Removal of Heavy-Metal Ions from Aqueous Solution with Nanochelating Resins Based on Poly(styrene-*alt*-maleic anhydride)

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ABSTRACT: Chelating resins have been considered to be suitable materials for the recovery of heavy metals in water treatments. A chelating resin based on modified poly(styrene-*alt*-maleic anhydride) with 2-aminopyridine was synthesized. This modified resin was further reacted with 1,2-diaminoethan or 1,3-diaminopropane in the presence of ultrasonic irradiation for the preparation of a tridimensional chelating resin on the nanoscale for the recovery of heavy metals from aqueous solutions. The adsorption behavior of Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ions were investigated by the synthesis of chelating resins at various pH's. The prepared resins showed a good tendency for removing the selected metal ions from aqueous solution, even at acidic pH. Also, the prepared resins were examined for the removal of metal ions from industrial wastewater and were shown to be very efficient at adsorption in the cases of Cu^{2+}, Fe^{2+}, and Pb^{2+}. However; the adsorption of Zn^{2+} was lower than those of the others. The resin was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis, and differential scanning calorimetry analysis. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 127: 2875–2883, 2013

INTRODUCTION

As industry expands, the contamination of water resources by heavy metals is a serious environmental problem worldwide. When heavy-metal ions are assimilated into living organisms, they accumulate in living bodies and cause serious disease, even at very low concentrations.[1–3] Therefore, many separation methods have been developed to remove heavy-metal ions from aqueous solutions, including reduction and precipitation, coagulation, reverse osmosis, electrodialysis, and adsorption.[3–11] Among these technologies, the adsorption of heavy-metal ions with chelating resins is highly popular because the resins are reusable, easy to handle, and have higher adsorption efficiencies and selectivities.

Metal-chelating polymers constitute an important class of versatile polymeric materials that have found widespread applications in environmental remediation and in the monitoring and separation of trace heavy-metal ions from aqueous solutions. Hence, numerous chelating resins have been prepared through the polymerization of conventional chelating monomers, such as acrylic acid,[12] allylthiourea,[13] vinyl pyrrolidone,[14] and vinyl imidaz-

ole.[15] Additionally, the modification of synthetic polymers[16–22] and natural polymer matrixes[13,23–26] by functionalization reactions has also been used to form chelating polymers. In the last case, they are normally produced by the incorporation of active chelating groups into a polymeric matrix. Such chelating groups may be covalently bound to a polymer matrix as pendent groups or incorporated into the repeating units of the polymer backbone by the polymerization of a suitable monomer containing the required chelating group. It has been demonstrated that the nature of the intervening groups connecting the active chelating ligands in chelating polymers plays an important role in the chelation process.[27]

In recent years, the development of high-performance adsorbents (chelating polymers) on the nanoscale for the removal of heavy-metal ions from aqueous solutions has been considered a research priority in the environmental field.[28]

Among synthetic polymers, poly(styrene-*alt*-maleic anhydride) (SMA) is a commercial industrial copolymer that is cheaper than any other polymer possessing a reactive group in the main chain or side chain for further functionalization.
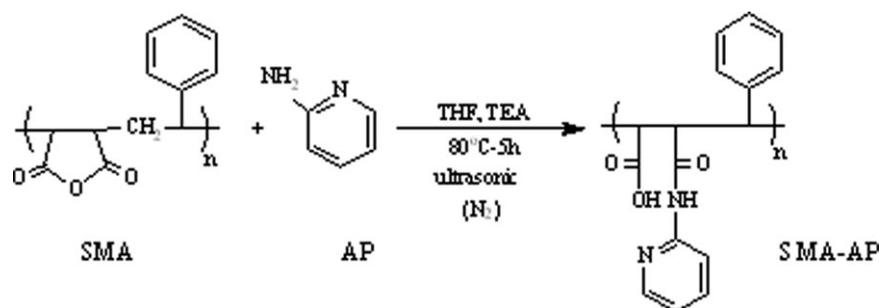
Scheme 1. Synthesis of the modified SMA.

In this study, a novel chelating resin was synthesized by the chemical modification of the SMA copolymer by 2-aminopyridine (AP) as a grafting agent under various conditions by the amidation reaction of maleic anhydride repeating groups in the copolymer backbone. Also, the prepared resins were further reacted by 1,2-ethylenediamin or 1,3-propylenediamin as a crosslinking agent to form tridimensional resins. The preparation of the crosslinked resins in the presence of ultrasonic irradiation along with vigorous magnetic stirring gave rise to polymeric particles on the nanoscale. The adsorption behavior of Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ions were investigated by synthesized chelating resins at various pH's.

EXPERIMENTAL

Material

Analytical-reagent grade $Fe(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Pb(NO_3)_2$ and other inorganic chemicals, including HCl and NaOH, were purchased from Merck (Germany) and were used without further purification. AP and the organic solvents, such as tetrahydrofuran (THF) and methanol, were also purchased from Merck and were used without further purification. The aqueous solutions were prepared by the dissolution of metal salts in deionized water.

Equipment

IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). The X-ray diffraction (XRD) spectra were recorded on an X'pert Philips X-ray photoelectron spectrometer (The Netherlands) with nonmonochromated Mg Kα radiation as the excitation source. Atomic absorption spectrophotometry (AAS; Shimadzu AA-6800, Japan) was used to determine the metal-ion concentrations in aqueous solutions. Differential scanning calorimetry (DSC) analyses of the prepared polymers were determined with a LENSES STAPT-1000 calorimeter (Germany) with scanning up to 600°C at a heating rate of 10°C/min. The inherent viscosity of the resulting SMA copolymer was obtained with an Ostwald viscometer at 25°C in a thermostatic water bath. The elemental analysis of one of the resins was performed by a CHN analyzer (2400 series II, PerkinElmer Co., USA). The morphology of the particles was examined via scanning electron microscopy (SEM; XL30 Philips, Netherland).

Synthesis of the Grafted SMA Copolymer by AP (SMA–AP)

The SMA copolymer was prepared by the free-radical polymerization of maleic anhydride and styrene at 70°C in the presence of benzoyl peroxide as an initiator.[29] For synthesis of the grafted
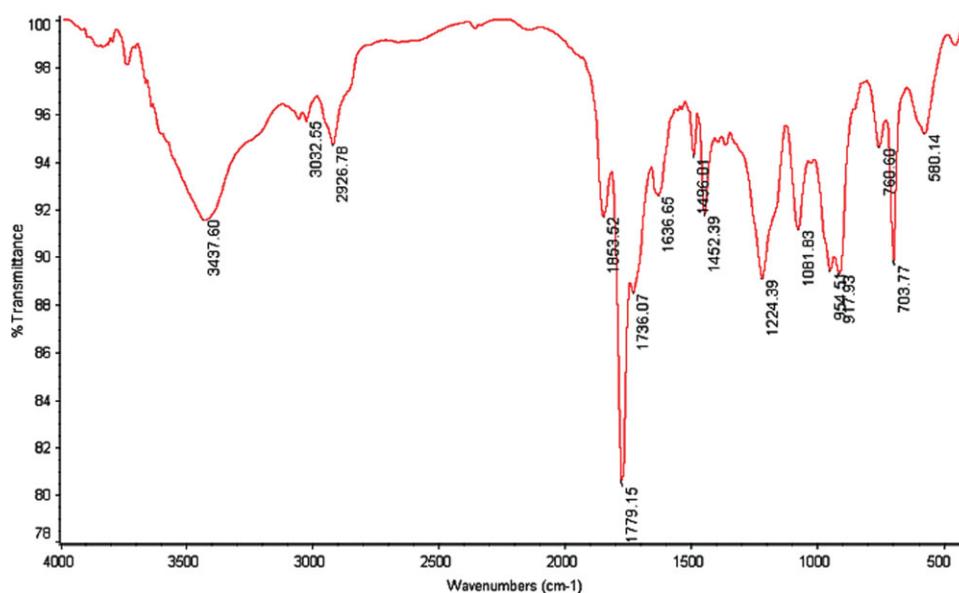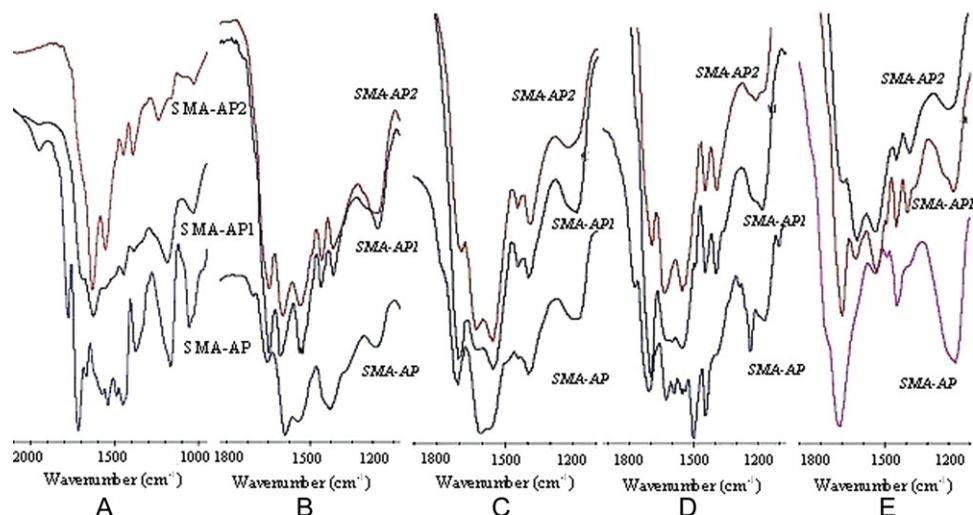

Figure 1. FTIR spectrum of the SMA copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. FTIR spectra of the SMA–AP, SMA–AP1, and SMA–AP2 copolymers (A) before complexation and (B–E) after complexation with selected metal ions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SMA copolymer, 3 g (0.015 mol) of SMA copolymer and 0.698 g (0.007 mol) of AP at a ratio of 1 : 0.5 were poured into a flask. Then, 0.5 mL (0.004 mol) of triethylamine (TEA) as a catalyst and 50 mL of THF as a solvent were charged in a three-necked, round-bottom flask equipped with a condenser, magnetic stirring bar, inlet and outlet for inert gas, and ultrasonic irradiation probe. The reaction mixture was refluxed under these conditions for 3 h. The precipitations were completed by the addition of n-hexane as a nonsolvent and were separated by filtration and washed by n-hexane several times. The product was dried in a vacuum oven for 24 h at 60°C (yield = 95%). The synthesis process of the first chelating resin is shown in Scheme 1.

Synthesis of the 1,2 Diaminoethane (SMA-AP1) and 1,3 Diaminoethane (SMA–AP2)

The SMA–AP1 chelating copolymer was prepared by the step-by-step reaction of the SMA copolymer with AP as a grafting agent and 1,2-diaminoethane as a crosslinking agent at a molar ratio of 1 : 0.5 : 0.25 in THF. The reaction mixture was refluxed for 3 h under inert gas in the presence of ultrasonic irradiation along with vigorous stirring. TEA was used as a catalyst in the reactions. The obtained product was filtered, washed thoroughly with THF, and dried in a vacuum oven at 60°C for 24 h. The yield of the reaction was 90%. The same procedure was repeated with 1,3-diaminopropane instead of 1,2-diaminoethane as the crosslinking agent for the preparation of SMA–AP2. The yield of the reaction was 98%. The elemental analysis of the SMA–AP2 resin was carried out and showed 63.18% C, 6.64% H, and 6.73% N.

Determination of the Adsorption Capacity for Single Metal Ions

Dynamic adsorption experiments were performed by the mixture of 50 mg of chelating resin with 50 mL of the metal-ion solution (50 ppm) in a flask with a magnetic stirrer at 25°C for 14 h. The pH values of the solutions were adjusted to 3, 6, and 9 by the addition of aqueous hydrochloric acid or sodium hydroxide solution. When the adsorption experiment was complete, the mixture

was filtered, and the residual metal-ion concentration was determined by AAS. The adsorption capacities (q's; mmol M^{2+}/g resin) under various conditions were calculated as follows:

$$q = \frac{(C_0 - C_f)V}{W} \quad (1)$$

where C_0 and C_f are the initial and final concentrations (mmol/L) of metal ions in the aqueous solution, respectively; V is the volume of the metal-ion solution (0.05 L); and W is the weight of the resin (0.05 g). The competitive adsorptions for mixtures of Cu^{2+}, Pb^{2+}, Fe^{2+}, and Zn^{2+} ions in the real sample under equal initial concentrations (10 ppm) were also studied according to the previous procedures.

Desorption of Metal Ions in Acidic Media

For the desorption of metal ions, aqueous 0.2M HCl was used. The resin–metal-ion complexes in which adsorption was carried out at pH 6 were immersed in the 0.2M HCl solution with a magnetic stirrer at 25°C for 1 h. After filtration, the final metal-
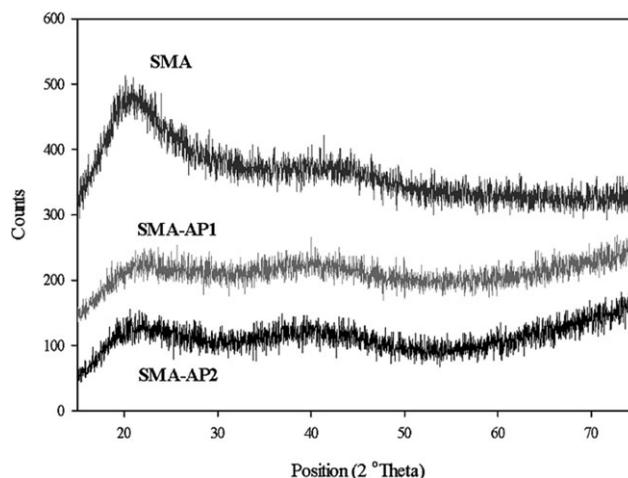
Figure 3. XRD patterns of the synthesized copolymers.
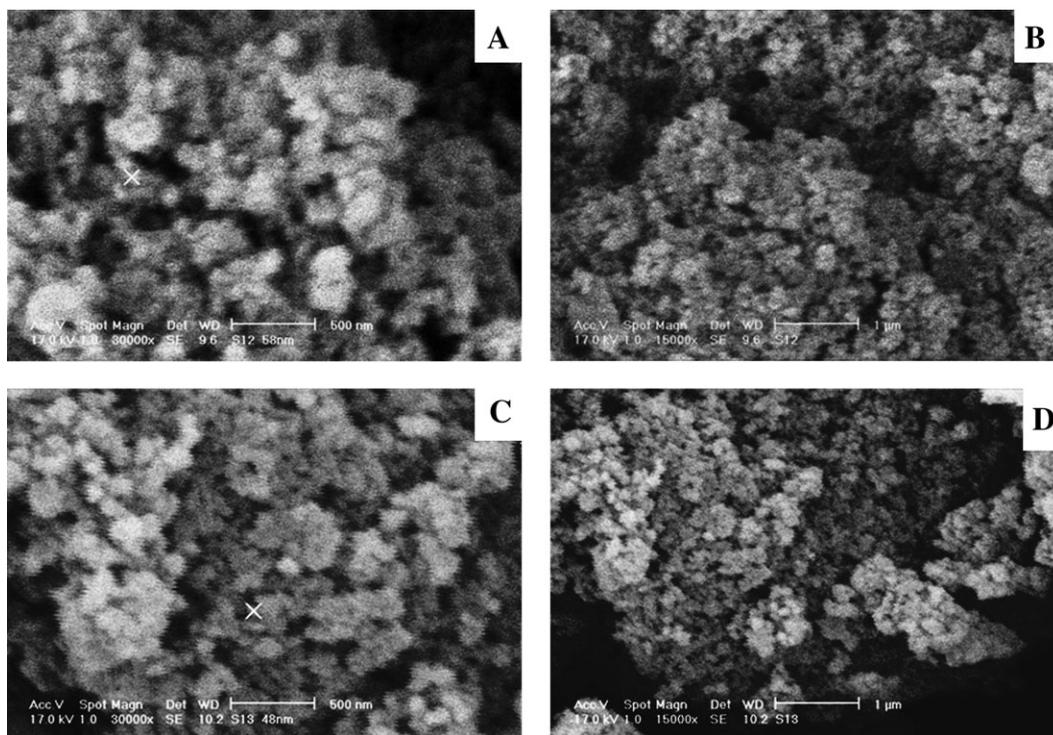
Figure 4. SEM images of the chelating resins (A) SMA–AP1 (scale = 500 nm), (B) SMA–AP2 (scale = 1 μm), and (C) SMA–AP2 (scale = 500 nm) and SMA–AP2 (scale = 1 μm).

ion concentrations in the solution were estimated by AAS. The desorption ratio (*D* %) was calculated as follows:

$$D(\%) = \frac{\text{Millimoles of metal ions desorbed to the HCl solution}}{\text{Millimoles of metal ions adsorbed onto resin}} \times 100$$

(2)

Swelling Index

A known weight (0.5 g) of fully dried SMA–AP, SMA–AP1, or SMA–AP2 was immersed in water. After a definite period of time, the polymer was filtered and blotted dry. The swollen polymer was weighed. The swelling index was determined by the ratio of the weight of the swollen polymer to the initial weight of the resin.

RESULTS AND DISCUSSION

Synthesis and Characterization of the SMA–AP Copolymers

The SMA copolymer was prepared by the method mentioned in ref. 29. Figure 1 shows the FTIR spectrum of the SMA copolymer. In this spectrum, the characteristic of anhydride bonds at

1735, 1784, and 1856 cm^{-1} are shown. The intrinsic viscosity of the resulting SMA copolymer was measured with an Ostwald viscometer at 25°C in THF solvent, and it was determined to be 0.32 dL/g.

The SMA–AP was prepared with the amidation of anhydride moieties of the SMA copolymer. The amine group of AP reacted with maleic anhydride repeating groups in the SMA copolymer backbone to form an alkylamide linkage and a carboxylic acid group. Amide bonds are significantly resistant to hydrolysis, so the resulting copolymer was stable in acidic and basic media. To prepare the tridimensional SMA–AP1 and SMA–AP2 copolymers, the reaction was carried out with a step-by-step reaction of the SMA copolymer with AP as a grafting agent and 1,2-diaminoethane or 1,3-diaminopropane as a crosslinking agent.

Figure 2(a) displays the FTIR spectra of the SMA–AP, SMA–AP1, and SMA–AP2 copolymers. The comparison of the SMA–AP spectrum with the SMA spectrum showed that the intensity of anhydride peaks decreased, and the formation of amide groups took place at about 1676 cm^{-1}. In the case of the SMA–

Table I. Adsorption Capacity for Single Metal Ions at Various pH's (3, 6, and 9)

	Adsorption capacity (mmol/g)											
	Fe^{2+}			Cu^{2+}			Zn^{2+}			Pb^{2+}		
Resin	3	6	9	3	6	9	3	6	9	3	6	9
SMA-AP	0.057	0.803	—	0.179	0.765	—	0.044	0.204	—	0.113	0.199	—
SMA-AP1	0.579	0.885	0.885	0.010	0.790	0.790	0.021	0.489	0.737	0.083	0.232	0.215
SMA-AP2	0.480	0.687	0.890	0.007	0.724	0.765	0.006	0.431	0.705	0.074	0.234	0.226

Table II. Adsorption Percentage for Single Metal Ions at Various pH's (3, 6, and 9)

	Adsorption percentage (%)											
	Fe^{2+}			Cu^{2+}			Zn^{2+}			Pb^{2+}		
Resin	3	6	9	3	6	9	3	6	9	3	6	9
SMA–AP	6.38	90.16	—	22.72	96.78	—	5.82	26.9	—	46.9	82.82	—
SMA–AP1	65.16	99.46	99.46	1.3	100	100	2.78	64.36	96.94	34.72	96.74	89.74
SMA–AP2	54.26	99.66	100	0.92	91.66	96.78	0.8	56.66	92.76	30.8	97.44	93.58

AP1 and SMA–AP2 copolymers, the FTIR spectra revealed that the grafting reaction was efficient and the anhydride peaks disappeared, and instead, the spectrum showed the characteristics of the absorption peaks of the carbonyl of amide at a lower frequency of about 1632 cm^{-1} and the carbonyl of carboxylate anion at about 1560 cm^{-1}. All of the pendant carboxylic acids of the resins were converted to free carboxylate ions because of the existence of aminopyridine groups in the neighborhoods.[30,31]

It is known that metal complexation to a certain polymeric ligand causes changes in the absorption spectra of the starting polymer.[32] FTIR spectroscopy has been used for the characterization of polymer–metal complexes because the frequency at which a characteristic group of the polymer absorbs is modified by metal-ion complexation, the shift or absence of a certain band present in the starting ligand, and the presence of new bands. Therefore, the first information about the structural changes caused by the complexation of the obtained chelated resin with Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} was provided by the FTIR spectra.

The shift of infrared absorption bands for the free carbonyl bond (C=O) of the carboxylate groups illustrated whether the bonding between the ligand and each metal ion in the solid phase was covalent or ionic. The more covalent it was, the higher the frequency shift was for the free carbonyl bond absorption. Figure 2(b–e) represents the FTIR spectra of the four kinds of metal ions adsorbed in the resins. In this study, the absorption band for C=O in the chelating group shifted to

higher frequencies with increasing covalent nature of the carbonyl band in the results of complexation with ionic metals and appeared about 1690–1710 cm^{-1}.[32] It was interesting that the absorption peaks at about 1710 cm^{-1} decreased with the diameter of metal ions adsorbed. The larger the diameter of the metal ion was, the smaller the electron attraction was, and the bond of metal ions with carboxylate tend toward ionic properties.

The bands at 1632, 1560, 1454, and 1242 cm^{-1} shifted to a lower frequency; this indicated that the metal coordination through the chelating ligands was done in the copolymer network. Also, the absorption bands characteristic of the aromatic parts of the matrix (1032, 914, 767, and 703 cm^{-1}) were not influenced by the metal complexation.

The XRD patterns of the synthesized copolymers are depicted in Figure 3. The diffraction patterns showed that the copolymers were amorphous. Indeed, there was only a broad diffraction hump at about $2\theta = 20°$; this indicated the amorphous nature of the copolymers. So, the presence of the grafting and crosslinking agent in the copolymer backbone did not effect the amorphous structure of the copolymer.

Table III. Percentage of Desorption for Single Metal Ions

	Percentage of desorption			
Resin	Fe^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
SMA–AP	97.8	95.4	98.5	97.7
SMA–AP1	94.2	94	98	95.5
SMA–AP2	94.1	96.6	98.1	95.8

Scheme 2. Structure of the metal–resin complex (n's = 1 and 2).

Figure 5. Removal percentage of metal ions from the treated industrial wastewater.

Table IV. k_d Values of the Crosslinked Copolymers for Single-Metal-Ion Adsorption

Resin	pH	k_d (mL/g)			
		Fe^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
SMA–AP	3	6.81×10	2.94×10^2	6.18×10	8.83×10^2
SMA–AP	6	9.16×10^3	3.01×10^4	3.68×10^2	4.82×10^3
SMA–AP1	3	1.89×10^3	1.32×10	2.86×10	5.32×10^2
SMA–AP1	6	1.84×10^5	—	1.81×10^3	2.97×10^4
SMA–AP1	9	1.84×10^5	—	3.17×10^4	8.94×10^3
SMA–AP2	3	1.19×10^3	2.20	1.20	4.45×10^2
SMA–AP2	6	7.13×10^5	1.10×10^4	1.31×10^3	3.81×10^4
SMA–AP2	9	—	3.00×10^4	1.28×10^4	1.46×10^4

Figure 4 shows the SEM micrographs of typical SMA–AP1 and SMA–AP2, in which the particles possessed an almost uniform distribution of size with spherical shapes. The diameter of the observed particles in the SEM images was estimated to be under 100 nm.

Determination of the Adsorption Capacity for Single Metal Ions

The adsorption capacities of the synthetic resins (SMA–AP, SMA–AP1, and SMA–AP2) for Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} were investigated in aqueous media. The results are summarized in Table I. It was observed that two resins, namely, SMA–AP1 and SMA–AP2, demonstrated a high affinity for selected metal ions, and these copolymers had more affinity than the SMA–AP. Also, the data in Table II indicated that with increasing pH, the adsorption capacity increased for all of the selected metals.

Sorption of Metal Ions as a Function of pH

The sorption behavior of any metals on the resins at different pH values was examined with a batch equilibration technique, and the results are summarized in Table II. The pH of the metal test solution was measured during the sorption process. After equilibration with the resin, a decrease in the pH of the solution was observed. This was attributed to the release of protons from the resin. In general, the adsorption of metal ions increased with increasing pH and reached a limiting value in each instance, which was followed by a decrease in adsorption beyond the limiting value. It is well known that the adsorption of heavy-metal ions by resins depends on the pH; this affects the chelation extremely as well as the physisorption processes.[33] Thus, the effect of pH on the adsorption capacities needed to be further investigated. The SMA–AP resin was dissolved completely in water at pH 9 because of its noncrosslinked nature, and its hydrophilicity was increased because of the deprotonation of its functional group.

The effect of crosslinking on the sorption revealed that the sorption capacity increased in the crosslinked samples by 1,2-diaminoethane and 1,3-diaminopropane compared to that in the noncrosslinked sample. Scheme 2 shows the metal binding onto the chelating resin.

There was an abrupt increase in the metal adsorption when the pH was raised from 3 to 9. The results indicate that with increasing pH from 3 to 6, the adsorption percentage increased for all of the selected metals, and it remained nearly unchanged from pH 6 to 9. This observation was more pronounced with Cu^{2+}, Fe^{2+}, and Pb^{2+}, where the binding capacity of the resin strongly increased with increasing pH of the medium, whereas the sorption of Zn^{2+} slightly increased as soon as the pH increased. The order of the adsorption percentage changed as follows: $Fe^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+}$. This behavior could be explained by the nature of the chelating groups on the resin backbone; the carboxylate groups of the prepared resins were weak acids, and the degree of protonation critically affected the ability of the resin to bind metal cations.

The adsorption of all of the metal ions on the resin was more favorable at a pH value of 9. At low pH values, a high concentration of H^+ could react with carboxylate ions (COO^-) and amine groups to form protonation. In other words, H^+ could compete with metal ions for adsorption sites and reduce the metal-ion adsorption capacity.[34,35] At the alkaline pH value, the carboxylate functional groups of the resin and the nitrogen of pyridine in the side chain of the resin formed a completely deprotonated form, so the metal uptake was intense.

Desorption of Metal Ions from The Chelating Resin

The desorption of the adsorbed metal ions from the chelating resins was also studied in a batch experimental setup. The chelating resin beads loaded to maximum amounts of the respective metal ions at pH 6 were placed within the desorption medium containing 0.2M HCl, and the amount of metal ions desorbed in 1 h was measured. The results in Table III show that for all of the metal ions, the recorded desorption ratios were up to 94%.

Table V. k_d Values of the Crosslinked Copolymers for Wastewater

Resin	k_d (mL/g)			
	Fe^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
SMA–AP1	1.182×10^5	—	8.709×10^3	8.364×10^2
SMA–AP2	3.484×10^4	3.990×10^5	7.953×10^3	1.101×10^5
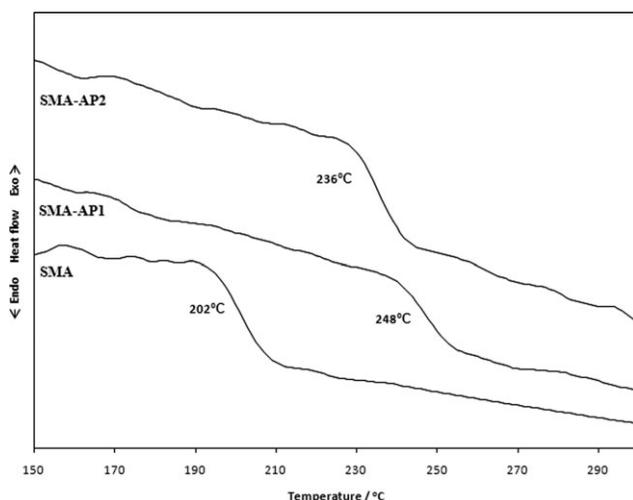
Figure 6. DSC thermograms of SMA, SMA–AP1, and SMA–AP2 copolymers.

Removal of Metal Ions from Industrial Wastewater from Akarak Armenia Factory

The used wastewater had the following characteristics. The appearance was turbid, the pH was 10.49, and the metal ions Fe^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Hg^{2+}, and Al^{3+} had concentrations of 18.5, 879.7, 0.2, 12.1, 0.8, 5.9, 5.7, 2.1, 1.9, and 1.6 ppb, respectively. The other ion concentrations were as follows: nitrate = 0.6 ppm, ammonium = 0.05 ppm, and sulfate = 0.21 ppm. The amounts of metal ions in the previously cited wastewater were poor, so the researchers decided to add an appropriate amount of each metal ion to the wastewater sample to achieve 50 mL of wastewater with a 40-ppm concentration. The share of each metal ion in this solution was estimated to be 10 ppm (Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}). To investigate the efficiency of the chelating resins SMA–AP1 and SMA–AP2 in the removal of metal ions from the real sample, 0.05 g from each of the resins was added to 50 mL of the aforementioned solution. The samples were stirred by a magnetic stirrer for about 10 h at room temperature. After they were stirred for a period of time and the mixture was filtered, the concentration of remaining metal ions in the filtrate was determined by AAS. Figure 5 displays the results of the experiments. The removal of metal ions from wastewater was efficient. On the basis of the results, we concluded that the nearly complete adsorption of all of the selected metal ions was achieved, but the adsorption of Zn^{2+} was lower than that of the others.

Determination of the Equilibrium Distribution Coefficient (k_d)

k_d was determined according to eq. (3):

$$k_d = \frac{\text{Amount of metal ions on the adsorbent}}{\text{Amount of metal ions in the solution}} \times \frac{V}{m} \quad (3)$$

where m is the weight of adsorbent (g).

The k_d value can be used as a valuable tool to study metal-cation mobility. High values of k_d indicate that the metal has been retained by the solid phase, whereas low values of k_d indicate that a large fraction of the metal remains in solution. k_d was
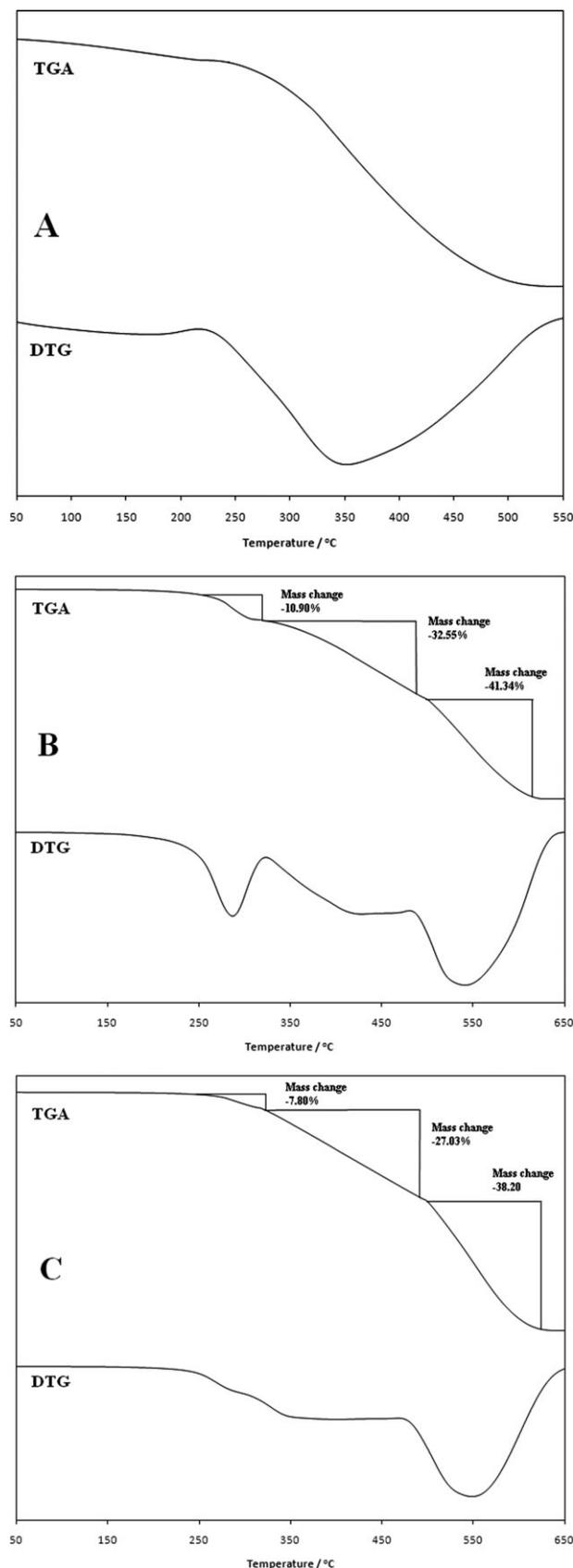
Figure 7. TGA/differential thermograms of the copolymers: (A) SMA, (B) SMA–AP1, and (C) SMA–AP2.

Table VI. Polymer Synthesized for Index Swelling

Resin	Time (h)								
	0.5	1	2	4	6	12	24	48	72
SMA–AP	0.070	0.114	0.152	0.190	0.236	0.299	0.310	0.317	0.320
SMA–AP1	0.022	0.040	0.053	0.069	0.077	0.108	0.157	0.163	0.163
SMA–AP2	0.029	0.050	0.088	0.100	0.110	0.127	0.188	0.195	0.196

calculated with the previous equation.[36] Tables IV and V shows the k_d values for the adsorption of single metal ions and the adsorption of metal ions from a real sample, respectively. These findings proved that the k_d values were approximately high in the cases of Fe^{2+}, Cu^{2+}, and Pb^{2+} ions, so the prepared chelating resins were good candidates for the removal of these metal ions from aqueous solutions. The prepared resins did not show a high tendency to remove Zn^{2+} ions from aqueous solutions at pH 6.

DSC
The DSC thermograms of the SMA, SMA–AP1, and SMA–AP2 copolymers are shown in Figure 6. The T_g of the SMA copolymer increased concomitantly with the existence of AP and a crosslinking agent in the structure of SMA copolymer in this study.

As shown, T_g increased as the amount of grafting agent increased, and this probably resulted from the enhanced molecular interactions due to hydrogen bonding in the copolymers.

A comparison of the SMA copolymer with a T_g of 202°C with the modified and crosslinked sample, showed that the crosslinked copolymers with more rigid structures, originating from the cyclic anhydride in the main chains of the copolymer, possessed higher T_g's, ranging from 236 to 248°C. The SMA–AP1, which had 1,2-diaminoethane, revealed a higher T_g than SMA–AP2, with 1,3-diaminopropane as a crosslinking agent. According to the DSC experiment, the polymer was amorphous because any endothermic melting peak of the copolymers was not observed in the temperature range, so these results confirmed the XRD analysis about amorphous structure of synthesized copolymers.

Thermogravimetric Analysis (TGA)/ Differential Thermogravimetry
The thermal properties of copolymers were evaluated by means of TGA/differential thermal analysis in an air atmosphere. The decomposition behavior of the synthesized copolymers is shown in Figure 7. All of the copolymers showed relatively high temperatures of decomposition and showed different decomposition maxima. TGA indicated that SMA–AP1 decomposed with three steps at 250 (10.90% mass change), 350 (32.55% mass change), and 500 (41.34% mass change), respectively, whereas SMA began to decompose in one step at 287°C. Also, the SMA–AP2 decomposed with three steps at 245 (7.80% mass change), 320 (27% mass change), and 500 (38.20% mass change), respectively. In the SMA–AP1 and SMA–AP2 copolymers, the initial weight loss at a temperature near 250°C was attributed to the formation of acid anhydride from the carboxyl groups with a

loss of water.[37] The two latter weight losses were attributed to decomposition of the modifying, crosslinking agents and, eventually, the aromatic groups.

This significant enhancement of thermal resistance by the presence of AP and amino alkanes was attributed to the formation of a network structure in the crosslinked copolymers.

Swelling Index
The swelling index values of the copolymers are reported in Table VI. The results clearly indicate that the uptake of water decreased with crosslinking resins in comparison with the non-crosslinking form. Also, the samples that were crosslinked with 1,3-diaminopropane demonstrated a higher value of swelling index relative to the crosslinked form with 1,2-diaminoethane. In fact, the crosslinked samples with 1,3-diaminopropane had large holes in the resin network compared to the samples that were crosslinked with 1,2-diaminopropane. In addition, the crosslinked resins could be used in a large range of pH, whereas the noncrosslinked resin (SMA–AP) could not be used at alkaline pH because it was a pH-sensitive resin dissolvable in alkaline pH as a result of deprotonation of its repeated functional groups and an increase in its hydrophilicity. The water uptake values (x's) were calculated with the following equation:

$$x = \frac{\text{Weight of the wet resin} - \text{Weight of the dry resin}}{\text{Weight of the dry resin}} \quad (4)$$

CONCLUSIONS
Chelating resins based on SMA were synthesized by the reaction of AP and 1,2-diaminoethane or 1,3-diaminopropane on the SMA backbone. Among the synthesized resins, SMA–AP1 and SMA–AP2 demonstrated a high affinity for the selected metal ions compared to SMA–AP, and the order of adsorption percentage changed as follows: $Fe^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+}$. The adsorption of all of the metal ions in acidic media was moderate, and it was favored at pH values of 6–9. The FTIR spectra revealed the carboxylate anions and secondary amine in the prepared chelating resin donated electron pairs to the metal ions. The k_d values were calculated for the prepared chelating resins, and the results indicate approximately high values in the case of Fe^{2+}, Cu^{2+}, and Pb^{2+} ions, so the prepared chelating resins are good candidates for the removal of these metal ions from aqueous solutions. The removal of metal ions from wastewater in this study was efficient, and it can be said that nearly complete adsorption was achieved in the case of Cu^{2+}, Fe^{2+}, and Pb^{2+}, and the adsorption of Zn^{2+} was lower than that of the others.

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