Synthesis of New Chelating Ion Exchange Resin with Hydroxamic and Amidoxime Groups and Study of Its Metal Binding Property

Violeta Neagu[1], I. Bunia[1], I. Plesca[1], M. Popa[2]

[1]*Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, Iasi 6600, Romania*
[2]*Gh. Asachi Technical University, Department of Macromolecules, Bd. D. Mangeron 71, Iasi 6600, Romania*

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ABSTRACT: The synthesis of a new chelating ion exchanger with hydroxamic and amidoxime groups was performed by an aminolysis reaction of an ethylacrylate/acrylonitrile/divinylbenzene copolymer with hydroxylamine in the presence of sodium ethoxylate. We studied the retention property of the new resin for Pb(II), Cd(II), Cu(II), Ni(II), Zn(II), Mn(II), and Fe(III) metal cations from aqueous solutions. The retention capacity depends on the contact time, the pH of the solution, and the types of counterions of the metal cations. Competitive adsorptions of $Pb(NO_3)_2$ + $Fe_2(SO_4)_3$, $Pb(NO_3)_2$ + $MnSO_4$, $Pb(NO_3)_2$ + $Cd(NO_3)_2$, and $Pb(NO_3)_2$ + $CuCl_2$ on the new chelating ion exchanger were performed. The results showed that the resin preferentially retained the Pb(II) ions from the binary aqueous mixtures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2956–2962, 2003

Key words: ion exchanger; functionalization of polymers; macroporous polymers; adsorption

INTRODUCTION

When heavy metals are released into the environment, they affect ecological life because of their tendency to accumulate in living organisms. Heavy metals are highly toxic metals and cause accumulative poisoning, cancer, and brain fever.[1] These metals are released into the environment in a number of different ways. Coal combustion, sewage wastewater, automobile emissions, the battery industry, mining activities, and the utilization of fossil fuels are just a few examples.

Various methods are proposed to remove heavy metal ions such as ion exchange, reverse osmosis, and electrodialysis techniques, which are efficient but expensive.[2,3] Chemical precipitation can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles is often a major disadvantage.

The search for an effective and economical method of removing toxic heavy metal ions requires the consideration of unconventional materials and processes that might have potential in this field. One of the efficient methods is adsorption.

Polymeric substances with the ability to complex metal ions are very common. They have both natural and industrial sources and are of great interest from the scientific and technological points of view. Chelating resins represent an important category of synthetic polymers with wide applicability to selectively removing metal cations. These substances display a large range of complexation properties that are due to electrostatic and steric effects. Several reviews cover many examples of the vast number of chelating groups that were incorporated into polymer networks.[4–7] The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic,[8] chromatographic,[9] and metal ion recovery processes.[10]

The desirable properties of chelating exchangers are a high capacity for the metal(s) of interest, high selectivity, fast kinetic–rapid equilibration with metal-containing solutions, and a high mechanical strength of the exchanger particles.

Polymer chelating resins containing the hydroxamic acid groups seem to have commercial potential, considering that these functional groups can form complexes with a wide range of metals.[11–15]

Another type of chelating polymer is that contain amidoxime functional groups. Literature data mentioned that the amidoxime groups formed stable complexes with different metal cations and, consequently, the polymers with the amidoxime groups

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Correspondence to: V. Neagu (vneagu@poni.icmpp.tuiasi.ro).

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can be successfully used for the preconcentration of trace metals from aqueous solutions.[16–20] One of the most important applications of these adsorbents is the recovery of uranyl ions from seawater.[21–24] For this reason, many research studies were focused on the synthesis of new chelating polymer structures with amidoxime and carboxyl groups by the radiation-induced grafting of acrylonitrile (AN) and acrylic acid onto polyethylene film and the subsequent amidoximation of polyacrylonitrile.[25]

The present article describes the synthesis of a new chelating polymer with the hydroxamic and amidoxime functional groups in the backbone structure and details its characterization by an adsorption study of Pb(II), Mn(II), Cd(II), Cu(II), Ni(II), Zn(II), and Fe(III) cations from aqueous solutions.

EXPERIMENTAL

Synthesis of ethylacrylate/acrylonitrile/divinylbenzene (EA/AN/DVB) copolymer

All the monomers were purified by distillation prior to use. The GC analysis of DVB gave the following result: 54% DVB and 30% ethylstyrene.

The EA/AN/DVB copolymers were obtained by suspension copolymerization of EA and AN with DVB using 1 wt % benzoyl peroxide as an initiator and benzine as a diluent [$D = 0.25$, $D =$ mL diluent/(mL diluent + mL comonomers)]. The aqueous phase consisted of 0.5 wt % ammonium salt of poly-(styrene-*co*-maleic anhydride). The organic/aqueous phase ratio was 1:3 (v/v) for all copolymerization processes. The reaction was allowed to proceed for 4 h at 65°C, 6 h at 75°C, and 4 h at 85°C. Following polymerization, the copolymer beads were washed with warm water and then extracted with dichloroethane in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers, and diluent; then they were vacuum dried at 50°C for 48 h. The copolymers were characterized by the apparent density (ρ_{ap}).[26]

Aminolysis reaction of EA/AN/DVB copolymer with hydroxylamine chlorohydrate

The aminolysis reaction was performed at 90–95°C under reflux for 16 h in a glass round-bottomed flask with a 50 wt % aqueous solution of hydroxylamine chlorohydrate in the presence of sodium ethoxylate as the catalyst. The flask was equipped with a stirrer, reflux condenser, and thermometer. The use of sodium ethoxylate as the catalyst is to release NH_2OH from the chlorohydrate form. After the reaction, the ion exchanger was separated by filtration, washed with water, and then regenerated with a 4% NaOH aqueous solution. The new chelating ion exchangers were characterized by the following features: the volume weight (W_v, g/mL), which is determined by the measurement of the weight loss of a known volume of fully hydrated resin in the desired ionic form, up to constant weight; and the volume (C_V, mEq/mL) and weight (C_{wt}, mEq/g) weak acid exchange capacities. These capacities were determined according to the following method: a known volume of the ion exchanger was reacted with a specific volume of 1*N* NaOH solution and the excess sodium hydroxide was measured by backtitration to the mixed indicator end point with a 1*N* HCl solution.[27]

TABLE I
Characteristics of Chelating Exchanger Precursors

Sample Code	Amount of Monomer (%) EA	AN	DVB	Apparent Density (g/cm^3)	Diluent
I	64.50	20	10	1.10	Benzine
II	56.70	20	15	0.80	Benzine

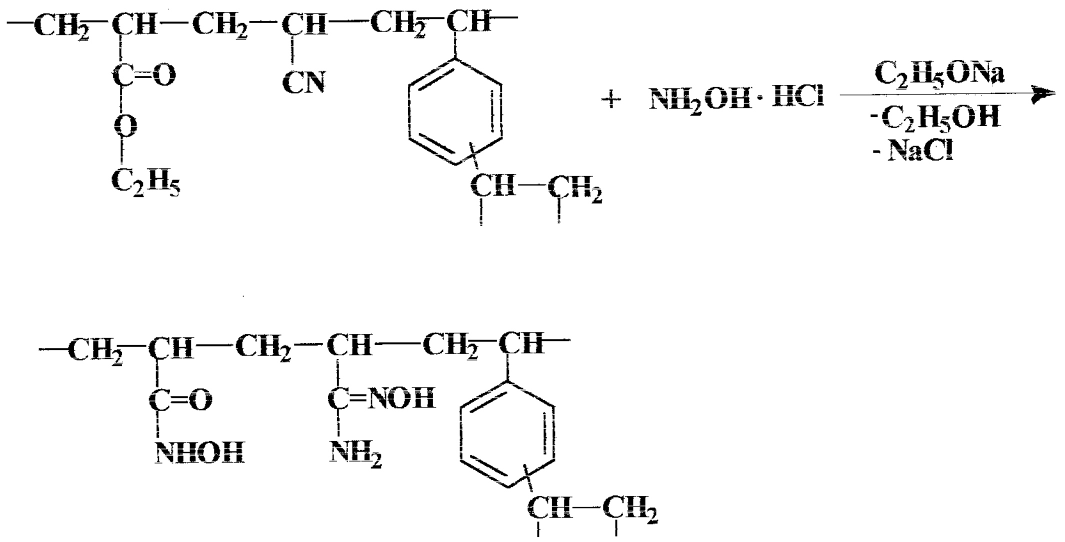
Heavy metal adsorption

Heavy metal adsorption from the single and double metal aqueous solutions were investigated in batch adsorption–equilibrium experiments. The effects of the contact time, pH value of the solution, and counterion type of metal cations on the adsorption capacity were studied.

Aqueous metal ion solutions (100 mL) with a $10^{-2}M$ concentration were treated with about 2.0 g of ion exchangers at a known humidity at room temperature. The adsorption flasks were shaken at desired contact times. The following metal aqueous solutions were used: $Cd(NO_3)_24H_2O$, $MnSO_47H_2O$, $Pb(NO_3)_2$, $CuCl_22H_2O$, $Cu(NO_3)_23H_2O$, $CuSO_45H_2O$, $NiCl_26H_2O$, $Ni(NO_3)_2$, $NiSO_46H_2O$, $Zn(NO_3)_2$, $ZnSO_47H_2O$, $Fe(NO_3)_3$, and $Fe_2(SO_4)_3$. At the end of contact time, the beads were separated from the adsorption medium and analyses for the heavy metal ions in aqueous solutions were performed with an atomic absorption spectrophotometer (AAS-300, Varian). The retention capacity (C_R) is the difference between the initial metal cation concentration and after first contact (mmol M/g dry sample).

RESULTS AND DISCUSSION

The new chelating ion exchanger was obtained by the aminolysis reaction of the EA/AN/DVB copolymer with hydroxylamine in the presence of sodium ethoxylate, as shown in the following:



This reaction was performed on two types of EA/AN/DVB copolymers with different morphologies. The information regarding the characteristics of the synthesized copolymers is presented in Table I.

The resulting products by the aminolysis reaction were characterized by the IR spectra and weak acid exchange capacity.

In the IR spectra (Fig. 1, spectrum b), the main characteristic absorption bands at 1657, 1620, and 900–950 cm^{-1} were due to —C═N—, —NH_2, and ═N—O— of the amidoxime groups, respectively. The decrease in the absorption at 2230 cm^{-1} (Fig. 1, spectrum b) compared to the IR spectrum of the original copolymer (Fig. 1, spectrum a) indicates the consumption of cyano groups as a result of the appearance of amidoxime groups. At the same time, the IR spectra (Fig. 1, spectrum b) show the characteristic absorption band at 1580 cm^{-1} that is due to ═NH bonds from the hydroxamic groups. In addition, the increase in the absorption at 1740 cm^{-1} indicates the presence of the $>$C═O bonds that belong to hydroxamic groups. The appearance of the absorption bands around 3300–3400 cm^{-1} is assigned to the —OH bonds of amidoxime and hydroxamic groups.

All of these observations permitted us to affirm that the aminolysis reaction of the EA/AN/DVB copolymer with hydroxylamine in the presence of sodium ethoxylate leads to the new ion exchanger with amidoxime and hydroxamic groups.

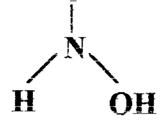
One of the most important characteristics for an ion exchanger is its ion exchange capacity. Table II presents the weak acid exchange capacity values for the compounds obtained in this study.

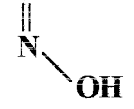
The new chelating ion exchangers were tested for the retention of different metal cations from aqueous solutions. Several of the most important factors that affect the adsorption of metal ions are the contact time, pH value, and metal contraions.

The data on the influence of the contact time and pH values on the retention capacity of different metal cations for the samples are presented in Table III. Table IV shows the influence of the contact time and contraions of the metal cations on the retention capacity of different metal cations for the tested ion exchangers. The retention capacity results in the competitive adsorption for the new chelating ion exchanger (I.CE) are presented in Table V.

The amidoximes exist predominantly in the *syn*-hydroxyamino form that is stabilized by an intramolecular hydrogen bond, and these compounds behave as bases in water. The amidoximes may coordinate as a nonionic group, but they generally undergo a metal-assisted hydroxyl proton dissociation upon coordination. The resins with this type of chelating group are very often used for the removal of metal cations from aqueous solutions.

Ion exchange resins bearing hydroxamic acid groups have long been of interest for removing specific metals from water. Hydroxamic acid exists in solution in the following two tautomeric forms:





The keto form predominates in an acid medium and the enol form in an alkaline medium. They are known to form complexes with a large number of metal ions. Most hydroxamic acid metal complexes have the following structure:

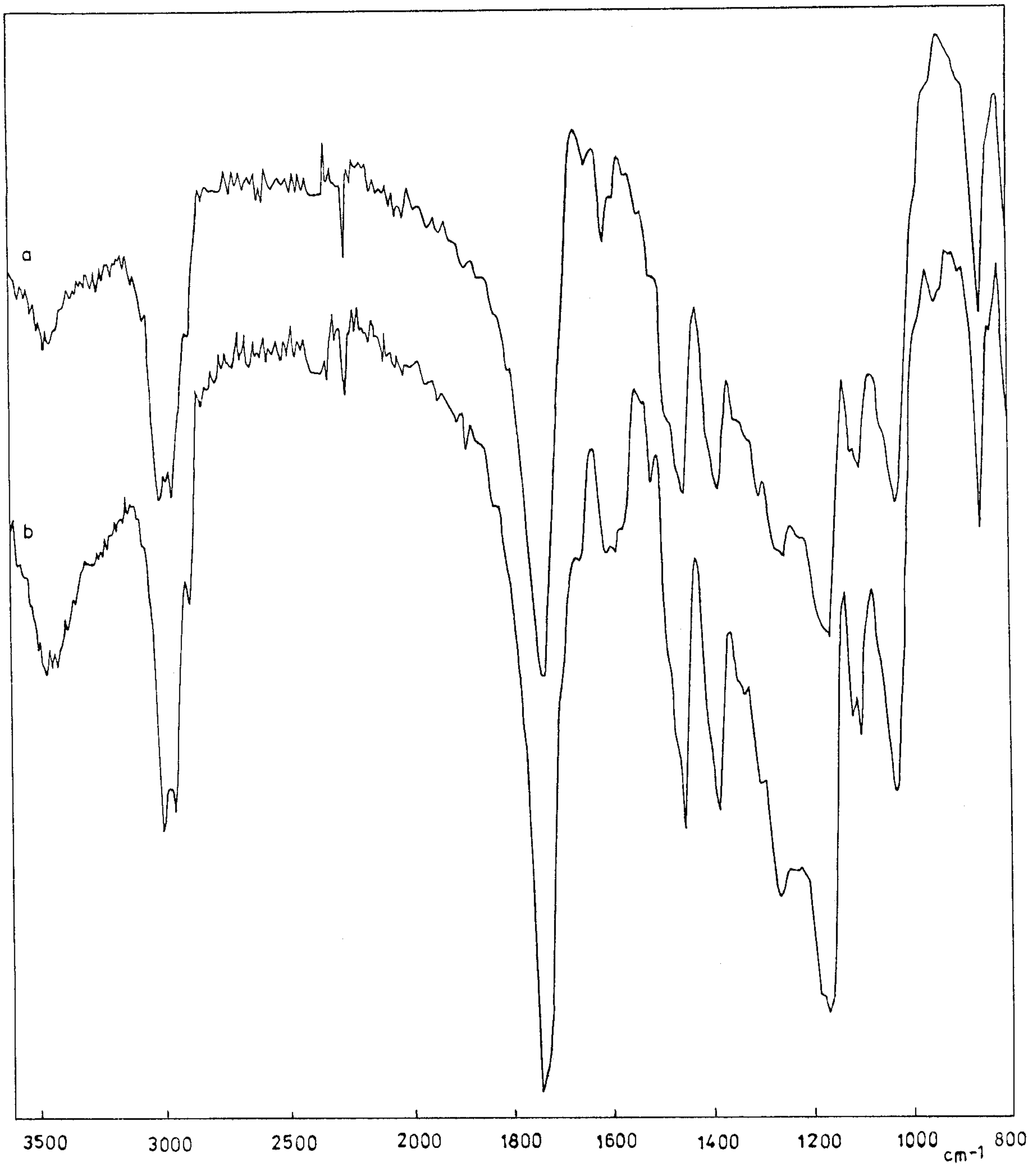
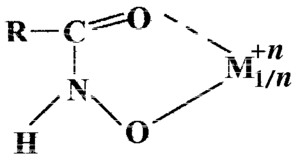


Figure 1 The IR spectra of the original copolymer (spectrum a) and the new ion exchanger I.CE (spectrum b).



Depending upon the valence state of the metal ion and the concentration of the hydroxamate group, more than one hydroxamate group will form a complex in solution. The situation with polymer-bound hydroxamate is different, however. The accessibility of more

TABLE II
Weak Acid Exchange Capacity for Synthesized Chelating Ion Exchangers

	Weak Acid Exchange Capacity		
Sample Code	C_v (mEq/mL)	C_{wt} (mEq/g)	Volume Weight (g/mL)
I.CE	0.86	1.30	0.67
II.CE	0.94	2.13	0.44

TABLE III
Influence of pH and Contact Time on Retention Capacity

Metal Cation	pH	C_R (mmol M/g Dry Sample)									
		I.CE					II.CE				
		2 h	4 h	6 h	24 h	48 h	2 h	4 h	6 h	24 h	48 h
Pb(II)	2	0	0	0	0	0	0	0	0	0	0
	5	2.80	3.00	3.04	3.11	3.25	2.00	3.10	3.13	3.18	3.23
Mn(II)	2	0	0	0	0	0	0	0	0	0	0
	5	0.38	0.54	0.65	0.67	0.70	0	0.17	0.21	0.32	1.22
Cd(II)	2	0	0	0	0	0	0	0	0	0	0
	5	0.17	0.23	0.88	0.89	1.30	0	0	0	0	0

than one hydroxamate group to a polyvalent cation is dependent upon several factors including free rotation of pendant —CO—NHOH groups, which is the rigidity imposed by the crosslinked backbone polymer.

The products obtained by the aminolysis reaction of EA/AN/DVB copolymer with hydroxylamine in the presence of sodium ethoxylate are new chelating ion exchangers with hydroxamic and amidoxime functional groups. From the characteristics of the EA/AN/DVB copolymers (Table I) it can be seen that the quantity of EA is higher than the quantity of AN, and therefore the presence of hydroxamic groups predominated. In the retention of the metal cations from aqueous solution, in this type of ion exchanger the hydroxamic groups took place as the major ratio to the complexation. On the other hand, the presence of the amidoxime groups led to the increase of the water content for the resins and consequently to the increased retention capacity for the metal cations. In our future work we will elaborate on the contribution of every functional group to the metal binding.

From Tables III–V it can see that the retention capacities of both chelating ion exchangers depend on the contact time; after many experiments, the retention equilibrium has been reached at 48 h for all metal cations. The studied samples did not retain the Pb(II), Mn(II), and Cd(II) cations at pH 2 (Table III). Therefore, the complexation behavior of heavy metal ions is more sensitive to pH changes, especially at lower pH. The inhibition of metal chelation with a decrease in the pH was observed by several authors and in different sorbents.[28,29] Thus, it is proposed that protons and metal ions compete for the same binding sites. Also, at low pH the amidoxime and hydroxamic groups behave very similarly because the amidoximes are rapidly hydrolyzed to hydroxamic acid. At pH 5 and at the equilibrium time, both chelating ion exchangers retain the cations in the following order: Pb(II) > Cd(II) > Mn(II) for the I.CE sample and Pb(II) > Mn(II) > Cd(II) for the II.CE sample. The Pb(II) retention capacity value is the same for both resins, but the situation is different for the other cations. This behavior could be explained by the differences of the stability constants of the formed complexes and the different morphological structures of the resins.

The behavior of both resins in the retention of metal cations is different because these chelating ion exchangers have different morphological structures and weak acid exchange capacity values. The II.CE resin has higher porosity and weaker acid exchange capacity values than the I.CE ion exchanger, which determines good results in the retention of the metal cations under study.

TABLE IV
Influence of Contact Time and Counterions of Metal Cations on Retention Capacity

Metal Cation		C_R (mmol M/g Dry Sample)									
		I.CE					II. CE				
		2 h	4 h	6 h	24 h	48 h	2 h	4 h	6 h	24 h	48 h
Cu(II)	Cl^-	0.43	0.43	0.43	0.64	0.86	0.18	0.31	0.31	0.60	1.81
	NO_3^-	0.23	0.25	0.40	0.41	2.30	0.11	0.14	0.16	0.17	0.22
	SO_4^{2-}	2.30	2.36	2.36	2.40	2.42	0.30	0.34	0.40	0.58	0.60
Ni(II)	Cl^-	0	0	0	0	0	0.26	0.29	0.34	0.35	0.47
	NO_3^-	0	0	0	0	0	0	0	0	0	0
	SO_4^{2-}	0	0	0	0	0	0.34	0.34	0.40	0.46	0.75
Zn(II)	NO_3^-	0	0	0	0	0	6.50	6.50	6.64	6.70	7.00
	SO_4^{2-}	0	0	0	0	0	0.20	0.26	0.70	0.76	0.82
Fe(III)	NO_3^-	0	0	0	0	0	0	0	0	0	0
	SO_4^{2-}	0	0.29	0.40	0.55	0.75	0.56	0.56	0.85	1.45	2.77

TABLE V
Retention Capacity for I.CE Sample in Competitive Adsorption

		C_R (mmol M/g Dry Sample							
		$Pb(NO_3)_2$ + $Fe_2(SO_4)_3$		$Pb(NO_3)_2$ + $MnSO_4$		$Pb(NO_3)_2$ + $Cd(NO_3)_2$		$Pb(NO_3)_2$ + $CuCl_2$	
Sample Code	Time (h)	Pb(II)	Fe(III)	Pb(II)	Mn(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)
I.CE	48	2.53	0.40	2.47	0.45	1.50	1.26	1.42	0.64

It is well known that a macroporous resin with many functional groups is more efficient than the gel type ones with few chelating sites in relation to the selective removal and recovery of heavy metal ions. A porous resin structure allows fast diffusion of the ions to the functional groups and therefore favors complexation. Besides, the other influencing factors in the retention of metal cations are the metal counterion nature and the stability constant of the metal ion. Every metal ion has own stability constant that leads to more or less stable complexes. The ionic form of the metal determines its hydrated ion radius and the size of the solvated species determines its mobility. The retention capacity increases when the hydrated ion radius and the size of the solvated species are low. For example, the II.CE resin has a higher retention capacity value for the Zn(II) cation from the nitrate solution than from the sulfate solution (Table IV).

Note from Table IV that the counterions of the metal cations influence the C_R values for Cu(II), Ni(II), Zn(II), and Fe(III) ions. In the case of Cu(II) ions, for the I.CE resin the highest C_R values were obtained in the $Cu(NO_3)_2$ and $CuSO_4$ aqueous solutions and for the II.CE resin they were obtained in $CuCl_2$. The Cu(II) retention capacity values for the studied resins are in the following order: $C_R\ (SO_4^{2-}) \approx C_R\ (NO_3^-) > C_R\ (Cl^-)$ for the I.CE ion exchanger and $C_R\ (Cl^-) > C_R\ (SO_4^{2-}) > C_R\ (NO_3^-)$ for the II.CE ion exchanger. For the same counterion type, the C_R values for the resins are the following: C_R (II.CE) $>$ C_R (I.CE) for the chloride solution, C_R (I.CE) $\gg$ C_R (II.CE) for the nitrate solution, and C_R (I.CE) $\gg$ C_R (II.CE) for the sulfate solution.

There is different behavior for the retention of Ni(II) ions; the I.CE resin did not retain the Ni(II) ions from chloride, nitrate, and sulfate solutions. It is not the same situation for the II.CE ion exchanger. This resin retained the Ni(II) ions from sulfate and chloride aqueous solutions. The Ni(II) retention capacity values are in the following sequence: $C_R\ (SO_4^{2-}) > C_R\ (Cl^-) > C_R\ (NO_3^-)$.

The I.CE resin did not retain the Zn(II) ions from nitrate and sulfate solutions, whereas the II.CE ion exchanger has Zn(II) retention capacity in the following order: $C_R\ (NO_3^-) \gg C_R\ (SO_4^{2-})$. The Fe(III) ions are retained on both chelating ion exchangers only from the sulfate solution. The highest retention capacity values were obtained for the II.CE resin.

We can affirm that the Cu(II), Zn(II), and Fe(III) retention capacity order for the studied ion exchangers is $C_R\ (CuSO_4) > C_R\ (Fe_2(SO_4)_3)$ for the I.CE resin and $C_R\ (Zn(NO_3)_2) > C_R\ (Fe_2(SO_4)_3) > C_R\ (CuCl_2)$ for the II.CE resin.

In the case of competitive adsorption (Table V), it was observed that the I.CE ion exchanger could be used in the selective retention of the Pb(II) cations from the binary mixtures of aqueous solutions: $Pb(NO_3)_2 + Fe_2(SO_4)_3$, $Pb(NO_3)_2 + MnSO_4$, $Pb(NO_3)_2 + Cd(NO_3)_2$, and $Pb(NO_3)_2 + CuCl_2$. It should be noted that the competitive adsorption capacities of the resins for all metal cations were lower than noncompetitive conditions.

CONCLUSIONS

New chelating ion exchangers by the aminolysis reaction of an EA/AN/DVB copolymer with hydroxylamine in the presence of sodium ethoxylate were obtained. The synthesized compounds were characterized by IR spectroscopy and weak acid exchange capacity.

Aminolysis reactions were performed on two types of EA/AN/DVB copolymers with different morphologies.

We studied the retention capacity of the new chelating ion exchangers for several metal cations from aqueous solutions. All the experiments led to the conclusion that the ion exchangers retain the metal cations and their retention capacities depend on the porosity of the resin structure, the contact time, the pH of the metal aqueous solution, and the counterions of the metal cations.

For the competitive adsorption, the I.CE resin could be used in the selective retention of the Pb(II) cations from the binary mixture of the aqueous solutions.

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