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Interaction between Methylchloroform and Surface Modified Activated Carbon in CF_4 Plasma

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The interaction between methylchloroform and a surface modified activated carbon, which was treated with tetrafluoromethane plasma, was evaluated on the basis of adsorption isotherms and physicochemical properties of the activated carbon. Tetrafluoromethane plasma-treated activated carbon could be used for the complete recovery of methylchloroform.

Global environmental pollution has reached an extremely serious stage. One of the most serious issues is the depletion of the ozone layer by chlorofluorocarbons (CFCs). 1,1,1-Trichloroethane (Methylchloroform) deplets the ozone layer. International agreements have been enacted to protect the ozone layer by regulating the release of chlorine atoms from compounds such as CFCs and halons. These chemicals are regulated by the ozone depletion potential (ODP).[1−4] Methylchloroform has an atmospheric lifetime of about 8 years and an ODP of 0.12. It is due to be phased out in 1996. A large quantity of methylchloroform has been used in industrial fields for a number of years and methylchloroform will be used until the year 2005. There is an urgent need for the recovery of the methylchloroform with minimal environmental impact. Recently, plasma treatment has become attractive, probably due to it being a dry process done at low temperature at a relatively low pressure gas.[5)] Tetrafluoromethane plasma-treated activated carbon has a hydrophobic surface. Hence, recovery efficiency of methylchloroform by plasma-treated activated carbon may be higher than that using untreated activated carbon. It is considered that methylchloroform molecule is first adsorbed to the fluorine group on the activated carbon surface. For the pilot recovery of methylchloroform, the adsorption isotherms of methylchloroform on tetrafluoromethane plasma-treated activated carbons were investigated.

Untreated activated carbon (U-AC) was obtained from Takeda Chemical Ind. Co., Ltd., Shirasagi G,. Japan. Details of the inductively coupled plasma apparatus have been previously described.6) U-AC (10.0 g) was placed in the plasma container, degassed for 2 h at 0.01 Torr (1Torr =133.322 Pa) and then stirred for 15 min at 110 ℃. The pressure of 0.5 Torr was maintained by adjusting the tetrafluoromethane flow rate. The other plasma treatment conditions were as follows: plasma treatment time is 15 min, frequency of electric discharge was 13.56 MHz, and output power was 40 W(PT-AC1), 60 W(PT-AC2), or 80 W(PT-AC3) (the maximum output power of this plasma apparatus is 100 W).

Table 1. Specific surface area, equi acid-base point, and number of adsorbed water molecules per unit surface area

Sample	Surface Area / $m^2 g^{-1}$	Equi Acid-Base Point	Number of Adsorbed Water Molecules / nm^{2-1}
U-AC	1120	8.4	0.577
PT-AC1	1020	3.6	0.478
PT-AC2	1070	3.6	0.378
PT-AC3	1110	3.5	0.782

The specific surface area, the equi acid-base point, and the number of adsorbed water molecules per unit surface area are shown in Table 1. The surface area was calculated using the B.E.T. equation used for nitrogen adsorption isotherms. The number of adsorbed water molecules per unit surface area was calculated by using the specific surface area and moisture adsorption isotherm. The equi acid-base point was measured as follows: approximately 0.1 g of activated carbon was put into 100 ml of deionized water, boiled for 5 min, and filtered. The pH of the solution was measured with a pH meter (Horiba Ltd., Kyoto, Japan).

The specific surface area of the PT-ACs was 0.5(PT-AC3) −9.0(PT-AC1)% smaller than that of U-AC. The surface pH of PT-ACs was smaller than that of U-AC. Ohte et al.7) reported that three types of fluorine groups are introduced by tetrafluoromethane plasma treatment: 1) the covalent bond type, insoluble in water and stable to heat, 2) the layer interstitial type, insoluble in water and unstable to heat, and 3) the adsorption type, soluble in water and unstable to heat. Hence, on the surface of the PT-ACs, weak fluorine-carbon bonds are formed, and on the interstitial layer and in the pores of the PT-ACs, strong fluorine-carbon covalent bonds are produced. It was concluded that the decreasing surface pH of PT-ACs was caused by dissolved fluorine. The number of adsorbed water molecules per unit surface area was then divided by the amount adsorbed as a monolayer by the specific surface area calculated from the nitrogen adsorption isotherms. The water adsorption showed that the tetrafluoromethane plasma treatment produced a more hydrophobic activated carbon except for PT-AC3. The number of hydrophilic groups of PT-AC3 was more than that of U-AC. The fluorine groups of only the covalent bond type are hydrophobic.8) It is considered that this result is due to the different type of fluorine groups introduced by the tetrafluoromethane plasma treatment because of the lower surface pH.

The adsorption isotherms of methylchloroform onto U-AC and the PT-ACs at 20 ℃ are shown in Fig. 1. The difference in the amount of methylchloroform adsorbed between U-AC and the PT-ACs was found to be due to the equilibrium pressure of less than 2 Torr. Since the fluorine groups were introduced on the tetrafluoromethane plasma treated activated carbon, the methylchloroform molecules were more easily adsorbed on the fluorine groups.

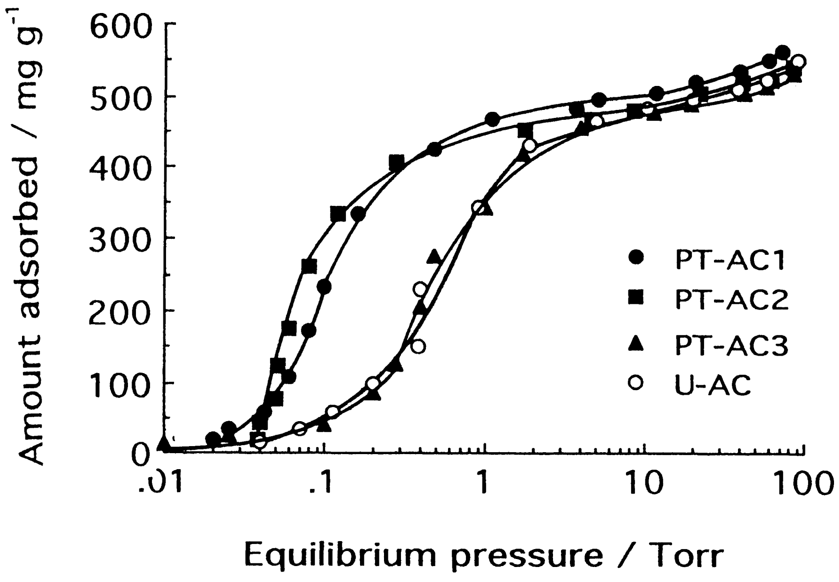

Fig. 1. Adsorption isotherms of methylchloroform onto U-AC and the PT-ACs at 20 ℃.

Table 2. Constants Wo and B of Dubinin-Radushkevich (D-R) plots

Sample	Constant Wo a)	Constant B b)
U-AC	0.396	0.022
PT-AC1	0.383	0.014
PT-AC2	0.405	0.012
PT-AC3	0.399	0.026

a) Wo, The limiting volume of the adsorption space (ml g^{-1}).

b) B, The affinity coefficient ($\times 10^{-6}$).

The activated carbon characteristics included a wide micropore volume distribution. The physical adsorption can be described by a theoretical model describing the volume filling of pores. The Dubinin-Radushkevich (D-R) equation ($W=Wo \cdot \exp[-(A/B)^2]$, $A=RT \cdot \ln(Ps/Po)$) can be strictly applied to a homogeneous system of micropores.[8)] The constants Wo and B of the D-R equation indicated the limiting volume of the adsorption space and the affinity coefficient, respectively. The D-R plots of methylchloroform adsorption isotherms onto U-AC and the PT-ACs are linear at equilibrium pressures of more than 1 Torr (correlation coefficient, 0.970 – 0.978). The D-R equation Wo and B constants are shown in Table 2. The Wo value does not change for the activated carbons, while the B value does. The relative standard deviation (R.S.D.) of Wo on U-AC and the PT-ACs is 2.03%, while that of B is 30.9%. These results indicated that the methylchloroform was adsorbed by specific adsorption sites, that is, the fluorine groups of the covalent bond type on the activated carbon surface.

It is concluded that: (1) the amount of methylchloroform adsorbed was increased with plasma treatment at a low equilibrium pressure, (2) the methylchloroform adsorbed selectively to fluorine groups of the only covalent type on the activated carbon surface, and (3) the interaction between methylchloroform and the activated carbon surface changed due to tetrafluoromethane plasma treatment.

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