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Chinese Chemical Letters 20 (2009) 1478–1482
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Study on the influence of humic acid of different molecular weight on basic ion exchange resin's adsorption capacity

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Received 14 April 2009

Abstract

In this paper, humic acid (HA) was ultra-filtered into different molecular weight sections and was characterized by multi-element analysis, UV_{254}/TOC, FT-IR and three-dimensional fluorescence spectrometric. Since humic acids of different molecular weights have different hydrophilic and molecular size, the maximum adsorption capacity of basic ion exchange resins appears on the humic acid whose molecular weight ranges from 6000 to 10,000 Da.

Keywords: Humic acid; Molecular weight; Basic ion exchange resin; Adsorption

Humic acid (HA) exits in environment widely. Since it can form trihalomethanes (THMs) when reacting with chlorine in the disinfection process [1], many researchers choose it as potential disinfection byproduct (DBP) in studies. Previous studies have demonstrated that basic ion exchange resin can remove HA effectively [2,3], and the world's first full-scale water treatment plant using ion exchange resin was commissioned at the Wanneroo water treatment plant (WTP) in Perth, Western Australia, in December 2001 [4]. This plant is the largest groundwater treatment facility supplying the city of Perth (population 1.4 million) and is capable of processing 225 mL/day at full capacity. Though it has been found that low molecular weight (MW) natural organic matter components compete for adsorption sites with target compounds during the adsorption, few scholars pay close attention to the MW of HA on resin's adsorption capacity. But in fact, MW of HA distributed widely [5], and their physical and chemical properties are different, and these differences may make noticeable effects on resin's adsorption capacity. In this paper, HA is ultra-filtered into different MW sections, and the adsorption performance of these HA of different MW on basic ion exchange resin is studied.

1. Experimental

Humic acid was purchased from Sigma (America) which was extracted from nature water. Basic ion exchange resins D-201 and D-301 were supplied by Nange (China).

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.07.013

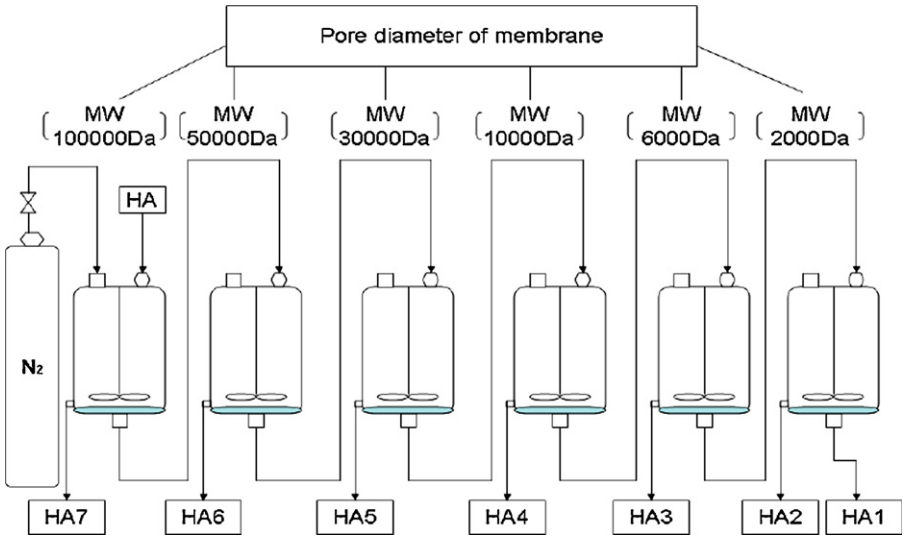

Fig. 1. Ultra-filtering of HA.

The process of ultra-filtering of HA was shown in Fig. 1. HA of different MW was characterized by multi-element analysis, UV_{254}/TOC, FT-IR and fluorescence spectrometric.

Equilibrium adsorptions of HA of different MW at 303 K were conducted as follows: 0.200 g of resin was introduced directly into ten 250 mL conical flasks, respectively, and then 100 mL aqueous solutions with different concentrations were added into those flasks, respectively. The flasks were completely sealed and placed in a G 25 model incubator shaker (New Brunswick Scientific) at 303 K and shaken under 120 r min^{-1}. The batch equilibrium test ran continuously over 120 h to ensure that the adsorption equilibrium had been reached and the concentrations of HA (C_e: mg L^{-1}) were determined using total organic carbon (TOC) analyzer. Thus, q_e (mg g^{-1}), the adsorption capacity, was calculated according to Eq. (1):

$$q_e = \frac{V_1(C_0 - C_e)}{W} \tag{1}$$

where V_1 is the volume of solution (L), W is the weight of dry resins (g).

2. Result and discussion

Composition characteristics of HA of different MW are shown in Table 1. The elemental contents of HA of different MW are similar to the averages reported in the literature, except that the oxygen content is slightly high [6]. Atomic ratios of H/C, O/C, and N/C are important indicators of the degree of aromatic condensation and maturity of humic acid [7]. The H:C ratio of HA of different MW is near 1, indicating that an aromatic framework exists in the chemical structure. The value of H/C and O/C increases as HA MW decreases, which indicates HA of lower MW have more hydrophilic group such as carboxyl or carboxylic acid.

Table 1
Results of E.A. of HA.

Samples	MW (Da)	C (%)	H (%)	O (%)	N (%)	S (%)	H/C	O/C	Ash (%)
HA1	<2000	31.73	3.04	63.58	1.38	0.27	1.15	1.50	0.08
HA2	2000–6000	35.62	3.07	59.62	1.37	0.32	1.03	1.25	0.15
HA3	6000–10,000	43.95	3.49	51.19	1.41	0.31	0.95	0.87	0.13
HA4	10,000–30,000	48.24	3.71	46.35	1.49	0.35	0.92	0.72	0.24
HA5	30,000–50,000	50.16	3.76	44.1	1.59	0.39	0.90	0.66	0.29
HA6	50,000–100,000	54.29	3.92	39.48	1.67	0.46	0.87	0.55	0.46

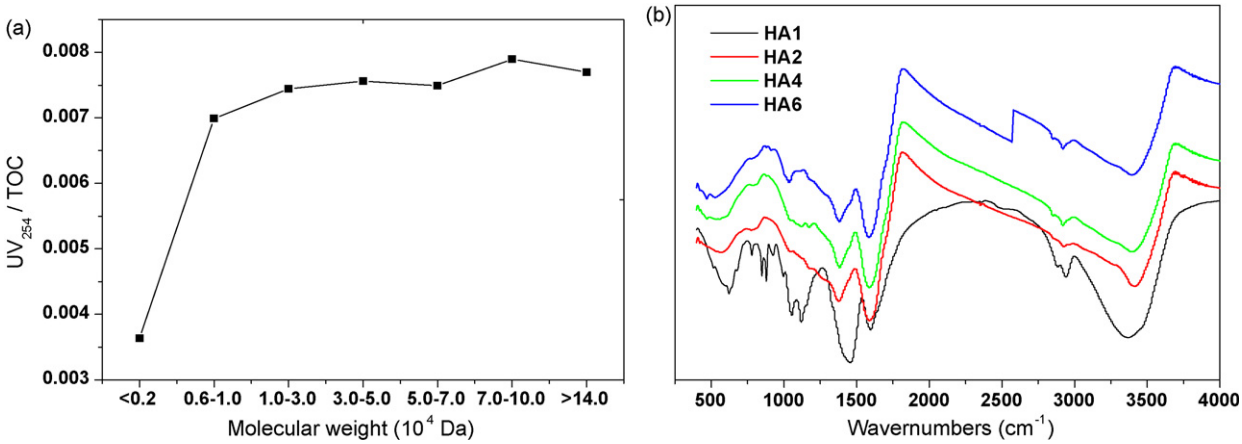

Fig. 2. (A) UV_{254}/TOC of HA; (B) FT-IR spectra of HA.

In Fig. 2(A), the value of UV254/TOC increases as HA MW increases, which indicates HA of higher MW is more aromatic. As shown in Fig. 2(B), though MW are different, FT-IR spectra of HA are similar, which indicates their chemical function groups are resemble.

As shown in Fig. 3, major fluorescence peaks of HA of different MW fall into similar locations of three-dimensional fluorescence (3DEM) spectra with its excitation and emission wavelength at 450 nm and 250 nm, respectively. Usually, the peaks on 3DEM spectra are the fixed-point characteristic of HA fingerprint [8]. Therefore, it could be assumed that fluorescence groups (i.e., aromatic conjugated systems) of HA of different MW are similar, which is consistent with the results of FT-IR spectra and fluorescence of HA.

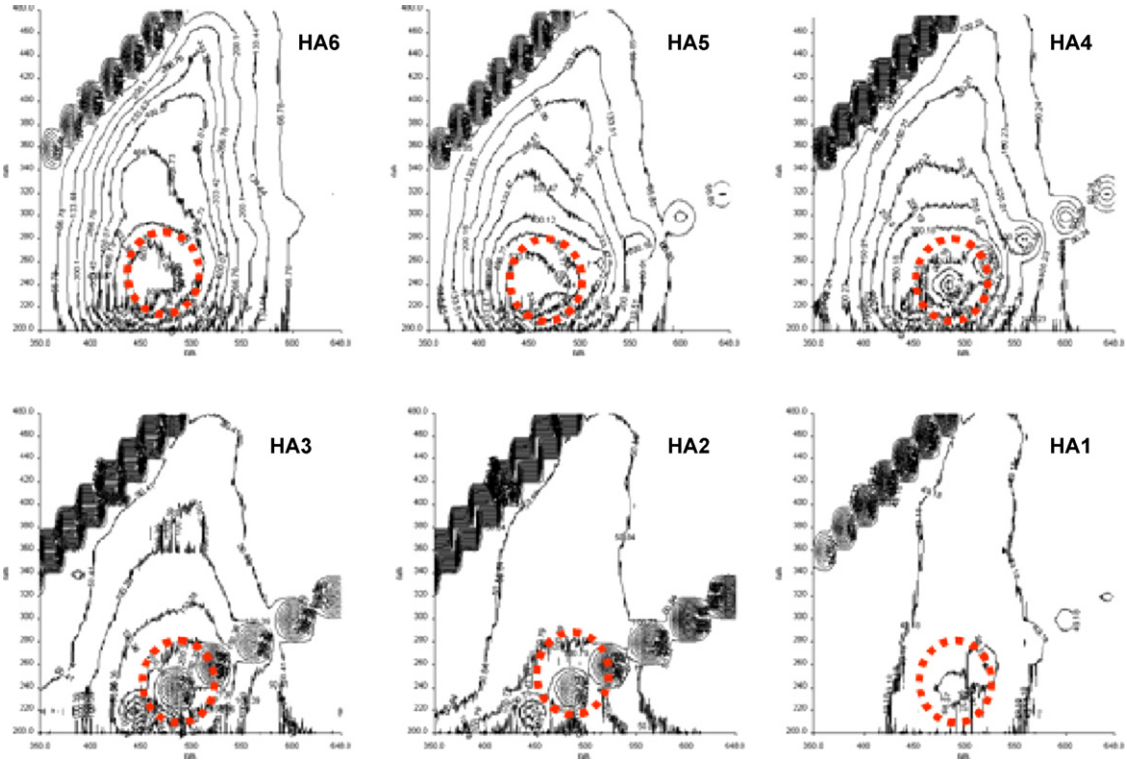

Fig. 3. 3DEM spectra of HA of different MW.

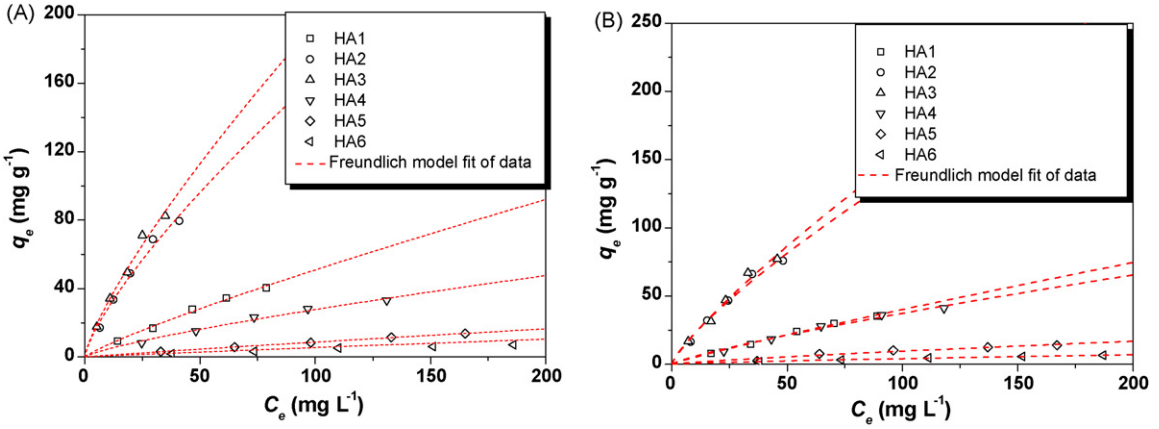

Fig. 4. Adsorption isotherms of HA with different MW on resins (A) D-201; (B) D-301.

Table 2
Freundlich equation fits of adsorption isotherms of HA at 303 K.

Adsorbent	Adsorbate	Freundlich equation		
		n	K_F	R^2
D-201	HA_1	1.13	0.87	0.995
	HA_2	1.17	3.65	0.987
	HA_3	1.20	4.52	0.992
	HA_4	1.16	0.53	0.989
	HA_5	1.09	0.13	0.990
	HA_6	1.19	0.09	0.986
D-301	HA_1	1.08	0.58	0.997
	HA_2	1.14	2.76	0.988
	HA_3	1.17	3.07	0.984
	HA_4	1.11	0.31	0.989
	HA_5	1.09	0.13	0.999
	HA_6	1.28	0.11	0.998

The equilibrium adsorption isotherms of HA on resins at 303 K are depicted in Fig. 4, and the isothermal equilibrium adsorption data for HA is fitted by Freundlich equation (Eq. (2)) [9]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), K_F and n are characteristic constants.

As shown in Table 2, Freundlich equations can fit adsorption isotherms well. The values of K_F, a relative indicator of absorbability in Freundlich theory, indicate that the adsorption force for HA3 (MW: 6000–10,000 Da) is much higher than that for other sections.

It can be explained as follows: (1) during the process of absorption, HA of higher MW is more likely to block the pores on resin's surface due to its high molecular size and thus decreases the absorption capacity of the resin. Meanwhile, the ionic degree of high MW HA is low, which is against ion exchange reaction. This, to some extent, decreases the absorption force of the resin. (2) HA of low MW contains too much hydroxyl, which boosts its hydrophilicity. Moreover, its hydrophilic neutral components also accumulate, which is also against the absorption force.

Acknowledgments

We gratefully acknowledge generous support provided by the National Nature Science Fund (No. 50778088) and China National Funds for Distinguished Young Scientists (No. 50825802) and Resources Special Subject of National High Technology Research & Development Project (863 project, No. 2006AA06Z383), China.

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