3		4.55		2.5		

Fig. 1. Adsorption equilibrium isotherm of CFC-113
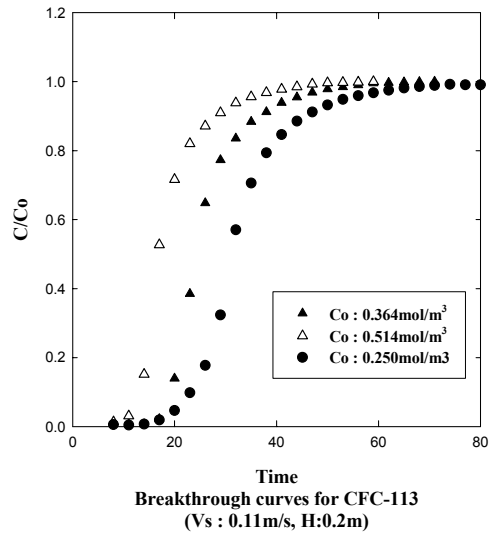

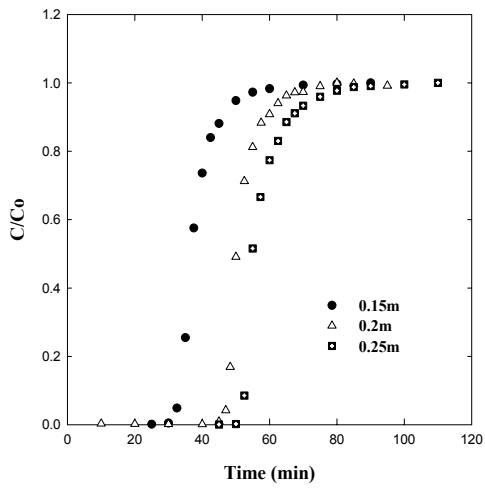Fig. 2. Effects of initial concentration on breakthrough curves of CFC-113 (Vs : 0.11m/s, H:0.2m)

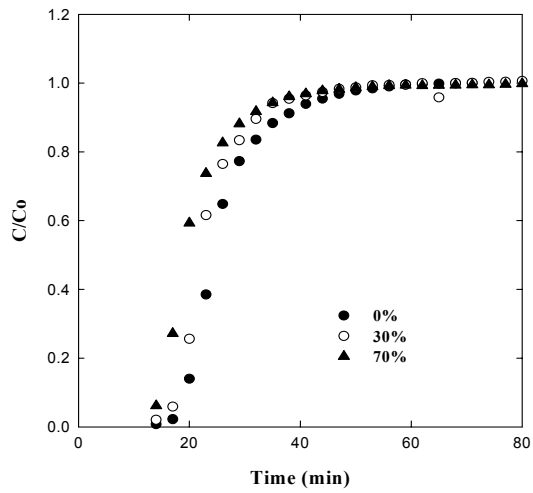Fig. 3. Effects of bed height on breakthrough curves of CFC-113 (Vs:0.11m/s, Co:0.364mol/m^3)

Fig. 4. Effect of relative humidity on breakthrough curves of CFC-113 (Vs:0.11m/s, H:0.2m, Co:0.364mol/m^3)