Effect of Various Fluoride Atom Species of Activated Carbon in CF_4 Plasma on Recovery of Trichloroethylene

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The surface modification of activated carbon using low temperature plasma of tetrafluoromethane was investigated to evaluate the removal of trichloroethylene. The plasma-treated, activated carbon underwent an immersion water and/or heat-treatment. The adsorption isotherms of trichloroethylene onto the activated carbons were measured to elucidate the relationship between the adsorption behavior of trichloroethylene and the introduced fluoride atoms. The trichloroethylene adsorption sites on plasma-treated, activated carbon are related to the fluoride atom species of the adsorption type, that is, the ion type.

Activated carbon is used in various industrial fields, such as solvent recovery, gas separation, catalysts, fractionation, purification, and deodorization.[1] Its properties include a large internal surface area, porosity, and hydrophobic surface. Recently, one method for its surface preparation is a plasma treatment[2] has become attractive. We have reported the characteristics of surface modified activated carbon by tetrafluoromethane plasma-treatment[3] and the recovery of the volatile halogenated hydrocarbons using plasma-treated activated carbon.[4,5] Ohte *et al.*[6] reported that surface modified carbon fibers using tetrafluoromethane plasma treatment revealed the following three types of fluorines introduced by plasma treatment: 1) covalent bond type, 2) layer interstitial type, and 3) adsorption type. The fluoride atom species of the covalent bond type is insoluble in water and stable to heat. The interstitial layer type is insoluble in water and unstable to heat. The adsorption type is soluble in water and unstable to heat. The presence of less fluorine on the surface of an activated carbon modified to the hydrophilic adsorbents, whereas the presence of more fluorine produced hydrophobic adsorbents.

Trichloroethylene (TCE) is used in large quantities as a solvent or detergent. We considered that TCE has the effect of ozone depletion because of the chloride atom in the TCE molecule and global warming. Therefore, TCE has to be recovered after use. No reports have appeared concerning the effect of fluoride atom species on trichloroethylene adsorption onto tetrafluoromethane plasma-treated, activated carbon. In the present study, we have investigated the adsorption characteristics of trichloroethylene on plasma treated, activated carbon in terms of the change in the physicochemical properties and adsorption isotherms due to plasma treatment.

The untreated activated carbon (U-AC) produced from nutshells was purchased from Takeda Chemical Industry Co., Ltd., Shirasagi G. Details of the inductively coupled plasma apparatus have been previously described.[7] Basically, approximately 4.0 g of U-AC was placed in the plasma container, degassed for 2 h at 0.01 Torr. The treatment time is for 15 min at 110 ℃. A pressure of 0.5 Torr was maintained by adjusting the tetrafluoromethane flow rate. The frequency of electric discharge was 13.56 MHz and the output power was 40 W (PT-AC) (the maximum output power of this plasma apparatus is 100 W). The PT-AC underwent immersion in water (IW-AC), heat treatment (HT-AC), or heat treatment and then immersion in water (HIW-AC). IW-AC was immersed in 500 ml of water for 14 days and then dried in a vacuum dessicator for 14 days. HT-AC was heated at 110 ℃ for 24 h. HIW-AC was treated using the combined methods. The specific surface area and pore volume distribution of the activated carbons were calculated from the B.E.T. equation and Dollimore and Heal method[8] used for the nitrogen adsorption isotherms, respectively. These details have been previously described. [7] The fluoride ion was determined by standard methods of analysis for hygienic chemists, that is, the lanthanum alizarin complexone method. Ten ml of immersion water was put into a 50 ml colored tube and 1 ml of alizarine complexone solution was added, followed by 20 ml of acetone in a 50 ml colored tube for a total volume of exactly 50 ml. The performed fluoride ion was measured at maximum wavelength of 420 nm using a Hitachi spectrophotometer U-1100 (Hitachi, Ltd., Tokyo, Japan).

Table 1. Specific surface area and pore volume distribution of activated carbon

Sample	Specific surface area	Pore volume distribution r < 20.5 Å	r > 20.5 Å
	$m^2 \bullet g^{-1}$	$ml \bullet g^{-1}$	
U-AC	1120	0.463	0.102
PT-AC	1020	0.423	0.082
IW-AC	1120	0.462	0.125
HIW-AC	930	0.368	0.119

The specific surface areas and the pore volumes of the activated carbons (U-AC, PT-AC, IW-AC, HT-AC, and HIW-AC) are shown in Table 1. The specific surface area slightly decreased with plasma-treatment. Hence, the surface of the activated carbon was etched by $F\bullet$ ($\bullet$ denotes a radical), $CF_3\bullet$, $CF_2\bullet$, $CF\bullet$, CF_3^+, CF_2^+, CF^+, C^+, F^-, C_2F_4, and C_2F_6 produced from the tetrafluoromethane plasma. We reported the structural analysis of the plasma-treated, activated carbon with treatment period.[3] The specific surface area and the total pore volume decreased with plasma-treatment. The specific surface area of IW-AC was as same as that of U-AC. Therefore, the fluoride atom introduced by plasma-treatment was liberated from the surface of plasma-treated, activated carbon when immersed in water. The heat treatment of PT-AC was available for fixing a fluoride ion onto the surface of the activated carbon, because the specific surface area of HIW-AC was the smallest of all carbons. It is evident that the tetrafluoromethane plasma-treatment affects the microporous structure of the activated carbon.

The pore volume of U-AC, PT-AC, IW-AC, and HIW-AC was determined using the Dollimore and Heal method from the nitrogen adsorption isotherm up to a relative pressure of 0.95. Pores with widths below 20 Å are described as micropores, those above 200 Å are macropores, and those with widths between 20 and 200 Å are called transitional pores. The adsorption behavior of the organic compounds onto the activated carbon depends on the physical properties of the adsorbents in the gaseous phase. Hence, the estimation of fine structure is very important. The pore volume of PT-AC was smaller than that of U-AC. Therefore, the fluoride atoms introduced onto the surface of the plasma-treated, activated carbon is seemingly responsible for decreasing the pore volume. The pore volume having a radius less than 20.5 Å on U-AC was the same as on IW-AC and that more than a radius of 20.5 Å on IW-AC was larger than a radius of U-AC because of washing. It is considered that decreasing the pore volume of HIW-AC was caused by the fixation or disappearance of the fluoride atoms on the surface of the activated carbon by heating.

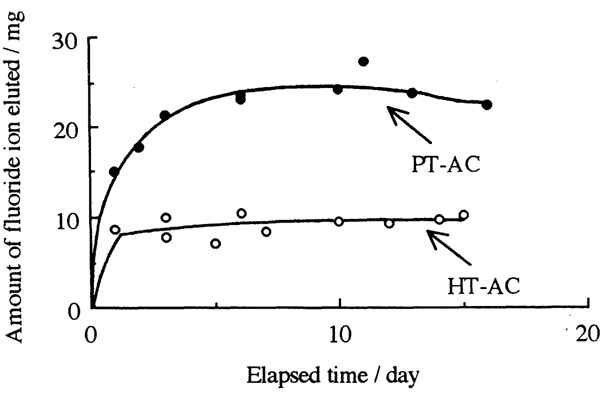

Figure 1. Amount of fluoride ion eluted from PT-AC and HT-AC with elapsed time.

The concentration of soluble fluoride ions on the plasma-treated, activated carbon versus elapsed time is shown in Figure 1. That of PT-AC increased after seven days of immersion. These results were compatible with that of Ohte *et al.*. That for HT-AC first increased, and then remained constant. The results indicated that 15 mg • g^{-1} of fluoride atom species disappeared and/or were fixed by heat-treatment at 110 ℃ for 24 h from PT-AC. The surface of the PT-AC provided fluoride atoms due to tetrafluoromethane plasma-treatment. There are only a few fluoride atoms on the surface of HIW-AC. These fluoride atoms were eluted within a couple of days.

We reported the effectiveness of plasma treatment for the recovery of methylchloroform and the adsorption properties of trichloroethylene onto the plasma-treated, activated carbon.[4] It shed light on the fluoride atom which increased the amount of adsorbed methylchloroform. Ohte *et al.* reported that the fluoride atoms of only the covalent bond type are hydrophobic. Therefore, it is postulated that the adsorption site of methylchloroform on plasma -treated, activated carbon was the fluoride atoms of the covalent bond type.[4] The adsorption isotherms of TCE onto U-AC, PT-AC, and HT-AC are shown in Figure 2. The amount of TCE adsorbed onto PT-AC and HT-AC was larger than that onto U-AC. That onto PT-AC and HT-AC was similar. It is assumed that the adsorbed amount was not influenced by the heat treatment of PT-AC. The adsorption isotherms of TCE onto U-AC, IW-AC, and HIW-AC are shown in Figure 3. The amount of TCE adsorbed onto HIW-AC was larger than that of U-AC and IW-AC. That onto U-AC and IW-AC was similar. Hence, we thought that the fluoride atom on the surface of the plasma-treated, activated carbon was fixed to the surface of the activated carbon for heating. The fluoride atoms of the adsorption type on the plasma-treated, activated carbon influences the increase in the amount of adsorbed TCE.

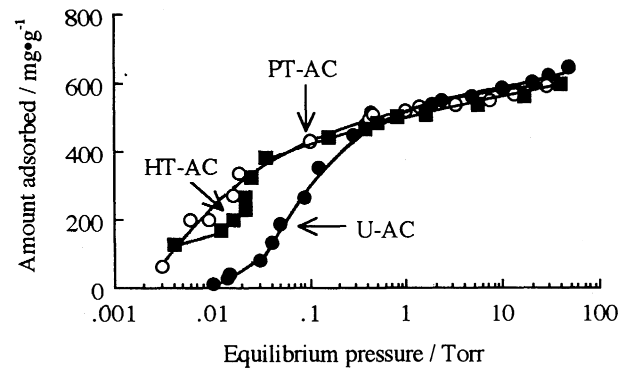

Figure 2. Adsorption isotherms of TCE onto U-AC, PT-AC, and HT-AC at 20 ℃.

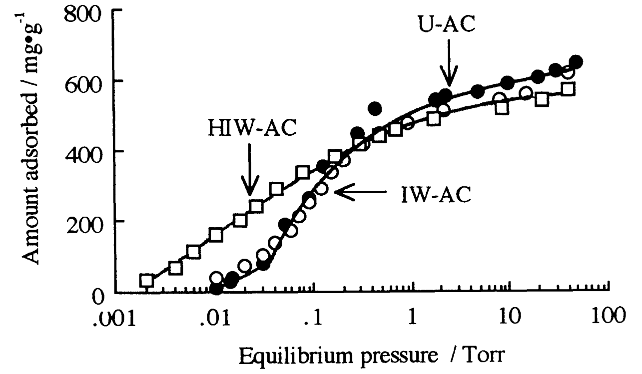

Figure 3. Adsorption isotherms of TCE onto U-AC, IW-AC, and HIW-AC AT 20 ℃.

References and Notes

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