

SYNTHESIS OF MACROPOROUS HUMIC ACID RESINS AND THEIR CHELATING PROPERTIES FOR HEAVY METAL IONS*

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ABSTRACT

Macroporous HA resins (HAR) can be prepared in pearl form by grafting HA onto crosslinked PS through azo or through ester and / or ether linkages. At pH 13 and the HA / PSNH₂ weight ratio 0.7—1.0, PSNH₂⁺Cl⁻ couples with HA and results in the formation of azo-type HA resin (HAR-A), which shows good adsorbility towards heavy metal ions. The Cu²⁺ sorption capacity of ester / ether type humic acid resin (HAR-E) is increased by lengthening the reaction time of HA and PSCH₂Cl. The structure of HAR is discussed on the basis of the IR spectra. The sorption capacity of HAR-A is 1.01 mmol / g for Cd²⁺ and 0.6—0.53 mmol / g for Ni²⁺, Mn²⁺, Cu²⁺, Co³⁺ and Zn²⁺, respectively. The calculated distribution coefficients of heavy metal ions on HAR-A can be arranged in the following order: Cu²⁺(8.7×10^3) > Cd²⁺(3.8×10^3) > Zn²⁺(2.4×10^3) > Ni²⁺(1.8×10^3) > Mn²⁺(4.9×10). At pH 6.5, Cu²⁺, Cd²⁺, Ni²⁺, Mn²⁺ can be quantitatively adsorbed by HAR-A and completely eluted with 1N HNO₃. HAR-A can be regenerated and reused. Trace quantities of the above-mentioned heavy metal ions in four samples of the natural occurring water and one sample of the tap water were analyzed by using HAR-A.

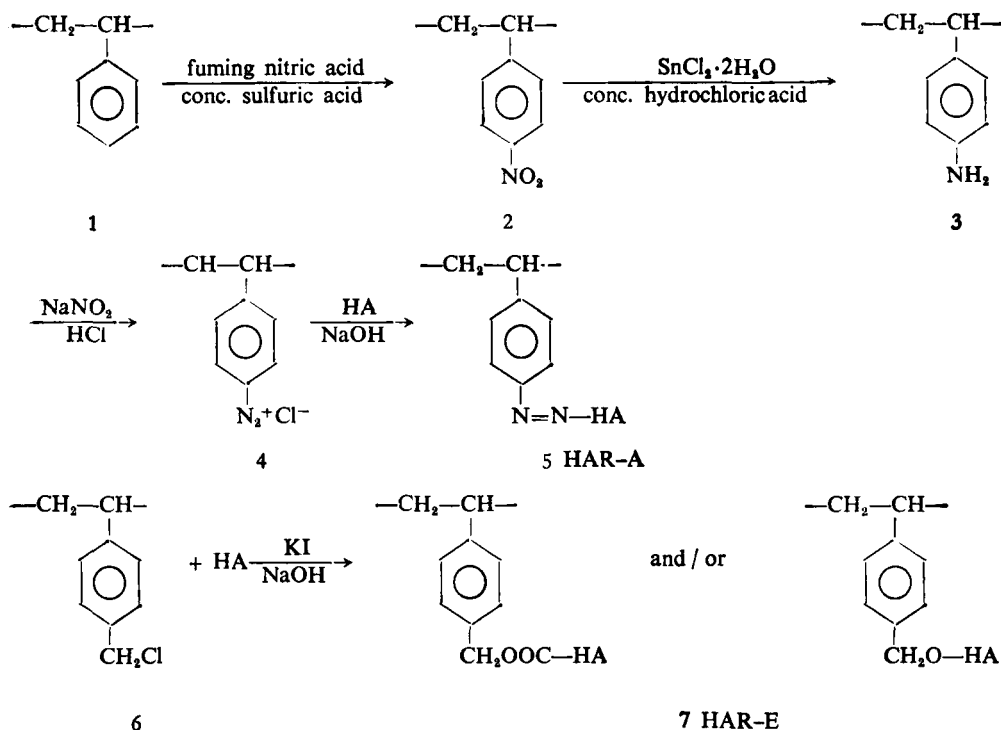
INTRODUCTION

The characterization^[1,2], sorption of metallic ions^[3-6] by humic acids (HA) and the adhesive^[7,8] and polycondensation type^[9-11] of humic acid resins (HAR), as well as coupling reaction of HA with diazonium salts of low molecular weight aromatic amines^[12-14] have been reported in the literature. Two kinds of new type HAR, azo type humic acid resin (HAR-A) and ester / ether type humic acid resin (HAR-E) have been synthesized by us according to the following scheme. They are both beadlike macroporous chelate resins, and HAR-A has excellent alkali-resistance in particular.

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The reactions of the resins shown in the above equations are confirmed by the IR spectra. The optimum conditions for HAR synthesis and their heavy metal ion sorption properties were studied. HAR-A can be regenerated and used repeatedly. Rate of sorption is satisfactory, $T_{1/2} \leq 3.5$ min. The distribution coefficients of several heavy metal ions in HAR-A have been determined. HAR-A can be used in enriching and estimating a trace amount of Cu^{2+} , Cd^{2+} , Ni^{2+} and Mn^{2+} in natural or tap water.

EXPERIMENTAL PART

1. Reagents

HA Zhaotong HA, Tulufan HA were isolated and purified according to the reference^[2].

PS Macroporous crosslinked polystyrene beads, degree of crosslinking 8% DVB, 20—60 mesh.

PSCH₂Cl Macroporous chloromethylated polystyrene beads, degree of crosslinking 6%, 40—80 mesh, chlorine content 18.01%.

Other reagents used in synthesis are of AR or CP grade, and those used in analysis are of GR grade or spectroscopically pure.

2. Synthesis of HAR-A

Resin 2 (PSNO₂) and resin 3 (PSNH₂) were synthesized according to the literature^[15]. Nitrogen content of resin 3 was determined to be 11.3%.

Resin 4 (PSN₂⁺Cl⁻) was prepared from resin 3 through diazotization as mentioned in the

literature^[16], the formed resin 4 was washed with ice-cold water to pH 3, and kept in refrigerator before use.

The UV spectra were taken from a 4 ppm solution of the purified HA in 0.05 N NaHCO₃ with a Shimadzu UV spectrophotometer model 210A. The IR spectra of the samples were recorded by the KBr-pellet method with a Perkin Elmer spectrophotometer model 683.

HA was first dissolved in 0.1 N NaOH and cautiously adjusted to the required pH by adding 5% NaOH solution. After cooled to 5°C, a weighed PSN₂⁺Cl⁻ resin was introduced into the solution in several portions with continuous stirring. Because of the trace acid remained in PSN₂⁺Cl⁻ resin and HCl produced in coupling, replenishing 5% NaOH solution from time to time was necessary. A pH meter was used to monitor the pH of the solution. Reaction was conducted under constant stirring below about 10°C for 5 hours and then left overnight. Next day the reaction mixture was heated to 70°C and stirred for another hour in order to decompose the residual diazonium groups. The product was separated by filtration with aspirator and washed thoroughly with 5% NaOH to remove any unreacted HA, then washed with water and treated with 2N HNO₃. The resin so obtained was transferred to a column with sintered glass plate at the bottom, rinsed with distilled water for 24 hours and then drained.

3. Synthesis of HAR-E

PSCH₂Cl beads were swollen with DMF, and then drained. The swollen resin was added to an aqueous solution containing HA, NaOH and KI, and the mixture was then reacted at 80°C under constant stirring for a predetermined time. Filtered by suction while hot, and washed thoroughly with distilled water and then with DMF and ether successively, dried in air.

Sample Zhaotong HA : PSCH₂Cl : NaOH : KI : H₂O = 5 : 2 : 1 : 1.5 : 125 (weight ratio)
PSCH₂Cl : NaOH : KI = 1 : 2.5 : 1 (mole ratio)

4. Determination of the sorption properties for heavy metal ions on HAR

(1) Determination of sorption rate and sorption capacity for heavy metal ions on HAR-A

Six portions of dried HAR-A weighing 0.2000 g each, were put into six beakers. Excess Cu²⁺, Cd²⁺, Co³⁺, Ni²⁺, Mn²⁺ and Zn²⁺ solutions were added respectively, made up to 200 ml and adjusted to pH 6.5 (unless otherwise specified). Stirred continuously at 25 °C. At definite intervals, the supernatant solution was withdrawn from each beaker and the metal ion concentration was determined with a Zeiss atomic absorption spectrometer model AAS-1 (AAS method). Parallel runs were made. Residual metal ions remaining in solutions after shaking 12 hours were determined by complexometric titration and their sorption capacities were calculated therefrom.

(2) Analysis of water samples

Two liters of filtered water sample was allowed to pass a HAR-A column of 120 (height) × 8 (diameter) mm at a rate of 4—5 ml / min. The heavy metal ions concentrated in it were eluted with 1N HNO₃ and determined by the AAS method (column method). Cu²⁺,

Cd^{2+} , Ni^{2+} and Mn^{2+} in samples of four natural water and one sample of tap water taken from Hangzhou were determined according to the same method described above.

RESULTS AND DISCUSSIONS

1. Choice of HA

Data listed in Table 1 illustrate that the sorption capacity of Cu^{2+} by Zhaotong HAR-A is larger than that of the Tulufan HAR-A.

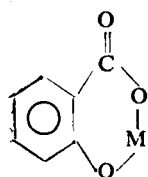
Table 1 Amount of Cu^{2+} adsorbed on different HAR-A

Name of HAR-A	Amount adsorbed (mg Cu^{2+} / g resin)
Zhaotong	14.3
Tulufan	12.1

* HA / $\text{PSNH}_2 = 1$ (weight ratio), coupled at pH 12.

** HAR-A 100 mg, Cu^{2+} 2 mg, pH 4, volume of solution 25 ml, 4 hours shaking, determined by AAS method (the same as for Fig. 1—3).

$\text{PSN}_2^+\text{Cl}^-$ couples with phenolic aromatic rings. As shown in Table 2, the Zhaotong HA having more phenolic hydroxyl groups, is more favorable for coupling. Furthermore, the HAR adsorbs Cu^{2+} mainly through the formation of chelate such as shown in the formula



. The OH / COOH in Zhaotong HA is 0.78 while that of the Tulufan HA is

0.31. The former prefers more the formation of chelates. Therefore, in this paper, HAR-A is generally referred to Zhaotong HAR-A unless otherwise specified.

Table 2 Characterization of functional groups^[3] in HA

	Carboxyl	Phenolic hydroxyl	Alcoholic hydroxyl	Carbonyl	Methoxyl
	(mmol group / g HA)				
Zhaotong HA	4.23	3.29	0.57	2.95	0.29
Tulufan HA	5.61	1.75	0.26	4.60	0

2. Influence of pH at coupling on the Cu^{2+} sorption in HAR-A

From Fig. 1, it is obvious that the coupling in different pH influences the sorption of

Cu^{2+} by HAR-A markedly. There is little difference in the pH range 10–11; but in the range 11–13, Cu^{2+} sorption by HAR-A increases abruptly as pH is increased. High pH favors the coupling of $\text{PSN}_2^+\text{Cl}^-$ with HA.

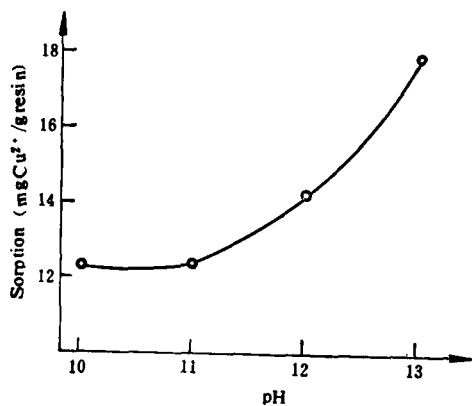


Fig. 1 Cu^{2+} sorption of HAR-A prepared at different coupling pH, $\text{HA} / \text{PSNH}_2 = 1$ (wt. ratio)

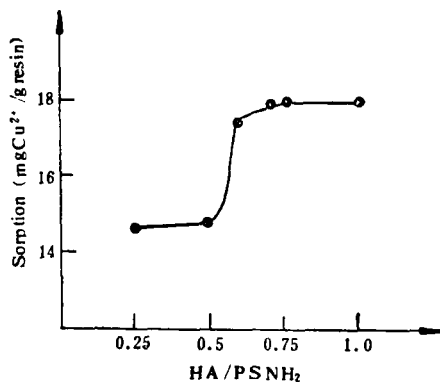


Fig. 2 Cu^{2+} sorption of HAR-A prepared at different $\text{HA} / \text{PSNH}_2$ weight ratios, coupling pH 13

3. Influence of $\text{HA} / \text{PSNH}_2$ on the sorption of Cu^{2+} by HAR-A

It can be seen in Fig. 2, that the Cu^{2+} sorption increases as the weight ratio of $\text{HA} / \text{PSNH}_2$ is in the range of 0.5–0.7, but flattens to the value of 17.9 mg Cu^{2+} /g resin as it is in the range of 0.7–1.0.

4. Influence of reaction time on Cu^{2+} sorption by HAR-E

It is illustrated in Fig. 3, that at fixed ratio of reactants, the sorption of Cu^{2+} by HAR-E increases with reaction time.

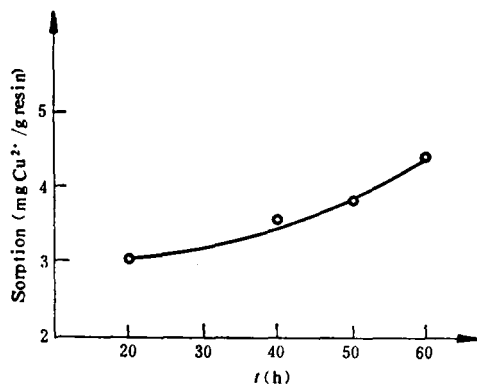


Fig. 3 Influence of reaction time on the sorption of Cu^{2+} by HAR-E

The resin increases in weight ca. 20–25% in the course of HAR-E synthesis. Though Zhaotong HA has comparatively more carboxyl and phenolic hydroxyl group, they are partially used in building ester / ether linkages, and hence the Cu^{2+} sorption of HAR-E is always inferior to that of HAR-A.

5. Structure of HAR

The UV spectra of HA in 380–180 nm range show a maximum absorption at 214–5 nm. It is probable due to the aromatic carboxyl groups of HA.

The IR spectra of PSNO_2 in Fig. 4 show a band at 1350 cm^{-1} which is the characteristic of nitro group. It disappears in PSNH_2 , but a new band appears at 1275 cm^{-1} pertaining

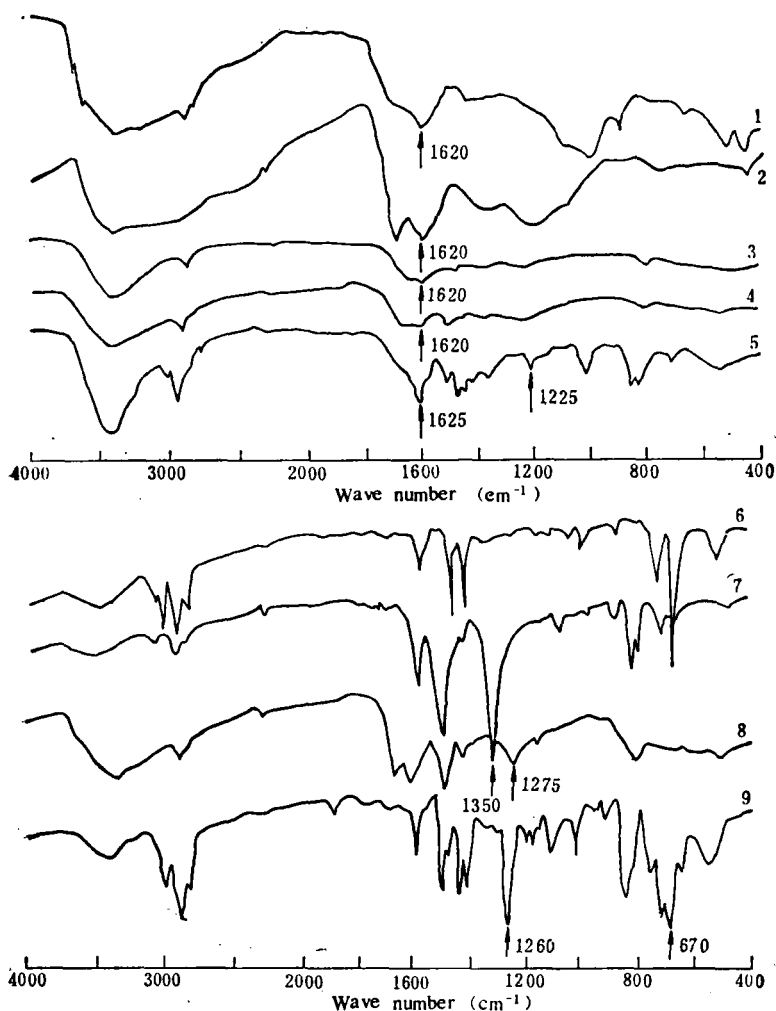


Fig. 4 The IR spectra of HA and resins

1. Zhaotong HA; 2. Tulufan HA; 3. Zhaotong HAR-A; 4. Tulufan HAR-A;
5. Zhaotong HAR-E; 6. PS; 7. PSNO_2 ; 8. PSNH_2 ; 9. PSCH_2Cl .

the aromatic primary amine. In the two HAR-A, 1275 cm^{-1} band disappears completely, and a band of COO^- at 1620 cm^{-1} originated from HA appears. IR spectra demonstrate the sequence of HAR-A synthesis.

PSCH_2Cl has a band at 670 cm^{-1} which is characteristic of $\text{C}-\text{Cl}$ and a band at 1260 cm^{-1} can be assigned as the nonplanar wagging of CH_2 [17,18]. In HAR-E bands at 670 and 1269 cm^{-1} disappear and a new band at 1225 cm^{-1} which can be attributed to the $\text{C}-\text{O}$ of newly formed ester / ether linkages rises.

6. Influence of pH on the sorption properties of HAR-A for heavy metal ions

The HAR-A used is prepared at $\text{HA} / \text{PSNH}_2 = 1$ and by coupling at pH 13. From Fig. 5, it is obvious that Cu^{2+} , Ni^{2+} , Co^{3+} , Zn^{2+} , Mn^{2+} , Cd^{2+} , Fe^{3+} is adsorbed completely at pH 3—6.5, 6—7, 6.5—7, 6.5—8.4, respectively. Sorption reaches 100%.

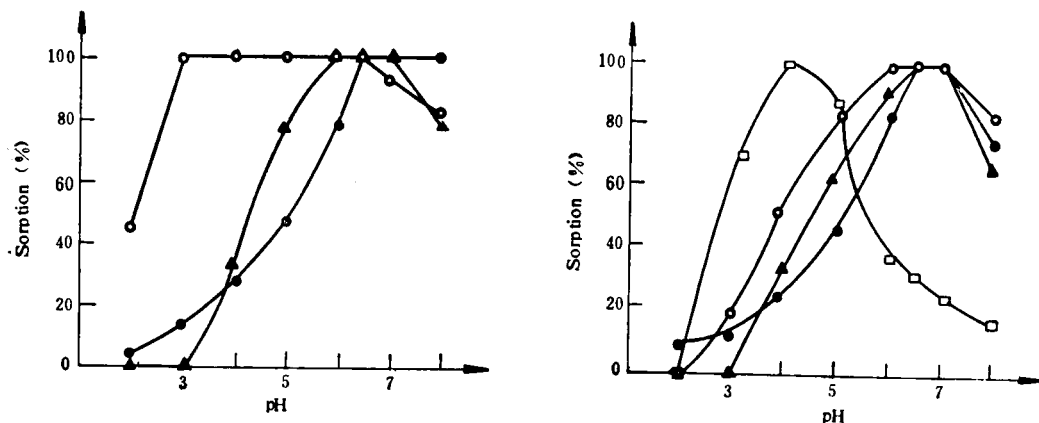


Fig. 5 Sorption of various heavy metal ions on HAR-A at different pH
Resin 100 mg, metal ion $50\text{ }\mu\text{g}$ each, buffer solution 5 ml, total volume 25 ml, shaking for 4 hours, determined by AAS method.

● Cd^{2+} ○ Cu^{2+} ▲ Co^{3+}

● Mn^{2+} ○ Ni^{2+} ▲ Zn^{2+} □ Fe^{3+}

7. Sorption rate and sorption capacity of HAR-A

The plateau of the curve on Fig. 6 indicates that equilibrium has been reached. Quantity adsorbed at this moment corresponds to the sorption capacity under the experimental conditions. Sorption capacities of the six heavy metal ions determined by AAS method and titration method are listed in Table 3.

Sorption rate is usually expressed in terms of $T_{1/2}$, the time required to reach half saturation. From Fig. 6, it is 3.5 and 3.0 min for Cd^{2+} and Cu^{2+} , respectively. HAR-A adsorbs Co^{3+} , Ni^{2+} , Mn^{2+} and Zn^{2+} very quickly, their $T_{1/2}$ are all less than one minute.

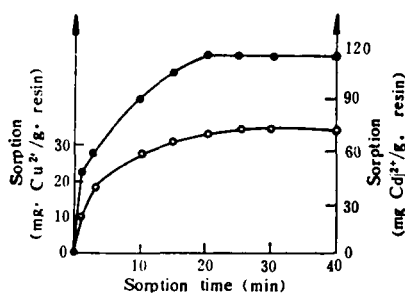
Fig. 6 Sorption rate of Cd^{2+} and Cu^{2+} on HAR-A● Cd^{2+} ○ Cu^{2+}

Table 3 Sorption capacities of HAR-A towards various heavy metal ions (mmol ion / g resin)

Method of determination	Kind of metal ion					
	Cu^{2+}	Cd^{2+}	Co^{3+}	Ni^{2+}	Mn^{2+}	Zn^{2+}
AAS method	0.56	1.01	0.55	0.60	0.59	0.53
Titration method	0.55	0.91	0.51	0.59	0.56	0.48

8. The distribution coefficients of various heavy metal ions on HAR-A

Adsorbability of a metal ion on a resin can be expressed in terms of distribution coefficient K_d , which is defined as^[19]:

$$K_d = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

The results of determination* are: $\text{Cu}^{2+}(K_d = 8.7 \times 10^3) > \text{Cd}^{2+}(3.8 \times 10^2) > \text{Zn}^{2+}(2.4 \times 10^2) > \text{Ni}^{2+}(1.8 \times 10^2) > \text{Mn}^{2+}(4.9 \times 10)$.

9. Choice of eluent

Data in Table 4 show that Co^{3+} adsorbed on HAR-A is difficult to be eluted by all the eluants tried, but Cu^{2+} , Cd^{2+} , Ni^{2+} and Mn^{2+} can be quantitatively eluted by 2N or 1N HNO_3 . We choose 1N HNO_3 as the eluant.

10. The analysis of heavy metal ions in natural and tap water

Considerable amounts of Na^+ , Ca^{2+} , Mg^{2+} are usually present in natural water, tap water and waste water. We have observed in the above-mentioned experiments that Na^+ in the HAc-NaAc buffer solution does not interfere in HAR-A sorption. Addition of 200 times of Ca^{2+} , Mg^{2+} in studying the adsorbabilities of Cu^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} on HAR-A by column

* 0.2000g HAR-A is added to a 200 ml solution containing 50 mmol metal ion of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , respectively. Shake for 4 hours and then analyze by AAS method.

Table 4 The results of elution with different eluants

Eluants	Recovery* (%)				
	Cu ²⁺	Cd ²⁺	Ni ²⁺	Mn ²⁺	Co ³⁺
2N HNO ₃	97.5	101.1	102.2	—	13.3
1N HNO ₃	100.8	99.6	102.2	100.0	13.3
0.5N HNO ₃	86.1	92.0	94.9	—	13.3
Saturated EDTA solution	75.3	82.8	93.3	84.6	—

* Resin bed: 120 (height) × 8 (diameter) mm; Cu²⁺, Cd²⁺, Ni²⁺, Mn²⁺, Co³⁺ 100 μg each in 30 ml mixed solution, rate flow 2—3 ml/min; eluted with 25 ml eluant; analyzed by AAS method.

method, also showed no effect.

Huanglongdong fountain with addition of different amounts of Cu²⁺, Cd²⁺, Ni²⁺, Mn²⁺ was passed through a HAR-A bed. The adsorbed ions were eluted and the recovery % of ions was determined by AAS method and the results are listed in Table 5. The standard recovery deviations of the above-mentioned ions were 2.08, 1.52, 1.46, 0.91, respectively.

Table 5 Recovery % of Cu²⁺, Cd²⁺, Ni²⁺, Mn²⁺

Heavy metal ions	Cu ²⁺			Cd ²⁺			Ni ²⁺			Mn ²⁺		
Added amount (g/l)	0	20	40	0	20	40	0	20	40	0	20	40
Determined amount (g/l)	13.1	33.0	50.8	14.3	33.5	54.5	8.8	29.7	51.2	143.8	165.0	182.5
Recovery %	—	99.5	94.3	—	96.5	100.8	—	104.5	106.0	—	106.0	96.8

Table 6 gives the results of analysis of Cu²⁺, Cd²⁺, Ni²⁺ and Mn²⁺ in four samples of natural waters and one sample of tap water of Hangzhou, using HAR-A column method.

Table 6 Amounts of Cu²⁺, Cd²⁺, Mn²⁺, Ni²⁺ in several water samples from Hangzhou

Water sources	Qiantong River	Hupao Spring	West Lake	Huanglongdong Spring*	Tap water
Cu ²⁺ (mg/l)	18.9	10.1	22.0	13.1	11.6
Cd ²⁺ (mg/l)	2.0	1.3	1.4	14.3	4.8
Ni ²⁺ (mg/l)	5.9	4.9	4.9	8.8	3.4
Mn ²⁺ (mg/l)	15.3	15.0	5.4	143.8	15.0

* Water samples collected after raining.

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