

Copolymer Resin. VII. 8-Hydroxyquinoline-5-sulfonic Acid–Thiourea–Formaldehyde Copolymer Resins and Their Ion-Exchange Properties

V. D. Mane, N. J. Wahane, W. B. Gurnule

Department of Chemistry, Kamla Nehru College, Sakardara, Nagpur 440009, India

Received 5 April 2008; accepted 5 July 2008

DOI 10.1002/app.29369

Published online 11 November 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 8-Hydroxyquinoline-5-sulfonic acid–thiourea–formaldehyde copolymer resins were synthesized through the condensation of 8-hydroxyquinoline-5-sulfonic acid and thiourea with formaldehyde in the presence of hydrochloric acid as a catalyst and with various molar ratios of the reacting monomers. The resulting copolymers were characterized with UV-visible, IR and ¹H-NMR spectral data, employed to determine the reactivity of monomers. The average molecular weights of these resins were determined with vapor pressure osmometry and conductometric titration in a nonaqueous medium. The chelation ion-exchange properties were also

studied with the batch equilibrium method. The resins were proved to be selective chelating ion-exchange copolymers for certain metals. The chelation ion-exchange properties of these copolymers were studied for Cu²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Fe³⁺ ions. The study was carried out over a wide pH range and in media of various ionic strengths. The copolymers showed a higher selectivity for Fe³⁺ ions than for Cu²⁺, Ni²⁺, Co²⁺, and Pb²⁺ ions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3039–3049, 2009

Key words: ion exchangers; polycondensation; resins; synthesis

INTRODUCTION

In recent years, there has been growing interest in the design and synthesis of copolymer resins because of their special properties and potential applications in ion exchange, wastewater treatment, organic synthesis, hydrometallurgy, catalysis, and separation of trace elements.^{1–3} 8-Hydroxyquinoline (oxine) is a monomer whose reactivity toward metal ions is well known from the literature,^{4,5} and it is widely used as a complexing agent.

Rivas and Villegas⁶ created crosslinked poly[3-(methacryloylamino)-propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide-*co*-2-acrylamidoglycolic acid by free-radical polymerization and tested the synthesized polymer as an absorbent under competitive and noncompetitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) by batch and column equilibrium procedures. They reported that resin metal-ion equilibrium was achieved before 1 h. The resin showed a maximum retention capacity value of 1.084 mequiv/g for Hg(II) at pH 2. The recovery of the resin was investigated at 20°C with different concentrations of HNO₃ and HClO₄.

Hegazy El-Sayed et al.⁷ prepared two hydrogels from *N*-vinyl-2-pyrrolidone/acrylic acid (NVP/AAC) and *N*-vinyl-2-pyrrolidone/acrylamide (NVP/AAM) for the separation of some heavy metal ions from wastewater. They studied the characterization, some selected properties, and the possibility of their practical use in wastewater treatment for heavy metals such as Cu, Ni, Co, and Cr. They reported that the maximum uptake for a given metal was higher for a treated NVP/AAC hydrogel than for an untreated NVP/AAC hydrogel and was higher for an untreated NVP/AAC hydrogel than for an NVP/AAM hydrogel.

Gurnule et al.⁸ synthesized a terpolymer resin through the condensation of salicylic acid and melamine with formaldehyde in the presence of an acid catalyst. They studied chelation ion-exchange properties of this polymer for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Fe³⁺, Cd²⁺, and Pb²⁺ ions. A batch equilibrium method was employed in the study of the selectivity of metal-ion uptake, involving the measurements of the distribution of a given metal ion between the polymer sample and a solution containing metal ions. The study was carried out over a pH range and in media of various ionic strengths. They reported that the polymer showed a higher selectivity for Fe³⁺, Cu²⁺, and Ni²⁺ ions than for Co²⁺, Zn²⁺, Cd²⁺, and Pb²⁺.

Correspondence to: W. B. Gurnule (wbgurnule@yahoo.co.in).

Erol and a coworker^{9,10} prepared new methacrylate monomers and their derivatives and copolymerized these monomers with various vinyl monomers. Reactivity ratios were calculated by the application of the conventional Fineman–Ross and Kelen–Tudos linearization methods. Vijayanand et al.¹¹ prepared copolymers with various contents of 4-nitro-3-methyl phenyl methacrylate and glycidyl methyl acrylate in the solvent methyl ethyl ketone with benzoyl peroxide as a free-radical initiator at 70°C. The characterization of the resulting polymers was performed with FTIR, ¹H-NMR, and ¹³C-NMR spectroscopy techniques.

This article describes the synthesis, characterization, and ion-exchange properties of copolymer resins derived from 8-hydroxyquinoline-5-sulfonic acid, thiourea, and formaldehyde.

EXPERIMENTAL

Materials

All chemicals were analytically pure or chemically pure; 8-hydroxyquinoline-5-sulfonic acid (Merck, India), thiourea (S.D. Fine Chemicals, Mumbai, India), and formaldehyde (S.D. Fine Chemicals) were used as received. Solvents purified by fractional distillation were used in the reaction.

Synthesis of the copolymer resin

Condensation of 8-hydroxyquinoline-5-sulfonic acid and thiourea with formaldehyde

A mixture of 8-hydroxyquinoline-5-sulfonic acid (2.436 g, 0.1 mol), thiourea (0.76 g, 0.1 mol), and formaldehyde (7 mL, 0.2 mol) in the presence of 200 mL of 2M hydrochloric acid as a catalyst was heated in an oil bath at 126°C for 5 h with occasional shaking.^{12,13}

The separated greenish resinous product was washed with hot water and methanol to remove unreacted monomer. The resinous product so obtained was washed with cold water, dried in air, and powdered. The powdered resins were washed with hot water and dried. Dried resins were then extracted with diethyl ether followed by petroleum ether for the removal of the 8-hydroxyquinoline-5-sulfonic acid–formaldehyde copolymer that might be present along with the copolymer. The resin was purified by dissolution in 8% NaOH and by reprecipitation through the dropwise addition of 1 : 1 HCl with constant and rapid stirring to avoid the formation of lumps. The process of reprecipitation was repeated twice. The copolymer resin so obtained was filtered, washed with hot water, dried in air, powdered, and stored *in vacuo* over anhydrous CaCl₂.^{12,13} The reaction is shown in Figure 1.

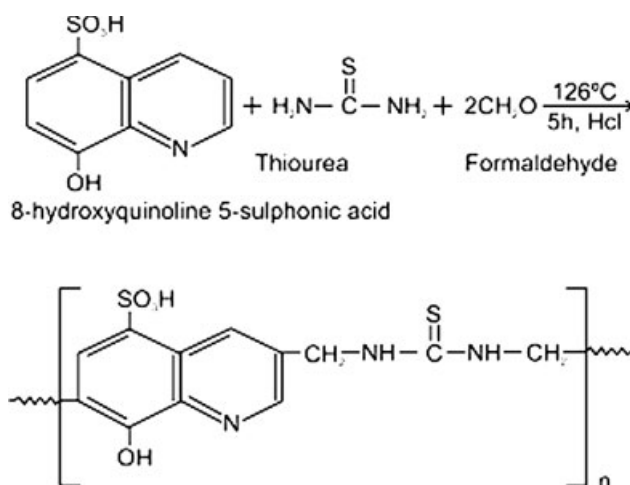


Figure 1 Preparation of the 8-HQ5-SATUF-I copolymer resin.

Different resin samples of 8-hydroxyquinoline 5-sulfonic acid, thiourea, and formaldehyde with ratios of 2 : 1 : 3, 3 : 1 : 4, and 4 : 1 : 5 were prepared with different molar ratios of the reactants.

Characterization of the copolymer resins

The copolymer resins were subjected to elemental analysis for C, H, and N on a Colemann CHN analyzer. The number-average molecular weights (M_n 's) were determined by conductometric titration in *N,N*-dimethylformamide (DMF) with ethanolic KOH as the titrant and with 25-mg samples. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for the neutralization of 100 g of the copolymer was made. An inspection of this plot revealed that there were many breaks. From this plot, the first break and the last break were noted. The calculation of M_n by this method is based on the following consideration: (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the breaks observed beyond the first break represent the stage at which phenolic hydroxyl groups of all the repeating units are neutralized. The following relation gives the average degree of polymerization (\overline{DP}):

$$\overline{DP} = \frac{\text{Total milliequivalent of base required for complete neutralization}}{\text{Milliequivalent of base for smallest interval}}$$

$$M_n = \overline{DP} \times \text{repeat unit weight}$$

The molecular weights of the resins were also determined by the vapor pressure osmometry (VPO) method with DMF as the solvent and benzyl as the calibrant. A Wescan model 233 vapor pressure osmometer was used for this purpose.

TABLE I
Summarized Procedures for EDTA Titrations of the Cations Under Investigation

Metal ion	Type of titration	pH range	Buffer	Indicator	Color change
Fe(III)	Direct	2–3	Diluent HNO ₃ /diluent NaOH*	Variamine blue	Blue to yellow
Ni(II)	Direct	7–10	Aqueous NH ₃ /NH ₄ Cl	Murexide	Yellow to violet
Co(II)	Direct	6	Hexamine	Xylenol orange	Red to yellow
Cu(II)	Direct	9–10	Diluent HNO ₃ /diluent NaOH*	Fast sulfone black-F	Purple to green
Pb(II)	Direct	6	Hexamine	Xylenol orange	Red to yellow

* No buffer used therefore pH was adjusted by using either dilute HNO₃ or dilute NaOH.

Electronic absorption spectra of the copolymers in dimethyl sulfoxide (DMSO) were recorded with a Shimadzu ultraviolet–visible (UV–vis) double-beam spectrophotometer fitted with an automatic pen chart recorder on thermosensitive paper in the range of 200–850 nm.

Infrared (IR) spectra of the 8-hydroxyquinoline-5-sulfonic acid–thiourea–formaldehyde (8-HQ5-SATUF) copolymer resins were recorded in nujol mull with a PerkinElmer Spectrum RX-I spectrophotometer in the range of 4000–500 cm⁻¹. ¹H-NMR spectra were recorded with a Bruker Advance-II 400-MHz ¹H-NMR spectrophotometer with DMSO-*d*₆ as the solvent.

Ion-exchange properties

Determination of metal-ion uptake in the presence of electrolytes of different concentrations. The following procedure was applied to study the effect of the nature of the various electrolytes and their concentrations on the amount of metal ions taken up by the copolymer resin samples. A finely powdered copolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of a known concentration. The pH of the solution was adjusted to the required value with either 0.1M HNO₃ or 0.1M NaOH. The suspension was stirred for a period of 24 h at room temperature. To this suspension, 2 mL of a 0.1M solution of the metal ion was added, and the pH was adjusted to the required value. The mixture was again stirred at 27°C for 24 h and filtered.¹³ The solid was washed, and the filtrate and washing were combined and estimated for the metal-ion content by titration against standard ethylene diamine tetraacetic acid (EDTA) with an appropriate buffer and a suitable indicator (Table I).¹⁴ A blank experiment was also carried out in the same manner without the addition of the polymer sample. The blank solution was again estimated for the metal-ion content. The amount of metal ions taken up by the copolymer in the presence of a given electrolyte of a known concentration was determined from the difference between the blank reading and the reading in the actual experiment.¹⁵ The experiment was repeated in the presence of several electrolytes of known concentrations

with five different metal ions: Fe(III), Co(II), Ni(II), Cu(II), and Pb(II). The same procedure was applied to all the molar ratios of the copolymer samples.

Evaluation of the rate of metal-ion uptake. To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the aforementioned type were carried out, in which the metal ion taken up by the copolymer resin was estimated from the time to room temperature (300 K) in the presence of 25 mL of a solution of NaNO₃. It was assumed that under the given conditions, the state of equilibrium was established within 24 h.^{15,16} The rate of metal-ion uptake was expressed as the percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium.^{15,17}

Evaluation of the distribution of metal ions at different pHs. The distribution of each one of the five metal ions [Fe(III), Ni(II), Cu(II), Co(II), and Pb(II)] between the polymer phase and aqueous phase was estimated at 300 K and in the presence of a solution of NaNO₃. The experiments were carried out as described previously in the pH range of 2–6.5. The distribution coefficient (*D*) was calculated with the following relationship:

$$D = \frac{\text{Weights (mgs) of metalions taken up by 1 g of copolymer}}{\text{Weight (mg) of metalion present in 1 ml of solution}}$$

RESULTS AND DISCUSSION

The synthesized 8-HQ5-SATUF copolymers were confirmed with UV–vis, IR, and ¹H-NMR techniques. All expected signals for 8-HQ5-SATUF were observed. High-performance liquid chromatography (thin layer chromatography) showed that the synthesized copolymers were 89.85% pure

All four 8-HQ5-SATUF copolymer resins were green in color. These purified resins were found to be soluble in DMF, DMSO, and aqueous sodium and potassium hydroxide solutions. The melting points were in the range of 240–254°C.

All four 8-HQ5-SATUF copolymer resins were analyzed for carbon, hydrogen, nitrogen, and sulfur at

TABLE II
Elemental Analysis Data and Empirical Formulas for the 8-HQ5-SATUF Copolymer Resins

Copolymer resin	% [found (calcd)]				Empirical formula of the repeating unit	Empirical formula weight
	C	H	N	S		
8-HQ5-SATUF-I	45.0 (44.3)	3.78 (3.38)	12.4 (12.9)	16.6 (15.4)	C ₁₂ H ₁₁ O ₄ S ₂ N ₃	325
8-HQ5-SATUF-II	47.6 (47.8)	2.70 (2.8)	10.2 (10.14)	17.3 (17.01)	C ₂₂ H ₁₈ O ₈ S ₃ N ₄	552
8-HQ5-SATUF-III	47.9 (48.0)	3.46 (3.1)	8.9 (8.7)	16.2 (15.8)	C ₃₂ H ₂₅ O ₁₂ S ₄ N ₅	799
8-HQ5-SATUF-IV	47.8 (48.64)	3.36 (3.0)	8.5 (8.1)	15.5 (16.1)	C ₄₂ H ₃₂ O ₁₆ S ₅ N ₃	1036

the Sophisticated Analytical Instrument Facility of Punjab University (Chandigarh, India). The results are presented in Table II. The elemental analysis data are in good agreement with the theoretical (calculated) data. The elemental analysis data were used to assign empirical formulas and empirical weights to these copolymer resins.

The M_n values of the 8-HQ5-SATUF copolymers were determined in fresh, triple-distilled pure DMF with ethanolic potassium hydroxide as the titrant. The experimental results are presented in Table III, and the conductometric titration curves are depicted in Figure 2.

An examination of conductometric titration plots indicates that there are several breaks before complete neutralization of all the phenolic hydroxyl groups. The first break in the plot is the smallest of all the breaks. It is assumed that this corresponds to a stage in titration when on average one phenolic hydroxyl group of each chain is neutralized. An examination of the conductometric data reveals that the size of most of the breaks is nearly equal to or is a whole multiple of the size of the first break. The titration curves of the copolymers indicate a sharp stepwise increase in the conductance until the stage neutralization of all the —OH groups. Beyond this stage, there is a continuous increase in the conductance. \overline{DP} of the 8-HQ5-SATUF copolymer sample was obtained from the ratio of total milliequivalents of base required to reach the final stage of neutralization to the milliequivalents corresponding to the first break in the plots of 8-HQ5-SATUF.

From Table III, it can be concluded that the molecular weights of the 8-HQ5-SATUF copolymers increase with an increase in the 8-hydroxyl-quinoline-5-sulfonic acid contents.

The molecular weights of the copolymer resins were also estimated by VPO (Table III). VPO has become a popular technique in molecular weight determination. The first step was to determine the calibration constant (K), which was obtained with benzil as a standard solute. Four sets of solutions of benzil in DMF with the approximate concentration (w/w) ratio of 2 : 4 : 8 : 10 were prepared. The measurements were carried out at 63°C. A drop of the benzil solution (lowest concentration) and a drop of the pure solvent were suspended on separate thermistor probes in a closed chamber saturated with solvent vapor. The thermistors were connected to form the legs of a Wheatstone bridge circuit. A constant voltage was applied. The difference between the solution and the activation of the two drops resulted in a differential mass transfer between them, and this resulted in a small temperature difference. The small temperature difference between the thermistors unbalanced the bridge; the resistance to bringing the bridge into balance was measured in terms of microvolts. For different concentrations, the same procedure was followed. A plot of voltage change ($\Delta\mu v$) versus the concentration would be linear, passing through the origin with a slope equal to K/m_2 . If molecular wt. of solute (m_2) is known, the value of constant K can be evaluated with the following relations:

$$\text{Slope} = K/m_2$$

$$M_n = K/\text{slope}$$

The first step in the measurement of M_n is the evaluation of constant K for a given solvent with a pure compound of a known molecular weight as a solute. The molecular weights of the copolymer samples,

TABLE III
Molecular Weight and Intrinsic Viscosity Data for the 8-HQ5-SATUF Copolymer Resins

Copolymer resin	First stage of neutralization (mequiv/100 g of copolymer)	Final stage of neutralization (mequiv/100 g of copolymer)	Degree of polymerization	M_n	
				By conductometry	By VPO
8-HQ5-SATUF-I	56	1,288	23	7,475	7,482
8-HQ5-SATUF-II	56	1,120	20	11,040	11,089
8-HQ5-SATUF-III	56	1,008	18	14,382	14,369
8-HQ5-SATUF-IV	56	896	16	17,176	17,188

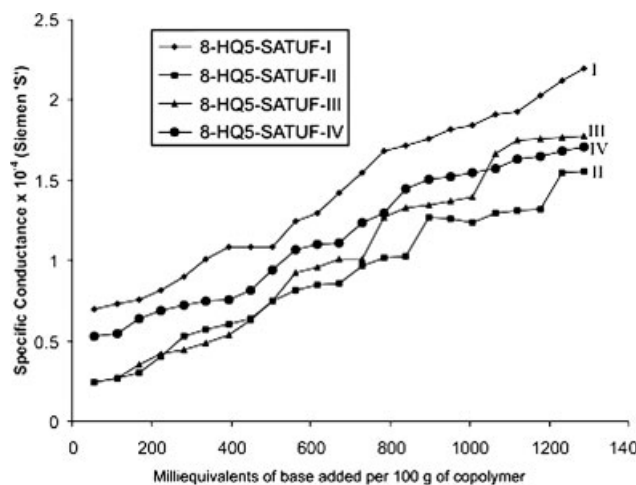


Figure 2 Conductometric titration curves of the 8-HQ5-SATUF copolymer resins.

estimated by conductometric titration and VPO, were comparable within the limits of the experimental error.

UV-vis spectra of all purified 8-HQ5-SATUF copolymer samples in spectroscopic-grade DMF were scanned in the region of 200–850 nm, and the results are shown in Figure 3. A perusal of the UV-vis spectra of the 8-HQ5-SATUF copolymers shows a similar nature. The spectra of these copolymers exhibit two absorption maxima in the regions of 240–260 and 320–360 nm. The bands at 240–260 nm indicate the presence of a C=S group containing a carbon-sulfur double bond in conjugation with the aromatic nucleus, and this is characteristic of the $\pi \rightarrow \pi^*$ transition. The less intense band is not clear. However, a shoulder merging in the 320–360-nm region can be seen in the UV-vis spectra. These should be assigned to $n \rightarrow \pi^*$ transitions.

The bathochromic shift (the shift toward a longer wavelength) from the basic values (257 nm and

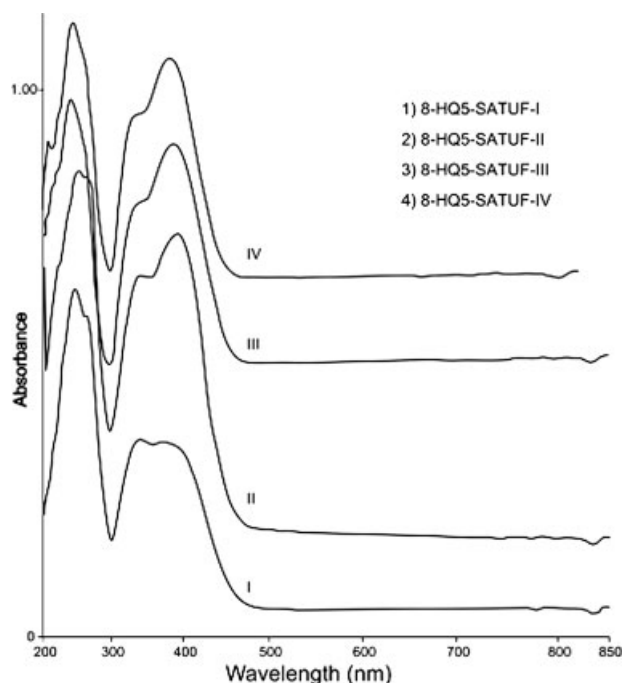


Figure 3 UV-vis spectra of the 8-HQ5-SATUF copolymer resins.

320 nm) may be due to the combined effect of conjugation and the phenolic hydroxyl group (auxochrome).

It can be observed from the UV-vis spectra of the 8-HQ5-SATUF copolymers that the maximum absorptivity (ϵ_{\max}) values gradually increased in the following order: 8-HQ5-SATUF-I < 8-HQ5-SATUF-II < 8-HQ5-SATUF-III < 8-HQ5-SATUF-IV.

The previously observed increasing order may be due to the introduction of more chromophores (>C=S group) and auxochromes (phenolic —OH group) into the repeat unit structure of the copolymer. This observation supports the proposed structures given in Figure 3.

TABLE IV
IR Spectroscopy Data for the 8-HQ5-SATUF Copolymer Resins

Frequency band observed for the copolymer resin (cm^{-1})				Assignment	Expected frequency band (cm^{-1})
8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV		
3506–3401(b)	3506–3399(b)	3507–3400(b)	3507–3401(b)	—OH stretching (phenolic)	3700–3300
3080(b)	3079–3102(b)	3080–3102(b)	3080–3102(b)	>NH stretching	3200–3300
1228–1138	1228–1136	1228–1130	1230–1132	>C=S (thiooxamide moiety)	1250–1150
1555–1601	1554–1601	1555–1600	1557–1602	Aromatic ring	1600–1500
954	953	953.9	954	Substitution in benzene skeleton	960
1045.5	1044.8	1045.5	1054		1080
1138	1136–1162	1136–1162	1136		1150
1228	1230.1	1232	1227		1230
1315	1280	1280	1310	>CH ₂	1300
1210	1195	1190	1205		1200
795	795	795	795		800

b = broad.

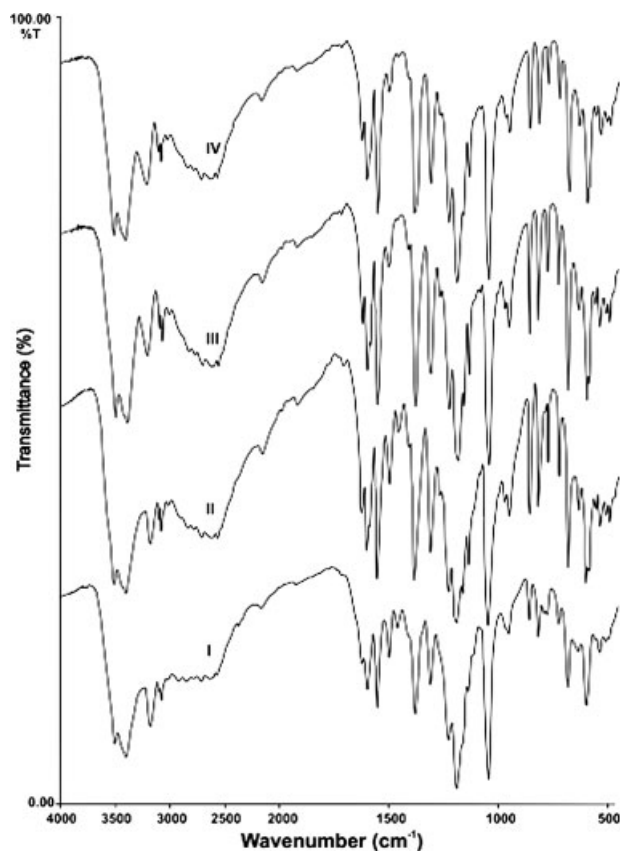


Figure 4 IR spectra of the 8-HQ5-SATUF copolymer resins: (I) 8-HQ5-SATUF-I, (II) 8-HQ5-SATUF-II, (III) 8-HQ5-SATUF-III, and (IV) 8-HQ5-SATUF-IV.

The IR spectra of all the 8-HQ5-SATUF copolymers were found to be similar, except for some differences in the intensities of a few peaks. The important IR bands along with their assignments are given in Table IV, and the spectra are incorporated in Figure 4.

A broad band appearing in the region of 3506–3401 cm^{-1} can be assigned to the stretching vibration of the phenolic —OH group.

The strong band at 1135–1228 cm^{-1} may be due to the stretching vibration of the >C=S group of the thio group. The spectra show a number of bands at about 795, 1205, and 1310 cm^{-1} , which can be ascribed to methylene groups. A sharp peak at 1610 cm^{-1} can be assigned to an aromatic skeletal ring. 1,2,3,5-Tetrasubstitutions of the aromatic benzene ring are recognized from bands appearing at 920, 1015, 1145, and 1265 cm^{-1} , respectively. The presence of the —NH— group in the thiourea unit can be ascribed to a broad band at 3102–3380 cm^{-1} , which seems to be merged with the broad band of the phenolic hydroxyl group. The presence of —NH— is further supported by the medium band at 660 cm^{-1} , which can be ascribed to the wagging vibration of —NH— of the thiourea unit in the copolymer resins.

NMR spectra of all four 8-HQ5-SATUF copolymers were recorded in the solvent $\text{DMSO-}d_6$ at the Sophisticated Analytical Instrument Facility of Punjab University. The spectra are presented in Figure 5, and the spectral data are listed in Table V.

The NMR spectra reveal that except for the 8-HQ5-SATUF-I and 8-HQ5-SATUF-II copolymers, the copolymers (8-HQ5-SATUF-III and 8-HQ5-SATUF-IV) show an intense signal around 3.0–4.0 δ (ppm), which is due to the methylenic proton of the $\text{Ar—CH}_2\text{—Ar}$ linkage. The signals in the range of 9.1–9.8 ppm (δ) are assigned to phenolic hydroxyl protons. The multiplet signals in the range of 7.5–8.0 ppm (δ) indicate the presence of aromatic protons. A weak, broad signal in the region of 5.2–5.24 ppm (δ) can be attributed to the proton of the —NH— bridges. Intense signals appearing in the region of 4.3–4.5 δ ppm (δ) indicate methylenic protons of the $\text{Ar—CH}_2\text{—N}$ moiety. The signal around 10 ppm (δ) can be assigned to the proton of the SO_3H group.

On the basis of physicochemical and spectral evidence, the most probable structures for all the newly

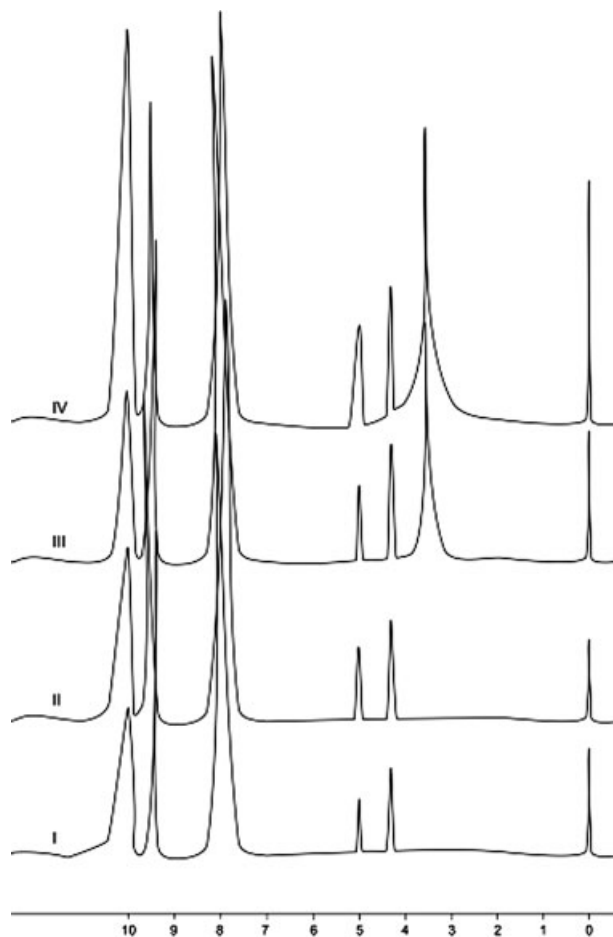


Figure 5 NMR spectra of the 8-HQ5-SATUF copolymers: (I) 8-HQ5-SATUF-I, (II) 8-HQ5-SATUF-II, (III) 8-HQ5-SATUF-III, and (IV) 8-HQ5-SATUF-IV.

TABLE V
¹H-NMR Spectral Data of the 8-HQ5-SATUF Copolymer Resins

Chemical shift observed for the copolymer resin (ppm)				Nature of protons assigned	Expected chemical shift (ppm)
8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV		
—	—	3.0–4.0	3.0–4.0	Methylenic proton of the Ar—CH ₂ —Ar linkage	3.93
4.3–4.5	4.3–4.5	4.3–4.5	4.3–4.5	Methylenic proton of the Ar—CH ₂ —N moiety	4.34
7.5–8.0	7.6–8.0	7.5–8.1	7.5–8.1	Aromatic proton (unsymmetrical pattern)	6.0–8.0
9.1–9.8	9.1–9.8	9.2–9.8	9.3–9.8	Proton of phenolic —OH	8–10
10.1	10.2	10.1	10.1	Proton of SO ₃ H	10–11
5.21	5.24	5.21	5.20	Proton of the —NH bridge	5.16

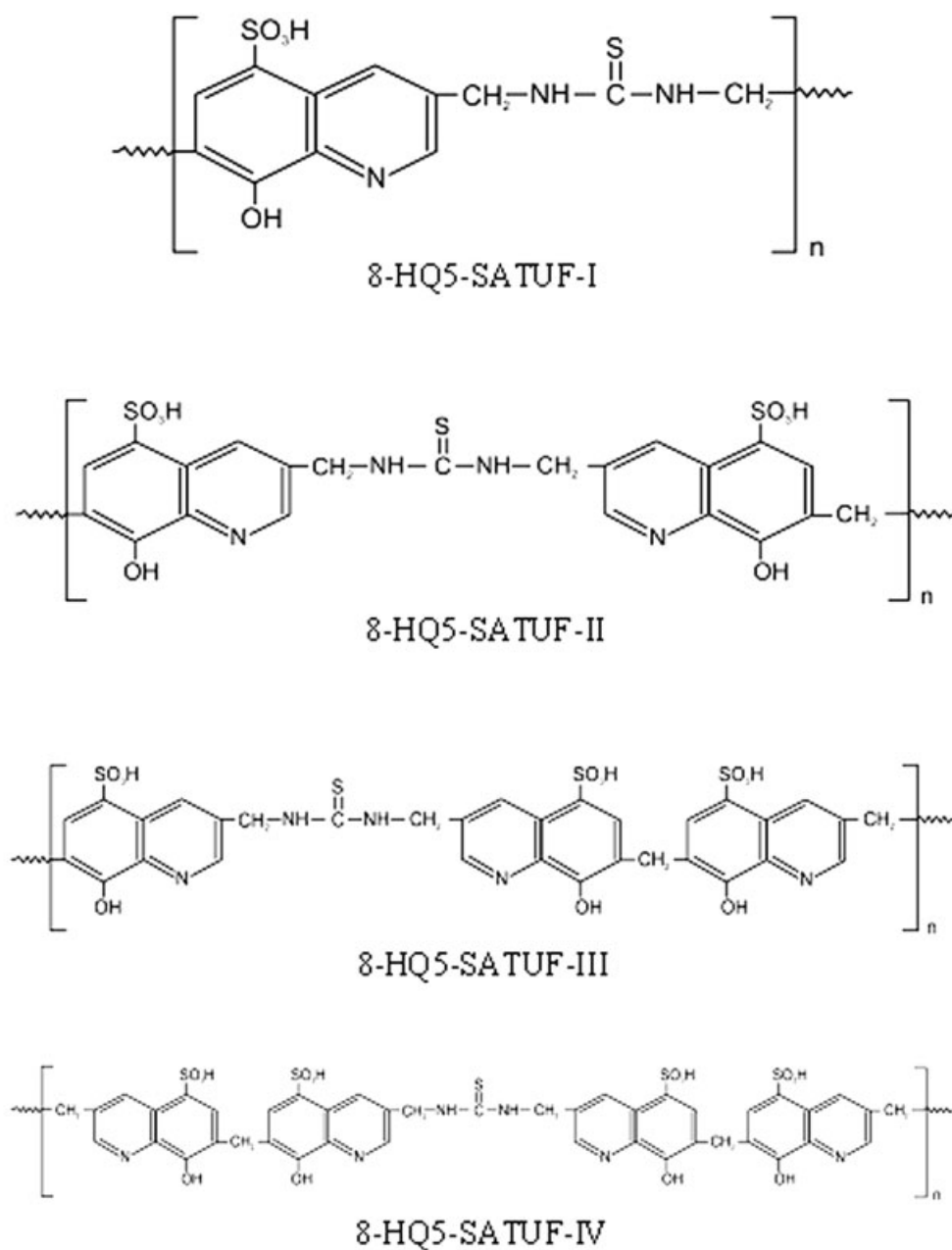


Figure 6 Suggested structure of the 8-HQ5-SATUF-I copolymer resin.

TABLE VI
Evaluation of the Influence of Different Electrolytes on the Uptake of Several Metal Ions

Metal ion	Electrolyte (mol/l)	Weight of metal ions taken up (mg)															
		NaClO ₄				NaCl				NaNO ₃				Na ₂ SO ₄			
		8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV	8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV	8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV	8-HQ5-SATUF-I	8-HQ5-SATUF-II	8-HQ5-SATUF-III	8-HQ5-SATUF-IV
Pb(II)	0.02	0.98	1.02	1.03	1.15	1.48	1.50	1.59	1.62	1.64	1.75	1.84	1.95	—	—	—	—
	0.07	0.75	0.84	0.77	0.89	1.37	1.40	1.45	1.54	1.43	1.54	1.65	1.72	—	—	—	—
	0.12	0.46	0.57	0.38	0.50	1.02	1.09	1.15	1.22	0.99	1.09	1.17	1.28	—	—	—	—
Cu(II)	0.54	0.35	0.28	0.25	0.38	0.75	0.89	0.99	1.02	0.65	0.76	0.85	0.95	—	—	—	—
	0.02	1.65	2.15	2.45	2.57	1.10	1.99	2.57	2.69	1.15	1.23	1.28	1.42	3.37	3.60	4.32	4.44
	0.06	2.17	3.08	3.38	3.50	2.08	2.78	3.30	3.42	1.67	1.90	2.05	2.18	2.68	3.15	3.44	3.56
	0.12	2.58	3.65	4.55	4.68	2.55	3.02	3.78	3.90	2.28	2.57	2.87	2.99	1.82	1.86	2.06	2.17
	0.52	3.07	3.90	4.98	5.10	3.20	3.58	4.02	4.14	2.65	3.25	4.17	4.30	0.97	1.07	1.24	1.37
Ni(II)	0.02	1.89	2.16	2.88	3.02	1.15	1.68	2.32	2.46	0.95	1.03	1.09	1.22	2.88	3.15	4.30	4.43
	0.07	2.12	2.88	3.57	3.70	1.65	1.02	3.55	3.67	1.60	1.88	1.97	2.09	2.37	2.45	3.53	3.38
	0.12	2.45	3.63	4.43	4.57	2.44	2.93	3.76	3.88	2.47	2.65	3.15	3.27	1.57	2.90	2.88	3.05
	0.55	2.59	3.72	4.65	4.75	2.95	3.68	4.47	4.59	3.02	3.45	4.02	4.15	0.80	1.18	1.40	1.58
Co(II)	0.03	1.70	1.79	1.89	1.92	1.87	1.80	1.89	1.93	1.93	1.55	1.85	1.98	1.72	1.73	1.85	1.95
	0.06	1.37	1.50	1.70	1.74	1.62	1.30	1.35	1.48	1.20	1.19	1.22	1.24	1.28	1.43	1.55	1.65
	0.12	1.05	1.16	1.27	1.39	1.02	1.04	1.02	1.15	0.98	1.07	1.08	1.20	0.87	1.15	1.22	1.32
	0.52	1.78	0.88	1.16	1.30	0.86	0.78	0.62	0.74	0.60	0.83	0.85	0.95	0.40	0.57	0.65	0.77
Fe(III)	0.02	1.03	1.06	1.12	1.19	0.28	0.39	0.42	0.50	1.08	1.11	1.16	1.23	1.37	2.48	2.58	2.66
	0.07	1.99	2.03	2.12	2.20	0.75	0.85	0.90	0.98	1.54	1.61	1.69	1.75	1.39	1.50	1.57	1.65
	0.12	2.27	2.32	2.38	2.43	1.59	1.67	1.73	1.80	1.88	1.97	2.00	2.06	1.28	1.38	1.45	1.58
	0.52	2.60	2.66	2.73	2.82	2.03	2.13	2.17	2.25	2.05	2.15	2.30	2.06	0.83	1.88	1.92	0.95

ions a = [M(NO₃)₂] = 0.1 mol./lit; presence of b = Volume = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

TABLE VII
Comparison of the Rates of Metal-Ion Uptake

Metal ion	Copolymer resin sample	Percentage of metal ions taken up at different times						
		1 h	2 h	3 h	4 h	5 h	6 h	7 h
Fe(III)	8-HQ5-SATUF-I	68	87	98	—	—	—	—
	8-HQ5-SATUF-II	69	88	99	—	—	—	—
	8-HQ5-SATUF-III	69	88	99	—	—	—	—
	8-HQ5-SATUF-IV	70	89	100	—	—	—	—
Cu(II)	8-HQ5-SATUF-I	47	54	69	84	96	—	—
	8-HQ5-SATUF-II	48	58	70	86	97	—	—
	8-HQ5-SATUF-III	48	58	70	86	97	—	—
	8-HQ5-SATUF-IV	49	59	72	90	99	—	—
Ni(II)	8-HQ5-SATUF-I	39	53	68	83	97	—	—
	8-HQ5-SATUF-II	40	56	69	93	97	—	—
	8-HQ5-SATUF-III	40	56	69	84	97	—	—
	8-HQ5-SATUF-IV	42	57	72	84	98	—	—
Co(II)	8-HQ5-SATUF-I	35	52	67	82	95	—	—
	8-HQ5-SATUF-II	37	53	68	53	96	—	—
	8-HQ5-SATUF-III	37	54	69	83	97	—	—
	8-HQ5-SATUF-IV	38	54	70	84	97	—	—
Pb(II)	8-HQ5-SATUF-I	21	32	48	63	80	90	—
	8-HQ5-SATUF-II	23	34	48	65	81	91	—
	8-HQ5-SATUF-III	24	36	50	66	81	91	—
	8-HQ5-SATUF-IV	25	35	50	66	82	92	—

synthesized and characterized copolymer resins are proposed (Fig. 6).

Ion-exchange properties

The results of the batch equilibrium study carried out with 8-HQ5-SATUF copolymer resin samples are presented in Tables VI–VIII. From this study, which was carried out with five metal ions with limited

variations of the experimental conditions, certain generalizations can be made about the behavior of the 8-HQ5-SATUF copolymer samples.

Influence of electrolytes on the metal-ion uptake

The data presented in Table VI reveal that the amount of metal ions taken up by a given amount of

TABLE VIII
Distribution Ratios (D)^a of Different Metal Ions as a Function of the pH

Metal ion	Copolymer resin	Distribution ratio of metal ions ^b at various pHs									
		1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe(III)	8-HQ5-SATUF-I	11.9	152.7	269.2	412.1	—	—	—	—	—	—
	8-HQ5-SATUF-II	14.8	168.4	280.0	413.1	—	—	—	—	—	—
	8-HQ5-SATUF-III	17.2	171.5	292.0	503.2	—	—	—	—	—	—
	8-HQ5-SATUF-IV	18.5	172.9	294.1	508.2	—	—	—	—	—	—
Cu(II)	8-HQ5-SATUF-I	—	—	—	42.1	91.1	177.7	154.1	1185.1	1590.1	1700.2
	8-HQ5-SATUF-II	—	—	—	48.6	97.8	196.1	375	1210.2	1610.2	1710.2
	8-HQ5-SATUF-III	—	—	—	52.7	112.8	201	392	1285.7	1630.5	1750.3
	8-HQ5-SATUF-IV	—	—	—	57.9	128.5	225	396	1310.1	1700.1	1780.5
Ni(II)	8-HQ5-SATUF-I	—	—	—	34.1	88.5	132.1	305.1	450.2	1015.2	1090.1
	8-HQ5-SATUF-II	—	—	—	35.5	95.1	105.1	370.2	460.1	1108.5	1182.2
	8-HQ5-SATUF-III	—	—	—	38.4	110.1	180.2	398.6	480.5	1362.7	1392.5
	8-HQ5-SATUF-IV	—	—	—	49.1	115.1	230.5	402.1	498.6	1390.7	1407.2
Co(II)	8-HQ5-SATUF-I	—	—	—	30.2	40.1	92.5	112.9	185.3	255.1	270.2
	8-HQ5-SATUF-II	—	—	—	32.1	44.6	98.2	145.7	199.4	280.4	282.1
	8-HQ5-SATUF-III	—	—	—	33.5	47.2	110.2	152.2	207.5	288.3	292.5
	8-HQ5-SATUF-IV	—	—	—	36.2	58.1	120.3	100.3	209.4	300.6	300.1
Pb(II)	8-HQ5-SATUF-I	—	—	—	43.2	25.6	49.2	90.4	112.7	208.5	209.1
	8-HQ5-SATUF-II	—	—	—	28.3	40.8	54.7	92.6	128.7	112.7	220.2
	8-HQ5-SATUF-III	—	—	—	29.1	42.5	61.2	99.6	158.4	225.4	230.5
	8-HQ5-SATUF-IV	—	—	—	30.1	44.2	63.4	100	162.4	228.2	223.6

^a D = Weight (mg) of metal ion taken up by 1 g of terpolymer/Weight (mg) of metal ions present in 1 mL of solution.

^b Metal ion uptake = (amount of metal ion absorbed \times 100)/amount of metal ion absorbed at equilibrium.

a copolymer resin depended on the nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride, and nitrate ions, the amount of ions taken up by the copolymer samples increased with the increasing concentration of the electrolyte, whereas in the presence of sulfate ions, the amount of the aforementioned ions taken up by the copolymer samples decreased with the increasing concentration of the electrolyte.¹⁸ Moreover, the amount of Co(II) and Pb(II) ions taken up by the copolymer samples decreased with the increasing concentration of the chloride, nitrate, perchlorate, and sulfate ions.^{15,18} This observation can be explained by the formation of complexes with Co^{2+} , Cu^{2+} , Fe^{3+} , Ni^{2+} , and Pb^{2+} metal cations.¹⁹ This type of trend has also been observed by other investigators in this field.

It was also observed that the amount of metal ions taken up by the 8-HQ5-SATUF copolymer resins increased in the following order: 8-HQ5-SATUF-I < 8-HQ5-SATUF-II < 8-HQ5-SATUF-III < 8-HQ5-SATUF-IV. This observed order may be due to the introduction of more and more ligand groups into the repeating unit (monomer) of the copolymer resin. It was also noted that a lower pH was not suitable when concentrated electrolytes were used. Moreover, the metal-ion adsorption by the copolymer resin samples was generally much better in the presence of a 1M perchlorate solution.

Evaluation of the rates of metal uptake

The rates of ion adsorption by all four 8-HQ5-SATUF copolymer resin samples were measured for Fe(III), Ni(II), Co(II), Cu(II), and Pb(II) ions to determine the time required to reach the equilibrium. The term *rate* refers to the change with time when they were in contact with the copolymer samples. The experimental results, which are presented in Table VII, show the dependence of the rate of metal-ion uptake on the nature of the metal ions. These results indicate that the time taken for the uptake of the different metal ions at a given stage depended on the nature of the metal ions under the given conditions. A careful examination of the experimental data, which are tabulated in Table VII, shows that Fe(III) ions required almost 3 h for equilibrium. Cu(II), Ni(II), and Co(II) ions required about 5 h, whereas Pb(II) ion required almost 6 h for equilibrium. The experimental results revealed that the rate of metal-ion uptake followed the order of Fe(III) > Cu(II), Ni(II), > Co(II) > Pb. It was further revealed that the rate of metal uptake followed this order: 8-HQ5-SATUF-I < 8-HQ5-SATUF-II < 8-HQ5-SATUF-III < 8-HQ5-SATUF-IV.

Distribution ratios of metal ions at different pHs

Table VIII shows the experimental results for the effect of the pH on the amount of metal ions distributed between two phases. The data presented in Table VIII indicate that the relative amount of metal ions taken up by the copolymer samples at equilibrium increased with the increase in the pH.

The study was carried out only up to pH 6.5 to prevent hydrolysis of the metal ions at higher pHs. In the case of Fe(III), the highest working pH was 2.5. The results indicate that the selectivity of the copolymer resin samples for Fe(III) ion was higher than that for the other metal ions, whereas the selectivity of the copolymer resin samples for Co(II) and Pb(II) ions was lowest. The other metal ions under study [Cu(II) and Ni(II)] showed intermediate selectivity.

The lower distribution ratio of Fe(III) can be attributed to steric hindrance.²⁰ The other four metal ions [Co(II), Pb(II), Ni(II), and Cu(II)] had a high distribution ratio over the pH range of 2.5–6.5. This could be attributed to low stability constants.²¹

Thus, in this study, the observed order of the distribution ratios of the metal ions measured in the pH range of 3–6.5 was found to be Fe(III) > Cu(II) > Co(II), Ni(II) > Pb(II). A similar trend was observed by earlier investigators.^{17,22} The results of this study are helpful in selecting the optimum pH for the selective uptake of a metal ion from a mixture of different ions. The selective uptake of the metal ions was studied by the adjustment of the optimum pH of 2.5. The lowering of the distribution ratios of Fe(III) was found to be small, and hence efficient separation could be achieved.

CONCLUSIONS

8-HQ5-SATUF copolymer resins based on the condensation reaction of 8-hydroxyquinoline-5-sulfonic acid and thiourea with formaldehyde in the presence of an acid catalyst were prepared. 8-HQ5-SATUF is a selective ion-exchange copolymer resin. The copolymer resin showed higher selectivity for Fe^{3+} and Cu^{2+} ions than for Co^{2+} , Ni^{2+} and Pb^{2+} .

References

- Kaliyappan, T.; Kannan, P. *Prog Polym Sci* 2000, 25, 343.
- Finn, R. C.; Zibieta, J. *Inorg Chem* 2001, 40, 2466.
- Patel, S. A.; Shah, B. S.; Patel, R. M.; Patel, P. M. *Iran Polym J* 2004, 13, 445.
- Lee, W.; Lee, S. E.; Kim, M. Y. *Korean Chem Soc* 2002, 23, 1067.
- Patel, M. M.; Kapadiya, M. A.; Patel, G. P.; Joshi, J. D. *J Appl Polym Sci* 2007, 106, 1307.
- Rivas, B. L.; Villegas, S. *J Appl Polym Sci* 2004, 91, 3679.
- Hegazy El-Sayed, A.; Abd El-Aal, S. E.; Abou Taleb, M. F.; Dessouki, A. M. *J Appl Polym Sci* 2004, 92, 2642.
- Gurnule, W. B.; Juneja, H. D.; Paliwar, L. J. *React Funct Polym* 2002, 50, 95.
- Erol, I. *J Polym Sci Part A: Polym Chem* 2004, 42, 3157.

10. Soykan, C.; Erol, I. *J Polym Res* 2004, 11, 53.
11. Vijayanand, R. S.; Kato, S.; Satokawa, S.; Kojima, T. *Eur Polym J* 2007, 43, 2046.
12. Jadhao, M. M.; Paliwar, L. J.; Bhave, N. S. *J Appl Polym Sci* 2005, 96, 1605.
13. Singru, R. N.; Zade, A. B.; Gurnule, W. B. *J Appl Polym Sci* 2008, 109, 859.
14. Masram, D. T.; Kariya, K. P.; Bhave, N. S. *e-Polymers* 2007, 75, 1.
15. Gurnule, W. B.; Rahangdale, P. K.; Paliwar, L. J.; Kharat, R. B. *Synth React Inorg Met Org Chem* 2003, 33, 1187.
16. Jadhao, M. M.; Paliwar, L. J.; Bhave, N. S. *Ind J Chem A* 2005, 44, 1.
17. Shah, B. A.; Shah, A. V.; Bhatt, R. R. *Iran Polym J* 2007, 16, 173.
18. Gurnule, W. B.; Rahangdale, P. K.; Paliwar, L. J.; Kharat, R. B. *React Funct Polym* 2003, 55, 255.
19. Rahangdale, S. S.; Zade, A. B.; Gurnule, W. B. *J Appl Polym Sci* 2008, 108, 747.
20. Gurnule, W. B.; Rahangdale, P. K.; Paliwar, L. J.; Kharat, R. B. *Ultrasound Sci* 2003, 15, 89.
21. Gurnule, W. B.; Rahangdale, P. K.; Kharat, R. B.; Paliwar, L. J. *Prog Cryst Growth Char Mater* 2002, 133.
22. Tarase, M. V.; Zade, A. B.; Gurnule, W. B. *J Appl Polym Sci* 2008, 2, 738.