# Chelation Ion-Exchange Study of Copolymer Resin Derived from 8-Hydroxyquinoline 5-Sulphonic Acid, Oxamide, and Formaldehyde

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**ABSTRACT:** Copolymers (8-HQ5-SAOF) were synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and oxamide (O) with formaldehyde (F) in the presence of acid catalyst. Four different copolymers were synthesized by using varied molar proportion of the reacting monomers. Copolymer resin composition has been determined on the basis of their elemental analysis and average molecular weights of these resins were determined by conductometric titration in nonaqueous medium. Viscometric measurement in dimethyl sulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. Electronic spectra, FTIR, and proton nuclear magnetic resonance spectra were studied to elucidate the structures. The newly synthesized copolymer proved to be a selective chelating ion-exchange copolymer for certain metals. The chelating ion-exchange properties of this synthesized copolymer was studied for different metal ions such as $Fe^{3+}$, $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$. A batch equilibrium method was used in the study of the selectivity of metal ion uptake involving the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion only for representative copolymer 8-HQ5-SAOF-I due to economy of space. The study was carried out over a wide pH range, shaking time, and in media of various ionic strengths. The copolymer showed a higher selectivity for $Fe^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions than for $Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3356–3366, 2010

**Key words:** ion-exchangers; synthesis; adsorption; degree of polymerization (DP); resins

## INTRODUCTION

The presence of heavy metals in the environmental area is a cause of concern due to their acute and long-term toxicity. Removal of these metals from the environment has become increasing interest and need to have certain analytical technique. Chelating ion-exchange technique has attained the status of unit operation in chemical industries and replaced the traditional methods of separation like distillation and others. Organic chelating ion exchanger is chiefly of interest for this due to their high ion uptake capacities. Also the synthesis of new copolymer resins attracted the attention of researcher because of versatile utility in our day-to-day life. Resins, as copolymer, which form special class of polymer are widely known for their uses. Various modified phenol-formaldehyde resins have large number of practical applications[1–3] viz. high thermal conducting material, excellent abrasive, ion exchangers, and many more other renowned applications are reported in the literature. Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture, and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, recipitation, and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacities and selectivity having physical and chemical stabilities.

Synthesis of various kinds of copolymer using varied organic compounds, their physico-chemical properties and applications were studied by various coworkers.[4,5] Jadhao et al.[6] have synthesized and studied the ion-exchange properties of 2,2,-dihydroxy biphenyl, urea, and formaldehyde copolymer resins. Extensive research work has been reported on copolymer resins derived from phenolic

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compounds-amine/amide-trioxane/formaldehyde from this department.[7,8] However, no work seems to have been carried out on synthesis and physico-chemical technique used for the characterization of newly synthesized copolymer resins derived from 8-hydroxyquinoline 5-sulphonic acid and oxamide with formaldehyde, and their chelating ion-exchange properties. This article includes the synthesis of these new copolymer resins, their systematic structural study with the help of elemental and spectral studies and other various physico-chemical techniques and chelating ion-exchange property of only one 8-HQ 5-SAOF-I copolymer due to economy of space.

This article has been described the development of a novel ion-exchanger resin process suitable for the desalination of waste water, which is high in Fe (III), Ni (II), and Cu (II) ions, to meet effluent discharge specifications. Ion-exchange column of synthesized copolymer resin can be used for removal of the iron, nickel, and copper metal ions as well as suspended solids in waste water. It can also be used in the removal of iron from boiler water in industries. The resin can also be used for the removal of iron and zinc from brass.

## EXPERIMENTAL

### Materials

The entire chemical used in the synthesis of various new copolymer resins were procured from the market and were analar or chemically pure grade. Whenever required, they were further purified by standard procedure. 8-Hydroxyquinoline 5-sulphonic acid and oxamide (Loba Chem, Mumbai) and formaldehyde (37% w/v) (S.D. Fine Chem, Mumbai) were used for synthesis of new copolymer resins.

### Synthesis of 8-HQ5-SAOF copolymer resins (8-HQ5-SAOF-1)

The new copolymer resin 8-HQ5-SAOF-1 was synthesized by condensing 8-hydroxyquinoline 5-sulphonic acid (2.43 g, 0.1 mol) and oxamide (0.88 g, 0.1 mol) with 37% formaldehyde (7.4 mL, 0.2 mol) in a mol ratio of 1 : 1 : 2 in the presence of $2M$ 200 mL HCl as a catalyst at 130°C $\pm$ 2°C for 6 h in an oil bath with occasional shaking to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered, and then extracted with diethyl ether and then with petroleum ether to remove 8-hydroxyquinoline 5-sulphonic acid-formaldehyde copolymer, which might be present along with 8-HQ5-SAOF copolymer. The yellow color res-

inous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 8-HQ5-SAOF-1 in shown in Figure 1.

The copolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered, and reprecipitated by gradual dropwise addition of ice cold 1 : 1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample 8-HQ5-SAOF-1 thus obtained was filtered, washed several times with hot water, dried in air, powdered, and kept in vacuum desicator over silica gel. The yield of the copolymer resin was found to be 75%.

Similarly other copolymer resins viz. 8-HQ5-SAOF-2, 8-HQ5-SAOF-3, and 8-HQ5-SAOF-4 were synthesized by varying the molar proportions of the starting materials, i.e., (2 : 1 : 3), (3 : 1 : 4), and (4 : 1 : 5), respectively, with little variation of experimental condition (Fig. 2). The sample yield (%) and reaction details are tabulated in Table I.

### Characterization of copolymer resins

The viscosities were determined using Taun-Fuoss viscometer at six different concentrations ranging from 1.00% to 0.031% of copolymer in dimethyl sulphoxide (DMSO) at 30°C. The intrinsic viscosity [η was calculated by relevant plots of the Huggins' eq. (1) and Kraemer's eq. (2)].

The number average molecular weights ($\overline{M}n$) were determined by conductometric titration in non-aqueous medium such as DMSO using ethanolic KOH as a titrant. Form the graphs of specific conductance against milliequivalents of base (Fig. 3),
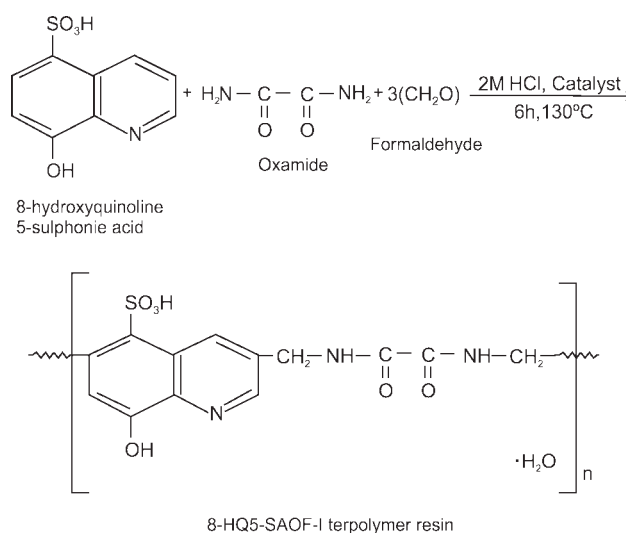


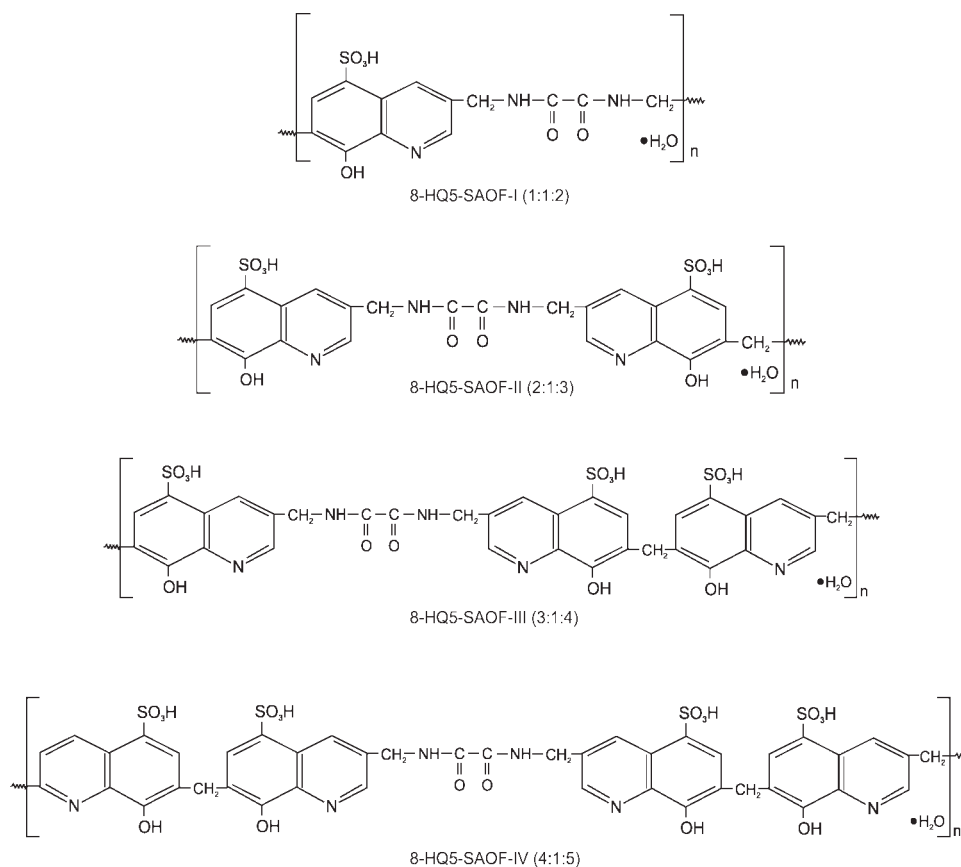**Figure 1** Reaction and suggested structure of representative 8-HQ5-SAOF-1 copolymer resin.

**Figure 2** Suggested structure 8-HQ5-SAOF copolymer resins.

first and last break were noted from which the degree of copolymerization ($\overline{\text{DP}}$) and the number average molecular weight ($\overline{\text{M}}$n) have been calculated for each copolymer resins.

Electron absorption spectra of all copolymer resins were recorded in DMSO (spectroscopic grade) on shimadzu double beam spectrophotometer in the range of 200–850 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Infrared spectra of four 8-HQ5-SAOF copolymer resins were recorded on PerkinElmer-983 spectrophotometer in KBr pallets in the wave number region of 4000–400 cm$^{-1}$ at SAIF, Punjab University, Chandigarh. Nuclear magnetic resonance (NMR) spectra of newly synthesized copolymer resins have been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-$d_6$ at sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Ion-exchange property was studied by batch equilibrium technique.

### Ion-exchange property

The ion-exchange property of the 8-HQ5-SAOF-I copolymer resin was determined by the batch equilibrium method developed by Gregor and De Geiso et al. with seven metal ions viz. Fe$^{3+}$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ in the form of metal

nitrate solution. The ion-exchange study was carried out to investigate the following three aspects.

### Influence of different electrolyte on the amount of metal ion uptake

The following experimental procedure was applied in order to study the effect of the nature of various electrolyte and concentrations on the amount of metal ion taken up by copolymer resin sample. A total of 25 mg copolymer resin was suspended in 25 mL electrolyte solution of known concentration. The pH of this suspension was adjusted before and after stirred for 24 h at 30°C, to this add 2 mL of 0.1$M$ metal ion solution, adjusted pH again to the required value, and stirred again 24 h. The suspension then filtered and filtrate was titrated against standard EDTA solution. Similarly, the blank experiment was also carried out in the same manner without adding copolymer sample. The amount of metal ion uptake was calculated from the difference between at blank experiment and the reading in actual experiment.

### Evaluation of rate of metal ion uptake

The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain

**TABLE I**
**Synthesis and Physical Data of 8-HQ5-SAOF Copolymer Resins**

| Terpolymer | Reactants | | | Catalyst 2M HCl (mL) | Yield (%) | Colour | Melting point (K) | Elemental Analysis | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 8-Hydroxy quinoline-5-sulphonic acid (mol) | Oxamide (mol) | Formaldehyde (mol) | | | | | % of C Found (Cal.) | % of H Found (Cal.) | % of N Found (Cal.) | % of S Found (Cal.) |
| 8-HQ5-SAOF-1 | 0.1 | 0.1 | 0.2 | 200 | 75 | Yellow | 436 | 43.11 (44.38) | 3.21 (3.93) | 11.36 (11.79) | 8.18 (8.98) |
| 8-HQ5-SAOF-2 | 0.2 | 0.1 | 0.3 | 200 | 75 | Yellow | 441 | 45.98 (46.62) | 3.15 (3.55) | 8.97 (9.46) | 10.23 (10.81) |
| 8-HQ5-SAOF-3 | 0.3 | 0.1 | 0.4 | 200 | 80 | Yellow | 445 | 47.12 (47.71) | 3.05 (3.37) | 8.84 (8.43) | 10.85 (11.56) |
| 8-HQ5-SAOF-4 | 0.4 | 0.1 | 0.5 | 200 | 75 | Yellow | 449 | 47.82 (48.36) | 2.96 (3.28) | 7.14 (7.87) | 11.68 (12.01) |

time related to that at the state of equilibrium. To estimate the time require to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described earlier were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 30°C (in the presence of 25 mL of $1M$ NaNO$_3$ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 h.The polymer may adsorbed maximum at equilibrium state.

% of amount of metal ions taken up at different time

$$= \frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal in absorbed at equilibrium}}$$

Evaluation of the distribution of metal ion at different pH

The distribution of each of seven metal ions was determined between copolymer phase and aqueous phase in pH range.

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}}$$
$$\times \frac{\text{Volume of solution (mL)}}{\text{Weight of resin (g)}}$$

## RESULTS AND DISCUSSION

All the newly synthesized purified 8-HQ5-SAOF copolymer resins were found to be yellow in color. The copolymers are soluble in solvents such as DMF, DMSO, and THF, whereas insoluble in almost all other organic solvents. The melting points of these copolymers were determined by using
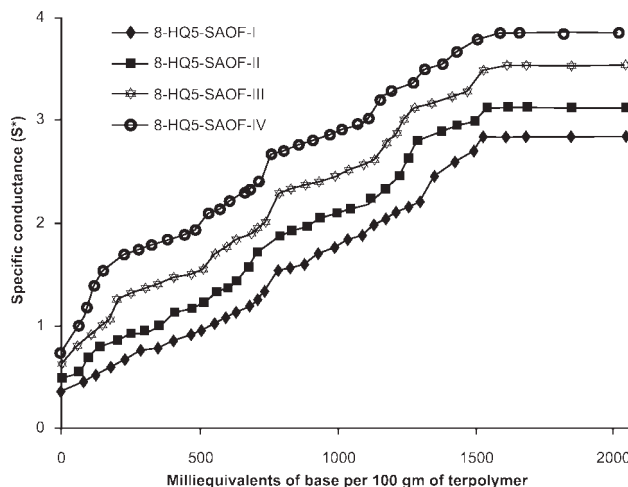


**Figure 3** Conductometric plots of 8-HQ5-SAOF copolymer resins.

electrically heated melting point apparatus and are found to be in the range of 436–449 K. The melting points of the copolymer resins have been determined by electrically heated melting point apparatus (The New York Quinine and Chemical Works, Brooklyn, NY). These resins were analyzed for carbon, hydrogen, and nitrogen content. The sulfur content was analyzed by using messenger method. The details of synthesis of copolymer along with color, melting point, yield, and elemental analysis are incorporated in Table I. The copolymer that has been used in this investigation was prepared by the reaction given in Figure 1.

The number average molecular weight ($\overline{M}n$) of this copolymer has been determined by conducto-metric titration method in nonaqueous medium and using standard potassium hydroxide (0.05$M$) in absolute ethanol as a titrant. The results are presented in Table II. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized. From the plot, the first and last breaks were noted (Fig. 3). The average degree of copolymerization ($\overline{DP}$), and hence, the number average molecular weight ($\overline{M}n$) of all copolymer have been determined using the formula.



**Figure 4** Viscometric plots of 8-HQ5-SAOF copolymer resins.

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

$$\overline{M}n = \overline{DP} \times \text{Repeat unit weight}$$

It is observed that the molecular weight of copolymer resins increases with increase in 8-hydroxyquinolinic 5-sulphonic acid content. This observation is in agreement with the trend observed by earlier workers.[9,10]

Viscosity measurements were carried out at 300 K in freshly triple distilled DMSO using Tuan-Fuoss Viscomer, at six different concentrations ranging from 1.00% to 0.031%. Reduced viscosity and inherent viscosity were plotted versus concentration for each set of data, getting liner plots. The intrinsic viscosity [η] was determined by the corresponding linear plots (Fig. 4). Huggins' ($K_1$) and Kraemer's ($K_2$)
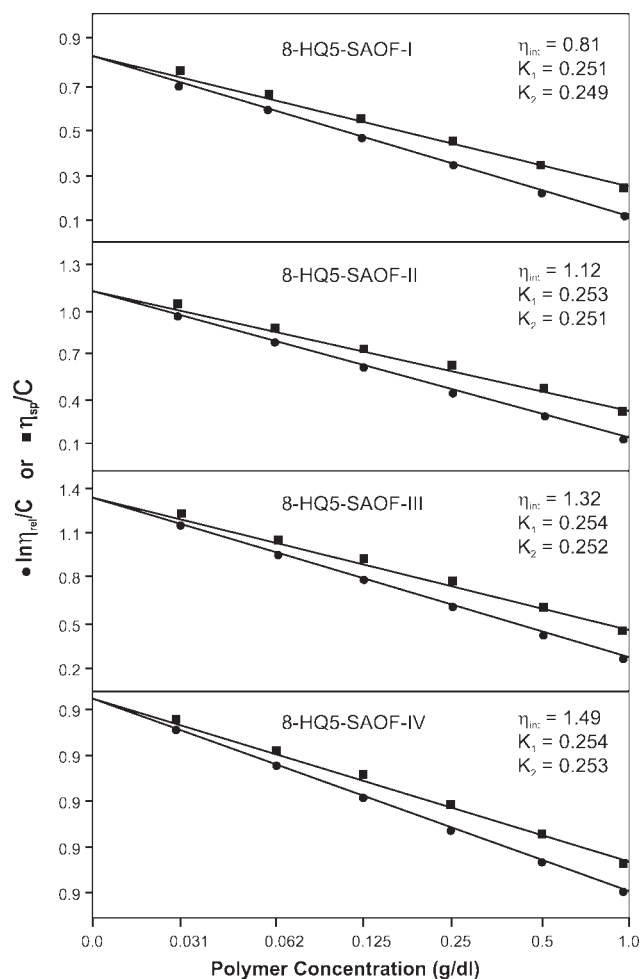
constants were determined by the slope of corresponding liner plots by expressions 1 and 2.

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 \times C \tag{1}$$

$$\ln \eta_{rel}/C = [\eta] - K_2[\eta]^2 \times C \tag{2}$$

According to the above relations 1 and 2, the plots of $\eta_{sp}/C$ and $\ln \eta_{rel}/C$ against $C$ were linear with slopes of $K_1$ and $K_2$, respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give the value of intrinsic viscosity [η] in both plots, which have been found to be closed agreement with each other. The calculated values of the constants $K_1$ and $K_2$ (Table II) in most

**TABLE II**
**Molecular Weight and Viscometric Data of the 8-HQ5-SAOF Copolymer Resins**

| Copolymer | Empirical formula of repeat unit | Empirical weight of repeat unit (gm) | Average degree of polymerization ($\overline{DP}$) | Average molecular weight ($\overline{Mn}$) | Intrinsic viscosity $[\eta]$ (dl/g) | Huggins constant $K_1$ | Kraemer's constant $K_2$ | $K_1 + K_2$ |
|---|---|---|---|---|---|---|---|---|
| 8-HQ5-SAOF-1 | $C_{13}H_{14}N_3O_7S$ | 356 | 16.5 | 5874 | 0.81 | 0.251 | 0.249 | 0.500 |
| 8-HQ5-SAOF-2 | $C_{23}H_{21}N_4O_{11}S_2$ | 592 | 17.0 | 10,064 | 1.12 | 0.253 | 0.251 | 0.504 |
| 8-HQ5-SAOF-3 | $C_{33}H_{28}N_5O_{15}S_3$ | 830 | 18.0 | 14,940 | 1.32 | 0.254 | 0252 | 0.506 |
| 8-HQ5-SAOF-4 | $C_{43}H_{45}N_6O_{19}S_4$ | 1067 | 18.5 | 19,739 | 1.49 | 0.252 | 0.251 | 0.503 |

cases satisfy the relation $K_1 + K_2 = 0.5$ favorably.[11] It was observed that copolymer having higher ($\overline{Mn}$) shows higher value of $[\eta]$, which are in good agreement with earlier coworkers.[11,12]

The UV–visible spectra (Fig. 5) of all the 8-HQ5-SAOF copolymer samples in pure DMSO were recorded in the region 200–850 nm at a scanning rate of 100 nm min$^{-1}$ and a chart speed of 5 cm min$^{-1}$. All the four 8-HQ5-SAOF copolymer samples gave two characteristics bands at 310–330 nm and 240–260 nm. These observed positions for the absorption bands have different intensities. The more intense band 240–260 nm is due to ($\pi \rightarrow \pi^*$) allowed transition of quinoline ring, which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromospheres groups like $\rangle$C=C, $\rangle$C=N, and —SO$_3$H groups and the less intense 310–330 nm may be due to ($n \rightarrow \pi^*$) forbidden transition in $\rangle$C=N and —SO$_3$H groups. Thus $\pi \rightarrow \pi^*$ transition indicates the presence of aromatic nuclei and $n \rightarrow \pi^*$ transition indicates the presence of —NH and —OH group. The bathochromic shift from the basic value viz. 230 nm and 310 nm may be due to combined effect of conjugation (due to chromospheres) and phenolic hydroxyl groups as well as —NH groups (auxochrome). The hyperchromic effect is due to the presence of —OH and —NH groups, which act as auxochrome.[13] From the spectra of 8-HQ5-SAOF copolymer resins, it is observed that $\varepsilon_{max}$ value gradually increases in the order of 8-HQ5-SAOF-1 < 8-HQ5-SAOF-2 < 8-HQ5-SAOF-3 < 8-HQ5-SAOF-4. The increasing order of $\varepsilon_{max}$ values may be due to introduction of more and more aromatic ring and auxochrome phenolic —OH and —NH groups in the repeated unit of the copolymer resins or it may due to distortion of the chromospheres brought about by ring strain or by steric hindrance or it may due to increase in possibility of interaction of nonbonding electrons to the $\pi$ electrons system. The observation is found to be in good agreement with proposed structures of above copolymer resins (Fig. 2).

The IR spectral data are tabulated in Table III and IR spectra of all four 8-HQ5-SAOFcopolymer are depicted in Figure 6. The IR spectral studies revealed that all these copolymer gave rise to nearly similar pattern of spectra. A broad absorption band appeared in the region 3500–3540 cm$^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxyl (—OH) groups exhibiting intramolecular hydrogen bonding.[14] A sharp strong peak at 1500–1550 cm$^{-1}$ may be ascribed to aromatic skeletal ring. The bands obtained at 1010–1016 cm$^{-1}$ suggest the presence of methylene (—CH$_2$) bridge.[15] The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/weak absorption bands appeared at 956–960, 1070–1080, 1140–1150 and 1120–1130 cm$^{-1}$, respectively. The presence of sharp and strong band at 3150–3160 cm$^{-1}$ indicates the presence of —NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.
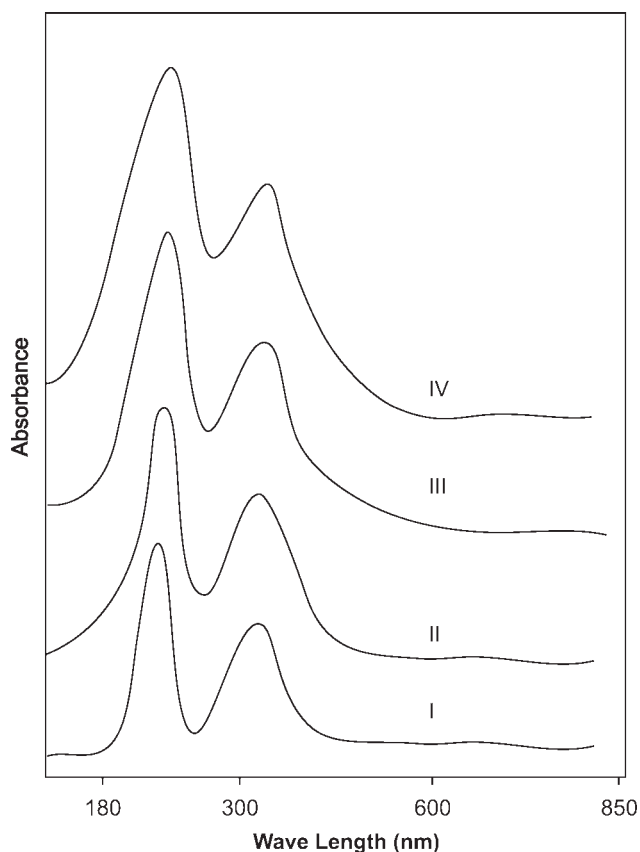


**Figure 5** UV–visible spectra of 8-HQ5-SAOF copolymer resins.

TABLE III
IR Frequencies of 8-HQ5-SAOF Copolymer Resins

| Observed band frequencies (cm$^{-1}$) | | | | Assignment | Expected band frequencies (cm$^{-1}$) |
|---|---|---|---|---|---|
| 8-HQ5-SAOF-I | 8-HQ5-SAOF-II | 8-HQ5-SAOF-III | 8-HQ5-SAOF-IV | | |
| 3500 (b,st) | 3505 (b,st) | 3507 (b,st) | 3510 (b,st) | —OH phenolic intermolecular hydrogen bonding | 3750–3200 |
| 3150 (b,st) | 3153 (b,st) | 3158 (b,st) | 3160 (b,st) | ⟩NH stretching (amide/imide) | 3200–3000 |
| 1650 (sh,st) | 1653 (sh,st) | 1657 (sh,st) | 1660 (sh,st) | ⟩C—O stretch (oxamide moiety) | 1600–17500 |
| 1500 (sh,st) | 1522 (sh,st) | 1538 (sh,st) | 1550 (sh,st) | Aromatic ring (substituted) | 1500–1600 |
| 1412 (m,sh) | 1412 (m,sh) | 1413 (m,sh) | 1413 (m,sh) | SO$_3$H stretching | 1410 |
| 1010 (sh,st) | 1013 (sh,st) | 1015 (sh,st) | 1016 (sh,st) | ⟩CH$_2$, i.e., methyl stretching | 1270–900 |
| 1302 (sh,st) | 1305 (sh,st) | 1308 (sh,st) | 1310 (sh,st) | —CH$_2$ bending (wagging and twisting) | 1280–1370 |
| 1203 (sh,st) | 1203 (sh,st) | 1204 (sh,st) | 1204 (sh,st) | | |
| 810 (sh) | 812 (sh) | 813 (sh) | 815 (sh) | —CH$_2$— plane bending | 1150–800 |
| 956 (m) | 957 (m) | 958 (m) | 960 (m) | 1,2,3,5 substitution in aromatic ring | 950 |
| 1070 (m) | 1073 (m) | 1075 (m) | 1075 (m) | | 1058 |
| 1140 (m) | 1144 (m) | 1148 (m) | 1150 (m) | | 1125 |
| 1120 (sh) | 1123 (sh) | 1124 (sh) | 1124 (sh) | | 1122 |

sh, sharp; b, broad; st, strong; m, medium; w, weak.

The NMR spectra of all four 8-HQ5-SAOF copolymers were scanned in DMSO-$d_6$ solvent. The spectra are given in Figure 7 and the spectral data are given in Table IV. From the spectra, it is revealed that all 8-HQ5-SAOF copolymer gave rise to different pattern of $^1$H-NMR spectra, because each of 8-HQ5-SAOF 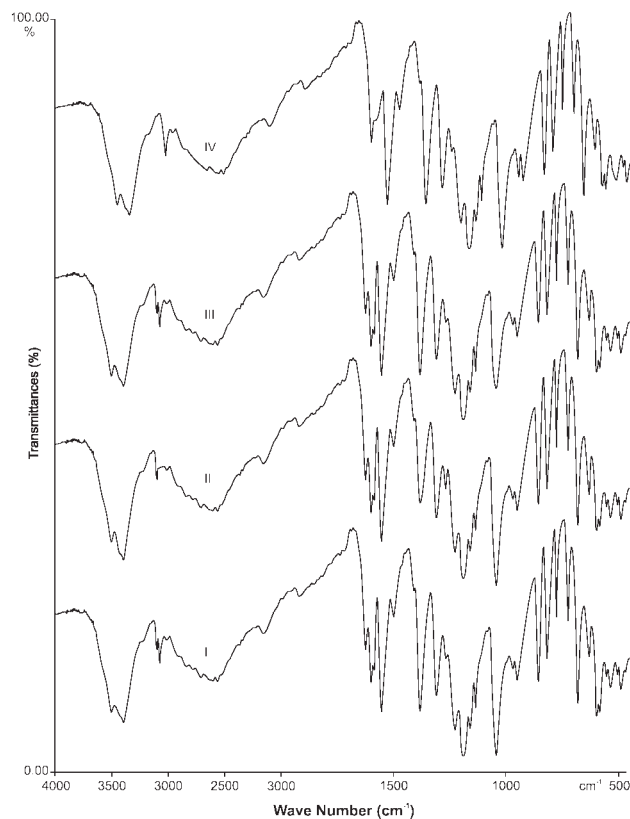copolymer possesses set of proton having different electronics environment. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature.[16] The singlet obtained in the region of 5.12–4.92 (δ) ppm may be due to the methylene proton of Ar—CH$_2$—N moiety. The signals in the region of 7.30–7.39 (δ) ppm are attributed to protons of —NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region of 8.21–8.18 (δ) ppm may be attributed to aromatic proton (Ar—H). The signals in the range of 9.08–9.02 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic —OH indicates clearly the intramolecular hydrogen bonding of —OH group.[17,18] The signals in the range of 10.02–10.08(δ) ppm are attributed to proton of —SO$_3$H groups.

SEM enables imaging to surface feature of 10–10$^5$ times magnification and resolution of features down to 3–100 nm depending upon the sample. Surface analysis has been found to be of great use in understanding the surface features of the materials. The morphology of the synthesized and purified terpolymer resins under investigation has been reported by scanning electron microscopy, which is shown in Figure 8. The white bar at the bottom of the SEM microscopy represents the scale. The morphology of the terpolymer resin shows fringed, scattered, and miscellaneous model of the crystalline amorphous structure.[19] The fringier and scattered represent transition material between the crystalline and amorphous phases. This tends to draw attention away from the details of the fine structure and gives little insight into the structure of large entities such as spherulites. The SEM photographs exhibit such spherulites which are the aggregate of crystalline
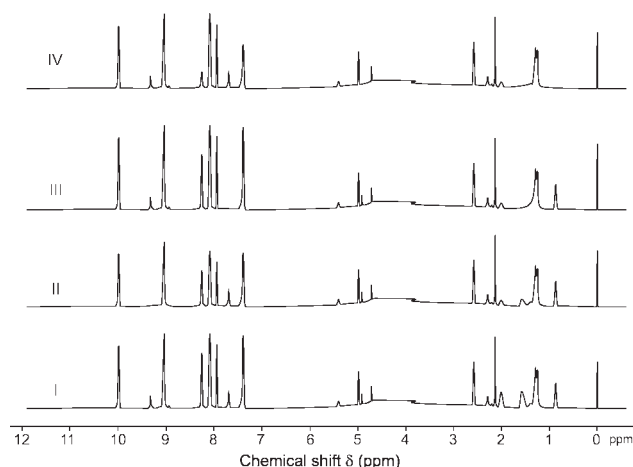


Figure 6 IR Spectra of 8-HQ5-SAOF copolymer resins.

**Figure 7** ¹H-NMR Spectra of 8-HQ5-SAOF copolymer resins.

present along with the some amorphous regions. The amorphous region shows secondary structural feature such as corrugations and having shallow pits. The spherulites structure of the 8-HQ5-SAOF copolymer resin indicates the presence of crystalline structure of the polymer. The corrugation in the surface area with deep pits shows the amorphous nature of the terpolymers. Thus SEM micrographs of 8-HQ5-SAOF-1 copolymer resin indicate the presence of transition structures between crystalline and amorphous. The amorphous nature depends on acidic character of reacting monomers. In the presence copolymer resins, the monomers having more acidic character (as 8-hydroxyquinoline 5-sulphonic acid is acidic in nature) and, therefore, shows more amorphous nature. The more amorphous nature shows more ion-exchange property; hence, the 8-HQ5-SAOF copolymer resin can be used as ion exchanger in the purification purpose.

On the basis of all the physico-chemical and spectral evidences, and foregoing results and discussion, the most probable structures have been proposed for 8-HQ5-SAOF copolymer resins under investigations as shown in Figure 2.

## Ion-exchange property

With a view to ascertain the selectivity of the 8-HQ5-SAOF-I copolymer resin for the selected metal

ion, it was studied the influence of various electrolytes on selectivity, the rate of metal uptake and the distribution ratios of the metal ions between the copolymers and solution containing metal ions. This study made certain generalization about the behavior of the copolymer resin sample.[20,21]

### Influence of different electrolyte on the metal ion uptake

The data presented in Figures 8–11 indicate that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentrations of electrolyte present in the solution. In the presence of perchlorate ($ClO^{4-}$), Chloride ($Cl^-$), and nitrate ($NO^{3-}$) ions the uptake of $Fe^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions increase with increasing concentration of the electrolyte, whereas in the presence sulfate ion ($SO_4^{2-}$), it is decreased with increasing concentration of electrolyte. Moreover, the uptake of $Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions decreases with increasing concentrations of the $Cl^-$, $NO^{3-}$, $ClO_4^-$ and $SO_4^{2-}$, which can be explained on the basis of the stability constant of the complexes of metal ions with ions of electrolytes.[20] It has been noticed that the lower pH was not suitable when concentrated electrolytes were used. The result shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration of the electrolyte increases, the ionization decreases, number of ligands (negative ions of electrolyte) decrease in the solution which forms the complex with less number of metal ions, and therefore, more number of ions may available for adsorption. Hence, on increasing concentration, uptake of metal ions may be increased, which is the normal trend. This normal trend disturbed due to the formation of stable complex with more number of metal ions with electrolyte ligands, which decrease the number of metal ions available for adsorption, hence uptake decreases.
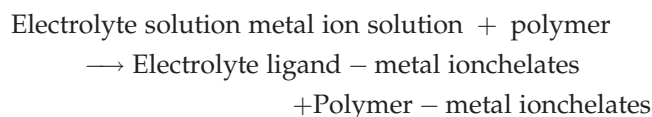
Electrolyte solution metal ion solution + polymer

⟶ Electrolyte ligand − metal ionchelates

+Polymer − metal ionchelates

### TABLE IV
**¹H-NMR Spectral Data of 8-HQ5-SAOF Copolymer Resins**

| Observed chemical shift (δ) ppm | | | | | |
|---|---|---|---|---|---|
| 8-HQ5-SAOF-I | 8-HQ5-SAOF-II | 8-HQ5-SAOF-III | 8-HQ5-SAOF-IV | Nature of proton assigned | Expected chemical shift (δ) ppm |
| 5.12 | 5.05 | 4.98 | 4.92 | Methylene proton of Ar—CH₂—N moiety | 3.00–3.5 |
| 7.30 | 7.34 | 7.37 | 7.39 | Proton of —NH bridge | 5.00–8.00 |
| 8.21 | 8.19 | 8.19 | 8.18 | Aromatic proton (Ar—H) | 6.2–8.5 |
| 9.08 | 9.07 | 9.05 | 9.02 | Proton of phenolic —OH involved intramolecular hydrogen bonding | 8.00–10.00 |
| 10.00 | 9.99 | 10.00 | 9.99 | Proton of SO₃H group | 9–10 |
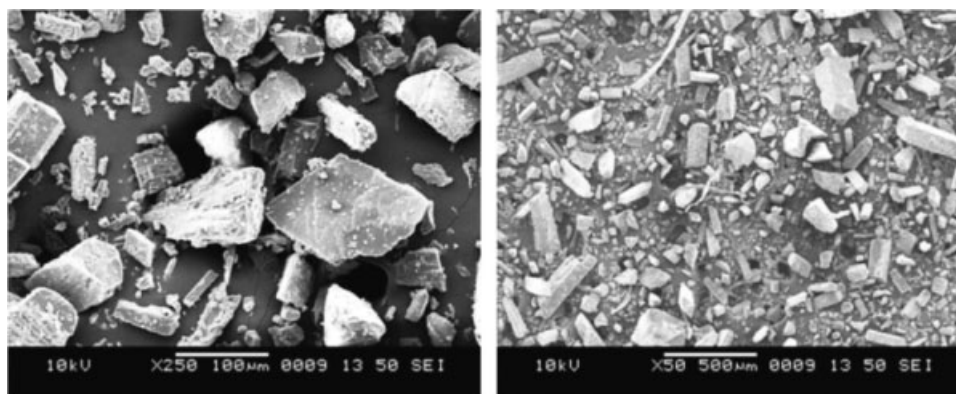
**Figure 8** SEM micrographs of 8-HQ 5-SAOF-1 copolymer resin.

If electrolyte ligand–metal ion complex is weak than polymer metal ion chelates, the more metal ion can form complex with polymer, hence uptake of metal ion is more. If this complex is strong than polymer–metal ion chelates, more metal ions form strong complex with electrolyte ligand which make metal uptake capacity lower by polymer

The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the 8-HQ5-SAOF-1 copolymer resin is found to be higher when comparing with the other polymeric resins.[22]

Evaluation of rate of metal ion uptake

The data presented in Figure 13 indicates that the rate of metal ion uptake depends upon nature of metal ion.[21] The rate of metal ions means the change in concentration of metal ion in aqueous solution containing copolymer sample. The rate of metal uptake was determined to find out the shortest pe-

riod of time for which equilibrium could be carried while operating as close to equilibrium conditions as possible. As shaking time increases, the polymer gets more time for adsorption, hence uptake increases. The result shows the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different mental ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions require about 3 h for the establishment of the equilibrium (95–100% metal uptake), whereas Cu (II), Ni (II), Co (II), and Zn (II) ions required about 5 or 6 h.[21] The rate of metal ions uptake thus follows the order Cu (II) > Ni (II) > Co (II) ≈ Zn (II) > Cd (II) ≈ Pb (II) for the copolymer (Fig. 12). The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post-transition metal ions such as Cd (II) exhibits other trend, the rate of uptake is in the comparable that of Pb (II) because of difference in the orbital.
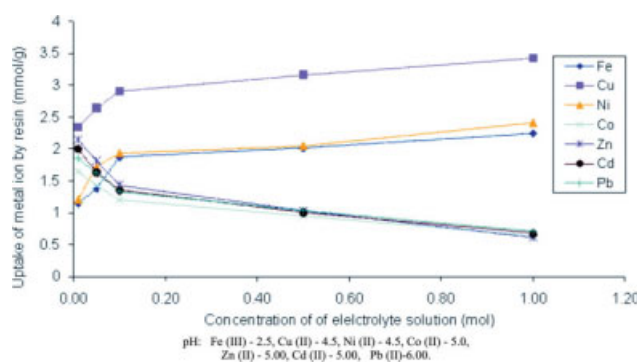


**Figure 9** Uptake of several metal ions by 8-HQ5-SAOF-1 copolymer resin at five different concentrations of electrolyte solution NaNO₃. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
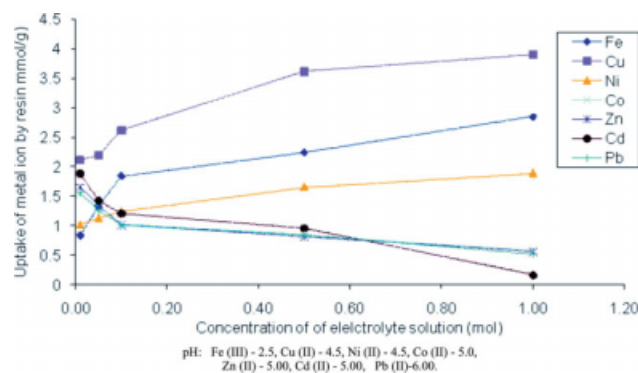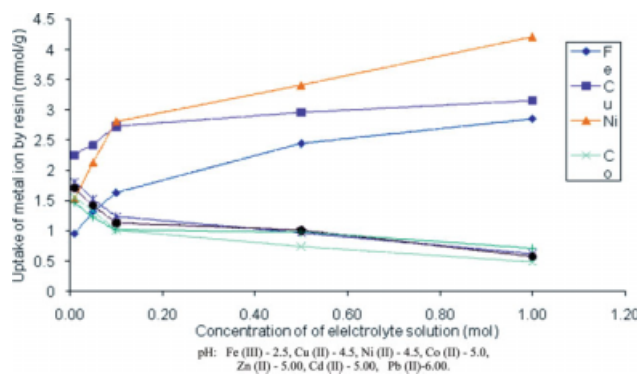


**Figure 10** Uptake of several metal ions by 8-HQ5-SAOF-1 copolymer resin at five different concentrations of electrolyte solution NaCl. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

**Figure 11** Uptake of several metal ions by 8-HQ5-SAOF-1 copolymer resin at five different concentrations of electrolyte solution NaClO$_4$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



**Figure 13** Comparison of the rate of metal ion uptake by 8-HQ5-SAOF-I copolymer resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

## Evaluation of the distribution rate of metal ions at different pH

The data presented in Figure 13 indicates that the relative amount of metal ion taken up by 8-HQ5-SAOF-I copolymer resin at equilibrium increases with increasing pH of the medium; however, the magnitude of increase is different for different metal cations.[22] The result indicates that copolymer resin sample takes up $Fe^{3+}$ ion more selectively than any other ions under study. The order of distribution ratio of metal ions measured in pH range 2.5–6.5 is found to be $Fe^{3+} > Cu^2 \approx Ni^{2+} > Co^{2+} \approx Zn^{2+} > Cd^{2+} \approx Pb^{2+}$. The study was carried from pH 2.5–6.5 to prevent hydrolysis of metal ions at higher pH. For metal ion $Fe^{3+}$, the highest working pH is 3, where distribution ratio is medium, because $Fe^{3+}$ forms octahedral complex with electrolyte ligand, showing crowding effect (steric hindrance), which may lower the distribution ratio of $Fe^{3+}$ ions. The value of distribution ratio at particular pH thus
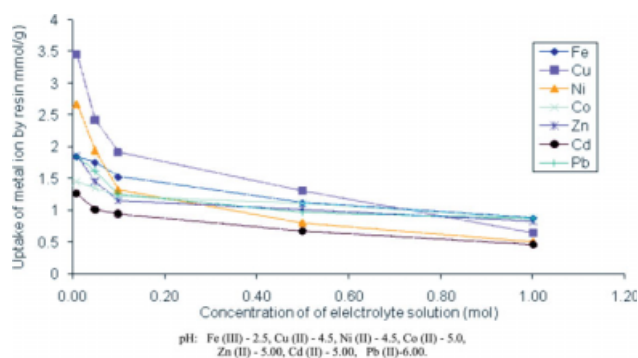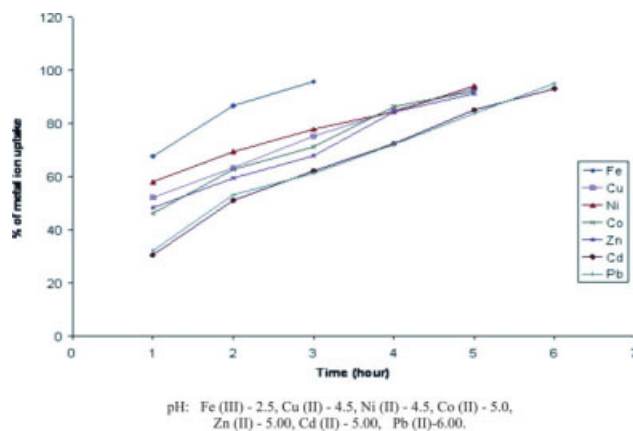
depends upon the nature and the stability of chelates with particular metal ion. The data of distribution ratio show a random trend in certain cases. This may be due to the amphoteric nature of the 8-HQ5-SAOF-1 resin.

From the result, it reveals that with decrease in atomic number, the ion uptake capacity is increased. In case of Cd (II) and Pb (II), purely electrostatic factors are responsible. The ion uptake capacity of Cd (II) is lower owing to the large size of its hydrated ion than that of Cu (II). The steric influence of the methyl group and hydroxyl group in 8-HQ5-SAOF-1 resin is probably responsible for their observed low binding capacities for various metal ions. The higher value of distribution ratio for Cu (II) and Ni (II) at pH 4–6.0 may be due to the formation of more stable complex with chelating ligands. Therefore, the polymer under study has more selectivity of $Cu^{2+}$ and $Ni^{2+}$ ions at pH 4.0–6.0 then other ions, which form rather weak complex. Although at pH 3, the



**Figure 12** Uptake of several metal ions by 8-HQ5-SAOF-1 copolymer resin at five different concentrations of electrolyte solution Na$_2$SO$_4$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
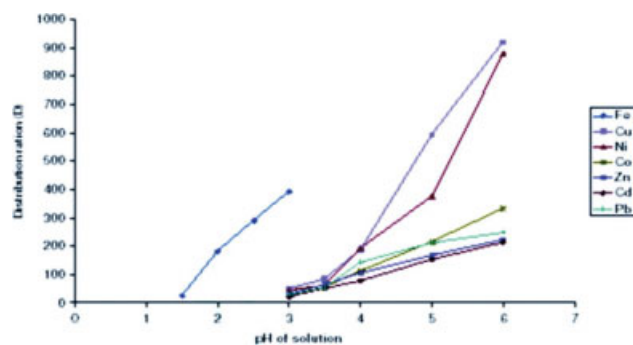


**Figure 14** Distribution ratio (D) of various metal ions as function of different pH by 8-HQ5-SAOF-I copolymer resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymer has more selectivity of $Fe^{3+}$ ions because at this pH $Fe^{3+}$ ion has highest distribution ratio than other metal ions (Fig. 14). The order of distribution ratio of metal ions measured in pH range 2.5–6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Co (II) ≈ Zn (II) > Cd (II) ≈ Pb (II). Thus, the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions.

## CONCLUSIONS

Copolymer 8-HQ5-SAOF, based on the condensation reaction of 8-hydroxyquinoline 5-sulphonic acid, oxamide and formaldehyde in the presence of acid catalyst, was prepared by using varied molar proportion for the reacting monomers. Copolymer 8-HQ5-SAOF is yellow in color, partly soluble in methanol, and completely soluble in DMF and DMSO, and insoluble in almost all other common solvents. From the elemental analysis, UV–visible, FTIR, NMR spectral studies, the proposed structure of the 8-HQ5-SAOF copolymer resins were determined. The copolymer resins can be used as cation ion-exchangers for the separation of transition metal ions. The resins can also be used for removal of toxic metals. The resins can form polychelates with certain metal ions. Therefore, it can be used for the separation of metal ions from the mixture.

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