

ADSORPTION OF CHLOROFORM AND TRICHLOROETHYLENE IN WATER WITH A NEW KIND OF HYPERCROSSLINKED RESINS*

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Abstract In this paper two newly developed hypercrosslinked resins were used to treat micropolluted drinking water and their static and kinetic adsorption were investigated at 293 K. The results show that these two adsorbents are superior to Amberlite XAD-4 for removing chloroform and trichloroethylene in aqueous solutions. The breakthrough capacity and the total capacities from mini-column adsorption studies for chloroform and trichloroethylene on XAD-4, ZH-01 and ZH-00 are calculated respectively under experimental conditions

Keywords Hypercrosslinked resin, Drinking water, Micropollution, Chloroform, Trichloroethylene, Adsorption, Activated carbon

INTRODUCTION

As a result of human activities, numerous hazardous organic compounds are introduced into environmental waters, especially groundwater. The quality of water sources has deteriorated in recent times, leading to an increase in the amount of chlorine required for purifying water, which results in the reaction between residual chlorine and organic compounds and brings about some by-products (DBPs) such as chloroform and trichloroethylene and other multihalogenated hydrocarbons in tap water. In these DBPs, the amount of chloroform and trichloroethylene is larger than that of the others, and they must be removed because of their carcinogenicity and even some accumulation effects^[1].

Adsorption has been considered to be the best available technology for removing organics from water in the US Safe Drinking Water Act^[2]. Granular activated carbon (GAC) is a well-tried adsorbent for deodorization, decoloring and removing the organics from water. However, some researches have revealed that GAC cannot efficiently remove the chlorinated organics^[3], especially chloroform and carbon tetrachloride^[4, 5]; when the concentration of some halogenated organics is lower than 5 µg/L, it will lose its efficiency completely^[6]. The adsorption resin is another kind of adsorbent which is widely employed for isolation and purification of organic substances, treatment of wastewaters, solid phase extraction, and so on. A variety of adsorbing materials has been developed and tested, such as Amberlite XAD, Lewatit, Tenax GC, Hitachi polysorb. Since the adsorption ability is strongly dependent on the nature of the polymers and on the solutes in water, hypercrosslinked polymers having high surface area and the right micropore network were developed and studied^[7].

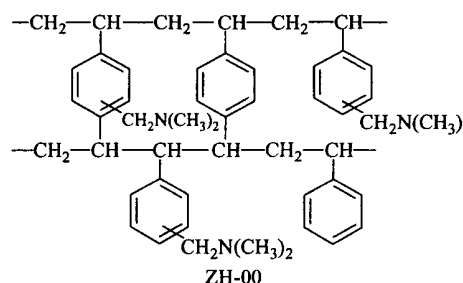
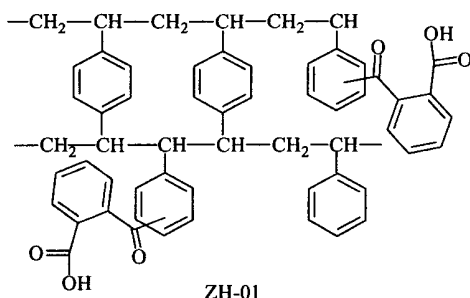
We have previously prepared new types of hypercrosslinked adsorbents ZH-01 and ZH-00, respectively, modified by 2-carboxylbenzoyl and amine functional group, and investigated comparatively the static and the

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kinetic adsorption of chloroform and trichloroethylene on Amberlite XAD-4, ZH-01 and ZH-00.



MATERIALS AND METHODS

Materials

Styrene, divinylbenzene (purity: 50.4%), chloromethyl methyl ether, phthalic anhydride, dimethylamine, chloroform, trichloroethylene, aluminum chloride, zinc chloride, dibenzoyl peroxide and phenol were available commercially and used without further purification. Photographic-grade gelatin was obtained from Yancheng Dafeng Gelatin Plant (Yancheng, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Simulated micropollutants, phenol, chloroform and trichloroethylene were dissolved in deionized water without pH adjustment. Physical properties of chloroform and trichloroethylene are listed in Table 1.

Table 1. Physical property of chloroform and trichloroethylene

Compounds	Molecular weight	Solubility (g L ⁻¹)*	Henry's constant (1.01 × 10 ⁵ Pa μmol ⁻¹)*	Molecular volume (nm ³)**
Chloroform	119.39	7.4–10	3.434 × 10 ⁵	0.132
Trichloroethylene	131.40	1.1	2.907 × 10 ⁶	0.148

* Values from the handbook of the Merck Index (Merck); ** Calculated values with HyperChem

Characterization of Adsorbents ZH-01 and ZH-00

The adsorbents, ZH-01 and ZH-00 were synthesized as described in the literature^[8]. The specific surface area and the pore distribution of resins were determined in dry state with a Micromeritics ASAP 2010 M surface area measurement instrument (Micromeritics Instrument, Norcross, USA). Infrared spectra of the polymeric adsorbent before and after the post-crossing reaction (Figs. 1 and 2) were obtained from a Nicolet 170 SX IR

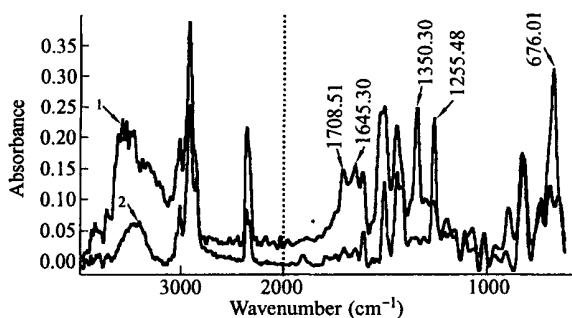


Fig. 1 IR spectra of chloromethylated copolymer of styrene and divinylbenzene before and after the Friedel-Crafts reaction, in which 1 is for ZH-01 resin and 2 is for chloromethylated macroporous copolymer of styrene-divinylbenzene

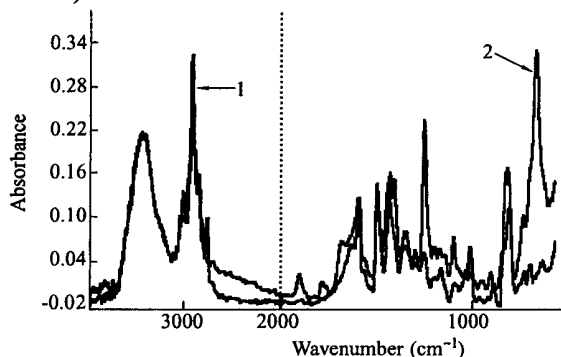


Fig. 2 IR spectra of chloromethylated copolymer of styrene and divinylbenzene before and after the reaction, in which 1 stands for ZH-00 resin and 2 stands for chloromethylated macroporous copolymer of styrene-divinylbenzene

Spectrometer (USA) with KBr pelleted samples. Compared with chloromethylated copolymer of styrene and divinylbenzene, the vibration bands of $\text{C}-\text{Cl}$ for ZH-01 and ZH-00 at about 670 cm^{-1} decrease considerably, and the bands at 1708.51 cm^{-1} and 1645.30 cm^{-1} in ZH-01 and at 2769.17 cm^{-1} in ZH-00 suggest that the 2-carboxylbenzoyl and dimethylamine groups are successfully bonded onto ZH-01 and ZH-00 resins, respectively. The chlorine content was measured according to the method of Volhard.

Analytical Method

The concentration of chloroform or trichloroethylene in water was determined in a vial using the headspace method and a gas chromatograph (Shimadzu Model GC-4CM) equipped with an electron capture detector: the headspace in a closed vial which had been kept at 298 K over 2 h was injected into the gas chromatograph and the concentrations were determined. Adsorption tests to obtain the isotherms of chloroform or trichloroethylene were carried out according to the procedure reported by Urano *et al.*^[9]

Adsorption Isotherms

Isotherms were obtained by variation of the ratio of solution volume to the adsorbent mass (0.080–0.250) at constant initial concentration of adsorbates (35 mg/L), and the mixture was agitated about 24 h to reach equilibrium using a horizontal shaker operated at 130 r/min.

Mini-Column Adsorption

Column adsorption was conducted using a $10\text{ cm} \times 4.6\text{ mm}$ I.D. stainless-steel column with a $2\text{ }\mu\text{m}$ stainless-steel frit connected with a 6672 reciprocating pump (Beijing Analytical Instrument Plant) at room temperature. The length of the filter could be varied with 1 mm glass beads to ensure that 0.300 g adsorbents was included. The adsorbate solution with initial concentration of 100 mg/L was used to carry out column sorption tests under identical operation at a flow rate of 0.5 mL/min, and the outlet concentration of each 20 min was determined by the above GC method. Column adsorption was used to compare the removal efficiency for tap water onto three adsorbents at different flow rate.

RESULTS AND DISCUSSION

Selection of Adsorbents

Some adsorbents including macroporous Amberlite XAD-4, MX-4^[10], hypercrosslinked AM-1^[8], NJ-8^[11], ZH-01 and ZH-00 were used for adsorbing phenol from its aqueous solutions of initial concentration 200, 400, 600, 800 and 1000 mg/L at 293 K. The concentrations of phenol were measured at 275 nm using a HPLC assembled from a Waters 600 controller, a Waters 600 pump (Waters Assoc., USA) and a Waters Dual λ Absorbance Detector.

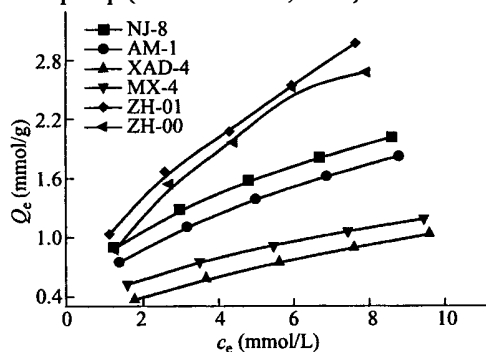


Fig. 3 Equilibrium adsorption isotherms of phenol from water on six adsorbents at 293 K

Experimental results (Fig. 3) show that ZH-01 and ZH-00 have a relatively favorable advantage over other adsorbents for removing organics in water. The typical properties of the above adsorbents are listed in Table 2. It can be seen from Table 2 that specific surface area is obviously not the only predominant factor for adsorbing

It can be seen from Table 2 that specific surface area is obviously not the only predominant factor for adsorbing organics using these adsorbents because AM-1 has the smallest surface area. Besides, the difference in polarity, the microporous structure and pore distribution of different adsorbents will be the other important factors that affect the adsorption.

Table 2. The typical properties of the six adsorbents

Property	XAD-4 ^[9]	MX-4 ^[9]	AM-1 ^[8]	NJ-8 ^[11]	ZH-01	ZH-00
Polarity	Nonpolar	Moderate polar	Moderate polar	Moderate polar	Moderate polar	Moderate polar
Specific surface area (m ² /g)	880	1114.2	590	906	1118	726.5
Average diameter (nm)	5.80	5.84	8.60	2.50	1.20	1.3
Micropore area (m ² /g)	3	90.6	340	529.0	686	393.8
Average particle size (mm)	~0.5	~0.5	~0.5	~0.5	~0.5	~0.5
Porosity (mL/g)	1.0	1.6	0.52	0.52	0.69	0.59
Residual chlorine content	0	0	3.5%	3.5%	2.8%	0.76%

* All the values were measured in our study.

Equilibrium Adsorption of Chloroform and Trichloroethylene

The equilibrium adsorption isotherms of chloroform and trichloroethylene from water on Amberlite XAD-4, ZH-01 and ZH-00 resins at 293 K are shown in Figs. 4(a) and 4(b), respectively, which indicate that hypercrosslinked adsorbents have satisfactory adsorbing efficiency. The isothermal equilibrium adsorption data for ZH-01 and ZH-00 were processed and compared with those for XAD-4 employing the rearranged Langmuir and Freundlich^[12] adsorption models, which may be expressed respectively as

Langmuir equation $c_e/q_e = c_e/Q_m + 1/(K_L Q_m)$ (1)

Freundlich equation $\ln Q_e = \ln K_F + 1/n \ln c_e$ (2)

where Q_e is the equilibrium adsorption capacity (mmol/g), c_e is the equilibrium concentration (mmol/L), Q_m is the maximum surface coverage (formation of the monolayer) of the adsorbent (mmol/g), K_L is the adsorption energy constant (L/g), and K_F and n are the characteristic constants. The evaluated constants for both equations for chloroform and trichloroethylene are shown in Table 3. Conformation of the data in the Langmuir isotherm model indicates the homogeneous nature of the adsorbent surface^[13] and the formation of the monolayer coverage of the adsorbate molecule over the adsorbent surface under the experimental condition.

Table 3. The evaluated constants of isotherms for chloroform and trichloroethylene

Adsorbate	Adsorbent	Langmuir			Freundlich		
		K_L	Q_m	R^2	K_F	n	R^2
Chloroform	XAD-4	11.23	0.237	0.9981	0.528	2.853	0.9935
	ZH-00	23.30	0.275	0.9902	0.580	2.138	0.9918
	ZH-01	53.06	0.379	0.9900	1.398	1.946	0.9996
Trichloroethylene	XAD-4	52.18	0.327	0.9915	1.446	2.680	0.9983
	ZH-00	141.4	0.335	0.9902	1.585	2.154	0.9964
	ZH-01	269.9	0.394	0.9800	3.731	1.875	0.9998

From Table 3, it is quite obvious that our set of experimental data also corresponds well to the Freundlich adsorption law for Amberlite XAD-4, ZH-01 and ZH-00 resins for all the correlative factors R^2 are larger than 0.98, and the results indicate that the adsorption capacities for ZH-01 and ZH-00 are significantly higher than that on Amberlite XAD-4 for chloroform and trichloroethylene, which can be confirmed by the value of K_F , a relative indicator of adsorption capacity according to the Freundlich theory^[14]. The high K_F and low n values show that ZH-01 and ZH-00 can be used for removing chloroform and trichloroethylene of different concentrations in water^[14]. It is obvious that that surface areas of adsorbents play an important role in adsorptive process as shown in Table 2 and Figs. 4(a) and 4(b). However, from the calculated values of Q_m listed in Table 3, the microporous structures of adsorbents are also an important factor affecting adsorption. Due to the right molecular volume of

adsorbates, the adsorbates can be adsorbed tightly in the fine pores of the ZH-01 and ZH-00. In comparison with chloroform, trichloroethylene has the structure of double bond, which leads to stronger interaction between the trichloroethylene molecules and the adsorbents and results in the higher adsorption capacities. All these data in Table 3 show on the basis of the two above isothermal models that ZH-01 and ZH-00 will exhibit their potential at even higher concentrations in column operations^[14].

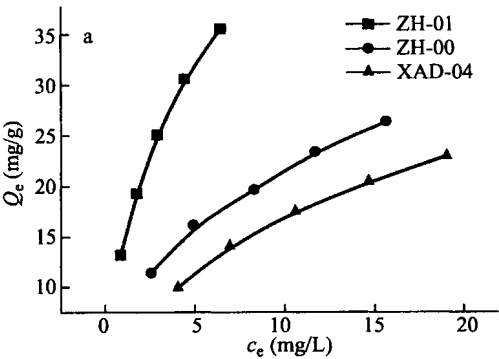


Fig. 4a Equilibrium adsorption isotherms of chloroform from water on Amberlite XAD-4, ZH-01 and ZH-00 resins at 293 K

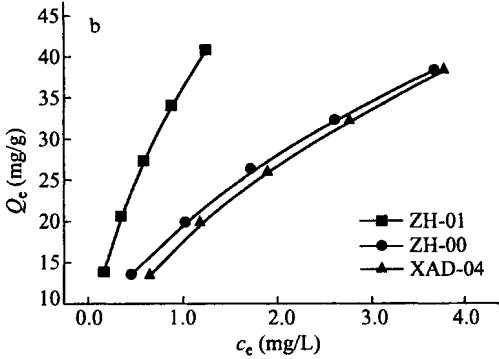


Fig. 4b Equilibrium adsorption isotherms of trichloroethylene from water on Amberlite XAD-4, ZH-01 and ZH-00 resins at 293 K

Mini-Column Adsorption Curves of Two Adsorbates

The adsorption capacity obtained from the column adsorption depends upon the diameter of the column, the flow rate, and some other experimental factors. For comparison, all these parameters were set constant in the present study. At a flow rate of 0.5 mL/min and an initial adsorbate concentration of 100 mg/L, the calculated results for the breakthrough capacity (mmol/g) and the total capacity (mmol/g) are listed in Table 4 and the adsorption curves are shown in Figs. 5(a) and 5(b). The results of removing low concentrations of chloroform and trichloroethylene from tap water at different flow rates are shown in Table 5, the flow rate of 60 mL/min will be the best choice, which shows that ZH-01 and ZH-00 have excellent prospects for micropolluted water treatment.

Table 4. The calculated results of the breakthrough capacity (mmol/g) and the total capacity (mmol/g) for three adsorbents

	XAD-4		ZH-01		ZH-00	
	Breakthrough capacity	Total capacity	Breakthrough capacity	Total capacity	Breakthrough capacity	Total capacity
Chloroform	0.198	0.218	0.313	0.366	0.205	0.255
Trichloroethylene	0.286	0.311	0.322	0.385	0.278	0.319

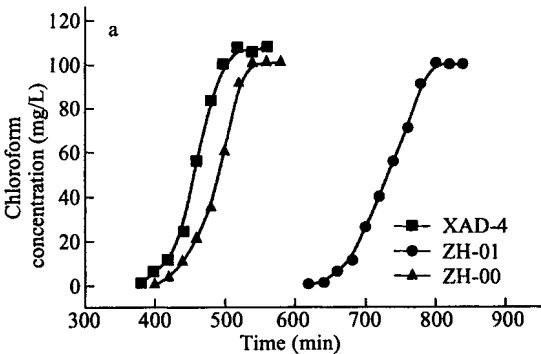


Fig. 5a Adsorption curves of chloroform on three adsorbents

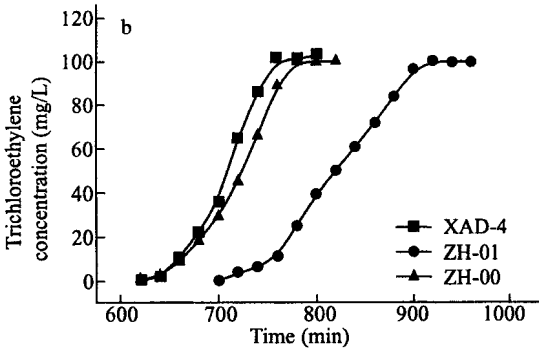


Fig. 5b Adsorption curves of trichloroethylene on three adsorbents

Table 5 Results of removing low concentrations of chloroform and trichloroethylene from tap water at different flow rates with ZH-01 and ZH-00

Amount of adsorbates ($\mu\text{g/L}$)	Flow rate (mL/min)	ZH-01		ZH-00	
		1* ($\mu\text{g/L}$)	2*	1* ($\mu\text{g/L}$)	2*
Chloroform 9.519	60	0.032	99.7%	0.216	97.7%
	80	0.375	96.1%	0.797	91.6%
	100	0.457	95.2%	1.321	86.1%
Trichloroethylene 17.046	60	0.312	98.2%	0.625	96.3%
	80	1.809	89.4%	2.660	84.4%
	100	3.009	82.3%	4.235	75.2%

*1 Denotes the residual amount of adsorbates after treatment, and 2 Denotes the yield of elimination

CONCLUSION

Two new hypercrosslinked polymeric adsorbents (ZH-01 and ZH-00) removing chloroform and trichloroethylene from their aqueous solutions were prepared, and the equilibrium adsorption capacities for chloroform and trichloroethylene are markedly higher than those on XAD-4, which can be attributed to its high specific surface area, high micropore area and the right adsorbate molecular volume.

All the isotherm data for chloroform and trichloroethylene on XAD-4, ZH-01 and ZH-00 can be satisfactorily fitted with the Langmuir and the Freundlich equations. High K_F and low n values show that ZH-01 and ZH-00 can be used for removing chloroform and trichloroethylene in water with different concentrations.

Mini-column adsorption studies for chloroform and trichloroethylene on XAD-4, ZH-01 and ZH-00 show that breakthrough capacity and the total capacities on ZH-01 and ZH-00 are higher than those on macroporous resins such as XAD-4, which is consistent with the elimination yields of treating the trace chloroform and trichloroethylene in tap water.

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