

# Trihalomethanes adsorption on activated carbon fiber

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**Abstract**—The mechanism of activated carbon fiber (ACF) adsorption trihalomethanes (THMs) was studied. It was found that ACF adsorption THMs was exothermic, the physico-adsorption principally, but not a complete monolayer adsorption. The adsorptive capacities of ACF increased as the four species of THMs became more hydrophobic, and as the chlorine atoms in  $\text{CHCl}_3$  were substituted by more bromine atoms. The result of fixed-bed reactor adsorption was fitted to that of isotherm experiments.

**Keywords:** trihalomethanes; adsorption; ACF.

## 1 Introduction

Trihalomethanes (THMs) involving  $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  are observed frequently in chlorinated water (Rook, 1974).  $\text{CHCl}_3$  and  $\text{CHBr}_3$  were proved to cause liver or lung cancer in rats and mice (USNCI, 1977; Theiss, 1977). Granular activated carbon (GAC) adsorption is one of the common treatments carried out presently for controlling THMs in drinking water. However, the adsorptive capacity of GAC was limited, and new type adsorbents with both large adsorptive capacity and adsorptive rate are preferable. Recently developed adsorbent, activated carbon fiber (ACF), may satisfy this demand and may be a promising material for further application. ACF, compared with GAC, has more open micropore on the surface directly and specific surface areas (Zeng, 1988). It's greatly interesting in the use of ACF for removing organic contaminants in water (Zeng, 1988; Tanada, 1991). Few studies had made a series attempt to elucidate ACF adsorption THMs yet (Sakoda, 1991).

The aim of this paper is to investigate the mechanisms and the impact factors on ACF adsorption THMs in water more fully.

## 2 Experimental studies

### 2.1 Materials

ACF (Materials Science Institute, Zhongshan University, Guangzhou, China) with 10–15  $\mu\text{m}$  diameter, 1000–1500  $\text{m}^2/\text{g}$  specific surface areas and 0.60–0.70  $\text{cm}^3/\text{g}$  micropore volume was selected as adsorbent. Prior to experiments, the ACF was pretreated as fol-

lows to remove water soluble and volatile impurities. The ACF used for isotherms was boiled in distilled water for 2h with exchange of the distilled water after 1h, subsequently rinsed with a plenty of fresh distilled water and dried in an electric oven at 120°C overnight. After the above pretreatment, the ACF was ground to fine powder and dried overnight again. The ACF used for column adsorption runs was not ground. THMs (China National Environmental Monitoring Center) including  $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$ , were chosen as primary adsorbates.

## 2.2 Isotherm measurements

Adsorption isotherms of the four species of THMs were measured by the batch adsorption method. Precisely weighted 0.4–1.0g of ACF was immersed in 250 ml vials containing four species of THMs solution without any free head space. Then the vials were immediately sealed with a Teflon film of 0.05 mm thick, or with a rubber stopper. The sealed vials were placed in a constant temperature magnetic stirrer, well stirring for 2 hour. After equilibrium, the THMs concentration in the mixture was measured by the head space method. Details of this analysis were described later. In preliminary experiments (kinetics studies), the mixtures were allowed to be stirred for 0.2, 0.5, 1.0, 2.0, 3.5 and 4.3 hours, and subsequently the THMs concentrations were analyzed to design the appropriate adsorption time sufficiently long for establishing the adsorption equilibrium. It was assured that 2.0 hour was almost enough to achieve the equilibrium for ACF.

## 2.3 THMs analytical method

Samples were incubated in dark at  $40 \pm 2^\circ\text{C}$  for 40 minutes before analysis. The concentrations of THMs were determined by the head space method which was recommended by Urano *et al.* (Urano, 1983) with slight modifications. A gas chromatograph, HP5890 series II, was equipped with an electron capture detector and a glass column. A stationary phase of 7% OV-101 on chromosorb A HP AW DMCS (80–100 mesh) was used for separation of THMs. The flow rate of  $\text{N}_2$  (99.999%) as carrier was controlled at 35 ml/min. The temperature of the column, injection port and detector was kept at 80, 100 and  $250^\circ\text{C}$ , respectively.

## 2.4 Fixed-bed reactor adsorption

2.65g ACF was packed in a glass column (15 mm i.d.). The ACF bed length,  $L$ , was 15 cm. The THMs solution through a flowmeter was introduced into this column using a peristaltic pump at a flow rate of 5 L/h, corresponding to a linear velocity,  $v$ , of 77.15 m/h. THMs concentrations in the influent and effluent of the column were analyzed periodically.

# 3 Results and discussion

## 3.1 Kinetics of adsorption of THMs

The kinetics of adsorption of THMs on ACF is presented in Fig. 1. Generally, as the adsorption time extended, the percentage of the four

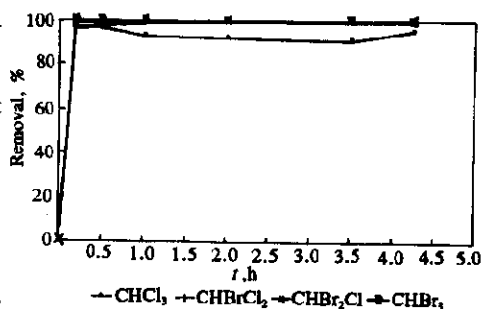


Fig. 1 THMs removals by ACF

species of THMs removing increased. While the adsorption time was longer than 0.5h, the removal percentage of three bromine substituted THMs ( $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$ ) was almost up to 100%, and that of  $\text{CHCl}_3$  was more than 90%.

### 3.2 Adsorption isotherms of THMs

Langmuir and Freundlich adsorption isotherms for THMs on ACF at 25°C were graphically shown in Fig. 2 and 3, respectively. The isotherms were not fit in with Langmuir equation well, but successfully correlated by Freundlich Equation (1), and the parameters determined and cited from the literature are listed in Table 1.

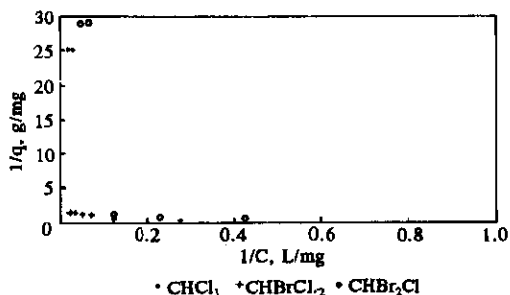


Fig. 2 Langmuir isotherms of THMs on ACF at 25°C

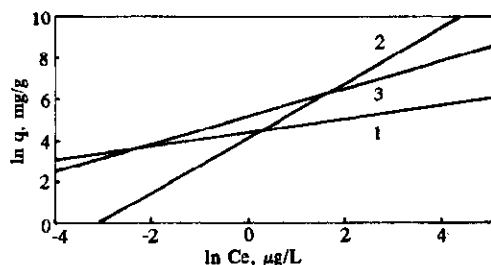


Fig. 3 Freundlich isotherms of THMs on ACF at 25°C  
1.  $\text{CHCl}_3$  2.  $\text{CHBrCl}_2$  3.  $\text{CHBr}_2\text{Cl}$

Table 1 Freundlich equation's parameters

Compound	Temperature, °C	K	1/n	Reference
$\text{CHCl}_3$	35	0.036	1.346	This work
	25	0.084	3.021	This work
	20	0.084	0.730	Sakoda's
	20	0.110	0.730	Sakoda's
	10	0.153	1.718	This work
$\text{CHBrCl}_2$	35	0.051	0.989	This work
	25	0.062	0.746	This work
	20	0.267	0.709	Sakoda's
	20	0.378	0.709	Sakoda's
	10	0.197	0.194	This work

$$q = k \cdot C^{1/n}, \quad (1)$$

where  $q$  is adsorptive capacity, mg/g;  $k$  is constant;  $C$  is equilibrium concentration,  $\mu\text{g/L}$ ;  $1/n$  is constant. It's noted that the adsorption of THMs onto ACF was not a complete monolayer over a sorptive surface. The  $\text{CHCl}_3$  adsorptive capacity of ACF investigated in this work was comparable with or slightly larger than those in Sakoda's work, but the  $\text{CHBrCl}_2$  adsorptive capacity was lower. Qualitatively, the data showed that the adsorptive capacities of ACF increased with substitution of bromine for chlorine atoms, as observed for isotherms of GAC reported by Lafrance and Alben (Lafrance, 1985; Alben, 1988).

### 3.3 Effects of temperature and experimental heats of adsorption

The adsorption of THMs on ACF at 4, 15, 25 and 37°C is obtained and shown in Fig. 4. From the temperature dependency of the isotherms, the heats of adsorption were calculated by:

$$\ln k = -\Delta H/R(1/T_1 - 1/T_2),$$

where  $\ln k$  is  $\ln(C_2/C_1)$ ;  $\Delta H$  is the heat of adsorption;  $R$  is the gas law constant;  $T$  is the absolute temperature,  $K$ .

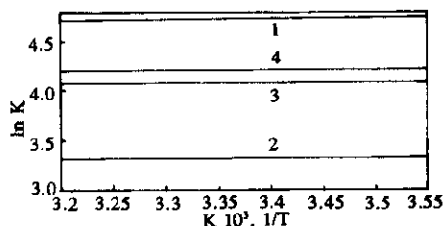


Fig. 4 Effect of temperature on the adsorptive capacities of ACF

1.  $\text{CHCl}_3$  2.  $\text{CHBrCl}_2$   
3.  $\text{CHBr}_2\text{Cl}$  4.  $\text{CHBr}_3$

The values of  $\Delta H$  for  $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  were  $-0.83$ ,  $-0.22$ ,  $-0.12$ , and  $-0.10$   $\text{kJ/mol}$ , respectively. It was clear that the values of  $\Delta H$  were all below zero, i. e., the adsorption of THMs on ACF was exothermic, and the absolute values of the  $\Delta H$  were all less than  $10$   $\text{kJ/mol}$ . This suggested that the adsorption of THMs was physico-adsorption principally. Compared with the  $\Delta H$  of  $\text{CHCl}_3$  on FT15 (ACF) reported by Sakoda (Sakoda, 1991), which the values was  $-40.76$   $\text{kJ/mol}$ , the adsorption heats in our experiments were much greater. The reason remains to be studied further.

### 3.4 Effects of the physicochemical characteristics of adsorbates

The relationship between THMs physicochemical characteristics and the adsorptive capacities of ACF are listed in Table 2. It showed that the adsorptive capacities increased as the compounds became more hydrophobic, i. e., increased with the solubilities of THMs in water decreasing; increased with the 1-octanol/water distribution coefficients ( $K_{ow}$ ) raising; and increased with the molecular weight (MW).

Table 2 Relationship between THMs properties and the adsorptive capacities of ACF

Adsorbates	Properties			Adsorptive capacities, mg/g
	$K_{ow}@$	$S, \mu\text{mol/L}^\#$	$MW^*$	
$\text{CHCl}_3$	91.20	4.575	119.5	0.231
$\text{CHBrCl}_2$	125.89	4.383	164.0	0.186
$\text{CHBr}_2\text{Cl}$	173.78	4.191	208.5	0.267
$\text{CHBr}_3$	239.88	3.999	253.0	0.792

@, 1-octanol/water distribution coefficients; #, solubility; \*, molecular weight

To sum up, on the basis of the isotherm studies and the relationship between THMs properties and the adsorptive capacities, it would be expected that the mechanisms of ACF adsorption THMs was exothermic, physico-adsorption principally, but not a complete monolayer adsorption.

### 3.5 Effects of pH value

In this paper, it showed that pH value had no effect on the adsorptive capacity of ACF

(Table 3).

**Table 3 Relationship between adsorptive capacities and the pH value of water**

pH	Adsorptive capacities, mg/g			
	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
2.6	0.10	0.11	0.17	0.19
3.7	0.10	0.11	0.17	0.19
5.8	0.10	0.11	0.17	0.18
7.5	0.11	0.11	0.18	0.20
9.6	0.10	0.12	0.17	0.18
10.9	0.10	0.12	0.18	0.19

### 3.6 Effects of the concentrations of adsorbates

The amount of THMs adsorbed on ACF was increased with the initial concentrations of THMs (Fig. 5).

Almost all possible impacts on the adsorptive capacities of ACF were investigated in this study. Some effect factors, including the physicochemical characteristics of adsorbates, pH value of water and concentration of adsorbates, were studied for the first time. These would provide useful reference to the practically applying the ACF adsorption for the THMs control in drinking water.

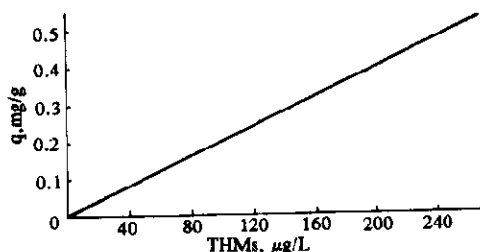


Fig. 5 Effect of initial concentration of THMs on the adsorptive capacities

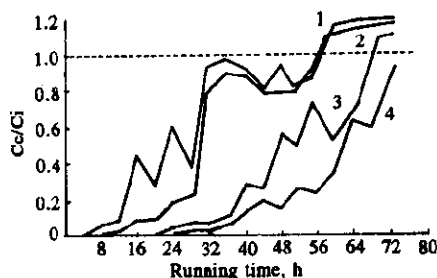


Fig. 6 Breakthrough curves of THMs on a ACF column at 25°C

$C_e$ : effluent concentration;

$C_i$ : influent concentration

1. CHCl<sub>3</sub> 2. CHBrCl<sub>2</sub>

3. CHBr<sub>2</sub>Cl 4. CHBr<sub>3</sub>

### 3.7 Fixed-bed reactor adsorption

The column was initially fed by a THMs solution containing CHCl<sub>3</sub> 37.0–76.5 µg/L, CHBrCl<sub>2</sub> 24.4–50.1 µg/L, CHBr<sub>2</sub>Cl 29.8–98.8 µg/L, CHBr<sub>3</sub> 21.4–89.6 µg/L, and the total THMs concentration 112.6–315.0 µg/L. The breakthrough curve of ACF for the four species of THMs is shown in Fig. 6. Four important conclusions could be drawn from the curve and Table 4. First, the effluent concentration of the four species of THMs from ACF column were not detected for an initial period of time. It's indicated that ACF was very effective in adsorbing THMs, and the four species of THMs were much adsorbable onto ACF.

Secondly, the effluent concentrations of the four species of THMs were increased gradually as the operation time extended. The column will be breakthrough as the effluent concentrations were equal to the influent concentrations.

$\text{CHCl}_3$  and  $\text{CHBrCl}_2$  were breakthrough first almost at the same time (about running 50 hours); followed  $\text{CHBr}_2\text{Cl}$  (about at 65 hours); however,  $\text{CHBr}_3$  was not breakthrough in the whole running time (70 hours). After exhausted, the effluent concentrations exceeded the influent concentrations on numerous occasions. It's indicated that deadsorption of THMs from ACF was occurring. Thirdly, the more chlorine atoms in  $\text{CHCl}_3$  were substituted by bromine atoms, the more cumulative mass loading. It's proposed that the affinities of ACF for THMs increased with bromine substitution. Fourthly, the species of THMs with lower boiling points appeared first in the effluent, that is, the column was exhausted first for  $\text{CHCl}_3$ , then for  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$ , but  $\text{CHBr}_3$  was not been found breakthrough in this experiment. Compared with the result of Sakoda's, in which the cumulative mass loading of the FT15 and FC200X ACF packed column for  $\text{CHCl}_3$  was about 0.38 and 0.18 mg/g respectively before breakthrough occurring, the cumulative mass loading of the ACF used in this work for  $\text{CHCl}_3$  was much higher (0.24 mg/g; Table 4).

Table 4 Relationship between the boiling points of adsorbates and the cumulative mass loading

THMs	Points, °C	Cumu. mass load., mg/g
$\text{CHCl}_3$	62	2.04
$\text{CHBrCl}_2$	89	2.10
$\text{CHBr}_2\text{Cl}$	120	4.29
$\text{CHBr}_3$	150	5.00

In general, the result of fixed-bed reactor experiments was fitted to the data of isotherm adsorption studies.

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