

ADSORPTION OF HUMIC SUBSTANCES BY MACRO WEAKLY BASIC ION-EXCHANGE RESIN AND THEIR EFFECTS ON REMOVAL OF Cu^{2+} AND Pb^{2+} *

Jin-nan Wang^{a, b}, Yang Zhou^{a, b}, Ai-min Li^{a, b**}, Li Xu^{a, b} and Ling Xu^{a, b}

^a State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, China

^b Research Center of Organic Toxic Substance Control and Resource Reuse of Jiangsu Province, Nanjing 210038, China

Abstract Adsorption of humic, tannic and gallic acids by a macro weakly basic ion-exchange resin JN-01 was studied. The adsorption capacity of this resin for gallic and tannic acids is much higher than that for humic acid, which can be explained on the basis of both their molecular size and ionization degree. Furthermore, humic acid is separated into different components with molecular weight in the range from 2000 Da to 100000 Da by ultra-filter, and their adsorption isotherms on resin JN-01 indicate that humic acid's molecular weight is an important factor which makes significant influence on adsorption. Finally, changes in the amount of Cu^{2+} and Pb^{2+} adsorbed on resin JN-01 as a function of the concentration of each of these three acids were studied. A large increase in the heavy metal ions uptake is observed in the presence of humic substance, such advantages are due to the interactions between the heavy metal ions and the unbound functional groups of the adsorbed organic acids.

Keywords: Adsorption; Humic substance; Macro weakly basic ion-exchange resin; Removal; Heavy metal.

INTRODUCTION

Humic substances (HS) exist in soils, rivers, lakes and other water-body, and are usually aromatic and acidic in nature^[1]. Special attention has been given to HS following the discovery of chlorinated hydrocarbons in water supplies since about 1970. Previous studies have demonstrated that these potentially carcinogenic such as trihalomethanes (THMs) can be formed in the presence of HS during the chlorine disinfection^[2]. So removing HS as much as possible prior to chlorination can reduce the formation of chlorinated hydrocarbons.

The current technologies to remove dissolved organic matter (DOM) from water include coagulation, adsorption, nano-filtration (NF) and biological methods^[3–8]. Among these technologies, adsorption is the most common approach for removing organic pollutants from water with high efficiency and simple operation conditions^[9, 10]. Though macro weakly basic ion-exchange resin has been used to remove organic pollutants from wastewater^[11, 12], adsorption for humic substance still remains not well studied. In this work, adsorption of humic, tannic and gallic acids by weakly basic ion-exchange resin is studied. In order to investigate the effect of molecular weight (MW) of humic acid (HA) on adsorption, mix humic acid is ultra-filtered into sections of different molecular weight. Finally, the effects of humic substance on the removal of heavy metal ions are also studied.

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** Corresponding author: Ai-min Li (李爱民), E-mail: liaimin99@vip.sina.com

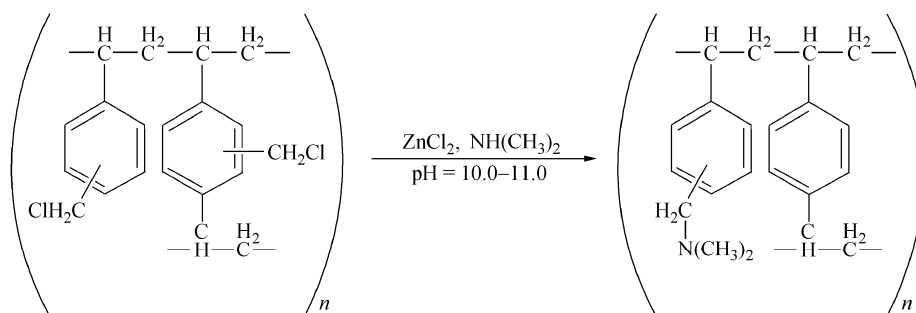
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MATERIALS AND METHODS

Chemicals

HA (solubility = 0.08 g/100mL, pK_{a1} = 6.1, pK_{a2} = 9.4), tannic acid (solubility = 100 g/100mL, pK_a = 4.9) and gallic acid (solubility = 1.1 g/100mL, pK_a of '—COOH' = 4.5, pK_a of '—OH' = 10) were supplied by Sigma (America). Macro weak ion-exchange resin JN-01 was synthesized as follows (Scheme 1): In a two necked round-bottom flask, 50.0 g of chloromethylation of the low-crosslinked macroporous styrene-divinylbenzene copolymers was swollen in 200 mL of dimethylamine (40%), 4.0 g $ZnCl_2$ was added, then adjust the pH = 10.0–11.0, and the mixture was stirred continuously at 303 K for 16 h and 318 K for 8 h. Then polymer beads were poured into an acetone bath containing 1% hydrochloric acid. Finally, polymer beads were filtered and then extracted with ethanol for 8 h in a Soxhlet apparatus and dried under vacuum at 333 K for 8 h.



Scheme 1 Preparation process of JN-01

Preparation of Humic Acid with Different Molecular Weight

Humic acid (HA) with different molecular weight was prepared by the UF installation. The MW of HA was in the range from 2000 Da to 100000 Da, and the separation process is shown in Fig. 1.

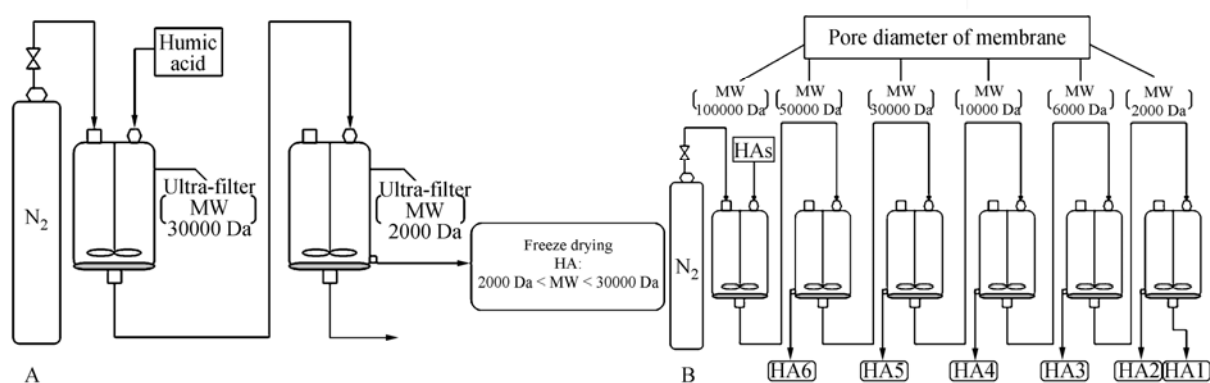


Fig. 1 (A) Separation of HAs used in adsorption tests at different temperatures; (B) Separation of HA1–HA6 with different molecular weight by UF

Analytical Methods

The concentration of humic substance in solutions was determined by a total organic carbon (TOC) analyser. The concentration of heavy metal ions in solutions was determined by a P-E 5000 atomic absorption spectrophotometer.

Static Adsorption Assay

Equilibrium adsorptions of HAs, TA and GA were conducted at 283, 303 and 323 K as follows: 0.200 g of resin JN-01 was introduced directly into a 250 mL conical flask, 100 mL aqueous solution of certain acid was added into each flask. The flasks were completely sealed and placed in a G 25 model incubator shaker (New

Brunswick Scientific) at a pre-settled temperature 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 acid (c_e) were determined. Thus, q_e (mg g^{-1}), the adsorption capacity, was calculated according to Eq. (1):

$$q_e = V_1(c_0 - c_e)/W \quad (1)$$

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

Effect of Humic Acid's Molecular Weight on Resin's Adsorption Capacity

The effects of humic acid's molecular weight on resin's adsorption capacity was tested as follows: 0.200 g of resin was introduced into a 250 mL conical flask, 100 mL solutions containing different concentrations of humic acid with certain molecular weight was added into each flask. The flasks were kept in a thermostated shaker bath at 303 K for 5 days, and then the acid concentration was measured, and the amounts of acids adsorbed by resin were calculated and plotted as a function of humic acid's molecular weight.

Effect of Humic Substance on Removal of Heavy Metals

The effects of GA, TA, and HAs on the removal of heavy metal ions by resin JN-01 were tested as follows: solutions containing different concentrations of these metal ions, between 20 mg L^{-1} and 100 mg L^{-1} , resin (0.2 g) and certain acid (concentration = 40 mg L^{-1}) were prepared and kept in a thermostated shaker bath at 303 K for 5 days, and then the heavy metal ions concentration was measured, and the amounts of heavy metal ions adsorbed by the resin were calculated and plotted as a function of humic substance.

RESULTS AND DISCUSSION

Characterization of Adsorbent JN-01 and HA

Characterization of JN-01 is listed in Table 1.

Table 1. Characterization of JN-01

Adsorbent	Total exchange capacity (mmol g^{-1})	Surface area ($\text{m}^2 \text{g}^{-1}$)	Average pore diameter (nm)	Micro volume ($r^* < 2 \text{ nm}$, $\text{cm}^3 \text{g}^{-1}$)	Mes/macro volume ($r^* > 2 \text{ nm}$, $\text{cm}^3 \text{g}^{-1}$)	Particle size (mm)
JN-01	≥ 4.5	41.3	9.5	0.014	0.12	0.4–0.6

* r is the diameter of the pore.

As shown in Table 2, the results of element analysis of HA is similar to the averages reported in the literature, except that the oxygen content is slightly high^[13, 14]. Atomic ratios of H/C, O/C, and N/C have been also used to investigate the structure in humic acid and to elucidate the structural formulae of humic acid^[15] because they are important indicators of the degree of aromatic condensation and maturity of humic acid^[16]. To further investigate the characteristics of the HA, atomic ratios of H/C, O/C, and N/C are calculated from the elemental analysis results. The H/C ratio value is slightly higher than 1, indicating that an aromatic framework exists in the chemical structure. The N in HA may have been formed from the biodegradation of protein. The O/C ratio indicates the carbohydrate and carboxylic acid reflect the content of humic acid.

Table 2. Composition characteristics of HA with different molecular weight

Samples	Molecular weight (Da)	C (%)	H (%)	O (%)	N (%)	S (%)	H/C (%)	O/C (%)	N/C (%)	S/C (%)	Ash (%)
HAs	2000–30000	21.25	3.48	71.53	1.34	0.31	16.37	336.61	6.30	1.46	0.03
HA1	< 2000	11.49	3.04	82.5	1.38	0.27	27.41	718.02	12.01	2.34	0.08
HA2	2000–6000	19.13	3.07	75.31	1.37	0.32	16.04	393.67	7.16	1.67	0.15
HA3	6000–10000	23.46	3.14	71.68	1.41	0.31	13.38	305.54	6.01	1.32	0.13
HA4	10000–30000	31.38	3.57	63.21	1.49	0.35	11.37	201.43	4.75	1.11	0.24
HA5	30000–50000	38.15	3.76	56.11	1.59	0.39	9.85	147.07	4.16	1.02	0.29
HA6	50000–100000	39.29	4.10	54.48	1.67	0.46	10.43	138.66	4.25	1.17	0.46

Equilibrium Adsorption

The equilibrium adsorption isotherms of HA, TA and GA on resin at different temperatures are depicted in Fig. 2. The isothermal equilibrium adsorption data for different acid are fitted and compared with those for JN-01 by means of the rearranged Freundlich adsorption models^[17]:

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (2)$$

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. The constants evaluated by application of isotherm equations are listed in Table 3.

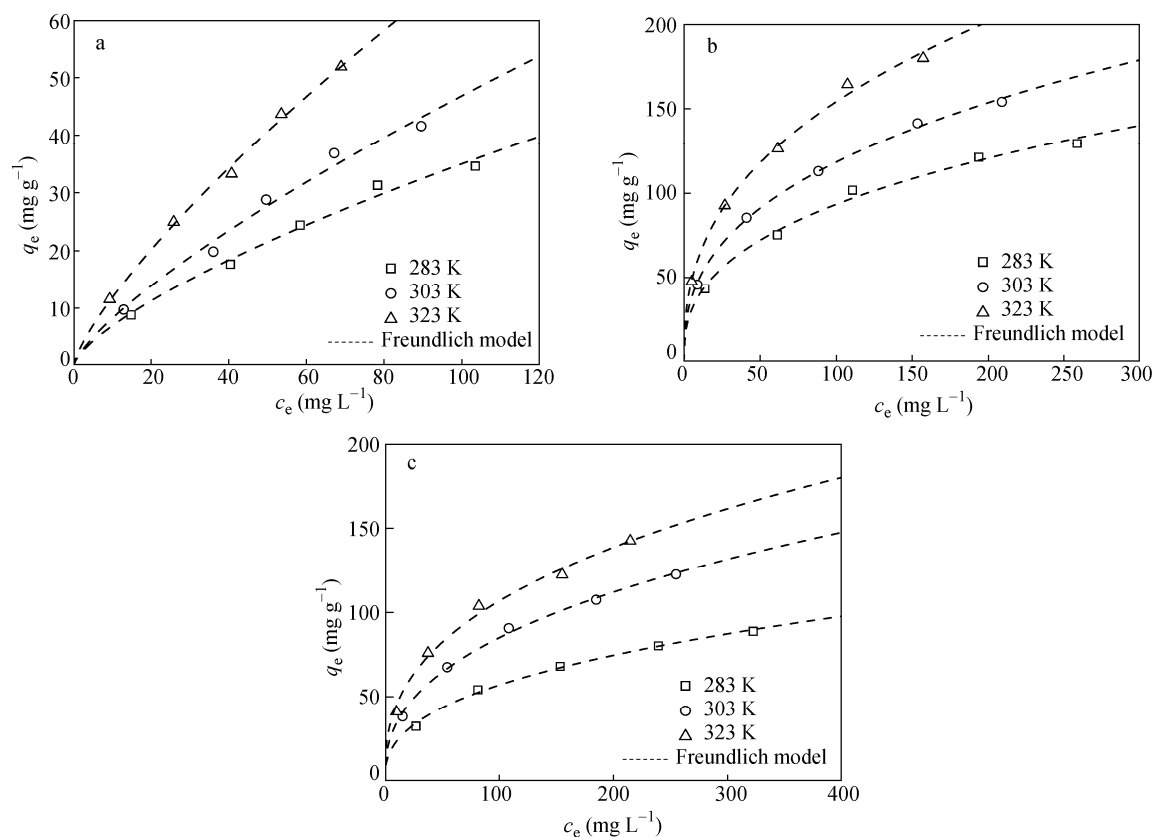


Fig. 2 Adsorption isotherms of humic substance on resin JN-01 at different temperature
a) HA; b) TA; c) GA

Table 3. Freundlich equation fit of the adsorption isotherms of humic substance at 283, 303 and 323 K

Adsorbate	Temperature (K)	Freundlich equation		
		n	K_F	R^2
HAs	283	1.37	1.24	0.994
	303	1.29	1.32	0.990
	323	1.34	2.17	0.998
TA	283	2.62	16.00	0.995
	303	2.59	19.95	0.999
	323	2.54	25.20	0.998
GA	283	2.46	8.74	0.995
	303	2.41	12.54	0.997
	323	2.50	16.88	0.992

Freundlich equation is reliable because all the correlation factors (R^2) are larger than 0.98. The values of K_F , a relative indicator of adsorption capacity in the Freundlich theory, indicate that the resin adsorption capacity of TA and GA was higher than that of HAs. This is in agreement with the previous report^[17], where high molecular weight was found to decrease the sorption of organic compounds onto the polymeric adsorbents from aqueous solutions. Besides, higher ionic degree of TA and GA is also beneficial to improving the resin's adsorption capacity.

The isosteric enthalpies of adsorption are calculated with a derivative Van't Hoff equation^[18]:

$$\ln(1/c_e) = \ln K_0 + (-\Delta H/RT) \quad (3)$$

where ΔH is the isosteric enthalpy of adsorption, R is the gas constant, c_e is the equilibrium concentration of solute at the absolute temperature T , and K_0 is a constant. At different temperatures (283, 303, and 323 K), c_e was obtained from the well-fitted isotherms. ΔH was calculated from the slope of line plotted by $\ln c_e$ versus $1/T$, as shown in Figs. 3(a)–3(c).

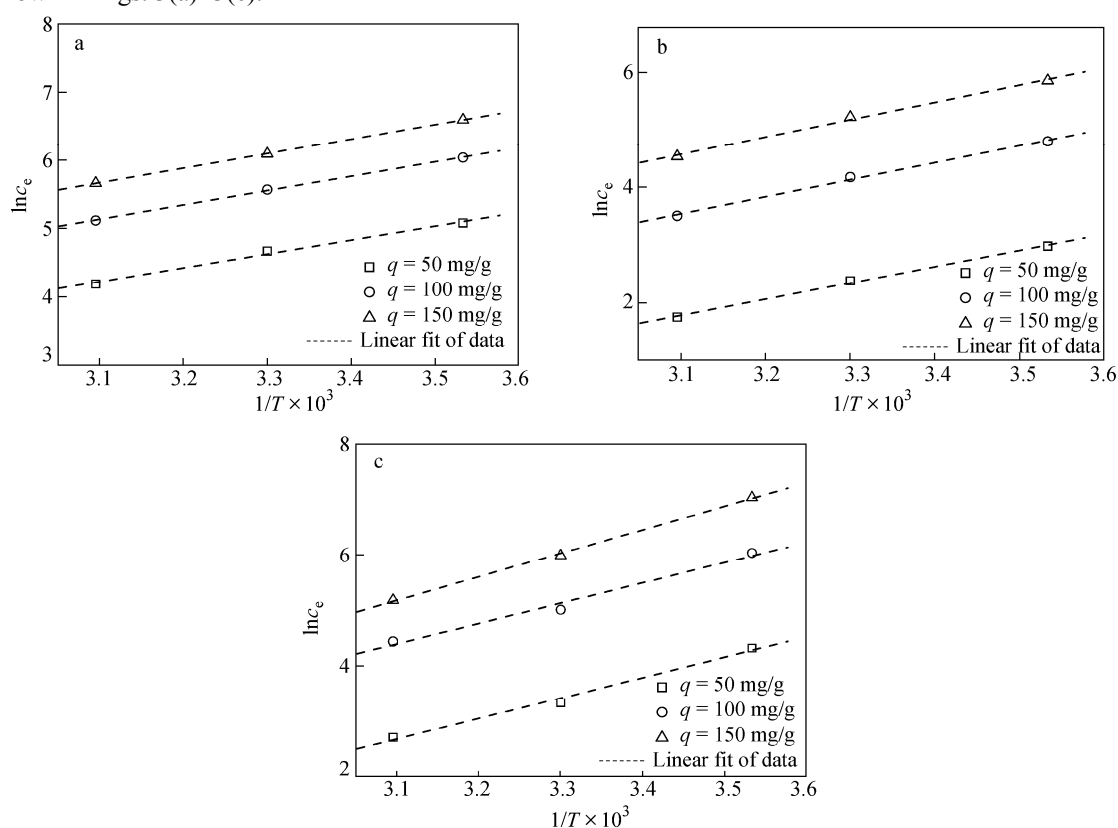


Fig. 3 $\ln c_e$ versus $1/T$
a) HAs; b) TA; c) GA

The calculated isosteric adsorption enthalpies of HA, TA and GA on JN-01 resin are summarized in Table 4.

Table 4. Isosteric adsorption enthalpy (ΔH , kJ mol^{-1}) calculated at different adsorption capacity of JN-01 for humic substance over the temperature range 283–323 K

Adsorbate	ΔH (kJ mol^{-1})		
	$q = 50$ (mg g^{-1})	$q = 100$ (mg g^{-1})	$q = 150$ (mg g^{-1})
HAs	16.86	17.40	17.71
TA	25.54	24.55	25.14
GA	30.42	30.31	35.25

Values of the enthalpy changes (always positive) of humic substance are indicative of an endothermic reaction, and their magnitudes show that the adsorption of HA on JN-01 resin may be dominated by chemical adsorption. But the adsorption enthalpies of HAs are significantly lower than the usual chemical adsorption enthalpy value ($43\text{--}140\text{ kJ mol}^{-1}$), indicating physical adsorption force such as hydrogen bond, π - π stacking and cation- π bonding also play an important role in adsorption process (Fig. 4, R' represents the basic structural unit of natural organic acids). Comparing with HAs and TA, the adsorption enthalpies of GA on JN-01 are significantly higher, which indicate the chemical adsorption (ion-exchange) is the main adsorption force during the process of adsorption of GA.

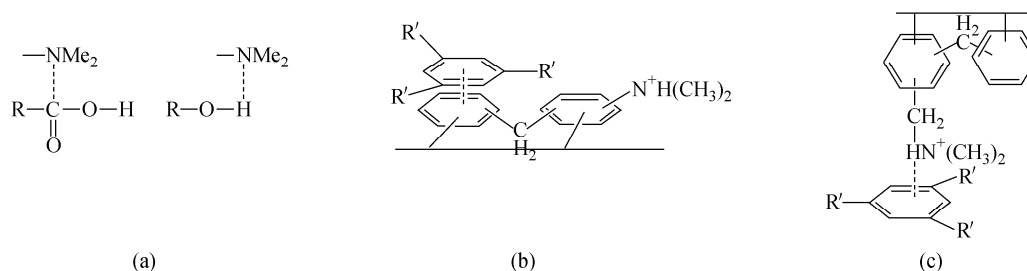


Fig. 4 (a) Hydrogen bond, (b) π - π stacking, (c) cation- π bonding

Effect of Humic Acid's Molecular Weight on Resin's Adsorption Capacity

Traditionally, the adsorption capacity of fractions of humic substances with different molecular sizes displays an inverse dependence on molecular size, when it is expressed on an adsorbent mass basis. Nevertheless, normalizing the amount adsorbed on the basis of the available adsorbent surface area accounts for the size exclusion behavior displayed by the molecular size fractions, resulting in convergence of their adsorption capacities.

As shown in Fig. 5, though the molecular weight of HA3 is higher than that of HA1 and HA2, the adsorption capacity of JN-01 for HA3 is the highest. It indicates that the adsorption capacity is reduced if the molecular weight of HA is higher than 10000 Da or lower than 6000 Da. The adsorption isotherms can be fit by Freundlich equation, and all constants are listed in Table 5.

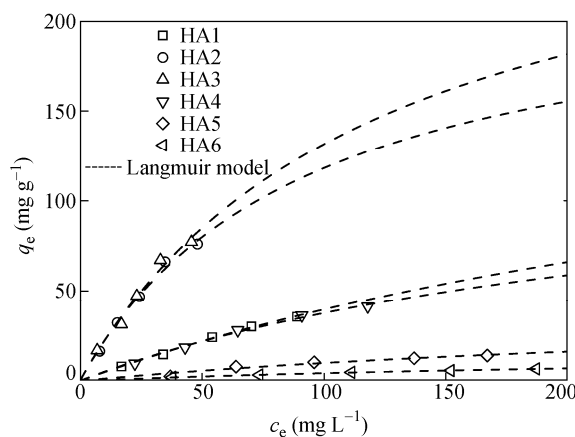


Fig. 5 Adsorption isotherm of humic acid with different molecular weight on resin JN-01 at 303 K

As shown in Table 5, Freundlich equation can fit the data well with $R^2 > 0.98$. The ' K_F ' of HA3 is higher than that of other components which indicates that molecular volume of HA is not the major factor for resin's adsorption capacity, and chemical properties of HA may play an important role during the adsorption process. In Fig. 6, the value of UV_{254}/TOC of HA increases as molecular weight increases, and it indicates aromatic of HA increases as molecular weight increases. In Table 2, atomic ratios of H/C and O/C increase as molecular weight

decreases, which indicates the hydrophilicity of HA increases as molecular weight decreases. Since either higher aromatic or hydrophilicity of HA can reduce resin's adsorption capacity, the amounts of JN-01 adsorption of HA3 is the highest.

Table 5. Results obtained from the Freundlich equations applied to the adsorption isotherms of humic acid with different molecular weight on JN-01 at 303 K

Adsorbate	Molecular weight (Da)	Freundlich equation		
		n	K_F	R^2
HA1	MW < 2000	1.08	0.578	0.997
HA2	2000 < MW < 6000	1.14	2.764	0.988
HA3	6000 < MW < 10000	1.17	3.07	0.984
HA4	10000 < MW < 30000	1.11	0.307	0.989
HA5	30000 < MW < 50000	1.09	0.128	0.999
HA6	50000 < MW < 100000	1.28	0.112	0.998

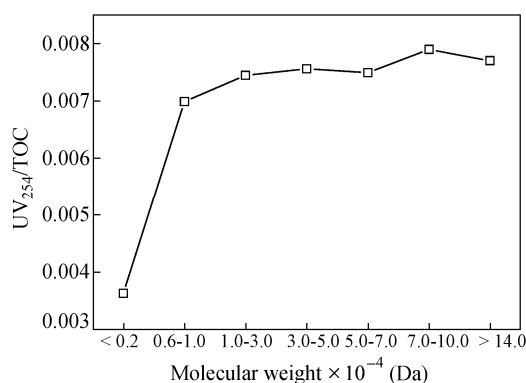


Fig. 6 UV₂₅₄/TOC of HA with different molecular weight

Effect of Humic Substance on the Removal of Heavy Metal Ions

As shown in Fig. 7, the adsorption capacity of JN-01 for heavy metal ions increases in the presence of humic substance. Weakly basic ion-exchange resin may adsorb heavy metal ions by these ways: (1) “—N<” of weak basic ion-exchange resin can serve as the electron donor and heavy metal ions can serve as the electron acceptor, and forms N···M²⁺ (2) heavy metal ions can form cation- π bonding with resin's benzene rings. All data are fitted by Langmuir equation^[17]:

$$1/q_e = 1/(bc_e) + 1/Q_m \quad (4)$$

From it, the monolayer saturation adsorption capacity of adsorbate, Q_m , the constant, b , and the adsorbent-adsorbate relative affinity in the adsorption process, Q_m and b , were obtained and listed in Table 6, and the value of constants is listed in Table 6.

From Table 6, it can be seen that Langmuir equation can fit the adsorption isotherms well. Both monolayer saturation adsorption capacities for metal ions and adsorbent-adsorbate relative affinity increase in the presence of humic substance. It can be explained as follows: in the presence of humic substance resin may adsorb humic substance first, and un-bonded function groups of the natural organic acid which has been adsorbed by resin can form conjugations with heavy metal ions, as a result, the adsorption capacity of resin for heavy metal ions increases.

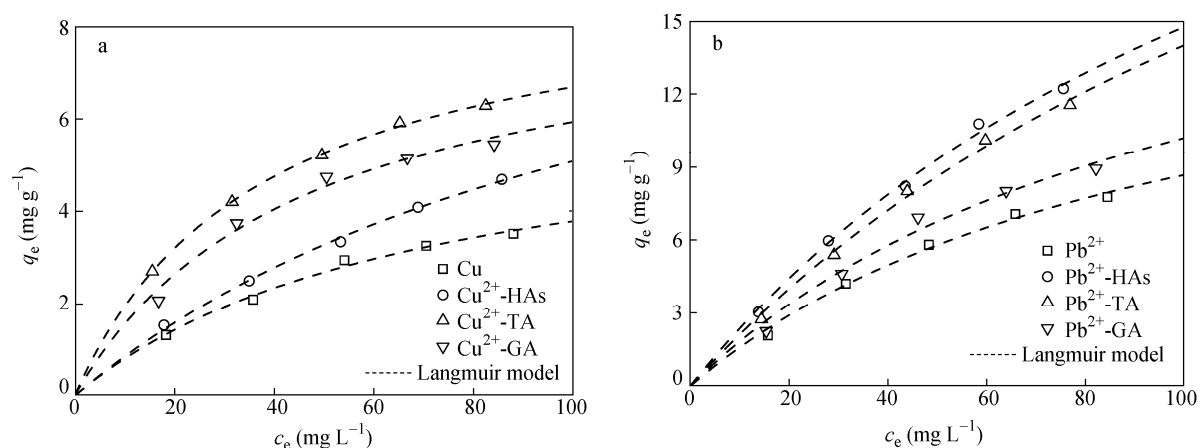


Fig. 7 Adsorption isotherms of heavy metal ions on JN-01 in the presence of humic substance
a) Adsorption of Cu^{2+} on JN-01; b) Adsorption of Pb^{2+} on JN-01

Table 6. Langmuir equation fit of the adsorption isotherms for Cu^{2+} and Pb^{2+} at 303 K in the presence and absence of humic substance

Adsorbate	Humic substance ($c = 40 \text{ mg L}^{-1}$)	Langmuir equation		
		b	Q_m	R^2
Cu^{2+}	In the absence of humic substance	0.089	6.66	0.996
	In the presence of HAs	0.101	9.35	0.997
	In the presence of TA	0.245	9.20	0.999
	In the presence of GA	0.155	10.87	0.985
Pb^{2+}	In the absence of humic substance	0.158	40.00	0.993
	In the presence of HAs	0.237	43.86	0.998
	In the presence of TA	0.199	64.52	0.998
	In the presence of GA	0.171	82.64	0.987

CONCLUSIONS

The following conclusions can be drawn from the conducted studies:

(1) Humic substance can be removed by macro weakly basic ion-exchange resin JN-01. Resin's adsorption capacity for tannic and gallic acids is higher than that for humic acid, and it is due to the higher ionic degree and lower molecular weight of tannic and gallic acids.

(2) Though humic acid's molecular weight can affect resin's adsorption capacity, the hydrophobic and aromatic features of humic acid may play an important role in its removal. The adsorption capacity of JN-01 for humic acid with molecular weight in the range of 6000–10000 Da is the highest.

(3) Though isosteric enthalpies of adsorption indicated that chemical adsorption force dominates the adsorption process of natural organic acids, physical adsorption force is important for JN-01 adsorption for humic and tannic acids.

(4) The adsorption capacity of macro weakly basic resin for heavy metal ions increases in the presence of humic substance due to bridging bonds between metal ions and these acids.

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