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Adsorption Characteristics of Trichloroethylene and 1,1,1-Trichloroethane onto Activated Carbon Fiber in Gaseous Phase

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Trichloroethylene (TCE) and 1,1,1-trichloroethane (methylchloroform:MC) are major volatile chlorinated hydrocarbons, and the production amounts of these compounds run up to about 80,000-100,000 tons a year in Japan.

TCE and MC were observed in groundwater in Japan as well as in the United State, so that the environmental contamination by these compounds became a serious problem (Nakamuro 1986, Westrich *et al* 1984).

TCE and MC cause vertigo, headache, drunkenness and fatigue depending on central nervous system depress, and also liver or kidney lesion by inhalation as general toxicities (Ikeda 1980).

For prevention of the poisoning to workers, the permissible concentrations of TCE and MC vapors in work area have been set at 50ppm and 200ppm, respectively by Japan Association of Industrial Health. In the United Statrs, those values are set at 100ppm and 350ppm by American Conference of Governmental Industrial Hygienists, respectively (Ikeda 1980).

In addition, TCE is considered to be carcinogenic because it cause liver cancer in mice (Nakamuro 1986). Furthermore, MC is considered to destroy the Ozone Layer. Though it is presumed that 40-70% of used TCE and MC in factories is exhausted to the atmosphere, there is no regulatyion now concerning the exhaustion of TCE and MC to the atmosphere. So that regards should be paid to the intake of TCE and MC from the atmosphere as well as from drinking water (Urano *et al* 1988).

In this paper, we studied the adsorption removal of TCE and MC by activated carbon fibers (ACFs) in gaseous

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phase pointing to the prevention against TCE and MC diffusion to the atmosphere and inhalation to workers.

MATERIALS AND METHODS

ACF A-10, A-15 and A-20 supplied from Osaka gas Co., Ltd. were used as adsorbents. Special grade of TCE (99.5%) and MC (95%) were obtained from Wako Pure Chgemical Ind.

The adsorption isotherms of TCE and MC onto ACF were determined in an all-glass vacuum system. The equilibrium amounts adsorbed at relative pressure up to 0.8 were measured by a gravimetric method by using a B.E.T. apparatus with a spring balance. The specific surface area and the pore size distribution of ACF were measured with a B.E.T. apparatus by a volumetric method using super high purity nitrogen gas at its boiling temperature (Brunauer *et al* 1938, Dollimore and Heal 1964).

RESULTS AND DISCUSSION

Physical properties of ACFs are listed in Table 1. The specific surface area and the pore volume became larger according to the grade number of ACFs, but only A-10 had the micropores of less than 7.5Å in radius.

Table 1. Physical Properties of ACFs.

	specific surface	pore volume (ml/g)		
ACF	area (m^2/g)	r<7.5Å	r<20Å	r<100Å
A-10	918.1	0.256	0.446	0.510
A-15	1432.1	0.000	0.778	0.828
A-20	1754.0	0.000	0.875	0.924

Figure 1 shows the adsorption isotherms of TCE (Fig.1-a) and MC (Fig.1-b) at 20°C. The amounts of TCE and MC adsorbed onto A-20 were largest. The amounts of TCE and MC adsorbed became larger according to the grade numbers of ACFs, and the amounts adsorbed onto A-20 were about twice of those onto A-10 in the range above 0.5 of relative pressures. The amounts of TCE adsorbed were larger than those of MC onto all ACFs.

With lower temperature, the amounts of TCE and MC adsorbed were large. The maximum values of the isosteric differential heats of TCE and MC adsorption

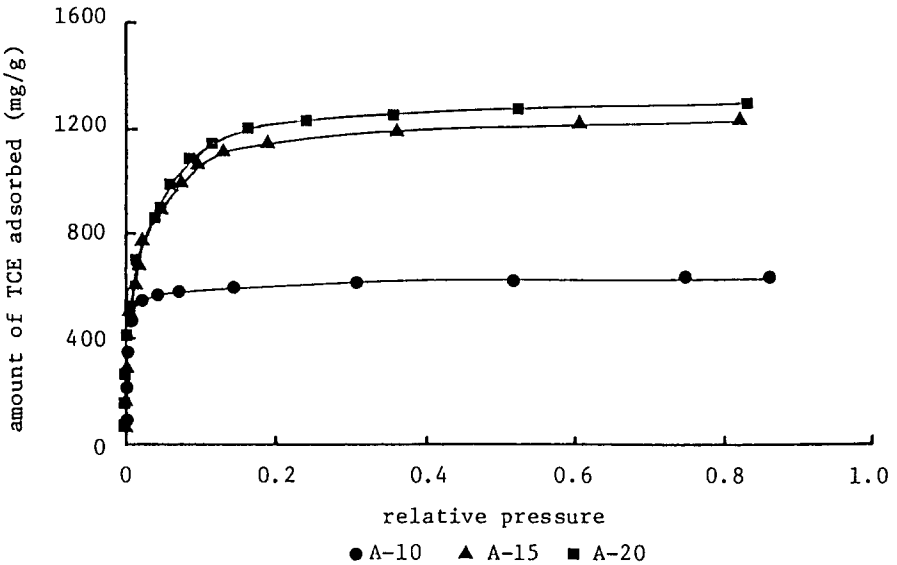

Figure 1-a. Adsorption Isotherms of TCE onto ACFs at 20°C.

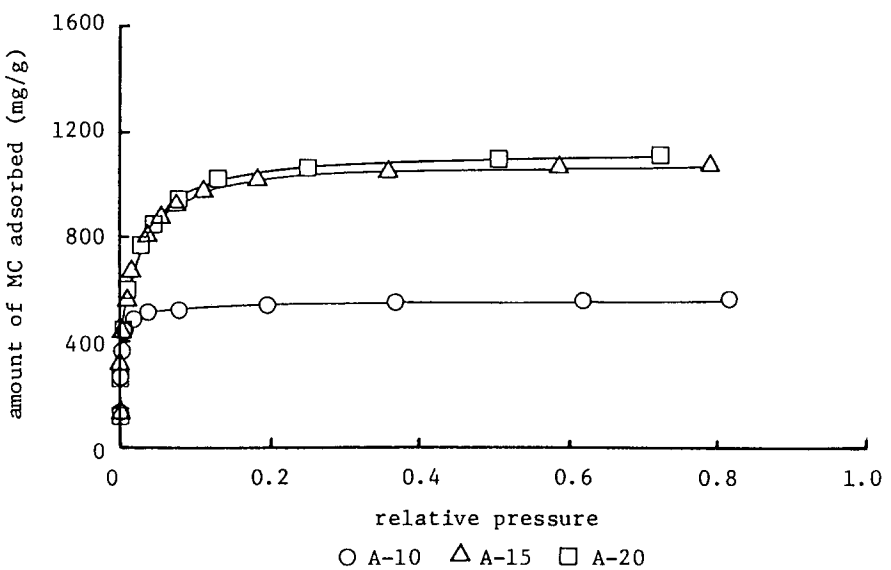

Figure 1-b. Adsorption Isotherms of MC onto ACFs at 20°C.

of A-20 were both about 20 kcal/mol, and this value was smaller than about 3 times as large as the condensation heats of TCE (31.5 kcal/mol) and MC (7.95 kcal/mol). Therefore, the adsorption of both TCE and MC onto ACFs were considered to be physical adsorption.

The physical adsorption of a gas into pores can be described by a theoretical model of the volume filling of pores. The Dubinin-Radushkevich (D-R) equation can be strictly applied only to homogeneous system of micropores. The D-R equation is expressed by following formula (marsh and Rand 1970),

$$W=W_0 \exp[-(A/\beta)^2]$$
$$A=[\ln(Ps/Pe)]\ RT$$

where W is the amount adsorbed at relative pressure Pe/Ps (ml/g), W_0 is the limiting volume of adsorption space (ml/g), R is the gas constant (1.987 cal/K mol), T is the absolute temperature, A is the decrease of free energy of adsorption (cal/mol) and is the similarly coefficient (ratio of molar volume of adsorbate to molar volume of benzene).

Figure 2 shows the D-R plots of the adsorption isotherms of TCE (Fig.2-a) and MC (Fig.2-b) onto ACFs. The D-R plots of A-15 and A-20 were straight lines and corresponded to type A in the classification of Rand (1976). On the other hand, the D-R- plots of A-10 were not straight lines and did not corresponded to any classification of Rand. The amounts of TCE and MC adsorbed onto A-15 and A-20 were larger than those onto A-10 at high pressures, while at very low pressures, the amounts adsorbed onto A-15 and A-20 were smaller than those onto A-10.

By differentiating the D-R equation in the logarithmic form, following equation was obtained.

$$-dW/d(A/\beta)=2W_0\,(A/\beta)\exp[-(A/\beta)^2]$$

Figure 3 shows the distributions of W with A/β for the adsorption of TCE (Fig.3-a) and MC (Fig.3-b). Experimental $-dW/d(A/\beta)$ distributions were obtained by the differentiation of the characteristics curves of W versus A/β. The maximum distributions of A-15 and A-20 located at A/β 1.6-2.4 (TCE) or 1.4-2.0 (MC), while those of A-10 located around A/β 4.6 (TCE) or 3.6 (MC).

The $-dW/d(A/\beta)$distribution is considered to be the qualitative measure of pore size distribution of very small micropores (Rand 1976, Boki *et al* 1987). Therefore, the results indicated that TCE and MC were adsorbed almost into the micropores of small values of D/d (D:pore diameter; d:molecular diameter, TCE=5.0A, MC=4.2A) with higher free energy of adsorption in A-10.

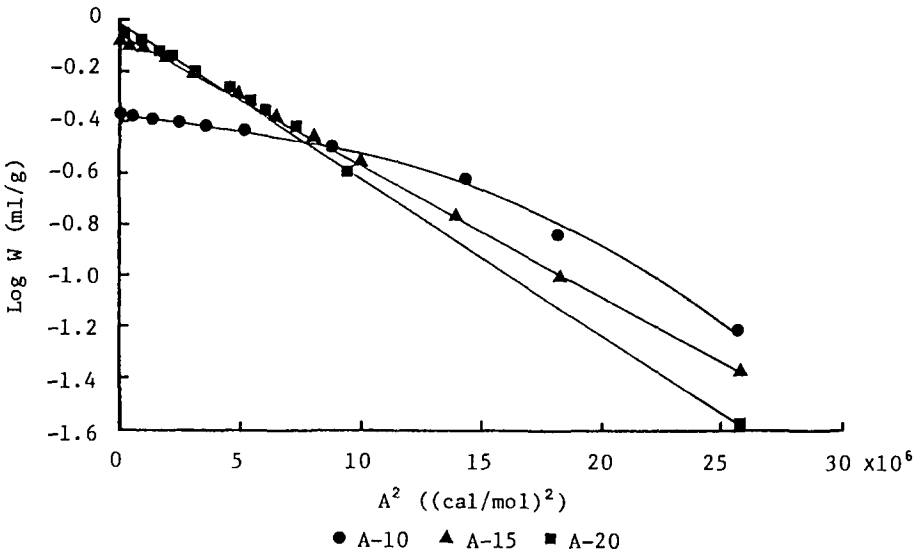

Figure 2-a. Dubinin-Radushkevich Plots of Adsorption Isotherms of TCE onto ACFs.

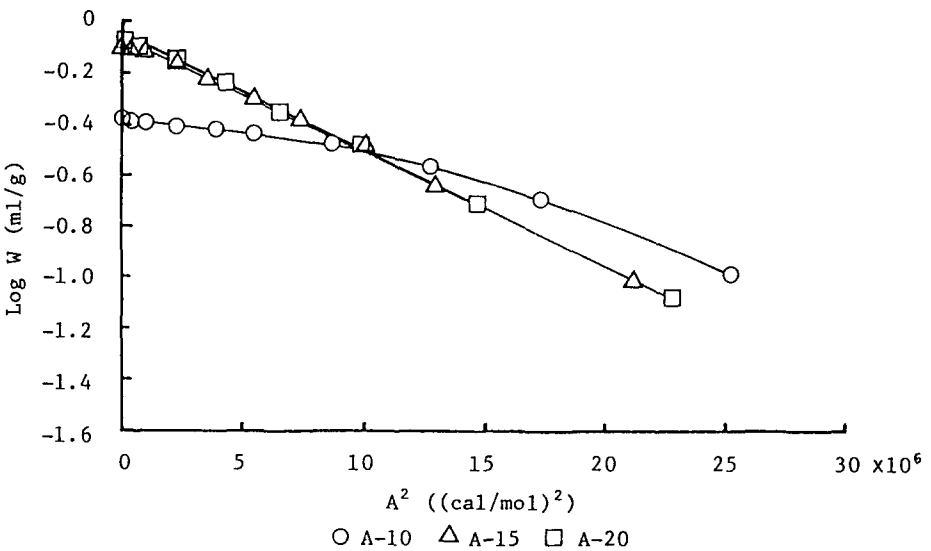

Figure 2-b. Dubinin-Radushkevich Plots of Adsorption Isotherms of MC onto ACFS.

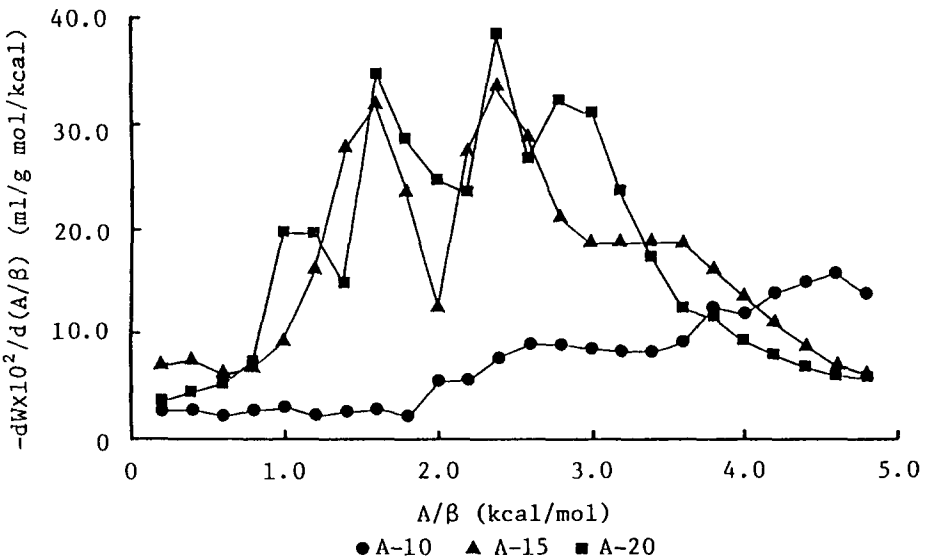

Figure 3-a. Comparison of Distribution of W with A/β for the Adsorption of TCE onto ACFs.

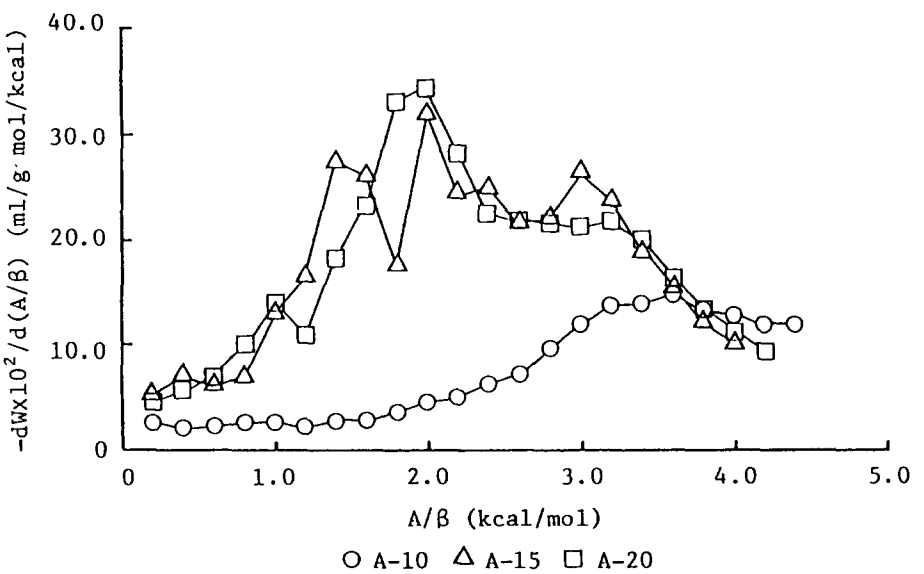

Figure 3-b. Comparison of Distribution of W with A/β for the Adsorption of MC onto ACFs.

While in A-15 and A-20, TCE and MC were adsorbed both in micropores of small values of D/d and in transitional pores of larger values of D/d.

Comparing the $-dW/d(A/\beta)$ distributions of TCE with those of MC, it was recognized that TCE was adsorbed into smaller pores than MC, though molecular diameter of TCE is larger than that of MC. This result is considered to be due to the hydrophobicities of TCE and MC [the solubilities of TCE and MC into water are 1.10 g/l (25°C) and 1.32 g/l (20°C), respectively], and the surface of ACF is hydrophobic.

The limiting volume of adsorption, W_0 was estimated by extrapolation of the intercept to $A^2=0$ of regression lines described in Figure 2 [in the case of A-10, regression lines in the range up to $A^2=10\times10^6$ (TCE) or $A^2=12\times10^6$ (MC) were used] by the least squares method. W_0 and the ratios of W_0 to the micropores volume W_{20} are listed in Table 2.

Table 2. Limiting Volume of Adsorption Space (W_0) and Ratios of W_0 to Micropore Volume of ACFs.

ACF	TCE-W_0 (ml/g)	$\frac{\text{TCE-}W_0 \times 100}{W_{20}*}$ (%)	MC-W_0 (ml/g)	$\frac{\text{MC-}W_0 \times 100}{W_{20}*}$ (%)
A-10	0.428	96.0	0.415	93.0
A-15	0.883	114.5	0.847	136.2
A-20	0.964	110.2	0.891	109.6

* W_{20} : pore volume of less than 20 Å in radius.

In the case of A-10, W_0 was smaller than W_{20}. But in the cases of A-15 and A-20, W_0 was larger than W_{20}. From the results, it was concluded that most parts of TCE and MC were adsorbed only in micropores (less than 20A in radius) in the case of A-10, while they were adsorbed both in micropores and in transitional pores. This conclusion was consistent with the results of the $-dW/d(A/\beta)$ distributions and the pore size distributions of ACFs.

It was suggested that A-10 having very small pores was more suited for removing TCE and MC at very low pressures with the view of prevention against the inhalation of TCE and MC to workers in work area, while A-15 and A-20 having large pore volumes at higher pressures with the view of prevention of the air pollution by TCE and MC.

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