

# Synthesis of Glycidyl Methacrylate Containing Diethanol Amine and Its Binary Copolymers with Ethyl Methacrylate and Butyl Methacrylate as Nano-Size Chelating Resins for Removal of Heavy Metal Ions

M. A. Abd El-Ghaffar, N. R. El-Halawany, S. A. Ahmed

*Polymers and Pigments Department, National Research Center, Dokki, Cairo, Egypt*

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**ABSTRACT:** One of the most important applications of chelating and functional polymers is their capability to recover metal ions from their solutions. This study concerns the synthesis of a hydrophilic glycidyl methacrylate (GMA) monomer-bearing diethanol amine (DEA) chelating group from the reaction of GMA and DEA. The formed adduct (A) was characterized via FTIR and mass spectra and subjected to homopolymerization and binary copolymerization with ethyl methacrylate and butyl methacrylate. The copolymerization process was carried out via a semi-batch emulsion polymerization technique by using potassium persulphate/sodium bisulphite as a redox pair initiation system and sodium dodecyl benzene sulphonate as an emulsifier at 65°C. The obtained polymers were characterized via FTIR, thermal gravimetric analysis, and UV-VIS. Volume-average diameters ( $D_v$ ) in

nanoscale range for the prepared polymers were confirmed by transmission electron microscope investigation. It was shown that the obtained nano-size chelating polymers have a powerful adsorption character toward transition metal ions ( $\text{Cu}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Ni}^{+2}$ , and  $\text{Co}^{+2}$ ) and efficient selectivity for  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  ions at normal pH. The effects of pH, time, and different comonomer feed compositions on the uptake of metal ions were studied. The reaction between the obtained chelating resins and different metal ions was confirmed to be a second-order reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3063–3073, 2010

**Key words:** nanosize chelating polymers; semi-batch emulsion polymerization; recovery of heavy metal ions; selectivity

## INTRODUCTION

Heavy metal ions in wastewater represent a real threat to the environment as well as to human beings. Many techniques have been applied to remove the heavy metals or to recover the precious elements from wastewater. Among these methods are neutralization, precipitation, ion exchange, adsorption, and solvent extraction.<sup>1</sup> Nowadays chelating resins have high potential applications for the selective removal of metal ions from industrial wastewater.<sup>1</sup> Many chelating resins with different functionalities have been used to bind various metal ions from wastewater and drinking water. Among these functionalities are those that contain oxygen, nitrogen, and sulfur atoms as active sites such as iminoacetic acid,<sup>2</sup> Schiff bases,<sup>3</sup> hydroxamic acid,<sup>4</sup> amidoxime,<sup>5</sup> thiol,<sup>6</sup> amine,<sup>7</sup> etc. Many studies have been done to show the behavior of those chelating resins toward different metal ions.<sup>8–14</sup>

Glycidyl methacrylate (GMA) is a useful monomer because the epoxy group can undergo ring-opening reaction with various nucleophiles.<sup>15–23</sup> Several types of controlled polymerization, such as group transfer polymerization,<sup>24</sup> nitroxide-mediated polymerization,<sup>25</sup> atomic transfer radical polymerization,<sup>26</sup> and reverse addition-fragmentation chain transfer,<sup>27</sup> have been used in the polymerization of GMA.

Recent studies reported the uptake of some heavy metals or the recovery of some precious elements by using GMA/divinyl benzene and other chelating resins.<sup>28–30</sup>

In the present study, we prepared GMA bearing diethanol amine (DEA) containing chelating function hydroxyl groups and its copolymers as chelating resins for the removal of undesired heavy metal ions from wastewater.

## MATERIALS AND METHODS

### Materials

GMA, ethyl methacrylate (EMA), butyl methacrylate (BMA), and DEA were products of Aldrich Chemical Company (St. Louis, MO). All other chemicals were Prolabo (Prolabo Chemicals, Leicestershire,

Correspondence to: M. A. Abd El-Ghaffar (mghaffar50@yahoo.com).

United Kingdom), products and were used as received.

### Synthesis of adduct (A) (GMA-DEA)

Into a 500-mL three-necked round flask, 0.1 mol GMA and 0.1 mol DEA were added dropwise and stirred continuously at 300 rpm in an ice bath for 3 h. A pale yellowish viscous liquid adduct (A) was obtained and purified by separation in a separating funnel from petroleum ether to remove the unreacted (GMA) monomer.

### Polymerization of adduct (A)

The homopolymerization of adduct monomer (A) was conducted under emulsion conditions. The following ingredients were mixed in a 250-mL three-necked round flask: 87.635 g deionized water (0.27 and 0.416 g) and potassium persulphate/sodium bisulphite (KPS/NaBS), respectively, as a redox pair initiation system, 1 g sodium dodecyl benzene sulphonate (SDBS) as an emulsifier, and finally, 12.365 g (0.05 mol) of monomer (A). The polymerization reaction was done under continuous stirring at 500 rpm at 65°C for 3 h. The obtained cross-linked homopolymer (AH) was purified by Soxhlet extraction from water and hexane and dried in an electric oven at 60°C.

### Semi-batch emulsion copolymerization of adduct (A) with EMA

The following ingredients were mixed: 1 g SDBS, 0.27 g KPS, 0.416 NaBS, 90 mL distilled water, and finally, comonomers of different feed compositions of EMA and monomer adduct (A) were charged into a three-necked flask in a semi-continuous process in two steps starting with EMA and after 30 min the adduct monomer (A) was added dropwise. The reaction was sustained with continuous stirring at 65°C for 4 h. The resulting chelating copolymer was purified by Soxhlet extraction from water and hexane. The product was dried in an electric oven at 65°C.

### Semi-batch emulsion copolymerization of monomer (A) with (BMA)

The copolymerization of adduct (A) and BMA of different feed monomer compositions was done as previously mentioned.

### Instrumental analysis

#### Mass spectra

Mass spectrometry was done by using a Finegan SSQ 7000, National Research Center.

#### FTIR spectra

FTIR analysis was carried out by using a Perkin-Elmer FTIR analyzer (Micro Analytical Unit, Cairo University).

#### Thermal gravimetric analysis

TGA was conducted under a constant rate of nitrogen flow by using a Perkin-Elmer 7 series and Shimadzu-TGA 50 H thermal analysis system. The heating rate was 10°C/min.

#### Transmission electron microscope

The TEM (model EM10; Zeiss, Germany) works at 60 kV, magnification ranges between 2500 and  $5 \times 10^5$ , and resolution to 0.5 nm.

#### Morphometry study

The morphometric study of the TEM photographs was performed by using a Leica QWin 500 image analyzer in Image Analysis Unit (Pathology Dept., NRC).

#### UV-VIS spectra

UV-VIS absorption spectra were performed by using a UV-2401 PC UV-VIS recording spectrophotometer (Shimadzu).

#### Atomic absorption spectra

The atomic absorption spectra for the different metal ions in their blend solutions were conducted by using a Perkin-Elmer model Z5100 atomic absorption spectrometer.

### Uptake measurements

#### Preparation of solutions

Stock solution (1%) of metal ion under investigation was prepared in distilled water. Buffer solutions of pH 5, 9, and 7 were used for the experiments and carried out at controlled acidic, basic, and neutral conditions, respectively.

#### Metal ion uptake experiments

Dry resin (0.1 g) was added to a test tube containing 10 mL of different transition metal ion solutions of known concentration for a definite time. The residual concentrations of different metal ions under investigation were determined via UV-VIS spectrophotometer by using different standard curves for the metal ions under study.

### Effect of pH on the uptake of metal ion

Uptake experiments under controlled pH were carried out following the above procedure for uptake experiments. The pH was adjusted by using the suitable buffer.

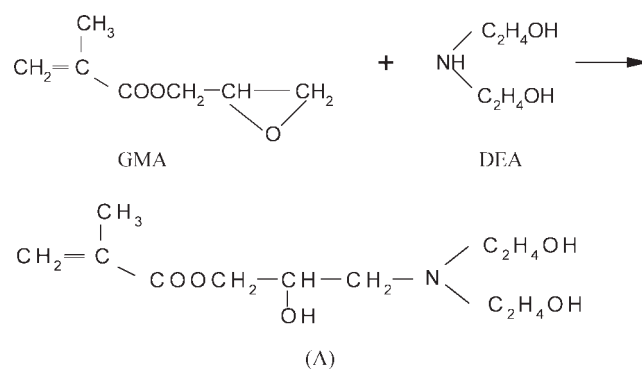
### Regeneration of the resin

Regeneration of the resin was performed by introducing 0.1 g of the resin in a column. Then 50 mL of  $\text{Cu}^{+2}$  ion solution (0.1M) was added to the tested resin. After reaching the maximum uptake, the resin was washed with deionized water several times. The resin then was subjected to elution by using different molar concentrations of HCl. The concentration of the released  $\text{Cu}^{+2}$  ions was detected via UV-VIS spectrophotometer.

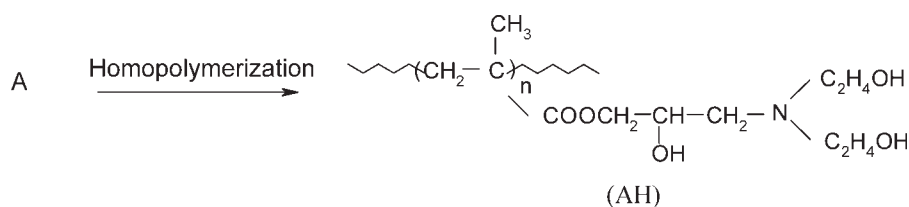
## RESULTS AND DISCUSSION

GMA-based cross-linked polymers have advantages over other polymer supports due to ease functionalization through the epoxide groups involved. Also,

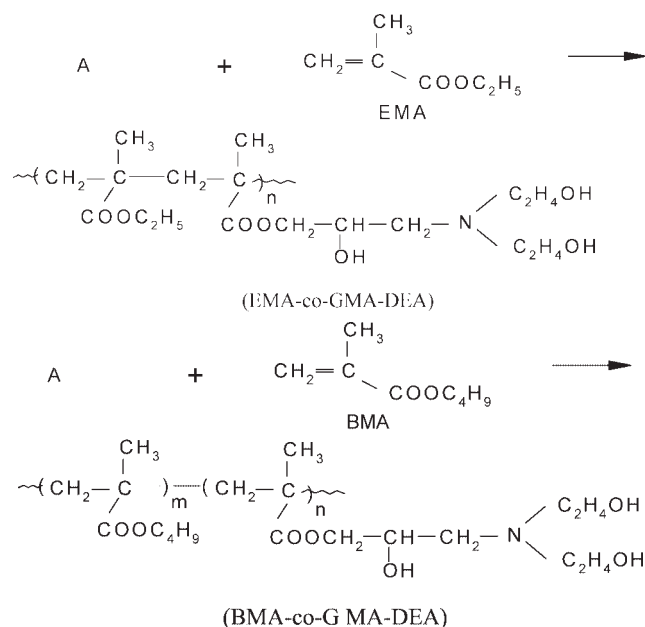
remarkable resistance of its ester linkage to acid and base hydrolysis is an additional advantage to using a ligand-carrying polymer.<sup>31</sup> In the present study, GMA monomer bearing DEA chelating function was prepared according to the following scheme:



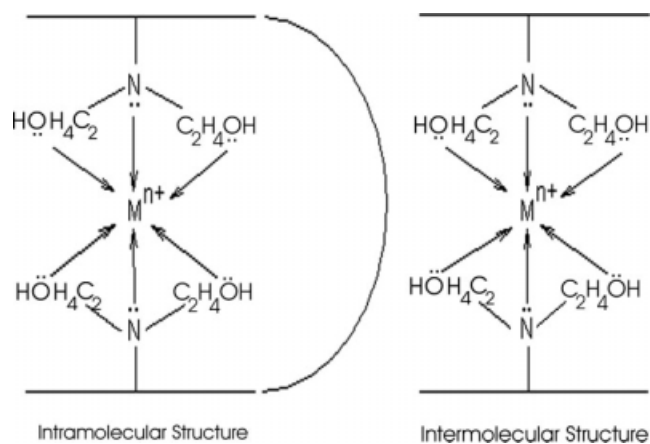
The adduct monomer (A) was then homopolymerized via emulsion pathway at 65°C using a redox pair initiation system to give the homopolymer (AH).



The adduct (A) with different feed compositions was also binary copolymerized with EMA and BMA by semi-batch emulsion copolymerization technique according to the following schemes:



The prepared chelating resins can form a complex with different metal ions according to the following schemes:



where M may be  $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Fe}^{+3}$ , and  $\text{Cr}^{+3}$ .

### Characterization of adduct (A)

#### FTIR spectra

Analysis of IR spectra of adduct (A) is shown in Figure 1. The characteristic band at  $1298 \text{ cm}^{-1}$  is

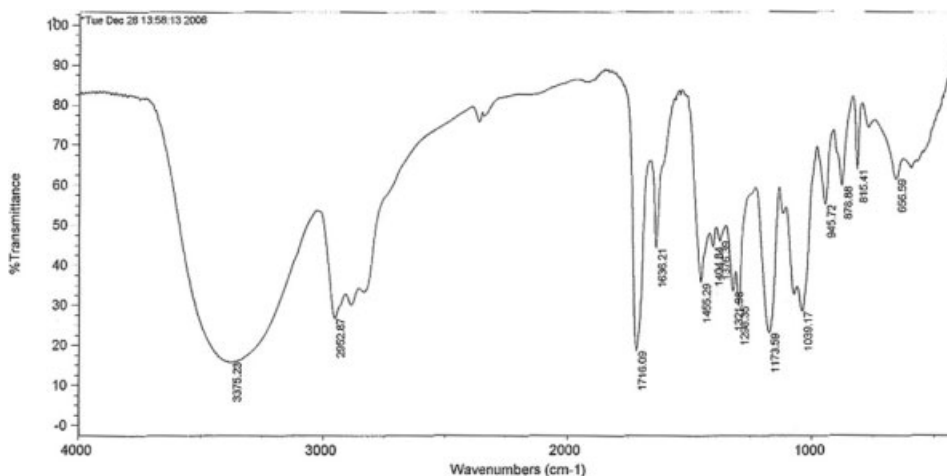


Figure 1 FTIR spectra of GMA-DEA (A).

attributed to the presence of a tertiary amine group (i.e., confirm the addition of the amino group of DEA to the oxarane ring of GMA monomer, which results in the formation of tertiary amine). Also, the disappearance of a symmetrical stretching band at  $1260\text{ cm}^{-1}$  of epoxy ring of GMA monomer indicates that the DEA was connected to GMA monomer. Other characteristic bands correspond to  $\text{C}=\text{O}$  at  $1715\text{ cm}^{-1}$  and  $\text{CH}_2$ ,  $\text{CH}_3$  at  $2962\text{ cm}^{-1}$  were also seen.

#### Mass spectra

Mass spectrum gives information about the structure of the GMA-DEA adduct. Figure 2 shows that the maximum molecular weight is 248, which corresponds to the molecular weight of the formed adduct ( $M_w = 247$ ). The excess in the molecular weight may be attributed to hydrogen abstraction.

Therefore, the adduct (A) was successfully prepared according to the above result. The spectra confirm the formation of GMA-DEA adduct.

#### Characterization of polymers

##### FTIR spectra

FTIR spectra of the prepared chelating polymers are shown in Figure 3(a–c). The figures show bands in the  $1450$  to  $1470\text{ cm}^{-1}$  region arising from  $\text{CH}_2$ ,  $\text{CH}_3$  groups too close together to enable the two groupings to be readily differentiated, especially in view of the small shifts that may be induced by changes of state. However, the overall intensity in the  $1450\text{ cm}^{-1}$  region is directly proportional to the number of such groupings present, as reported by Francis.<sup>32</sup> It was reported also by Thompson and Torkington<sup>33</sup> that the absorption bands at  $1450$  to  $1470\text{ cm}^{-1}$  give rise to  $\text{CH}_2$  and  $\text{CH}_3$  groupings due to hydrogen

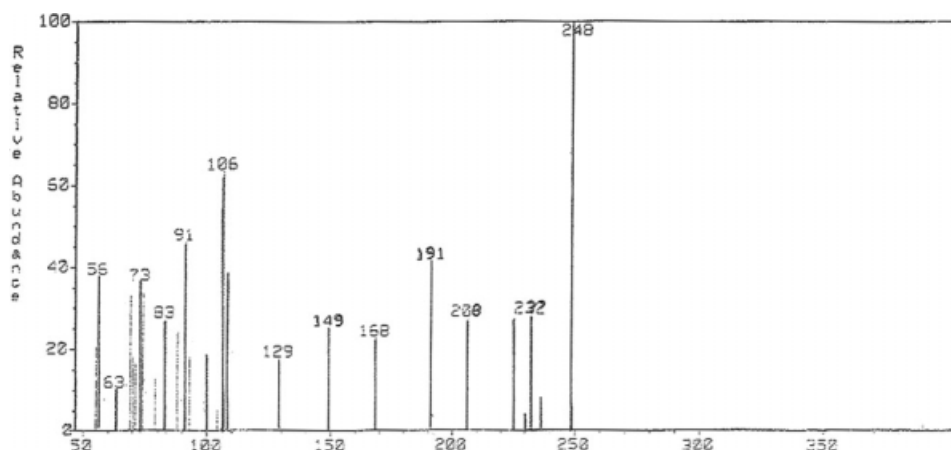
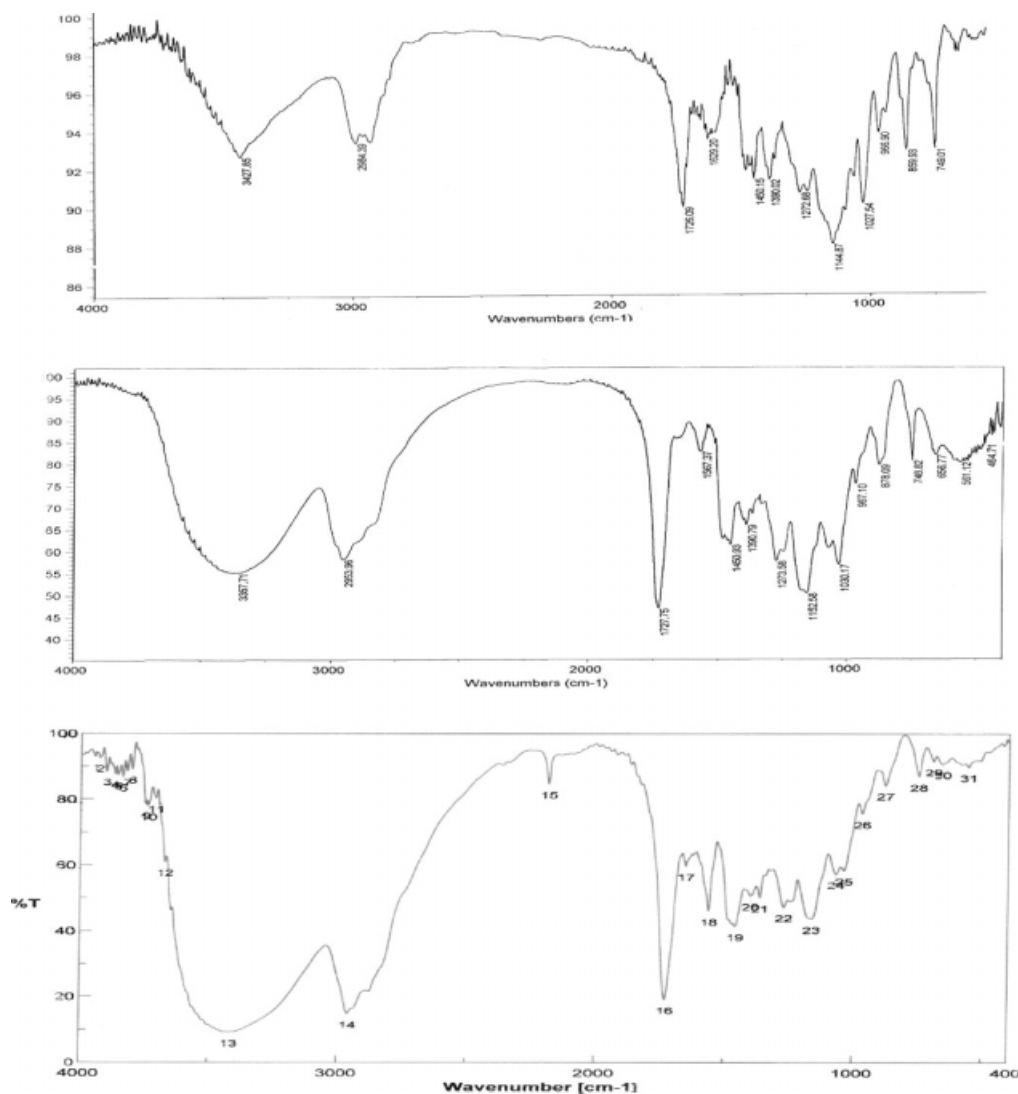


Figure 2 Mass spectra of GMA-DEA (A).



**Figure 3** FTIR spectra of (a) EMA homopolymer, (b) A-co-EMA, and (c) A-co-BMA.

bonding vibrations as reported by Francis. It is now accepted that  $\text{CH}_2$  deformation gives rise to absorption very close to  $1465\text{ cm}^{-1}$  and asymmetrical  $\text{CH}_3$  deformation to absorption at  $1450\text{ cm}^{-1}$ . Absorption bands at  $2983\text{--}2984\text{ cm}^{-1}$  correspond to CH stretching of  $\text{CH}_3$  and  $\text{CH}_2$  groups for the EMA homopolymer and shift to  $2953\text{ cm}^{-1}$  in Figure 1(b) for EMA-co-A and to  $2963\text{ cm}^{-1}$  in Figure 1(c) for BMA-co-A. The characteristic band at  $1726\text{ cm}^{-1}$  corresponds to the carbonyl stretching vibration. Other broad bands at  $3000\text{--}3600\text{ cm}^{-1}$  for copolymers b and c are characteristic for the OH groups.

#### TGA of the prepared polymers

Figure 4(a–c) shows the TG curves for EMA homopolymer (a), adduct homopolymer (b), and copolymer of adduct and EMA (c). It is clearly seen from the mentioned figures that EMA homopolymer retains its initial mass up to  $180^\circ\text{C}$  and, at  $250^\circ\text{C}$ , it

retains about 91% of its initial mass; after that, a quick decomposition occurred. A great loss in the mass, about 35% at  $300^\circ\text{C}$ , and a complete decomposition took place for this EMA homopolymer at  $350^\circ\text{C}$ . On the other hand, the adduct homopolymer AH [Fig. 4(b)] and the copolymer EMA-co-A [Fig. 4(c)] showed slight polymer degradation from room temperature to about  $200^\circ\text{C}$ , equaling 5–6% for both, due to dehydration or loss of bonded water. After that, partial decomposition took place, ranging from 40 to 42% weight loss at  $330\text{--}350^\circ\text{C}$  for both polymers. At  $500^\circ\text{C}$  the adduct homopolymer AH and EMA-co-A copolymer retained 10 and 8% of their initial masses, respectively.

#### Transmission electron microscope

TEM was used to measure the average particle diameter ( $D_i$ ) and number of particles for different polymers as reported in previous publication.<sup>34</sup>

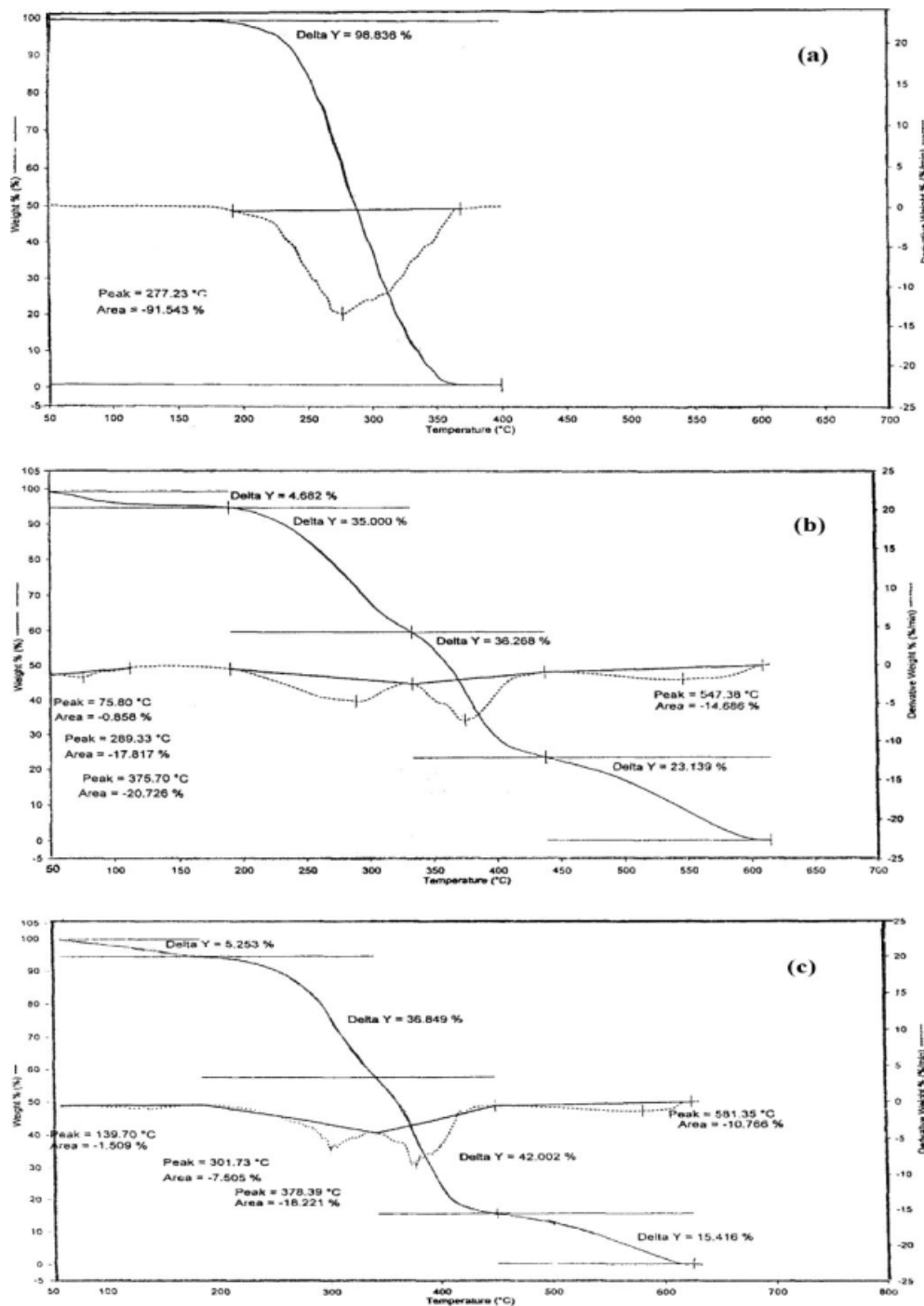


Figure 4 TGA diagrams of (a) EMA homopolymer, (b) AH, and (c) EMA-co-A.

The various average particle diameters and the number of particles were determined with a computer program by using the following relationships:

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \quad (1)$$

where  $D_n$  is the number-average particle diameter,  $D_i$  is the actual particle size, and  $N_i$  is the number of particles of size,  $D_i$ , which can be obtained from the photographic pictures, and

$$D_w = \left( \frac{\sum N_i D_i^6}{\sum N_i D_i^3} \right)^{1/3} \quad (2)$$

where  $D_w$  is the weight-average particle diameter

$$D_v = \left( \frac{\sum N_i D_i^3}{\sum N_i} \right)^{1/3} \quad (3)$$

where  $D_v$  is the volume-average particle diameter

**TABLE I**  
Data of the Morphology Characteristics for EMA Homopolymer and Its Copolymer with Adduct (A)

Polymer	$D_v$ (nm)	$D_n$ (nm)	$D_w$ (nm)	$D_w/D_n$
EMA	7.2015	6.7315	9.0244	1.34
A-co-EMA	8.3317	7.321	11.644	1.59

$$PDI = D_w/D_n$$

where PDI is the polydispersity index.

The particle size distributions of copolymer lattices of EMA homopolymer and EMA/A copolymers prepared at fixed initiator and emulsifier concentrations and performed at fixed temperature (65°C) were determined by using TEM. The micrographs (1<sub>a</sub> and 1<sub>b</sub>) and the data given in Table I illustrate that these copolymeric systems have produced spherical lattice particles in the range of nanosize scale. It is clear from the data of PDI shown in Table I that these polymers showed polydispersity.

### Metal ion uptake

Heavy metals are toxic pollutants that should be removed from wastewater due to their undesired effects on human physiology and also from an ecological point of view.<sup>35</sup>

### Effect of comonomer composition

The uptake of Cu<sup>+2</sup> ions by EMA-co-A and BMA-co-A copolymers as a function of different comonomer feed compositions at 27°C and normal pH is shown in Tables II and III and Figures 5 and 6. It is clear from the figures and the data listed in the tables that the metal ion uptake increases as the concentration of adduct (A) monomer increases. This behavior can be reasonably attributed to the increase in the number of functional hydroxyl and nitrogen groups of

**TABLE II**  
Uptake of Cu<sup>+2</sup> Ions by (EMA-co-A) of Different Comonomer Feed Compositions at 27°C After 24 h at Normal pH and Initial Metal Concentration of 1% (0.05865 mol)

Resins	Mol % (EMA-co-A)	Uptake (mmol/g)
A <sub>1</sub>	(30 : 70)	0.7890
A <sub>2</sub>	(35 : 65)	0.4673
A <sub>3</sub>	(40 : 60)	0.1455
A <sub>4</sub>	(45 : 55)	0.1425
A <sub>5</sub>	(50 : 50)	0.1395
A <sub>6</sub>	(55 : 45)	0.1308
A <sub>7</sub>	(60 : 40)	0.1220

**TABLE III**  
Uptake of Cu<sup>+2</sup> Ions by (BMA-co-A) of Different Comonomer Feed Compositions at 27°C After 24 h at Normal pH and Initial Metal Concentration of 0.05% (0.0293 mol)

Resins	Mol % (EMA-co-A)	Uptake (mmol/g)
A <sub>8</sub>	(60 : 40)	0.1067
A <sub>9</sub>	(55 : 45)	0.1149
A <sub>10</sub>	(50 : 50)	0.196
A <sub>11</sub>	(45 : 55)	0.2939
A <sub>12</sub>	(40 : 60)	0.3521
A <sub>13</sub>	(35 : 65)	0.4201
A <sub>14</sub>	(30 : 70)	0.4667

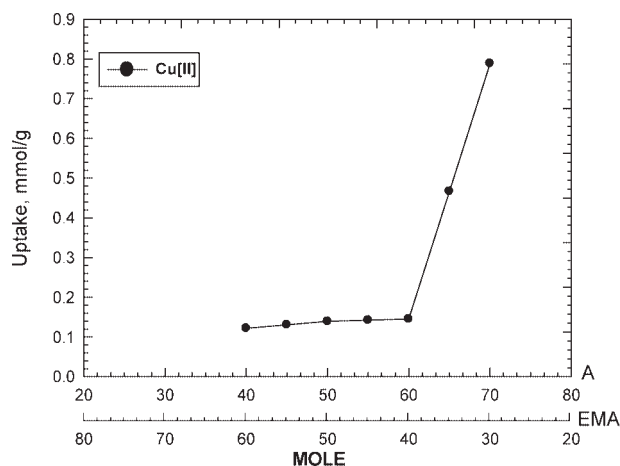
the formed adduct (A), which are responsible for the chelation with Cu<sup>+2</sup> ions.

### Effect of time

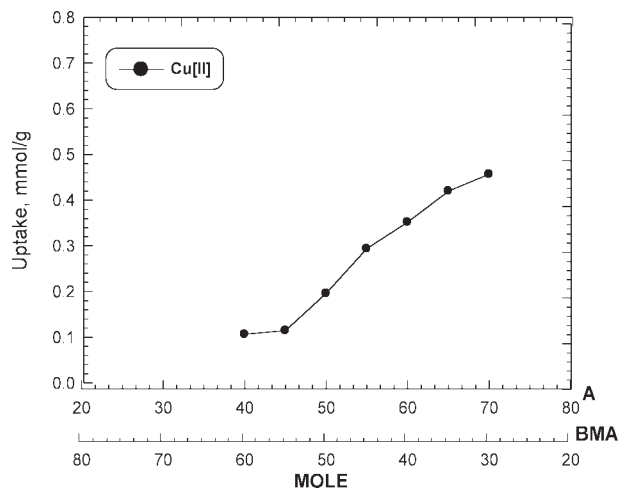
Figure 7 as well as Table IV show the change in the uptake of Co<sup>+2</sup> ions from its aqueous solution at natural pH as a function of time by resins AH, A<sub>1</sub>, and A<sub>11</sub>. It is seen from the data given that the Co<sup>+2</sup> ion uptake increases with increasing time, whereas complete uptake equilibrium was achieved within 24 h for AH homopolymer and resins A<sub>14</sub> and A<sub>1</sub>, respectively.

### Pseudo second-order kinetics

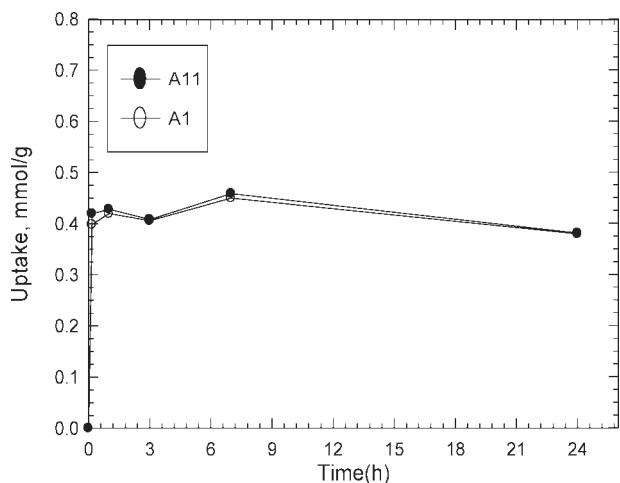
Figure 8 and Table V show that the adsorption of Co<sup>+2</sup> ions on resin A<sub>1</sub> is a second-order reaction (i.e., it depends on both concentrations of the tested resin and the concentration of the metal ion under investigation).



**Figure 5** Effect of comonomer concentrations of (EMA-co-A) on the uptake of copper ions (Cu<sup>2+</sup>) at 27°C and normal pH.



**Figure 6** Effect of comonomer concentrations of (BMA-co-A) on the uptake of copper ions ( $\text{Cu}^{2+}$ ) at  $27^\circ\text{C}$  and normal pH.



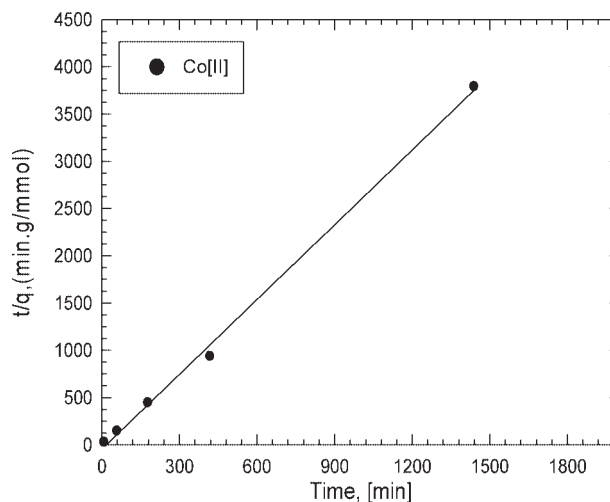
**Figure 7** Effect of time on the uptake of  $\text{Co}^{2+}$  ions at  $27^\circ\text{C}$  and normal pH.

**Effect of pH**

The adsorption of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cr}^{3+}$  ions by adduct homopolymer (AH), resin  $\text{A}_1$ , and resin  $\text{A}_{14}$  at different pH values are shown in Figure 9(a-

**TABLE IV**  
Uptake of  $\text{Co}^{2+}$  Ions by the Resins  $\text{A}_{14}$ ,  $\text{A}_1$ , and AH as a Function of Time at  $27^\circ\text{C}$  and Normal Ph

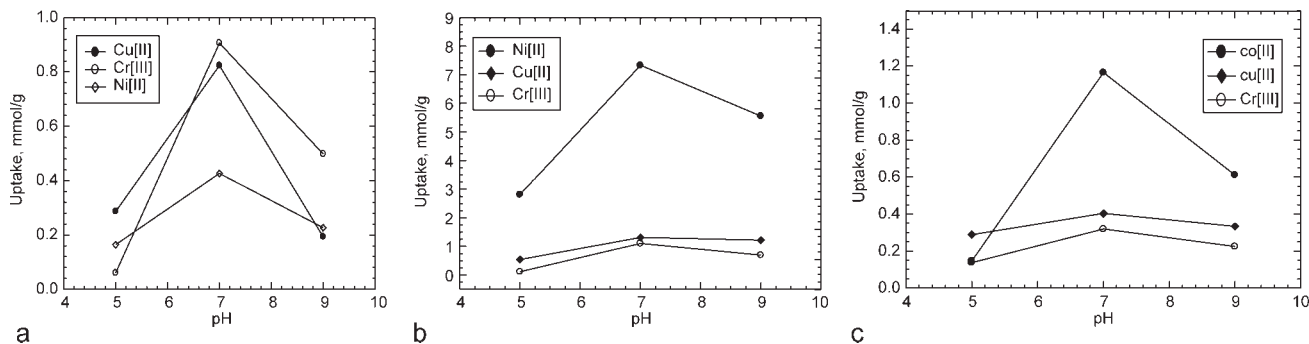
Time (min)	Uptake (mmol/g)		
	AH	$\text{A}_{11}$	$\text{A}_1$
0	0	0	0
15	1.266	0.4196	0.3982
60	1.311	0.4282	0.4196
180	1.3482	0.4082	0.4058
420	1.4283	0.4589	0.4498
1440	1.4691	0.3819	0.3801



**Figure 8** Pseudo second-order kinetics for the uptake of  $\text{Co}^{2+}$  by resin  $\text{A}_1$  at  $27^\circ\text{C}$ .

**TABLE V**  
Parameters of the Pseudo Second Order for the Adsorption of  $\text{Co}^{2+}$  Ions on the Studied Resin  $\text{A}_1$

Metal ion	Pseudo second order		
	$K_2$ (g/(mmol min))	$q_e$ (mmol $\text{g}^{-1}$ )	$R^2$
$\text{Co}^{2+}$	0.1467	0.3787	0.9979



**Figure 9** Effect of pH on uptake of different metal ions by resin: (a) AH, (b)  $\text{A}_1$ , and (c)  $\text{A}_{14}$  at  $27^\circ\text{C}$ .

c) and illustrated in Table VI. It is clearly seen from the data that the adsorption of the selected metal ions is very limited at lower pH (pH 5) and the



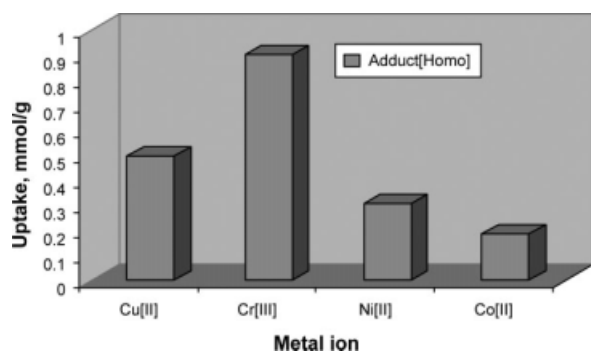
**TABLE VI**  
Uptake of Different Metal Ions by Resins AH, A<sub>1</sub>, and A<sub>14</sub> as a Function of pH at 27°C

Resin	pH	Uptake (mmol/g)		
		Ni <sup>+2</sup>	Cu <sup>+2</sup>	Cr <sup>+3</sup>
AH	5	0.1644	0.0607	0.2866
	7	0.4262	0.9067	0.8234
	9	0.2271	0.4981	0.1938
A <sub>1</sub>	5	2.8130	0.5431	0.1136
	7	7.3291	1.3157	1.1009
	9	5.5590	1.2173	0.6953
A <sub>14</sub>	5	0.14709	0.289	0.1375
	7	1.16494	0.4033	0.3192
	9	0.61108	0.333	0.2246

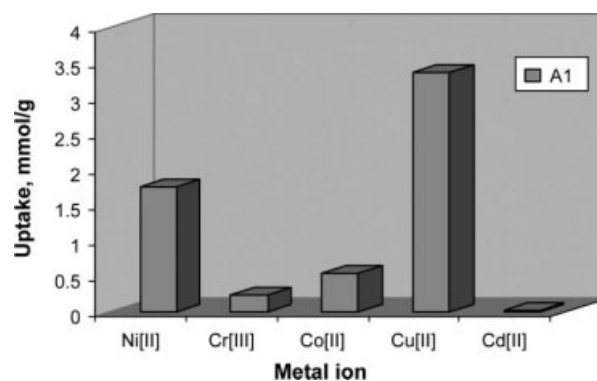
adsorption capacity reached maximum values at pH 7 and showed observed lowering in the adsorption capacity at pH 9. The decrease of uptake in acidic media may be attributed to the protonation of the lone pair of electrons on nitrogen and/or the lower dissociation extent of the hydroxyl groups, which hinder the interaction of metal ion. This assumption is in accordance with the data reported by Luo and Huang.<sup>35</sup> The maximum uptake at pH 7 is doubtful to be attributed only to the interaction of the free metal ions with active sites on the chelating resin. At pH 9, the observed lower uptake of metal ions may be attributed to the partial desorption of metal ions from the chelating resins in the form of soluble M-amine complex, which agrees well with the results reported by Atia et al.<sup>36</sup>

### Maximum metal ion uptake

Maximum ion uptake of different metal ions after 24 h at normal pH by resins AH and A<sub>1</sub> are shown



**Figure 10** Maximum ion uptake of different metal ions by adduct homopolymer AH after 24 h at 27°C and normal pH.



**Figure 11** Maximum ion uptake of different metal ions by resin A<sub>1</sub> after 24 h at 27°C and normal pH.

in Figures 10 and 11. The figures show maximum adsorption capacity for Cr<sup>+3</sup> and Cu<sup>+2</sup> ions by AH and maximum uptake for Cu<sup>+2</sup> and Ni<sup>+2</sup> ions by resin A<sub>1</sub>.

### Metal ion selectivity

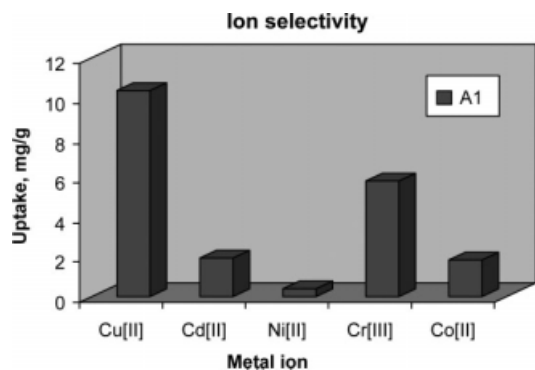
To evaluate the selectivity of the best chosen resin A<sub>1</sub> toward different metal ions, the capacity of the resin was determined by using a number of single metal ion solutions, which are common contaminants in ground, river, and wastewater, such as Ni<sup>+2</sup>, Co<sup>+2</sup>, Cu<sup>+2</sup>, and Cd<sup>+2</sup> at normal pH and initial concentration of 0.5%. The results are given in Table VII and illustrated in Figure 12. It is clearly seen from the data that resin A<sub>1</sub> showed much higher affinity toward Cu<sup>+2</sup> and Ni<sup>+2</sup> ions but much less affinity toward Cr<sup>+3</sup> and Co<sup>+2</sup> ions, where no adsorption for Cd<sup>+2</sup> ions was observed.

### Elution experiments

The elution of the studied metal ion (Cu<sup>+2</sup>) from the tested resin A<sub>1</sub> was examined by using different molar concentrations of HCl (0.3, 0.2, and 0.1M) as shown from the data given in Table VIII. Elution experiments were performed by using 0.1 g of the resin in the column and then loading with the metal ion under investigation (0.1M). After reaching the maximum uptake, the resin was washed carefully by flowing distilled water through the column. The

**TABLE VII**  
Ion Selectivity of Resin A<sub>1</sub> Toward Blend of Different Metal Ions at 27°C and Normal Ph

Metal	Uptake (mg/g)
Ni <sup>+2</sup>	7.230
Cr <sup>+3</sup>	1.860
Co <sup>+2</sup>	5.760
Cu <sup>+2</sup>	10.748
Cd <sup>+2</sup>	1.960



**Figure 12** Ion selectivity of resin A<sub>1</sub> toward blend of different metal ions at 27°C and normal pH.

resin loaded by the metal was then subjected for elution by using different acid concentrations. The concentration of the released metal ion was determined via UV-VIS spectra. The elution efficiency was calculated from the amount of metal ion sorbed on the resin and the desorbed amount in the elution medium according to the following equation:

Elution efficiency

$$= \frac{\text{Amount of metal ion desorbed to the elution medium}}{\text{Amount of metal ion sorbed on resin}} \times 100$$

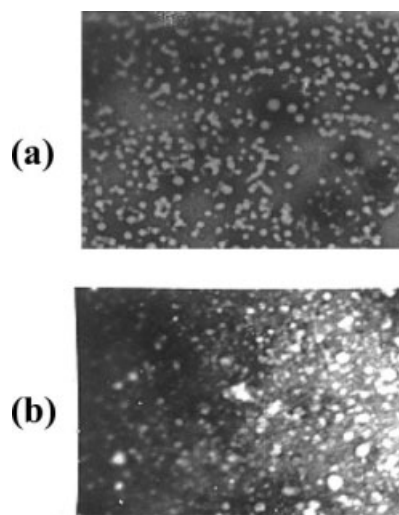
## CONCLUSIONS

Binary chelating copolymers of GMA bearing diethanol amine with EMA and BMA were synthesized via emulsion polymerization process for removal of heavy metal ions from wastewater. The prepared resins showed high performance and maximum uptake toward Cu<sup>+2</sup>, Ni<sup>+2</sup>, and Co<sup>+2</sup> ions. Volume-average diameter ( $D_v$ ) of the prepared polymer particles was confirmed to be in the nanoscale range. Parameters affecting metal ion uptake (e.g., effect of time, comonomer feed composition, and pH) were studied.

**TABLE VIII**  
Effect of Eluent Concentrations on the Elution Efficiency of the Tested Resin (A<sub>1</sub>)

Eluent Concentration	Adsorbed Uptake (mmol/g)	Desorbed Uptake (mmol/g)
(0.3M HCl)	0.1995	0.1855
(0.2M HCl)	0.18847	0.175
(0.1M HCl)	0.1684	0.158

The elution efficiency ranges from 90 to 93% for all concentrations.



**Graph 1** Morphology of (a) EMA homopolymer and (b) A-co-EMA at fixed initiator, emulsifier concentration, and temperature.

The following results can be demonstrated:

1. The metal ion uptake increases with increasing the time and also the monomer adduct content in the feed.
2. The adsorption capacity of the selected metal ions is very limited at lower pH values [e.g., (pH 5)] and reached maximum value at pH 7; on the other hand, the sorption capacity value at pH 9 was reduced due to partial desorption of metal ions from the chelating resins in the form of soluble M-amine complex.
3. The prepared chelating resins showed higher ion selectivity for Cu<sup>+2</sup> and Ni<sup>+2</sup> ions; the sorption capacities were 10.7 and 7.2 mg/g, respectively.
4. HCl with different molar concentrations was found to be effective eluting agents because it gave elution efficiency of about 93% and the regenerated resin may be used repeatedly for recovery of metal ions without significant activity loss.

## References

1. Watera, L. G. A.; Driessena, W. L.; Glenyby, M. W.; Reedijka, J.; Schroaderb, M. *React Funct Polym* 2002, 51, 33.
2. Yuchi, A.; Mukaie, K.; Sotomura, Y.; Yamada, H.; Wada, H. *Anal Sci* 2002, 18, 575.
3. Samala, S.; Acharyaa, S.; Dey, R. K.; Rayb, A. R. *Talanta* 2002, 57, 1075.
4. Taek-Seung, L.; Dong-Won, J.; Jai-Kyeong, K.; Sung, H. *Fiber Polym* 2001, 2, 13.
5. Egawa, H.; Nonaka, T.; Nakayama, M. *J Makromol Sci Chem* 1988, 11, 1407.
6. Massahiko, C.; Morio, N.; Tomoo, T.; Hisashi, T. *Talanta* 1979, 26, 911.

7. Mukherjee, A.; Biswas, M. *Appl Polym Sci* 1993, 50, 1485.
8. Nakayama, M.; Chikuma, M.; Tanaka, H.; Tanaka, T. *Talanta* 1982, 29, 503.
9. Egawa, H.; Nonaka, T.; Maeda, H. *Sep Sci Technol* 1985, 20, 653.
10. Trochimczuk, A. W.; Kol, B. N.; Barthowiak, D. J. *Eur Polym J* 2001, 37, 559.
11. Polakovi, J.; Kubov, J. *Anal Chim Acta* 2003, 488, 123.
12. Fortes, M. C. B.; Martins, A. H.; Benedetto, J. S. *Miner Eng* 2003, 16, 659.
13. Prabhakar, L. D.; Maryasaral, A. *Polym Int* 1997, 42, 149.
14. Haron, M. J.; Wan Yunus, W. M. Z.; Yong, N. L. *Chemosphere* 1999, 39, 2459.
15. Someya, Y.; Shibata, M. *Polymer* 2005, 46, 4891.
16. Loyens, W.; Groeninckx, G. *Polymer* 2005, 43, 5679.
17. Wang, W. X.; Griffiths, R. M. T.; Naylor, A.; Giles, M. R.; Irvine, D. J.; Howdle, S. M. *Polymer* 2002, 43, 6653.
18. Brar, A. S.; Dutta, K. *Macromolecules* 1998, 31, 4695.
19. Paul, S.; Ranby, B. *Macromolecules* 1976, 9, 337.
20. Shiho, H.; DeSimone, J. M. *Macromolecules* 2003, 34, 1198.
21. Zhang, M. C.; Kang, E. T. *Langmuir* 2000, 16, 9666.
22. Shanthi, C.; Rao, K. P. *Carbohydr Polym* 2001, 44, 123.
23. Ismet, K.; Ilter, Z.; Senol, D. *Polymer* 2002, 43, 6455.
24. Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J Am Chem Soc* 1983, 105, 5706.
25. Grubbs, R. B.; Dean, J. M.; Broz, M. E.; Bates, F. S. *Macromolecules* 2000, 33, 9522.
26. Krishnan, R.; Srinivasan, K. S. V. *Macromolecules* 2003, 36, 1769.
27. Zhou, J.; Zhou, D.; Zhu, X. L.; Chen, G. J. *J Polym Sci Part A: Polym Chem* 2004, 42, 2558.
28. Atia, A. A.; Donia, A. M.; Yousif, A. M. *J Appl Polym Sci* 2005, 97, 806.
29. Atia, A. A.; Donia, A. M.; Abou El-Enein, S. A.; Yousif, A. M. *J Sep Purif Technol* 2003, 33, 295.
30. Abd El-Ghaffar, M. A.; Abd El-Wahab, Z. H.; El-Wakeel, K. Z. *Hydrometallurgy*, 2009, 96, 27.
31. Bahire, F. S.; Niyazi, B. *React Funct Polym* 2001, 49, 151.
32. Francis, S. A. *J Chem Phys* 1950, 18, 861.
33. Thompson, H. W.; Torkington, P. *Trans Faraday Soc* 1945, 41, 246.
34. Badran, A. S.; Ayoub, M. M. H.; Abd El-Ghaffar, M. A.; Nasr, H. E.; Abd El-Hakim, A. A. *Eur Polym J* 1997, 33, 537.
35. Luo, C. S.; Huang, S. *Sep Sci Technol* 1993, 28, 1253.
36. Atia, A.; Donia, A. M.; El-Boraey, H. A.; Mabrouk, D. H. *J Sep Purif Technol* 2006, 48, 281.