ORIGINAL PAPER

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Dynamic adsorption and desorption of heavy metal ions on poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber

Received: 15 October 1997 / Revised: 17 March 1998 / Accepted: 20 March 1998

Abstract The dynamic adsorption and desorption properties, including the effect of pH value and flow rate on the adsorption, eluent acidity and volume, eluting velocity and re-use, of Cu(II), Pb(II), Zn(II), Cd(II), Mn(II), Ni(II), Co(II) and Hg(II) ions on the column loaded with poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber were investigated. The recovery of Mn(II), Co(II), Cd(II), Ni(II) and Zn(II) ions in the presence of Na, K, Ca and Mg ions was examined. The preconcentration of trace amounts of Mn(II), Co(II), Cd(II), Ni(II) and Zn(II) ions from model solution samples was carried out with satisfactory results. The amount of the metal ions detected after preconcentration and recovery by this technique was basically in agreement with the added amount. The method is rapid, precise and simple.

Introduction

In analytical chemistry, the preconcentration process is of great importance since it enables trace elements to be determined in combination with different identification methods [1, 2]. Sorption with chelating sorbents is very promising in this respect. The chelating resins have a high adsorption capacity for noble metals [3–8], but a slow sorption rate.

Fibrous sorbents hold great advantage for the concentration of microelements from natural waters. The large surface area and high kinetic properties of these sorbents and the possibility of using them in different sorption

modes, such as filters and films, make them useful to determine the concentrations of various microelements [9–11]. The chelating cellulose sorbents have recently been reported [12–17]. But owing to their poor performance in acid solution and lower sorptive capacity for metal ions, these sorbents cannot be widely applied. Although the poly(acrylamidoxime-carboxylic acid) chelating fiber has been developed for the concentration of multielements from various samples [18–20], the swelling effect of the fiber during elution limited its re-usability. Polyacrylacylisothiurea [21] and poly(acrylamidrazone-hydrazide) chelating fibers [22] have been synthesized and applied to the concentration-separation of trace amounts of Au(III), Pd(IV), Ru(III) and In(III), Sn(IV), Cr(III), V(V), Ti(IV).

A new type of poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber, called PAAP-II, was obtained through the following steps: 1) The polyacrylonitrile fiber was modified by hydrazine; 2) the hydrazine-modified fiber reacted with diethylenetriamine, and the aminated fiber was obtained; 3) the PAAP-II chelating fiber was prepared by introducing the phosphonic group into the aminated fiber. By infrared spectroscopic analysis, it was shown that the PAAP-II chelating fiber contained carboxyl, aminophosphonic and hydrazide groups. The synthesis and structure of the sorbent has been described in detail elsewhere [23].

However, the dynamic column adsorption and desorption properties of the poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber have not been reported previously. In this report, we investigate the preconcentration efficiency of the newly developed chelating fiber for heavy metal ions by means of the dynamic adsorption technique. The adsorption properties, including effect of flow rate and pH value on adsorption, and desorption conditions such as elution velocity, desorption acidity, eluent volume and re-usability are discussed in detail.

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Fig. 1 Effect of flow rate on the adsorption of metal ions by PAAP-II chelating fiber

Material and methods

Reagents and standards

The poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber was cut into 1 mm units, soaked in 1% NaOH solution for 3–4 h, and then suction-filtered, washed with distilled water, and dried at 60–65 °C overnight.

All chemicals were of analytical grade. Deionized water was used throughout the experimental procedure. The standard solutions (1000 mg/L) of Cu(II), Pb(II), Zn(II), Cd(II), Mn(II), Ni(II), Co(II) and Hg(II) were provided by Central Iron and Steel Research Institute, Ministry of Metallurgical Industry, China, and the test concentrations of these metal ions were further diluted to 2.0 mg/L prior to use.

Instrument and apparatus

A 3100 Enhanced Data System (Perkin-Elmer) and a Z-6100 (Hitachi) Atomic Absorption Spectrometer (AAS) were used for the determination of low and high concentrations of the single metal ions. The concentration of the mixed metal ions was determined by a Spectroflame ICP Argon-plasma Emission Spectrometer (Spectro Analytical Instruments Kleve, Germany). The pH values of the solutions were measured with a Model pH-3 C pH-meter (Shanghai Instrument Company). Glass columns of 20 cm length and 1 cm inner diameter were used for dynamic adsorption experiments and preconcentration of the trace metal ions.

Column adsorption procedure

The fiber column, containing 0.25 g PAAP-II chelating fiber, was prepared by spiraling a water slurry of the chelating fiber. The bed height of sorbent in the column was 3 cm.

A volume of 10 mL of 2 mg/L Cu(II), Pb(II), Zn(II), Cd(II), Mn(II), Ni(II), Co(II) and Hg(II) single metal ion solutions, previously adjusted to the desired pH value with diluted NH_4OH solution, was passed through the adsorption columns at flow rates of 1–8 mL/min. After the passage of the solutions, the columns were rinsed twice with 10 mL of deionized water. The concentrations of the metal ions in effluents were determined by AAS.

Desorption experiments

After the adsorption procedure, the adsorbed metal ions on the fiber column were eluted with different concentrations of diluted hydrochloric or nitric acid at eluting rates of 1–8 mL/min. The concentrations of metal ions were analyzed by AAS.

Re-use of the chelating fiber

A volume of 10 mL of a mixture containing 2 mg/L each of Cd(II), Mn(II), Ni(II), Co(II) and Cu(II), previously adjusted to $\text{pH } 6.0 \pm 0.3$ with diluted NH_4OH solution, was added to the fiber column at

Fig. 2 Effect of pH value on the adsorption of metal ions by PAAP-II chelating fiber

a flow rate of 3 mL/min. The metal ions extracted by the sorbent were desorbed with 30 mL of 6 mol/L hydrochloric acid at a flow rate of 2 mL/min. The column was rinsed twice with deionized water, then soaked in 1% NaOH solution, and substantially washed with deionized water until neutrality was reached. As in the above process, the experiment was repeated 10 times. The adsorption and desorption percentages were calculated each time.

Effect of interfering ions

A mixture, containing 20 μg each of Zn(II), Cd(II), Mn(II), Ni(II), Co(II) ions and 10–20 mg each of Na, K, Ca, Mg interfering ions in 100 mL solution at $\text{pH } 6.0 \pm 0.3$, was passed through the PAAP-II fiber column at a flow rate of 3 mL/min. The concentrations of the metal ions eluted with 40 mL of 6 mol/L hydrochloric acid were determined by ICP after the solution was concentrated to 50 mL.

Preconcentration of trace metal ions from model solution samples

A 1 L mixing solution, containing 15–20 $\mu\text{g/L}$ each of Zn(II), Cd(II), Mn(II), Ni(II) and Co(II), was passed through PAAP-II chelating fiber column at a flow rate of 3 mL/min. The column was

Fig. 3 Effect of eluent acidity and volume on desorption of (a) Cd, (b) Co, (c) Cu, (d) Mn, (e) Ni, (f) Pb, (g) Zn, (h) Hg ions from PAAP-II chelating fiber column (eluting rate 2 mL/min)

washed twice with 10 mL of deionized water, and then the adsorbed metal ions were eluted with 40 mL of 6 mol/L hydrochloric acid. The eluate was transferred to a 50 mL volumetric flask. The concentration of the eluted metal ions were determined by ICP.

Results and discussion

Effect of flow rate on the adsorption

Figure 1 presents the effect of the flow rate on the adsorption of metal ions by the poly(acrylamino-phosphonic-car-

boxyl-hydrazide) chelating fiber. At flow rates of 1–8 mL/min, Co(II), Cd(II), Pb(II), Ni(II) and Mn(II) ions can be adsorbed quantitatively, while the adsorption of Cu(II), Hg(II) and Zn(II) ions had a decreasing dependency at a flow rate of 6 mL/min; but an 85% adsorption can be attained.

Effect of pH value on the adsorption

The pH value is one of the most important factors influencing the adsorption behavior of metal ions on the fi-

Fig.4 Effect of eluting velocity on the recovery of metal ions from PAAP-II chelating fiber column

Table 1 The re-usability of PAAP-II chelating fiber

Times		Metal ions				
		Mn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)
1	Adsorption (%)	95.06	100.0	95.03	100.0	100.0
	Recovery (%)	94.60	92.30	102.1	92.03	80.10
2	Adsorption (%)	95.07	100.0	94.80	100.0	100.0
	Recovery (%)	98.50	97.25	107.9	96.50	86.20
3	Adsorption (%)	95.07	100.0	97.07	100.0	100.0
	Recovery (%)	97.50	94.08	102.1	97.25	90.41
4	Adsorption (%)	95.14	100.0	97.32	100.0	100.0
	Recovery (%)	98.50	91.82	112.8	92.73	92.22
5	Adsorption (%)	95.00	100.0	95.58	100.0	100.0
	Recovery (%)	96.53	95.41	94.69	93.04	91.02
6	Adsorption (%)	95.12	100.0	96.70	100.0	100.0
	Recovery (%)	95.82	92.92	103.3	93.14	87.23
7	Adsorption (%)	94.94	100.0	96.35	100.0	100.0
	Recovery (%)	99.88	98.01	98.30	91.02	90.67
8	Adsorption (%)	95.05	100.0	94.25	100.0	100.0
	Recovery (%)	98.50	92.24	102.1	93.42	91.87
9	Adsorption (%)	95.01	100.0	96.90	100.0	100.0
	Recovery (%)	96.95	92.89	105.0	96.85	89.55
10	Adsorption (%)	95.11	100.0	97.18	100.0	100.0
	Recovery (%)	98.50	97.63	102.1	92.06	88.33

Table 2 Effect of interfering ions (Na, K, Ca, Mg) on the recovery of metal ions

Conc.(mg/L) of Na, K, Ca, Mg	Recovery (%) ^a				
	Zn(II)	Cd(II)	Ni(II)	Mn(II)	Co(II)
100	102.1	94.50	99.01	95.47	98.21
200	100.3	96.32	101.3	97.82	97.30

^a The concentration of Zn(II), Cd(II), Ni(II), Mn(II), Co(II) ions is 0.2 mg/L

brous sorbent. The results in Fig. 2 show that these curves for Cu(II), Pb(II), Cd(II), Zn(II), Ni(II), Mn(II) and Co(II) exhibit a similar dependency on the pH value. For Cu(II) ion, the adsorption percentages were 99% above pH 3.0 and decreased rapidly in the pH range 1.0–3.0, while below pH 1.0 Cu(II) ion was scarcely adsorbed by the

PAAP-II fiber. The adsorption percentages of Pb(II) and Cd(II) ions by the sorbent reached 98% above pH 3.5. Zn(II), Mn(II) and Co(II), Ni(II) ions can be quantitatively adsorbed by the sorbent separately at pH 4.0, 4.5, 5.0.

However, one interesting difference was observed in the case of the adsorption of Hg(II) ion by the PAAP-II fiber. The adsorption percentage of Hg(II) ion remained above 95% even at lower pH value (pH = 1.5). This phenomenon is mainly contributed to the formation of a stable complex between the PAAP-II fiber and Hg(II) ion at lower pH value. Further investigations on the macromolecular structure and morphology of the PAAP-II fiber as well as on the coordination mechanism seem to be necessary for a better understanding of the property.

Eluent acidity and volume for desorption

The effects of the concentration and volume of hydrochloric or nitric acid on the desorption efficiency (recovery) of the metal ions from the chelating fiber column were investigated and the results are plotted in Fig. 3. All investigated metal ions showed a common trend to higher recovery at higher acidity and larger eluent volume of hydrochloric or nitric acid. Evidently, Cu(II), Co(II), Zn(II) and Ni(II) ions can be desorbed quantitatively with 15 mL of 2 mol/L hydrochloric acid from the column with 98% recovery. The recovery of Mn(II) and Cd(II) ions in 25 mL and 35 mL of 6 mol/L hydrochloric acid reached 96 and 90%, respectively. However, dilute hydrochloric acid was not as effective as dilute nitric acid for the recovery of Pb(II) and Hg(II) ions, which was 98% in 25 mL of 4 mol/L and 8 mol/L nitric acid, respectively.

Eluting velocity

The influence of elution velocity on the recovery of Cu(II), Pb(II), Zn(II), Cd(II), Mn(II), Ni(II), Co(II) and Hg(II) was studied under optimum eluent acidity and volume (see Fig. 4). The results revealed that eluting velocity variation in the range of 1–8 mL/min had no significant effect on the recovery of Cu(II), Pb(II), Zn(II), Mn(II), Ni(II) and Hg(II) and reached a recovery of 95% or more. But with respect to Cd(II) and Co(II) ions, the recovery decreased with increasing eluting rate.

Table 3 The recovery of trace amount elements from model solution samples

Elements	Added (μg)	Found (μg)					Average	Recovery (%) ^a
Mn(II)	18.08	18.80	18.33	19.30	18.65	18.77	103.8	± 3.5
Co(II)	15.62	16.00	15.02	16.07	16.68	15.94	102.0	± 6.9
Cd(II)	17.40	16.59	17.17	17.03	17.93	17.18	98.70	± 5.09
Ni(II)	18.89	19.58	18.70	19.51	19.27	19.27	102.0	± 4.0
Zn(II)	16.75	17.22	16.01	17.56	16.03	16.71	99.80	± 7.60

^a Average of 4 determinations with 95% confidence level

Stability and re-use of the fiber

After the dry chelating fiber had been stored at room temperature for about 2 years, the fiber was prepared by passing it through 1% NaOH solution and washing with deionized water until neutral, and then the column was repeatedly used ten times according to the re-use procedure. The results in Table 1 showed that for Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) ions, quantitative extraction (> 95%) was observed. However, except for Cd(II), the recovery of the other metal ions eluted with 30 mL of 6 mol/L hydrochloric acid from the chelating fiber column was above 90%. In addition, swell of the chelating fiber was not found after using it ten times.

Effect of interfering ions on the recovery of metal ions

In order to evaluate the possibility of selective recovery of Co(II), Cd(II), Mn(II), Zn(II) and Ni(II) ions in the presence of interfering ions, 10–20 mg each of Na, K, Ca, Mg ions as their chloride salts were added to a 100 mL mixed solution containing 20 μg each of the mentioned ions. The results, given in Table 2, showed that 1000-fold excesses of Na, K, Ca, Mg caused little interference with the recovery of the tested metal ions.

Preconcentration of trace amount elements from solution samples

A large 1 L volume of model solution samples, containing 15–20 μg each of Co(II), Cd(II), Mn(II), Zn(II) and Ni(II), was prepared for evaluating the possibility of enriching solution of low concentration. The results listed in Table 3 show that the amount of the metal ions detected after preconcentration and recovery by this technique is basically in agreement with the added value and the recovery of the added elements with 95% confidence level is in the range 92–109%. Clearly, this method offers a good precision.

Conclusion

The poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fiber shows good stability, fast adsorption and elution rate, and can be re-used efficiently. Above pH 5.0, Cu(II),

Pb(II), Zn(II), Cd(II), Mn(II), Ni(II), Co(II) and Hg(II) ions can be quantitatively adsorbed by the PAAP-II chelating fiber and the adsorbed ions can be desorbed under adequate eluting conditions. The column packed with the PAAP-II chelating fiber provides a very simple, rapid and reliable technique for the preconcentration of trace amounts of Mn(II), Co(II), Cd(II), Ni(II) and Zn(II) ions from the model solution samples with satisfactory results and is expected to be applicable to real samples.

Acknowledgement This work was supported by SKLEAC and Key Project of Resource and Eco-Environmental Research in the Chinese Academy of Sciences (No: KZ 952-S1-231).

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