Bull. Environ. Contam. Toxicol. (1997) 59:935-940

Bulletin of Environmental Contamination and Toxicology

Adsorption Characteristics of Trihalomethanes onto Activated Carbon Fiber from Quarternary Mixture Solution

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Received: 30 May 1997/Accepted: 26 September 1997

Chlorination of water has been contributed to prevent people from infectious diseases. In recent years, however, it has been reported that trihalomethanes (THMs) are produced during chlorination in the water purification process (Rook 1974, Bellar *et al* 1974, Bunn *et al* 1975). THMs in water are not readily decomposed biologically and THMs are believed to be carcinogenic (Thompson *et al* 1974, Schwetz *et al* 1974). Then the safety of the drinking water supply is in question.

In Japan, the Basic Environment Law was promulgated to comprehensively and systematically promote policies for environmental conservation to ensure a healthy environment in November of 1993. In article 16 of the law, the criteria for air, water, soil pollution, and noise were set by the Ministry of Health and Welfare of Japan. The maximum allowable level of total THMs in drinking water was established at 0.1mg/L. The levels for individual THMs, that for chloroform, bromodichloromethane, dibromochloromethane and bromoform were set at 0.06, 0.003, 0.1 and 0.09mg/L, respectively.

The current removal methods for the THMs are boiling, aeration and adsorption, which are effective because of their volatility and hydrophobicity. In the boiling and aeration treatments, the volatile THMs may escape from water merely to cause air pollution. The adsorption onto activated carbon effectively removes organic compounds from water. Activated carbon fiber (ACF), which is a new type of functional activated carbon, has been developed and its application to the field of environmental science is expected.

In this investigation, we studied the adsorption characteristics of THMs onto ACF from mixture solution for the safety of drinking water.

MATERIALS AND METHODS

THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) standard solution and purified water for the measurement of THMs (Wako Pure

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Chem. Co. Ltd.) were used. Quarternary mixture solution was prepared by mixing THM standard solution of same concentration and amount. Two kinds of ACFs (A-10, A-20) supplied from Osaka Gas Co. Ltd. Before use, ACF was washed in purified water. Then it was dried at 110°C for 48 hours and kept in a desiccator.

The specific surface area and the pore size distribution of ACFs were measured with a B. E. T. apparatus (Shibata P-700) using nitrogen gas at its boiling temperature (- 196°C) (Brunauer *et al.* 1938, Dollimore & Heal 1964). The base consumption of ACF was determined using the acid-base titration method (Boehm & Voll 1970). The surface pH was measured according to the method of Urano *et al.* (1976). The heat of immersion for water was determined with a twin conduction type microcalorimeter (Tokyo Riko TIC-22). The conditions for measuring of immersion were as follows: temperature, 25°C; weight of sample, approximately 20mg.

The amount of THM adsorbed was measured by isothermal run. A constant weight of ACF was precisely weighed out and placed in brown vials of 50 mL in volume. Quarternary mixture solution diluted with purified water was added the vial. Immediately, the vials were sealed up with Teflon sheet, butyl-gum septum and aluminum seal. After the vials were shaken at 25°C for 48 hours, they were allowed to stand at the same temperature. The equilibrium concentrations of THMs in the vials were measured by the head space method on a gas chromatograph equipped with an ECD (Hitachi 263-30). A glass column of 3m in length and 3mm in diameter was used. The packing used was silicone DC-550 on chromosorb WAW-DMCS. Super high purity nitrogen gas (99.999%) was used as carrier, at the flow rate of 50mL/min. The temperature of injection, column oven and detector were 250, 80 and 250°C, respectively.

RESULTS AND DISCUSSION

The physical properties of ACFs are indicated in Table 1. Specific surface area and pore volume of A-20 were about twice of those of A-10.

Table 1. Physical Properties of Activated Carbon Fibers.

ACF	specific surface area (m^2/g)	pore volume (mL/g) $r < 20$ Å	$r < 100$ Å
A-10	918.1	0.446	0.510
A-20	1754.0	0.846	0.904

The chemical properties of ACFs are indicated in Table 2. The base consumption of A-20 was greater than that of A-10. The surface pH of A-10 was neutral and that of A-20 was slightly acidic. It is assumed that A-20 has more acidic groups on the surface. The heat of immersion for water of A-20 was about 1.5 times larger than that of A-10. It is estimated that the surface of A-10 was more hydrophobic than A-20.

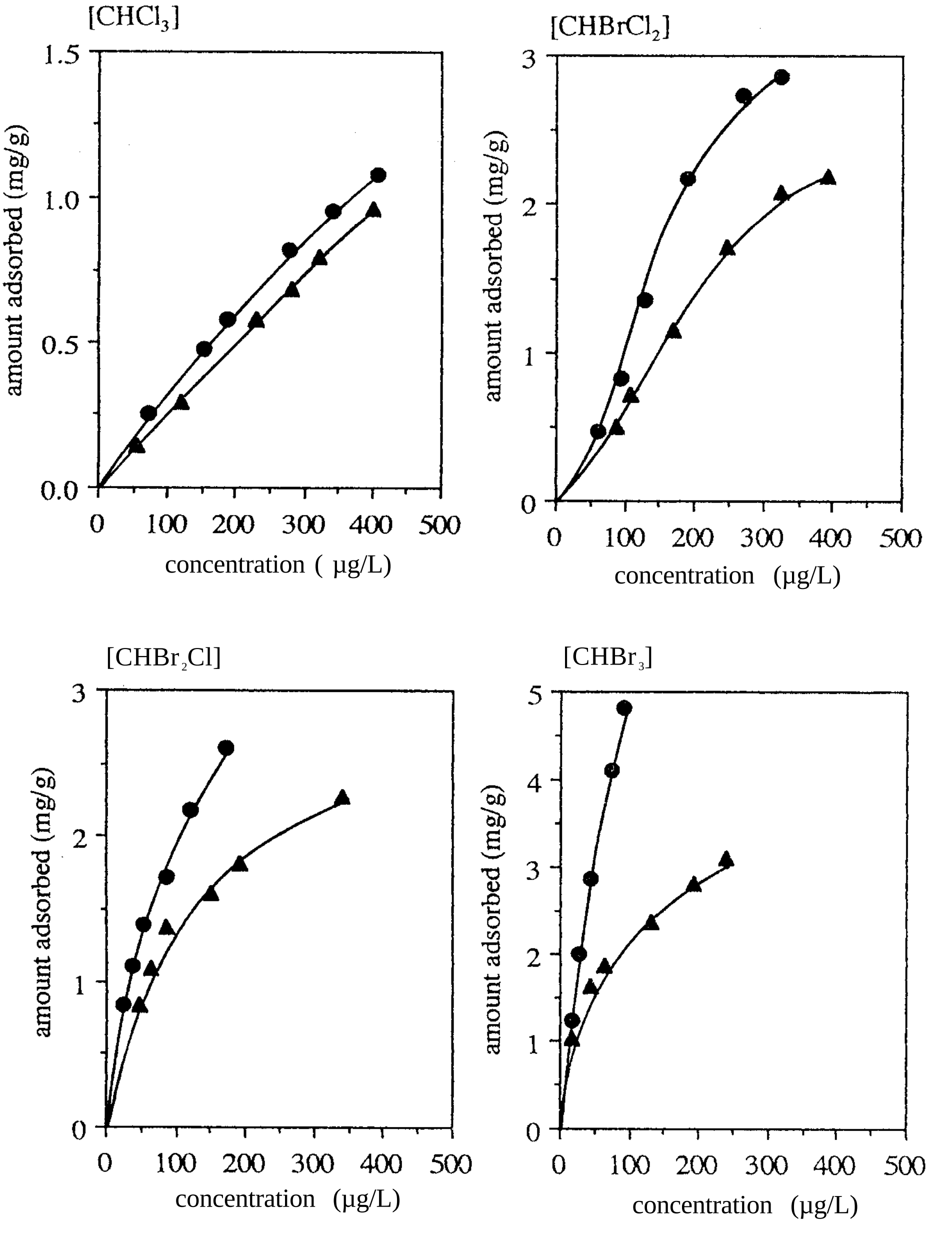

Figure 1. Adsorption Isotherms of THMs onto ACFs from Quarternary Mixture Solution. ●: ACF-10, ▲: ACF-20.

Table 2. Chemical properties of Activated Carbon Fibers.

ACF	base consumption (mEq/g)	surface pH	heat of immersion for water (J/g)
A-10	0.37	7.1	41.7
A-20	0.45	6.3	63.5

Figure 1 shows the adsorption isotherms of THMs from quarternary mixture solution. From the values of physical properties of adsorbents, it was estimated that A-20 should absorb large amounts of THMs. However, the amounts adsorbed were opposite that predicted by the physical properties.

The amounts of THMs adsorbed by weight per weight of ACF at 100μg/L of equilibrium concentration calculated from Freundlich equation are listed in Table 3. The amounts of THMs adsorbed onto A-10 were 1.6 times (chloroform), 1.6 times (bromodichloromethane), 1.5 times (dibromochloromethane) and 2.3 times (bromoform) larger than those onto A-20, respectively.

Table 3. Amounts of THMs Adsorbed at 100mg/L.

	amount adsorbed (mg/g)			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
A-10	0.41	0.72	1.99	5.25
A-20	0.25	0.45	1.33	2.33

The amounts of THMs adsorbed by millimolarity are listed in Table 4. The amount adsorbed onto A-10 was larger than that onto A-20. The difference between the amount adsorbed onto A-10 and A-20 was same as the case of the amount adsorbed by weight per weight of ACF. It was recognized that the THM with more bromine was easily adsorbed onto ACFs rather than the THM with more chlorine.

Table 4. Amounts of THMs Adsorbed at 100mg/L.

	amount adsorbed (mmol/g)			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
A-10	3.43	4.39	9.55	20.77
A-20	2.09	2.75	6.39	9.22

In general, the adsorption capacity of carbon adsorbent for organic pollutants depends on their physical properties (Giusti *et al.* 1974, Puri *et al.* 1976). And it is known that the existence of surface oxygen groups on the carbon, and the effect of surface oxygen groups on the adsorption characteristics is previously shown (Coughlin & Ezra 1968). Graham (1955) reported that the acidic groups on carbon play a very significant role in adsorption from an aqueous solution.

According to our results, the amount of THMs adsorbed onto ACFs was not affected by the physical properties of adsorbent. This result is similar to the report of Sakoda *et al.* (1987), which showed that the amounts of trichloroethylene and tetrachloroethylene adsorbed were inversely proportional to the specific surface area or pore volume. Moreover, it is reported that the contents of surface oxygen groups on carbon are related to the surface pH (Sugiura *et al.* 1985). Our results, which show that the base consumption of A-20 is larger than that of A-10, and that the surface pH of A-20 is acidic compared to that of A-10, are consistent with the report by Sugiura *et al.* (1985). Then it is estimated that the surface acidic groups are more common on A-20 than on A-10. Moreover, it is assumed that the surface of A-20 is more hydrophilic than that of A-10 from the result of the heat of immersion for water. Therefore, it is concluded that the greater the surface hydrophobicity of ACF, the larger the amount of THMs adsorbed.

The magnitude of adsorption was in the order of: bromoform > dibromochloromethane > bromodichloromethane > chloroform. It was recognized that the THM with bromine was easily adsorbed rather than the THM with chlorine. The electro negativity and electron affinity are 3.0 and 3.61eV for chlorine and 2.8 and 3.36eV for bromine, respectively. That is, it is thought that polarity of chlorine is greater than that of bromine. The polarity of a THM with chlorine would be greater than that with bromine. Therefore, it is concluded that the greater the polarity of the THM, the lower the amount of the THM adsorbed onto ACF.

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