

# Application of the Modified Polyacrylonitrile Fiber with Amino-Carboxyl-Tetrazine Groups for the Preconcentration of Trace Heavy Metal Ions

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**ABSTRACT:** A new fibrous sorbent containing ethylenediamine, carboxyl, and tetrazine groups based on polyacrylonitrile fiber was synthesized and developed for the preconcentration of heavy metal ions. The experimental parameters such as pH value, sorptive capacity, flow velocity, reuse, as well as eluent type and concentration were investigated in detail. All the studied metal ions can be quantitatively retained by the modified fiber under  $\text{pH} \geq 3.5$ , then eluted by using a mixture of 1 mol/L hydrochloric acid and 5% thiocarbamide as eluent warmed to 40°C. The column technique was applied for the concentration of Cu(II), Cd(II), Zn(II), Mn(II), Pb(II), Co(II), and Ni(II) ions in model samples with satisfactory results, and the relative standard deviations for the determination of metal ions were found to be less than 5%. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2631–2636, 1999

**Key words:** fibrous sorbent with amino-carboxyl-tetrazine groups; preconcentration of heavy metals; adsorption; elution

## INTRODUCTION

Ion exchange chelating fiber obtained by introduction of suitable functional groups: amidoxime,<sup>1,2</sup> bisamide,<sup>3</sup> amidrazone-acylhydrazine,<sup>4–6</sup> carboxyl-hydroxam-amidoxime,<sup>7–9</sup> and carboxyl-acylhydrazine-amidoxime<sup>10</sup> on various types of fibrous polymers: cellulose, polyvinyl alcohol, polyacrylonitrile, etc., have gained increasing importance in preconcentration and separation of trace elements, recovery of noble metals, and removal of toxic metal ions. They provide high efficiency and good kinetic property for purification procedures of water, and simpler analytical techniques for trace elements.

In our laboratory, the ion exchange chelating fibers containing carboxyl-tetrazine,<sup>11</sup> aminophosphonic-carboxyl-hydrazide,<sup>12</sup> and aminophosphonic-dithiocarbamate<sup>13</sup> were synthesized in succession, and used for the preconcentration of trace rare earth elements in sea water<sup>14</sup> and heavy metal ions in model water.<sup>15</sup>

From the obtained results it has been shown that the nitrogen-containing functional groups have high affinity for heavy metals, and the introduction of multifunctional groups provides possibilities for the simultaneous preconcentration of trace multielements. In this article, a new chelating fiber containing ethylenediamine, carboxyl, and tetrazine groups (amino-carboxyl-tetrazine groups) is synthesized through three reaction steps of polyacrylonitrile fiber with hydrazine, ethylenediamine, and aqueous caustic soda solution. The column adsorption and desorption properties of the fibrous sorbent, i.e., enrichment

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**Table I Sorptive Capacity  $Q$  (mmol/g) of the Modified PANF with Amino-carboxyl-tetrazine Groups for Metal Ions**

Metals	Cu(II)	Zn(II)	Cd(II)	Mn(II)	Co(II)	Ni(II)	Cr(III)	Pb(II)
pH	4.0	6.0	6.0	6.0	6.0	6.0	4.0	4.5
$Q$	1.19	0.99	0.96	0.96	0.92	0.90	0.80	0.66

$Q$ : maximum amount of metal ions adsorbed by dry chelating fiber in mmol/g.

acidity, flow rate, eluted acidity, and reuse, are discussed. The preconcentration of trace heavy metal ions in model water are carried out by the proposed method with satisfactory results.

## EXPERIMENTAL

### Material and Instrument

A 100 mmol/L stock solution of Cu(II), Cd(II), Cr(III), Zn(II), Mn(II), Pb(II), Co(II), and Ni(II) ions was prepared by dissolving analytical grade  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively, in 500 mL deionized water with 30 mL concentrated nitric acid. These solutions were further diluted to suitable concentrations.

A 1000-mg/L standard solution of each metal ion was provided by Central Iron and Steel Research Institute, Ministry of Metallurgical Industry.

A GGX-6A atomic absorption spectrometer (AAS) was used for the determination of single metal ion concentration. The determination of mixed metal ions was carried out by Spectroflame ICP Argon-plasma emission spectrometer (ICP-AES). A HZQ-C air-bath shaker was used for shaking the solution. The pH value was measured with a Model pH-3A pH-meter.

### Synthesis of the Chelating Fiber

The chelating fiber with amino-carboxyl-tetrazine was synthesized according to the following three stages: step 1:<sup>11</sup> Twenty grams of polyacrylonitrile fiber (PANF) and 800 mL of hydrazine was reacted in 1-L flat flange reaction vessel for 2.5 h at 90–94°C, then suction filtered, washed with water, and dried at 55–60°C overnight. The weight increase of the product was about 5.5%. Step 2: the mixture of dry hydrazine-modified fiber and 850 mL of ethylenediamine was heated to 95°C  $\pm$  1 for 4–8 h. The reaction mixture was cooled, suction-filtered, washed with deionized water, and dried at 55–60°C overnight. Step 3: the above dry product was reacted with 900 mL of 4% aqueous caustic soda solution for 5 h at 80°C  $\pm$  1 in a 1-L flat-flange reaction vessel. Afterward, the modified fiber was suction filtered, sequentially washed with deionized water, 1 mol/L hydrochloric acid and deionized water, then dried overnight. The fibrous sorbent containing amino-carboxyl-tetrazine groups was obtained.

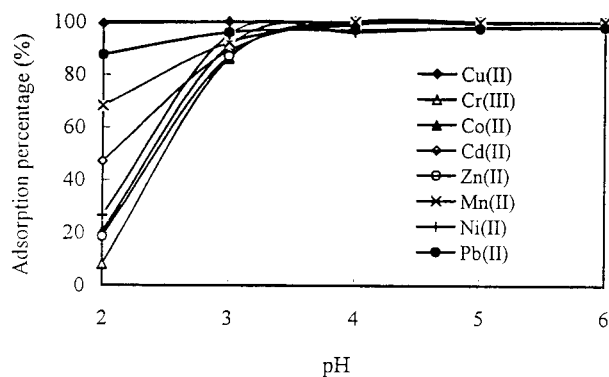
### Adsorption Capacity

The binding capacity of the sorbent was determined for each heavy metal ion by the batch technique. The modified fiber (100 mg each) was equilibrated by shaking for 24 h in 10 mL of 10 mmol/L heavy metal ions solution at 25°C  $\pm$  1. The adjusted pH value was 6.0 except for Cu(II), Cr(III), 4.0, and Pb(II), 4.5.

**Table II Comparison of Sorptive Capacity of Several Chelating Sorbents Containing Nitrogen**

Types of Sorbents	Metal Ions							
	Cu(II)	Zn(II)	Cd(II)	Mn(II)	Co(II)	Ni(II)	Cr(III)	Pb(II)
Sorbent I	1.45	0.38	0.19	—	0.34	0.40	—	0.72
Sorbent II	1.87	0.37	<0.01	—	0.25	0.09	0.03	0.52
Sorbent III	1.19	0.99	0.96	0.96	0.92	0.90	0.80	0.66

Sorbent I: the poly(acrylamidoxime) fiber,<sup>16</sup> Sorbent II: the modified starch containing amidoxime,<sup>17</sup> Sorbent III: the chelating fiber developed in this article.



**Figure 1** Dependence of sorption for metal ions on pH value.

### Column Preparation

The empty glass column was soaked in 8 mol/L nitric acid for 24 h before use, then drained and rinsed with deionized water several times. 300 mg (1-mm units) of the modified chelating fiber sorbent was suspended in deionized water, slurry packed in the column (i.d. 0.7 cm, height 3 cm), and finally rinsed with deionized water.

### Column Adsorption Procedure

Ten milliliters of 1 mg/L Cu(II), Cd(II), Cr(III), Zn(II), Mn(II), Pb(II), Co(II), or Ni(II) single or mixed ion solution, previously adjusted to the desired pH  $5.75 \pm 0.25$  with diluted ammonium hydroxide and nitric acid, was passed through the adsorption column at flow rates of 1–8 mL/min. The column was rinsed with 10 mL deionized water. The concentration of the metal ions in effluents was determined by AAS or ICP-AES.

### Desorption Procedure

After adsorption procedure, the retained metal ions on fiber column were eluted with appropriate eluent at eluting rates of 1 mL/min. The eluted single or mixed metal ions were determined by AAS or ICP-AES.

### Reuse of the Chelating Fiber

Ten milliliters of 1 mg/L Cd(II) ion solution, previously being adjusted to pH 5.5–6.0 with diluted  $\text{NH}_4\text{OH}$  solution, was added to the fiber column at a flow rate of 3 mL/min. The metal ions extracted by the sorbent were eluted with 10 mL of 1 mol/L hydrochloric acid at a flow rate of 1 mL/min. The column was rinsed twice with deionized water, then soaked in 0.1 mol/L  $\text{NH}_4\text{OH}$  solution, then substantially washed with deionized water until neutrality was reached. As the above performance, the experiment was carried out 10 times.

### Preconcentration Procedure

One liter mixture containing 50  $\mu\text{g/L}$  each of Zn(II), Cd(II), Mn(II), Ni(II), Cu(II), Pb(II), and Co(II), adjusted to pH 5–6, was passed through the modified PANF column at a flow rate of 3 mL/min, which was washed twice with 10 mL of deionized water, then adsorbed metal ions were eluted with 10 mL mixture of 1 mol/L hydrochloric acid and 5% thiocarbamide. The eluate was transferred to a 100 mL volumetric flask. The concentrations of the eluted metal ions were determined by ICP-AES.

## RESULTS AND DISCUSSION

### Sorptive Capacity

The binding capacity of sorbent is one of the most important factors to reflect the sorptive possibilities for metal ions from aqueous solution. The specific capacities of the modified PANF with amino-carboxyl-tetrazine groups are listed in Table I. The results show that the capacities of the fibrous sorbents are high enough for use in the preconcentration of trace heavy metal ions from solution samples. The specific capacities for the tested ions decrease following the sequence: Cu(II) > Zn(II) > Cd(II)  $\approx$  Mn(II) > Co(II) > Ni(II) > Cr(III) > Pb(II). The binding capacity

**Table III** Sorptive Percentage (%) of Single and Mixed Ions on the Modified PANF with Amino-carboxyl-tetrazine Groups, at a Flow Rate of 2 mL/min

Metals	Cu(II)	Zn(II)	Cd(II)	Mn(II)	Co(II)	Ni(II)	Cr(III)	Pb(II)
Single ion	99.4	98.5	99.0	99.2	97.8	96.9	99.2	98.5
Mixed ion	100.0	98.8	99.9	98.8	99.3	99.3	98.4	98.4

**Table IV** Desorption Percentage (%) of Single Metal Ions from the Modified PANF Column Using Hydrochloric Acid as Eluent

Concentration of HCl (mol/L)	Metals						
	Cd(II)	Co(II)	Mn(II)	Ni(II)	Cr(III)	Zn(II)	Cu(II)
0.5	102.9	99.0	100.8	94.5	95.7	98.6	
1.0	102.9	100.5	100.8	96.7	99.5	101.8	69.9
2.0	100.9	99.5	102.0	99.1	97.6	100.0	76.0
4.0	100.5	100.9	99.6	99.5	93.7	98.7	93.2
6.0	102.4	98.1	97.5	97.6	88.8	100.0	98.3

of a chelating sorbent depends on the content and structure of the chemical active groups that take part in the chelating reaction, as well as the adsorption conditions such as pH value, the state, and properties of sorbate in solution. The comparison of adsorption capacities of several chelating sorbents containing nitrogen is reported in Table II. With exception of Cu(II) and Pb(II), the prepared chelating fiber in this study surpasses the other sorbents containing a single functional group in its ability to bind the listed metal ions. The high capacities of the modified fibrous sorbent are mainly attributed to the existence of multifunctional groups with different properties such as amino, carboxyl, and tetrazine.

#### Effect of pH Value and Flow Rate on Adsorption

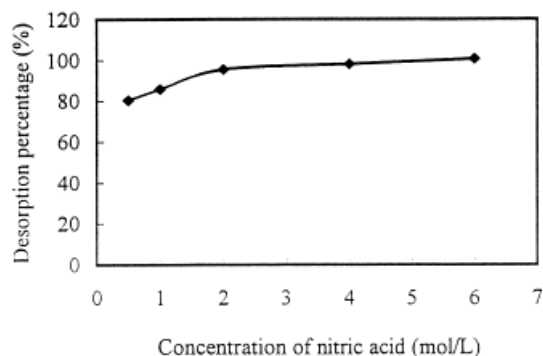
The effect of pH value on sorption is considered from two aspects: the functional groups surface structure of chelating sorbent, and the metal ion state in solution. The dependence of surface structure on pH value is contributed to the protonation and deprotonation behavior of acidic and basic groups. At different pH values the metal ions could exist in different forms. The results of the pH value effect on adsorption are shown in Figure 1. It can be seen that Zn(II), Cd(II), Mn(II), Co(II), Ni(II), and Cr(III) ions are adsorbed poorly on the fibrous sorbent at lower than pH 3.0. When the pH value of the solution is higher than 3.5, a quantitative sorption (>99%) of all tested metal ions is observed. However, for Cu(II) and Pb(II) ions, the adsorption percentages reach 99.4 and 87.5%, respectively, even at pH 2.0. Therefore, pH 6 is recommended as the optimum for the adsorption of metal ions.

The dependence of sorption for single or mixed ions on flow rate was studied at flow rates of 1–8 mL/min. In these cases, the quantitative recovery occurs. The results of adsorption for single or

mixed ions at flow rate of 2 mL/min are listed in Table III.

#### Selection of Eluent and Its Concentration

Up to now, the elution of heavy metal ions from various sorptive column has been tried by using mineral acids such as hydrochloric acid and nitric acid.<sup>18–20</sup> It was also found that 1% nitric acid in acetone was the most satisfactory combination in experiments using both ammonium pyrrolidine dithiocarbamate and 8-hydroxyquinoline;<sup>21,22</sup> however, as explained by Elci,<sup>23</sup> 2 mol/L nitric acid and 2 mol/L hydrochloric acid had an advantage with respect to 1 mol/L nitric acid in acetone for the selective recovery. To achieve quantitative elution of heavy metal ions from the modified fibrous sorbent, the various eluents were tested in this work. Table IV lists the recovery of single Cd(II), Co(II), Mn(II), Ni(II), Cr(III), Zn(II), and Cu(II) ions by using the different concentration of hydrochloric acid as the eluent. The results of elution performance show that, by using 10 mL of 0.5 mol/L hydrochloric acid, the quantitative elution can be obtained for all the tested metal ions

**Figure 2** Effect of nitric acid concentration on elution of the Pb(II) ion.

**Table V Desorption Percentage (%) of Mixed Metal Ions from the Modified PANF Column Using Various Eluent**

Eluent Type	Metals							
	Cr(III)	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
6 mol/L nitric acid	99.9	92.7	91.3	96.0	85.4	100.3	93.5	97.8
7 mol/L hydrochloric acid + 1% ascorbic acid	80.0	93.4	96.6	97.3	50.8	101.9	99.2	90.0
1 mol/L hydrochloric acid + 5% thiocarbamide	100.1	98.3	97.3	95.9	91.7	101.1	94.0	100.1
<sup>a</sup> 1 mol/L hydrochloric acid + 5% thiocarbamide	97.1	97.7	96.0	96.7	96.9	100.9	95.6	98.0

<sup>a</sup> The eluent warmed to 40°C.

except for the Cu(II) ion, which is 69.9% recovered. The higher concentration of hydrochloric acid is necessary for the recovery of the Cu(II) ion. In an effort to boost the recovery of the Cu(II) ion, a mixture of 1 mol/L hydrochloric acid and 5% thiocarbamide was tested as an eluent. The use of thiocarbamide, maybe forming a very stable complex with the Cu(II) ion, results in the quantitative desorption of the Cu(II) ion from the fiber matrix, which is 100.2% recovered. The diluted nitric acid was tested for the recovery of the Pb(II) ion, and the result is presented in Figure 2. The increased recovery is observed with the increase of nitric acid concentration, and 10 mL of 2 mol/L nitric acid-based eluent is effective for the quantitative elution of the Pb(II) ion, which is 95.4% recovered.

The simultaneous elution performance of mixed metal ions was carried out using 15 mL of 6 mol/L nitric acid, a mixture of 7 mol/L hydrochloric acid and 1% ascorbic acid, as well as a mixture of 1 mol/L hydrochloric acid and 5% thiocarbamide as eluent, respectively. The recoveries of all metal ions are presented in Table V. It can be seen that the recoveries of all the investigated metal ions except for Cu(II) are above 91% when 6 mol/L nitric acid is used as an eluent, while a mixture of 7 mol/L hydrochloric acid and 1%

ascorbic acid is not as effective for Cr(III) and Cu(II) ions, the recovery of which is only 80 and 50.8%, respectively. A mixture of 1 mol/L hydrochloric acid and 5% thiocarbamide is the most satisfactory eluent for all studied metal ions, the desorption percentages of which are above 91%, and the quantitative recoveries ( $\geq 95\%$ ) of these ions are found when the same eluent is warmed to 40°C.

From the results of the desorption experiment for single and mixed ions we can also conclude that the modified polyacrylonitrile fiber with amino-carboxyl-tetrazine groups has high affinity for the Cu(II) ion so that the diluted mineral acids as the eluent are not effective, and the additional complexant is necessary for the quantitative elution of the Cu(II) ion.

#### Reusability and Application for the Preconcentration of Trace Metal Ions

To evaluate the reusability of the modified PANF, the column adsorption and elution experiments were repeatedly performed. The results of Table VI show that the quantitative extraction and elution ( $>98\%$ ) are observed in each process. In addition, the swell of the fibrous sorbent is not found after using repeatedly.

**Table VI Reusability of the Modified PANF with Amino-carboxyl-tetrazine Groups**

	Experiment Times									
	1	2	3	4	5	6	7	8	9	10
Sorption (%)	100	100	100	100	98.6	99.1	98.6	100	98.2	100
Recovery (%)	97.7	98.6	98.6	98.6	99.1	100	100.1	100.5	99.5	99.1



**Table VII Recovery of Trace Elements from Model Solution**

Metals	Added ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )						Average ( $\mu\text{g}$ )	Recovery (%)
		1	2	3	4	5	6		
Cd(II)	46.4	45.1	42.7	43.2	43.3	45.7	44.9	44.2	95.3
Co(II)	47.2	45.4	45.3	43.1	46.5	45.6	43.6	44.9	95.1
Cu(II)	46.2	47.2	43.5	43.0	44.1	45.9	43.8	44.6	96.5
Mn(II)	46.3	44.7	44.5	43.4	45.1	45.9	44.7	44.7	96.5
Ni(II)	43.4	42.4	43.2	40.0	40.6	39.9	40.6	41.1	94.7
Pb(II)	54.6	52.1	52.9	52.3	53.6	54.6	52.5	53.0	97.1
Zn(II)	52.4	55.5	56.3	56.5	55.0	54.5	54.4	55.4	105.7

Relative standard deviation (RSD) less than 5%.

One liter of model solution samples containing Zn(II), Cd(II), Mn(II), Ni(II), Cu(II), Pb(II), and Co(II) mixed ions were prepared for evaluating the possibility of enriching trace elements. The results of six samples shown in Table VII demonstrate 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 recoveries of all the added elements are in the range 94–106%. This indicates the high reliability and validity of the method developed.

## CONCLUSION

The investigation of adsorption and desorption properties for heavy metal ions reveals that the modified PANF with amino-carboxyl-tetrazine groups exhibits high sorptive capacities, fast adsorption velocity, easy elution conditions, and perfect reusability. The new method provides a reliable technique for the preconcentration of trace heavy metal ions in model samples. It is possible that the technique here is applied to enrich trace elements in real samples prior to the determination.

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