

Preparation and Adsorption Properties of Resins Containing Amine, Sulfonic Acid, and Carboxylic Acid Moieties

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ABSTRACT: Completely water-insoluble resins containing amine, carboxylic acid, and sulfonic acid as ligand groups were synthesized by radical polymerization in solution. The yield was higher than 97%. The resins were characterized by FTIR spectroscopy and thermal analysis. The metal ion retention properties at different pH values were investigated by a batch method. Metal ions studied were: Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III). The metal ion

binding ability depended strongly on the pH. The retention properties were also tested under competitive conditions. Elution of the metal ion was investigated in acid medium at different concentrations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 700–705, 2003

Key words: adsorption; metal–polymer complexes; radical polymerization; resins; FTIR

INTRODUCTION

Polymeric reagents are being continuously developed and used for their complexation with metal ions for ion-exchange or selective adsorption purposes. These polymeric materials are custom-synthesized to remove certain metal ions or groups from aqueous media.¹ The polymeric ligands, having polyfunctional groups such as carboxylic, sulfonic, amide, amine, and ammonium groups, possess good hydrophilic and ion-exchange properties. These polymeric materials have been used for removal of metal ions such as Cu²⁺, Fe²⁺, Cd²⁺, Pb²⁺, Zn²⁺, and Hg²⁺ from water and have also been used in the treatment of radioactive liquid waste containing radioactive isotopes such as Cs⁺, Co²⁺, Sr²⁺, and Eu³⁺.^{2–11}

Among the common polymer-supported reagents are the sulfonic acid cation exchangers, usually based on styrene–divinylbenzene matrices as well as crosslinked polymers of acrylic and methacrylic acids. The sulfonic acids perform very well in a wide range of pH values, although they lack selectivity. The carboxylic acids, as weak acids, display enhanced selectivity toward divalent metal cations, but their useful pH range is limited.

The selective complexation of a targeted metal ion by a given ligand is an important objective for metal ion recovery processes.

It is well known that ligands with “soft”-type donors prefer interactions with “soft” (i.e., large and more easily polarizable) acceptors such as silver, gold, and mercury cations, for example.¹² High ligand affinity for these cations is used in the synthesis of selective extractants and resins. For example, resins with thiourea and alkyl substituted thiourea ligands show selectivity for noble metals,¹³ Au(III) and Ag(I),¹⁴ respectively.

The ion-exchange reaction is an extremely versatile reaction and is well suited for the complexation cations and anions through electrostatic binding. However, because of the wide range of materials and methods of synthesis it is not surprising that the physical form of the chelating exchanger may vary from rock-hard material to soft gel. The desirable properties of chelating exchangers are fourfold: (1) high capacity for the metal(s) of interest; (2) high selectivity; (3) fast kinetics/rapid equilibration; and (4) high mechanical strength and toughness of the exchanger particles.¹⁵

During the last few years we have been studying the ability of resins containing amide, amine, carboxylic, and ammonium groups^{11,16–24} to bind metal ions, particularly those with a negative environmental impact.

The aim of this study was to report the metal ion retention properties of resins containing sulfonic and carboxylic acids and to compare their metal ion binding properties under different experimental conditions.

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EXPERIMENTAL

Reagents

Acrylic acid (AA; Merck, Darmstadt, Germany) was purified by distillation. 3-(Dimethylamine)propylacrylamide (DAPA; Aldrich, Milwaukee, WI), 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA; Aldrich), *N,N'*-methylene-bisacrylamide (MBA; Merck), and ammonium persulfate (AP; Merck) were used as received without further purification.

Metal salts (Merck) were analytical grade; perchloric acid, nitric acid, and sodium hydroxide were all obtained from Merck.

Synthesis of the adsorbents

Poly[3-(dimethylamine)propylacrylamide-*co*-2-acrylamido-2-methyl-1-propane sulfonic acid] [P(DAPA-APSA)] was obtained by aqueous radical polymerization. DAPA (4 mmol) and APSA (4 mmol) were copolymerized in the presence of AP (0.2 mmol) and MBA (4 mol %) as initiator and crosslinking reagent, respectively, at 70°C for 24 h. The resin was washed repeatedly with water and dried under vacuum to constant weight. Yield: 99%. The dried resin was ground and the particle size of 180–250 μm was used in all the experiments.

Poly[3-(dimethylamine)propylacrylamide-*co*-acrylic acid] [P(DAPA-AA)] was obtained by aqueous radical polymerization. DAPA (0.1 mol) and AA (0.1 mmol) were copolymerized in the presence of AP (0.2 mmol) and MBA (4 mol %) at 70°C for 24 h. The resin was washed repeatedly with water and dried under vacuum to constant weight. Yield: 98%. The dried resin was ground and the particle size of 180–250 μm was used in all the experiments.

Sorption equilibrium procedure

A batch-type equilibrium procedure was used in all the sorption runs. The sorption equilibrium experiments included the effect of the pH values on sorption, determination of the maximum binding capacity, and selectivity sorption from mixtures of metal ions.

Dried samples (0.1 g each) of the chelating resin were equilibrated for 1 h in 10 mL metal ion solutions at 20°C. The various metal ion aqueous solutions were adjusted to the desired pH values with nitric acid or sodium hydroxide before equilibrium. The loaded sample resins were filtered and washed with distilled water. The concentration of metal ions in the filtrate was determined by atomic absorption spectroscopy. Batch metal uptake experiments under competitive conditions were also carried out. The following metal

ion mixture was made: batches of 0.1 g resin were added together with a mixture of 10 mL (4.4×10^{-4} M) of each metal ion Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III). After shaking for 1 h, the samples were handled as described above for noncompetitive conditions.

To obtain the maximum sorption capacity for Hg(II) ions, 50 mL of an aqueous solution (5.2×10^{-3} M) was shaken with 1 g of dry resin for 1 h at 20°C. The mixture in the flask was filtered and washed with distilled water and transferred into a calibrated flask. The process was repeated three times, the volume was maintained at 250 mL, and the metals were determined by atomic absorption spectroscopy.

Removal of mercury(II) ions

The loaded resin with mercury(II) (0.1 g) was stirred with HClO₄ (10 mL, 1 and 4M). The desorbed metal ions were collected and estimated as above.

Measurements

A Julabo air-batch shaker (Julabo Labortechnik GmbH, Germany) was used for shaking the solution at a desired temperature. The pH was measured with a Jurgens digital pH meter (Germany). A Unicam Solar 5M series atomic absorption spectrometer (UK) was used for the determination of single and mixed metal ions. The FTIR spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI). The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer (Polymer Laboratories, UK). Approximately 5 mg of the dry sample was heated at a 10°C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The water-insoluble P(DAPA-AA) and P(DAPA-APSA) were synthesized by radical copolymerization by using AP and MBA as initiator and crosslinking reagent, respectively. (See structural diagram.) An equimolar feed monomer ratio of DAPA with AA and APSA was employed. Yields were 98 and 99%, respectively. The particle size of the resin immediately after the polymerization was higher than 500 μm . The polymeric materials were ground and the particle size 180–250 μm was used for further metal ion retention properties.

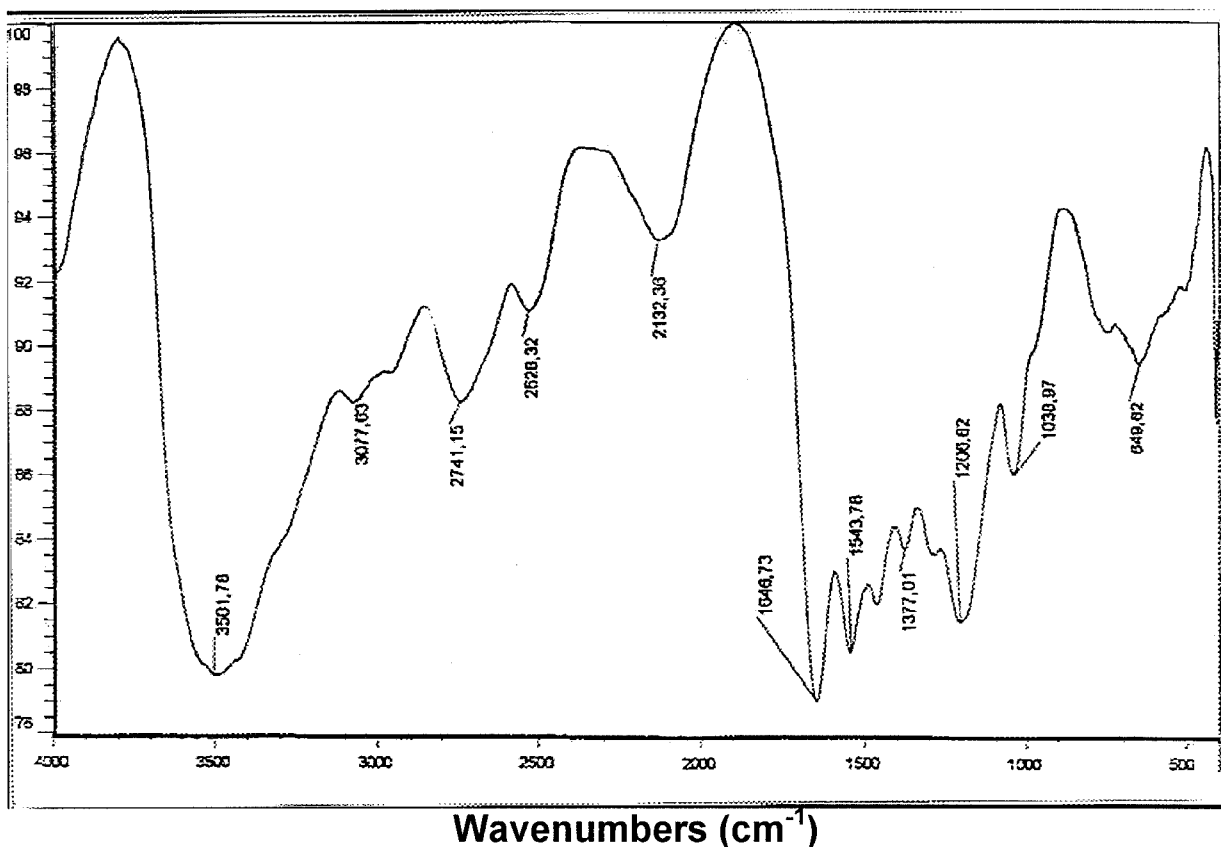
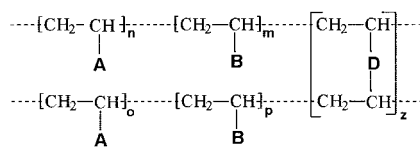
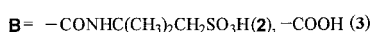


Figure 1 FTIR spectrum of the resin P(DAPA-APSA).



where



A	B	D	Acronym
(1)	---	(4)	P (DAPA)
(1)	(2)	(4)	P (DAPA-APSA)
(1)	(3)	(4)	P (DAPA-AA)

P(DAPA-APSA): Poly[N-3-(dimethylamino)propylacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid].

P(DAPA-AA) : Poly[N-3-(dimethylamino)propylacrylamide-co-acrylic acid].

The FTIR spectrum of P(DAPA-APSA) resin shows the most characteristic absorption bands at 3501 cm^{-1} attributed to NH (secondary amine), 1640 cm^{-1}

(stretching C=O, amide), and that between 1400 and 1450 cm^{-1} was associated with C—N (amide) (see Fig. 1).

The FTIR spectrum of DAPA-AA resin shows the most characteristic absorption bands at 3444 and 1632 cm^{-1} , which are attributed to the stretching of OH (carboxylic acid) and NH (secondary amine) and C=O (amide), respectively (see Fig. 2).

The sorption characteristics of the adsorbent toward copper(II), cadmium(II), zinc(II), mercury(II), lead(II), and chromium(III) were investigated in an aqueous solution, at pH 1–5, depending on the metal salt properties, using the batch equilibrium procedure. The sorption affinities of the adsorbent as a function of the pH are summarized in Figures 3 and 4.

For the resin P(DAPA-AA), at pH = 1, the highest retention values correspond to Cr(III) (90.3%, 1.521 mmol), Cu(II) (82.1%, 0.684 mmol), Cd(II) (82.8%, 0.498 mmol), and Zn(II) (87.4%, 0.872 mmol), and the lower retention values correspond to Hg(II) (44.3%, 0.166 mmol) and Pb(II) (45.6%, 0.168 mmol), respectively. The highest effect of the pH on the retention was observed for Hg(II) and Pb(II) ions. For Pb(II) the retention increased from 47.9% (0.168 mmol) at pH = 1 to 80% (0.280 mmol) at pH = 5. At pH = 2 the

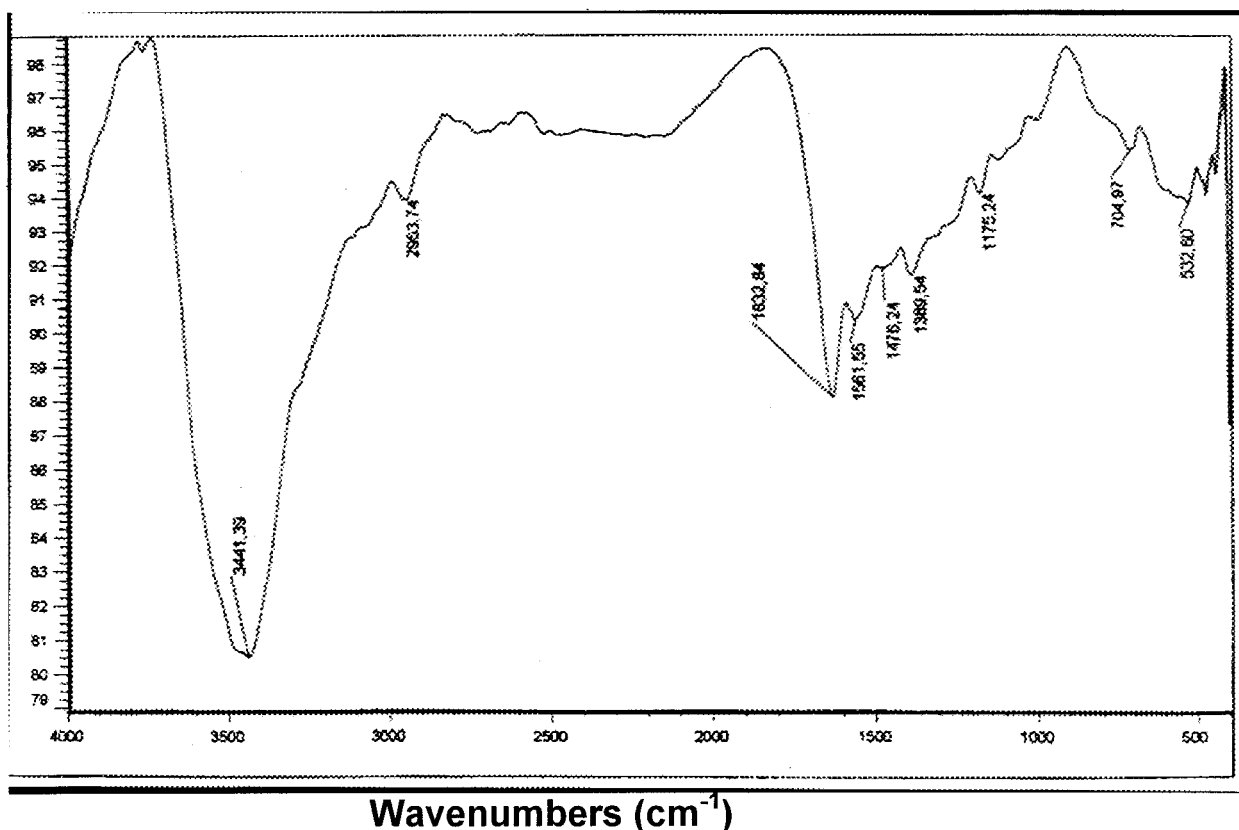


Figure 2 FTIR spectrum of the resin P(DAPA-AA).

retention of Hg(II) ions was 89.1% (0.333 mmol/mol repeat unit). The high sorption of Hg(II) may be attributed to at least two factors: stability constants for complex formation and conformational requirements.

For all the other metal ions no increase was observed over 10% in all the pH ranges. The highest retention value was observed for Cr(III) (97.3%, 1.639 mmol) at pH = 5. At this pH value the concentration of carboxylate and amine (nonprotonated) groups are increased, making them able to coordinate the metal ions more strongly.

For the resin P(DAPA-APSA), the retention of Pb(II) is the most sensitive to the effect of pH. It ranged from 45.6% (0.090 mmol) at pH = 1 to 62.8% (0.136 mmol) at pH = 5. Cr(III) shows the highest retention values, near 90% at all pH ranges. This could be attributed to the higher charge density of these ions. The lowest retention values were observed for Hg(II) ions. This metal ion was studied only to pH = 2 to avoid precipitation.

The equilibrium was achieved rapidly considering that the ligand group-metal interaction occurs in a

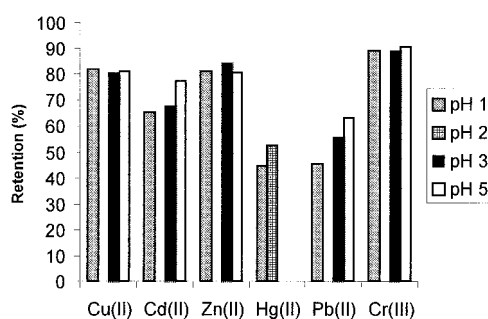


Figure 3 Effect of the pH on the retention properties of P(DAPA-APSA), for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III).

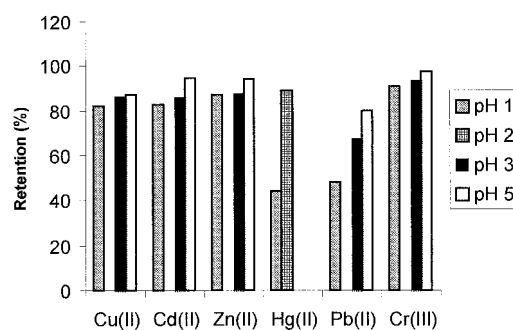


Figure 4 Effect of the pH on the metal ion retention properties of P(DAPA-AA) for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III).

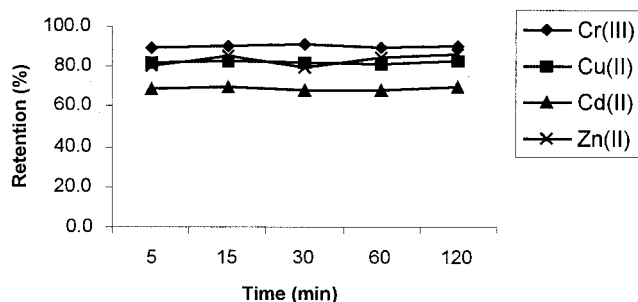


Figure 5 Effect of the contact time on the retention properties of P(DAPA-APSA) for Cu(II), Cd(II), Zn(II), Hg(II), and Cr(III).

heterogeneous medium. Thus, before 15 min the equilibrium was achieved for all the metal ions (see Fig. 5 and Table I).

The sulfonic acid and carboxylic acid groups have different levels of involvement in the retention of the metal ions. Thus, the sulfonic groups could interact electrostatically with the ions but the carboxylate groups could interact through a complexation. Both mechanisms should occur at different magnitudes, depending on the pH. At low pH the contribution of the electrostatic effect is stronger than that at higher pH where the complex formation should be more important.

To explore the application of the adsorbent, it is relevant to obtain knowledge on the maximum adsorption capacity of the resin toward Cu(II), Hg(II), Cd(II), Zn(II), and Cr(III) ions.

The resin P(DAPA-APSA) shows maximum retention capacity (MRC) values between 69.3% (1.27 meq/g) for Cu(II) and 85.4% (4.08 meq/g) for Cr(III). The resin P(DAPA-AA) has a high affinity with Hg(II) ions, 90.8% (6.59 meq/g) at pH = 2.

The maximum load capacity after three contacts was observed for the resin P(DAPA-AA) for Hg(II) (6.59 meq/g, 90.8%). The resin P(DAPA-APSA) shows the highest value for Cr(III) (4.08 meq/g dry resin, 85.4%) and the lowest value for Cd(II) (0.77 meq/g dry resin, 65.0%) (see Table II).

TABLE II
Maximum Retention Capacity (MRC) of the Resins P(DAPA-APSA) and P(DAPA-AA) for Cu(II), Cd(II), Zn(II), Hg(II), and Cr(III)

Resin	Metal ion	pH	Retention	
			(%)	(meq/g)
P(DAPA-APSA)	Cu(II)	3	69.3	1.27
P(DAPA-APSA)	Cd(II)	3	65.0	0.77
P(DAPA-APSA)	Zn(II)	3	79.3	1.46
P(DAPA-APSA)	Cr(III)	3	85.4	4.08
P(DAPA-AA)	Hg(II)	2	90.8	6.59

In these experiments, buffer solutions were deliberately not used to avoid any possible interference caused by the components of the buffer.

The metal ion retention under competitive conditions at pH = 3 demonstrates that there is not a significant difference with those metal ion retention properties observed under noncompetitive conditions. This behavior was similar for both resins. Only the resin P(DAPA-AA) shows a significant difference for Cd(II) (see Table III).

To recover the resin, different eluents were studied. The best results were obtained for the resin P(DAPA-APSA) loaded with Hg(II). This ion was removed between 93 and 95% with 1 and 4M HNO₃ and 1 and 4M HClO₄. It is necessary to consider that the elution was determined only after one contact and for 1 h. It should be possible to increase the elution by increasing the time of contact or changing the medium. Regeneration conditions remain to be studied in detail, given that metal uptake efficiencies of the regenerated polymers have not yet been investigated.

CONCLUSIONS

Crosslinked resins completely insoluble in water were synthesized by radical polymerization in high yields. The resins containing amine-carboxylic acid and amine-sulfonic acid groups in the side chain showed that the metal ion retention properties depended

TABLE I
Effect of Contact Time on the Retention Properties of P(DAPA-AA) for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III) at pH = 5

Metal ion	Contact time (min)									
	5		15		30		60		120	
	(%)	(mmol)	(%)	(mmol)	(%)	(mmol)	(%)	(mmol)	(%)	(mmol)
Cu(II)	90.2	0.751	89.5	0.746	90.7	0.755	87.2	0.726	90.4	0.753
Cd(II)	76.3	0.459	76.8	0.462	78.4	0.471	77.8	0.467	77.8	0.467
Zn(II)	38.2	0.415	41.2	0.449	42.4	0.461	42.4	0.461	42.4	0.461
Hg(II)	80.2	0.284	83.0	0.290	83.9	0.293	89.1	0.333	90.1	0.301
Pb(II)	74.4	0.260	75.6	0.265	79.3	0.278	80.0	0.280	81.8	0.286
Cr(III)	89.8	1.510	89.9	1.510	90.8	1.530	93.3	1.573	93.2	1.570

TABLE III
Metal Ion Retention Properties of the Resins P(DAPA-APSA) and P(DAPA-AA) from a Mixture of Metal Ions at pH = 3

	Metal ion (initial mmol) for resin		Retention			
	P(DAPA-APSA)	P(DAPA-AA)	P(DAPA-APSA)		P(DAPA-AA)	
			(%)	(mmol)	(%)	(mmol)
Cu(II)	0.086	0.166	75.4	0.066	81.8	0.136
Cd(II)	0.063	0.120	60.7	0.038	66.4	0.080
Zn(II)	0.104	0.199	80.6	0.084	77.3	0.154
Hg(II)	0.039	—	34.1	0.013	—	—
Pb(II)	0.037	0.070	48.7	0.018	72.0	0.050
Cr(III)	0.177	0.337	87.8	0.155	89.4	0.301

strongly on the pH. At pH = 5 the resins that contain carboxylate and amine groups significantly adsorbed the metal ions. The highest retention for Hg(II) ions was observed for the resin P(DAPA-AA) at pH = 2.

No important difference between the metal ion retention properties under noncompetitive and competitive conditions was observed, except that of Cd(II) for the resin P(DAPA-AA).

Adsorbed Hg(II) ions were relatively easily desorbed by using 1 and 4M HNO₃ and 1 and 4M HClO₄.

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