Adsorption Properties of Poly(acrylaminophosphonic-carboxyl-hydrazide)Type Chelating Fiber for Heavy Metal Ions

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ABSTRACT: In this article, the adsorption properties of poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibers for Cu(II), Cd(II), Co(II), Mn(II), Pb(II), Zn(II), Ni(II), and Cr(III) are investigated by a batch technique. Based on the research results of binding capacity, adsorption isotherm, effect of pH value on sorption, and adsorption kinetics experiments, it is shown that the poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibers have higher binding capacities and good adsorption kinetic properties for heavy metal ions. The sorption of the metal ions on the chelating fibers is strongly dependent on the equilibrium pH value of the solution. The adsorption isotherms of Cu(II) and Cd(II) on the chelating fiber exhibit a Langmuir-type equation. The adsorbed Cu(II), Cd(II), Zn(II), and Pb(II) could be eluted by diluted nitric acid.
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Key words: poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fiber; adsorption property; heavy metal ions

INTRODUCTION

The study of the removal of metal ions from aqueous solution, either for pollution control or for raw material recovery, has been taking on increasing importance in recent years. The chelating sorbents with a fibrous structure are increasingly used in removal of toxic metal ions and enrichment recovery of traces of elements from aqueous solution.[1,2] Such sorbents have a larger specific surface and very small diameter, assuring high kinetic properties. As a result, adsorption and concentration procedures become more convenient and easier.[3] Most research on ion-exchange chelating fibers has been done in two countries, the former U.S.S.R. and Japan, compiled in monographs[4,5] and a number of reviews.[1,6,7] Methods and technologies for the introduction of various types of chelating groups into polyacrylonitrile fibers have been developed. An ion-exchange chelating fiber containing carboxyl and tetrazine groups has been synthesized by B. W. Zhang,[8] T. Miyamatus,[9] and V. M. Zarechenskii.[10] Chang and Su et al. have prepared poly(acrylamidrazone-hydrazide) chelating fiber[11] and poly(acrylamindoxime-carboxylic acid) chelating fiber,[12] and used them to enrich-separate many elements from different matrices. A. N. Barash has synthesized a chelating fiber containing carboxyl-amidrazone-hydrazide groups.[13] I. N. Zamorova has reported a synthetic process of chelating fiber con-

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taining a sulfur-donor atom, and investigated its adsorption properties for the Ag(I) ion.[14] Polyacrylonitrile fiber has also been used in creating fibrous ion-exchangers containing amidoxime-hydroxam groups[15–17] and bisamide groups.[18] But the technique of attachment diethylenetriamine or triethylenetetramine and phosphonic groups to the modified polyacrylonitrile fiber to obtain poly(acryldiaminophosphonic-carboxyl-hydrazide) chelating fiber, called PAAP-2, or poly(acryltriaminophosphonic-carboxyl-hydrazide) chelating fiber, expressed as PAAP-3, has never been reported. The synthesis of PAAP-2 or PAAP-3 chelating fiber was carried out as followings: (1) the polyacrylonitrile fiber was modified by hydrazine; (2) the hydrazine-modified fiber reacted with diethylenetriamine or triethylenetetramine, and the aminated fiber was obtained; (3) PAAP-2 or PAAP-3 chelating fiber was prepared by introducing phosphonic into the aminated fiber. By infrared spectroscopy analysis it was shown that PAAP-2 or PAAP-3 chelating fiber contained carboxyl, aminophosphonic, and hydrazide. The synthesis and structure of the chelating fibers will be described in detail elsewhere.[19]

This investigation concerns adsorption properties of the PAAP-2 and the PAAP-3 chelating fiber with respect to Cu(II), Cd(II), Co(II), Cr(III), Mn(II), Pb(II), Ni(II), and Zn(II). Their binding capacities, adsorption isotherms, and kinetic properties are reported here.

EXPERIMENTAL

Materials and Reagents

Poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibers (PAAP-2 and PAAP-3) were cut into 1 mm long parts, and then soaked in 1% NaOH solution for 3–4 h, suction-filtered, washed with distilled water and dried over night at 60–65°C.

All reagents used were analytical reagent grade. Standard metal ion solutions (1000 mg/L) were provided by Central Iron and Steel Research Institute, Ministry of Metallurgical Industry.

Stock solutions (0.1 and 0.015 mol/L) of Cu(II), Cd(II), Co(II), Cr(III), Mn(II), Pb(II), Ni(II), and Zn(II) were prepared by dissolving appropriate quantities of $CuCl_2 \cdot H_2O$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $CoSO_4 \cdot 7H_2O$, $ZnCl_2$, $MnSO_4 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, and $CrCl_3 \cdot 6H_2O$, respectively, in 500 mL distilled water, 30 mL concentrated nitric acid was added, and the solution was diluted to 1 L with distilled water.

Instrument and Apparatus

A HZQ-C air-bath shaker was used for shaking the solution. The pH value was measured with a Model PHS-3C pH-meter. A 3100 EDS and a Z-6100 atomic absorption spectrometer were respectively used for the determination of single low and high metal ion concentrations. The determination of mixed metal ions was carried out by Spectroflame ICP Argon-plasma emission spectrometer (ICP-AES).

Adsorption Equilibrium Experimental

Batch studies were employed in all adsorption experiments. The adsorption equilibrium experiments included the determination of binding capacity, adsorption isotherm, and effect of pH value on adsorption.

Adsorption Procedures

Dried samples (0.10 g each) of poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibers (PAAP-2 or PAAP-3) were equilibrated by shaking for 24 h in 10 mL of metal ion solutions at 25°C. The various of metal ion solutions were adjusted to the desired pH value with aqueous ammonia prior to equilibrium. The loaded chelating fiber samples were suction filtered and washed with distilled water. The concentrations of metal ions in filtrate were determined by atomic absorption spectroscopy (AAS). All tested samples were run in triplicate.

Binding Capacity

PAAP-2 or the PAAP-3 chelating fiber (0.100 g) was equilibrated with 10 mL of 0.016 mol/L stock metal ion solutions at 25°C. The adjusted pH value was 4.5 for Cu(II), Pb(II), and Cr(III); 5.5 for Ni(II) and Co(II); 5.0 for Zn(II); 5.2 for Cd(II); 6.0 for Mn(II).

Adsorption Isotherm

The adsorption isotherms of the PAAP-2 chelating fiber were only determined for Cu(II) ion and Cd(II) ion at 25°C. The equilibrium pH value was 4.0 ± 0.25 for the Cu(II) ion solution and 5.2 ± 0.25 for the Cd(II) ion solution. The tested concentration was 0–5 mmol/L. The other conditions were similar to the determination of binding capacity.

Effect of pH Value on Adsorption

PAAP-2 or the PAAP-3 chelating fiber samples (0.100 g) were equilibrated with 10 mL of 0.001 mol/L metal ion solutions at 25°C. The tested pH value range was 1.0–7.0.

Adsorption Kinetics

Acording to the following described procedures, small- and large-scale batch studies, applying solutions containing either a single metal ion species or a mixture of several metal ions, were carried out to investigate the adsorption kinetic properties of the poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fiber for heavy metal ions. All of the metal ion solutions were adjusted to the desired pH values with diluted ammonia solution. Subsequently the metal solutions were added to the fiber samples, which were previously transferred into 1000-mL flasks. Mixing started immediately after addition of the tested metal ion solution to the fiber samples. After time interval of 2 min, 1.0 mL aliquots of the tested solutions were collected, centrifuged, and decanted to separate any remaining fiber. The actual concentration of metal ions in solution was determined by AAS or ICP-AES. In this case, the amounts of added metal ions did not exceed the saturation adsorption capacity of the chelating fiber for these metal ions. The experimental conditions are listed below.

Small-Scale Single Metal Ions

Fifty milliliters of standard metal ion solutions containing 0.3 mmol/L of tested metal ion; 0.200 g of PAAP-2 or PAAP-3 chelating fiber; pH = 6.0 ± 0.25.

Large-Scale Single Metal Ions

Five hundred milliliters of standard metal ion solutions containing 10 mg/L of tested metal ion; 0.80 g of PAAP-2 or PAAP-3 chelating fiber; pH = 6.3 ± 0.25.

Simultaneous Removal of Heavy Metal Ions

Five hundred milliliters of standard metal ion solutions containing 10 mg/L of each of tested metal ions; 0.80 g of PAAP-2 or PAAP-3 chelating fiber; pH = 6.3 ± 0.25.

Desorption Kinetics

The PAAP-2 or the PAAP-3 chelating fiber samples (0.20 g each) were respectively added to 100 mL of 10 mg/L Cu(II), Pb(II), Mn(II), Zn(II), and Cr(III) ion solutions, previously adjusted to a pH value of 6.0. After stirring for 4 h, the tested chelating fiber was suction filtered and washed with distilled water. The amount of adsorbed metal ions was determined indirectly according to the concentrations of metal ions in the filtrate and initial solution. Then 100 mL of 1 mol/L HNO_3 solution was added to the loaded fiber samples. After each interval of 2 min, a 0.5 mL solution sample was collected. The concentration of metal ions in solutions was determined by AAS.

RESULTS AND DISCUSSION

Binding Capacities of Heavy Metal Ions

More than one heavy metal ion is absorbed simultaneously by the chelating fibers due to the existence of combining several functional groups with different exchange characteristics such as carboxyl, amino, phosphonic, and hydrazide groups. The capacities of the PAAP chelating fibers for heavy metals are reported in Table I. The specific capacities of PAAP-2 and PAAP-3 chelating fibers for the tested metal ions decrease following the sequence: Pb(II) > Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) > Mn(II) > Cr(III), and Ni(II) > Pb(II) > Co(II) > Zn(II) > Cu(II) > Cd(II) > Mn(II) > Cr(III). The remarkable result is the higher binding capacities of PAAP-2 chelating fiber for all tested metal ions compared to that of PAAP-3 chelating fiber and high affinities of PAAP-2 chelating fiber for Pb(II) and Cu(II).

Table II shows a comparison of the binding capacities of several chelating sorbents. With the exception of chromium, the PAAP-2 chelating fiber surpasses the other chelating ion exchangers in its ability to binding the listed metal ions.

Effects of pH Value on Adsorption

Due to the protonation and deprotonation properties of the acidic and basic groups of the ion exchanger, its sorption behavior for metal ions is influenced by the pH value, which influences the surface structure of sorbents, the formation of metal ions, and the interaction between sorbents and metal ions. Therefore, the pH dependence of the adsorption for the metal ions was

Table I Specific Capacity *Q* (mmol/g) of Poly(acrylaminophosphonic-carboxyl-hydrazide) Chelating Fiber, Measured at Adequate pH Value

Metals	Pb(II)	Cu(II)	Ni(II)	Zn(II)	Cd(II)	Co(II)	Mn(II)	Cr(III)
pH	4.5	4.5	5.5	5.0	5.2	5.5	6.0	4.5
Q(PAAP-2)	1.55	1.47	1.40	1.39	1.36	1.25	1.17	0.76
Q(PAAP-3)	1.31	1.04	1.34	1.11	0.95	1.14	0.75	0.23

Conditions: solution volume, 10 mL; chelating fiber amount, 0.100 g; shaking time, 24 h; temperature, 25°C.

examined in detail. In Figure 1, the results show that these curves have similar dependence of pH value. For Cu(II), the degree of adsorption is constant at 99% above pH 3.0 and decreases rapidly in the pH range 1–3. Cu(II) ion is scarcely adsorbed below pH 1. The adsorption percentages for Pb(II) and Cd(II) increase in the pH range 1–3.5, reaching a constant level of 98% at pH $>$ 3.5. Zn(II) and Ni(II) as well as Mn(II), Cr(III), and Co(II), can be quantitatively adsorbed by the PAAP-2 chelating fiber separately at pH $>$ 4.0, 5.0, and 4.5.

In addition, the dependence on the pH value for the adsorption of the metal ions with the PAAP-3 chelating fiber is tested (see Fig. 2). The results reveal that Cu(II), Pb(II), Cd(II), Zn(II), and Cr(III) can be extracted above pH 4.5, while Co(II), Ni(II), and Mn(II) ions are completely adsorbed by the PAAP-3 chelating fiber at pH $>$ 5.0.

The affinity of ion exchange sorbents for metal ions is usually expressed in terms of distribution coefficients (D) at certain pH value. The distribution coefficients for the partitioning of the heavy metals between the PAAP chelating fibers and the liquid phase are summarized in Table III. From these results it is evident that the pH value influences the distribution coefficients of PAAP–metal chelates. At a low pH value, the D values for the listed metal ions are lower, but at pH $>$ 5.0, the sorption of metal ions on PAAP-2 chelating fiber leads to higher distribution coefficients ($>10^3$).

Adsorption Isotherms

The results showing the amount of Cu(II) and Cd(II) adsorbed by the PAAP-2 chelating fiber as a function of equilibrium solution concentrations are plotted in Figure 3. When these adsorption data of Cu(II) and Cd(II) are treated respectively by a linear regression analysis according to the Langmuir adsorption isotherm, the sorption parameters are obtained (see Table IV). The Langmuir-type equations for Cu(II) and Cd(II) are separately expressed as

$$Q = 1.16C/(0.0435 + C) \quad (1)$$

$$Q = 1.28C/(0.00192 + C) \quad (2)$$

where Q is the amount of metal ions adsorbed by the PAAP-2 chelating fiber in mmol/g, and C is the equilibrium concentration of metal ions in mmol/L.

Examination of Table IV and Figure 3 further reveals that the adsorption of Cu(II) and Cd(II) on the PAAP-2 chelating fiber exhibits Langmuir behavior in the concentration range studied.

Adsorption Kinetics

The adsorption kinetic properties of the metal ions by the PAAP chelating fibers are important for assessment of the suitability of this material to serve as a packed bed ion exchanger integrated in a through flow column. In cases where the ex-

Table II Comparison of the Metal Binding Capacities *Q* (mmol/g) for Various Chelating Sorbents

Metals	Pb(II)	Cu(II)	Ni(II)	Zn(II)	Cd(II)	Co(II)	Cr(III)
pH	5.0	5.0	5.0	5.0	5.0	5.0	—
PAADX[20]	0.72	1.45	0.4	0.38	0.19	0.34	—
pH	4.5	4.0	6.0	6.0	6.0	6.0	4.0
MPANF[8]	0.98	1.33	0.95	1.03	1.30	1.02	0.96
pH	4.5	4.5	5.5	5.0	5.2	5.5	4.5
PAAP-2	1.55	1.47	1.40	1.39	1.36	1.25	0.76

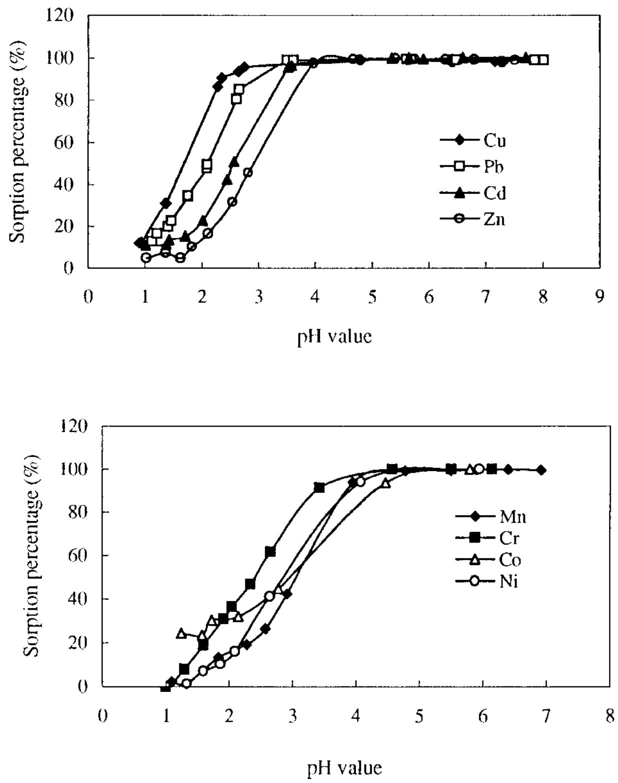

Figure 1 Effect of pH on sorption of metal ions with PAAP-2 chelating fiber.

change reaction seems to be too slow for an application of the fiber in combination with a dynamic flow system, the batch technique might be a reasonable alternative. The small-scale tests indicate a fast exchange reaction of the PAAP chelating fibers for the single metal ions (pH = 6.0). For the PAAP-2 chelating fiber, an extraction rate of 98% or greater yields for Cu(II), Cd(II), and Pb(II) after 6 min. The following results are achieved for the other metal ions: Mn(II), 96.41; Cr(III), 96.01; Co(II), 97.03; Ni(II), 92.61, and Zn(II), 97.5%. After a treatment time of 15 min, the adsorption rate of the listed metal ions is higher than 97% [see Fig. 4(a)]. With the PAAP-3 chelating fiber, slower sorption speeds compared to the results of the PAAP-2 chelating fiber are found. After 10 min, the adsorption percentages of Cu(II), Cd(II), Pb(II), Mn(II), Co(II), and Zn(II) respectively reach to 98.13, 96.82, 96, 95.72, 97.97, and 94.52%, but Cr(III) and Ni(II) are only removed to a degree of 51.45 and 61.6%. After 40 min, all tested metal ions are extracted to a degree higher than 97% except for Cr(III) and Ni(II), which are removed to a degree of 92.02 and 88.18% [see Fig. 4(b)].

The large-scale tests of the PAAP chelating fibers for the metal ions were carried out at pH 6.30. The adsorption kinetic curves of the PAAP-2 and PAAP-3 chelating fiber for heavy metal ions are shown in Figure 4(c) and (d). For Cu(II), Cd(II), Pb(II), Co(II), Zn(II), and Mn(II), the process remains fast or is accelerated, especially in the case of Ni(II). The extraction of the PAAP-2 chelating fiber for the listed metal ions is almost complete (97%) after 20 min. But in the case of the PAAP-3 chelating fiber, Cr(III) is only adsorbed to a degree of 90% and is approximately constant after 40 min.

Simultaneous Removal of Heavy Metal Ions

To determine the effectiveness of the chelating fibers for heavy metals removal from large water volumes, the adsorbents have to be evaluated in several ways. Figure 5(a) and (b) show the removal of the mixed heavy metal ions using certain amount of PAAP chelating fibers. It is evident that the adsorption of the PAAP-2 chelating fiber for Cd(II), Pb(II), Mn(II), Co(II), and Ni(II) is complete (99%), and remains constant after 5

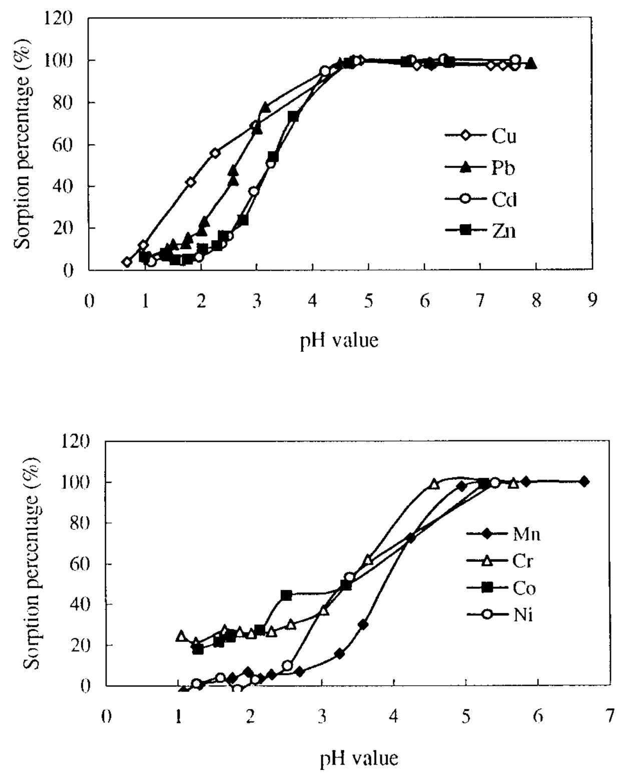

Figure 2 Effect of pH on sorption of metal ions with PAAP-3 chelating fiber.

Table III Distribution Coefficients (*D*) of Heavy Metal Ions Between the PAAP Chelating Fibers and Aqueous Phase

	pH					
	2.0	3.0	4.0	5.0	6.0	6.5
PAAP-2-Pb(II)	9.16×10	—	8.45×10^3	—	—	9.93×10^3
Cu(II)	6.37×10^2	2.12×10^3	—	1.12×10^4	—	5.39×10^3
Cd(II)	2.95×10	—	—	—	1.56×10^4	7.32×10^4
Zn(II)	1.99×10	8.37×10	3.49×10^3	—	1.36×10^4	9.86×10^3
Mn(II)	3.3×10	7.34×10	1.54×10^3	1.39×10^4	5.3×10^4	5.3×10^4
Cr(III)	5.69×10	1.61×10^2	—	—	1.45×10^5	—
PAAP-3-Pb(II)	2.97×10	2.08×10^2	—	—	7.42×10^4	—
Cu(II)	1.29×10^2	2.22×10^2	—	2.96×10^4	3.3×10^3	—
Cd(II)	6.34	5.95×10	1.7×10^3	1.43×10^4	—	7.29×10^4
Zn(II)	1.12×10	3.06×10	2.69×10^2	—	—	6.73×10^3
Mn(II)	6.97	1.86×10	4.68×10^2	4.15×10^3	5.31×10^4	1.07×10^5

Conditions: solution volume, 10 mL; chelating fiber amount, 0.100 g; shaking time, 24 h; temperature, 25°C; concentration of metal ions, 0.001 mol/L.

min. The different results are observed for Cu(II), Zn(II), and Cr(III), which the sorption of these three elements reaches to a highest degree of 97.49, 98.24, and 97.93% at 5 min; afterward, their adsorption percentages decrease slightly and are, respectively, 92.86, 96.53, and 97.44 at 1 h. The results are attributed to the existence of the competitive sorption among the metal ions. The same sorption behavior for the metal ions is observed in the case of the PAAP-3 chelating fiber. However, the lower efficiency is significant difference from the result of the PAAP-2 chelating fiber.

Desorption Properties of PAAP-2 Chelating Fiber

Basic investigation of the sorption properties of the PAAP chelating fibers exhibits the high affinity of the exchangers for heavy metal ions. To examine the applicability of the PAAP-2 chelating fiber, desorption properties of the heavy metal ions such as Cu(II), Cd(II), Pb(II), Mn(II), Zn(II), and Cr(III) were studied using 1 mol/L nitric acid as the eluent. The results are listed in Table V. The results show that Cu(II), Cd(II), Pb(II), Mn(II), and Zn(II) can be eluted satisfactorily to a degree of 93% after stirring for 40 min. Acid suspending and stripping for 1 h leads to a release of higher than 98% of adsorbed Cu(II), Pb(II), Mn(II), and Zn(II). However, it is remarkable that Cr(III) cannot be eluted quantitatively by 1 mol/L nitric acid or even after stirring for 2 h. The desorption percentage is only 30.57%. For this point, there are two explanations. One is that the metal complex of PAAP-2 chelating fiber with Cr(III) ion may be more stable. The other is that the complex mechanism and adsorption speciation of Cr(III) ion on PAAP-2 chelating fiber are different from that of the other metal ions. The further research on the complex mechanism

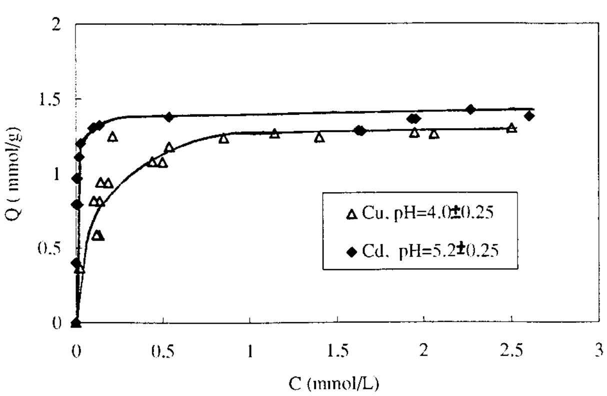

Figure 3 Adsorption isotherms of metal ions on the PAAP-2 chelating fiber.

Table IV Langmuir Adsorption Parameters for Cu(II) and Cd(II) on the PAAP-2 Chelating Fiber

	Adsorption Parameters		
Metal Ions	Q_0	A	r
Cu(II)	1.16	0.0435	0.9341
Cd(II)	1.28	0.00192	0.9815

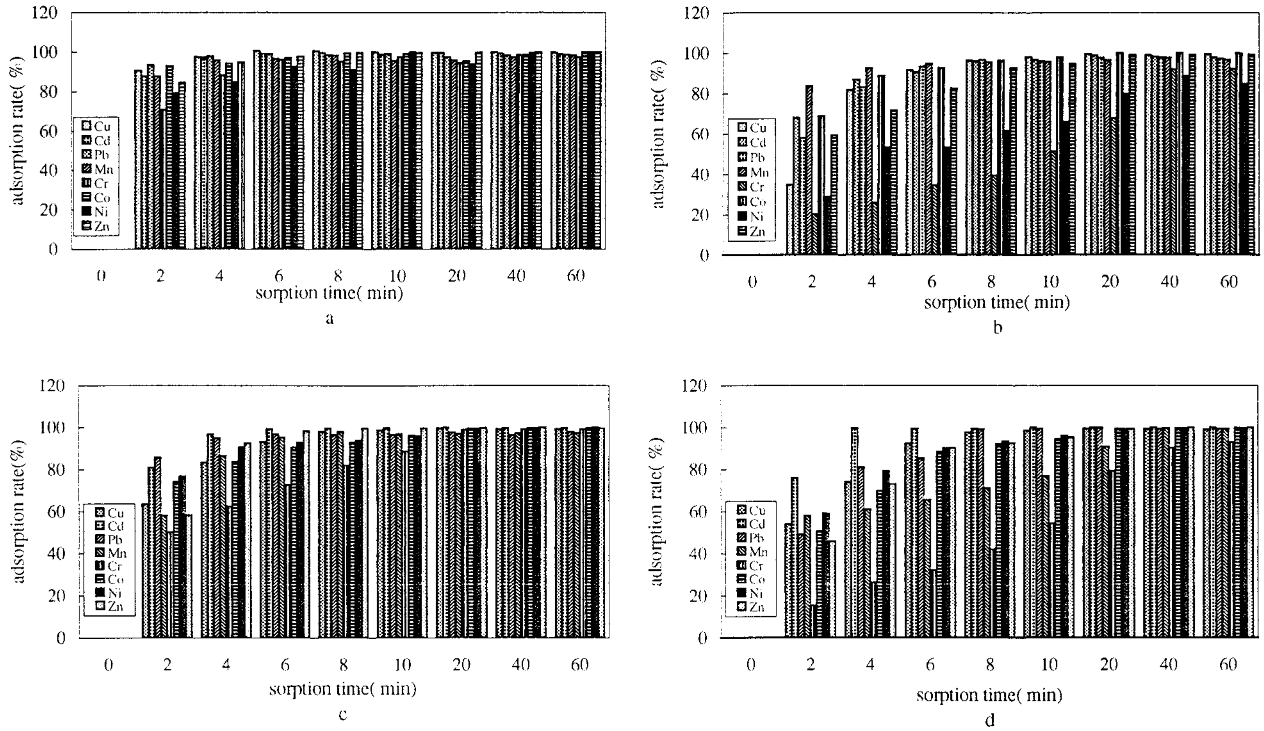

Figure 4 The adsorption kinetic curves of the PAAP chelating fibers for metal ions. (a) PAAP-2, small-scale test; (b) PAAP-3, small-scale test; (c) PAAP-2, large-scale test; (d) PAAP-3, large-scale test.

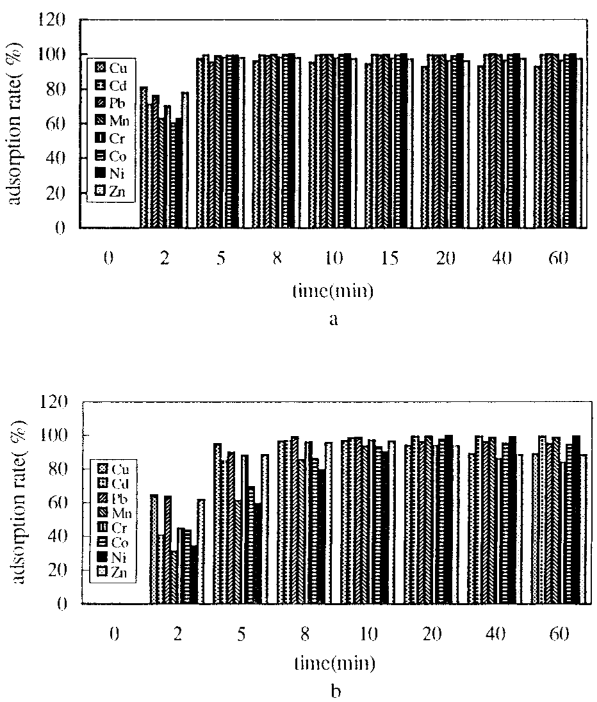

Figure 5 Simultaneous removal of heavy metal ions from the PAAP chelating fibers. (a) PAAP-2; (b) PAAP-3.

of metal ions on the chelating fiber is still under study.

CONCLUSION

In this article, the adsorption characteristics of PAAP chelating fibers for heavy metal ions were studied. From the experimental results and analysis above, the following conclusions were achieved.

1. The investigation of the poly(acrylaminophosphonic-carboxyl-hydrazide) chelating fibers reveals that the binding capacities of the PAAP-2 chelating fiber for Cu(II), Pb(II), Ni(II), Zn(II), Cd(II), Co(II), Mn(II), and Cr(III) are 1.47, 1.55, 1.40, 1.39, 1.36, 1.25, 1.17, and 0.76 mmol/g, and that of the PAAP-3 chelating fiber are 1.04, 1.31, 1.34, 1.11, 0.95, 1.14, 0.75, and 0.23 mmol/g, respectively.
2. The adsorption of the heavy metal ions on the chelating fibers is strongly dependent on the equilibrium pH value of solution. The metal ions cannot be absorbed by the modified fibers

Table V Desorption Rate (%) of the Metal Ions Using 1 mol/L Nitric Acid as Eluent

	Stirring Time (min)							
Metal Ions	2	4	6	8	10	20	40	60
Cu(II)	65.43	80.08	84.77	86.72	89.65	93.24	98.24	99.02
Pb(II)	41.99	61.78	74.83	76.95	83.01	87.64	93.86	99.60
Cd(II)	42.44	61.89	72.50	77.81	83.12	89.30	93.72	95.49
Mn(II)	33.01	38.14	48.51	51.48	58.75	66.15	93.74	113.0
Zn(II)	69.51	70.24	76.10	79.02	83.90	90.73	95.61	98.08
Cr(III)	6.45	8.76	11.06	12.14	13.67	17.97	22.43	24.88

at lower pH value range. With the increase of the pH value, the adsorption percentage for the metal ions exhibits sudden jump, and then remain constant.

3. The adsorption isotherms of Cu(II) and Cd(II) on the PAAP-2 chelating fiber fit very well to Langmuir behavior in the studied concentration range.
4. The kinetics of the modified fibers-metal ions interaction has been found to be sufficiently rapid and can be sorbed completely after several minutes of treatment time in most cases for the extraction of metal ions.
5. The loaded Cu(II), Mn(II), Cd(II), Mn(II), and Zn(II) on the PAAP-2 chelating fiber can be eluted by stirring for 40 min in 1 mol/L nitric acid. Therefore, it might be an effective tool for removal and accumulation of the heavy metal ions from natural waters and industrial effluents.

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