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Removal of hazardous metal ions from the polluted water by Copolymer Resin-III Derived from 8-Hydroxyquinoline 5-SulphonicAcid, Oxamide and Formaldehyde

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ABSTRACT

Copolymer resin (8-HQ5-SAOF-III) synthesized by the condensation of 8-hydroxyquinoline5-sulphonic acid and oxamide with formaldehyde in the presence of acid catalyst, was proved to be selective chelation ion-exchange copolymer for certain metals. The chelating ion-exchange properties of this copolymer were studied for Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) ions in the form of their metal nitrate solutions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involved in the measurements of the distribution of a given metal ion between the copolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range, shaking time and in media of various ionic strengths of different electrolytes. The copolymer showed a higher selectivity for Fe (III), Cu (II), and Ni (II) ions than for Co (II), Zn (II), Cd (II) and Pb (II) ions. Distribution ratios (D) of metal ions were found to be increased by increasing pH of the solutions; hence the resin can be used to recover certain metal ions from waste solutions and used for the purpose of purification of waste water and removal of iron from boiler water. The ion-exchange capacity of metal ions has also been determined experimentally and compare with other commercial resins. Besides ion exchange properties, the copolymer resin was also characterized by Viscometric measurements in dimethyl sulphoxide (DMSO), Uv-visible absorption spectra in non-aqueous medium, infra-red (IR) spectra and nuclear magnetic resonance (NMR) spectra. The physico-chemical and spectral methods used to elucidate the structure of 8-HQ5-SAOF –III resin. The morphology of the copolymer was studied by scanning electron microscopy (SEM); showing amorphous nature of the resin therefore can be used as a selective ion-exchanger for certain metal ions.

Keywords: Adsorption, degree of polymerization (DP), ion exchangers, metal-polymer complexes, resins, selectivity.

INTRODUCTION

Ion-exchange technique can remove traces of ionic impurities from water/process liquors and gives out a product of ultra pure quality in a simple efficient and techno-economically viable manner. Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radioisotopes and find large applications in water treatment and pollution control [1,2].Various hydroxyl benzoic acid-formaldehyde and 4-hydroxyacetophenone-biuret- formaldehyde copolymers have been reported and found use as ion-exchangers [3-5]. In an earlier communication [6-8] from this department a number of such copolymers have been reported. However, no work has been carried out on the synthesis, characterization and ion-exchange properties of the copolymer resins from 8-hydroxyquinoline5-sulphonic acid, oxamide and formaldehyde. The purpose of present study, is to explore the adsorption behaviour of seven metal ions Fe^{2+}, Cu^{2+}, Ni^{2+}, CO^{2+}, Zn^{2+}, $Cd^{2+}$and Pb^{2+} on the newly synthesized copolymer resin 8-HQ5-SAOF –III at different pH values, different concentration of different electrolytes and at different shaking time intervals. The adsorption behaviour of these metal ions is based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. The copolymer resin under investigations is found to be cation exchanger having both ion-exchange group and chelating group in the same polymer matrix and the resin can be used selectively for the purpose of purification of waste water. One of the important applications of chelating and functional polymer is its capability to recover metal ions from west solution. Hence the chelating ion exchange property of the 8-HQ5-SAOF –III copolymer resin was also reported for specific metal ions.

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 capacity and selectivity having physical and chemical stabilities [9, 10].

Trade Name	Functional Group	Polymer Matrix	Ion-exchange Capacity ($mmol.g^{-1}$)
Amberlite IR-120	$-C_6H_4SO_3H$	Polystyrene	5.0-5.2
Duolite C-3	$-CH_2SO_3H$	Phenolic	2.8-3.0
Amberlite IRC-50	-COOH	Methacrylic	9.5
Duolite ES-63	$-OP(O)(OH)_2$	Polystyrene	6.6
Zeocarb-226	-COOH	Acrylic	10.00
Dowex-1	$-N(CH_3)_3Cl$	Polystyrene	3.5
Amberlite IRA-45	$-NR_2$, -NHR, $-NH_2$	Polystyrene	5.6
Dowex-3	$-NR_3$, -NHR, $-NH_2$	Polystyrene	5.8
Allassion A WB-3	$-NR_2$, $-N^+R_3$	Epoxy-Amine	8.2

The present paper has been described the development of a novel ion-exchanger resin process suitable for the desalination of waste water which is high in Fe (II), Ni (II) and Cu (II) ions, to meet effluent discharge specifications. Ion Exchange column of 8-HQ5-SAOF–III 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 [11].There are many useful reports on ion-exchange separation methods in chemical processes [12, 13]. Some commercially available ion-exchange resins are given below

MATERIALS AND METHODS

The chemicals used were all of A.R. or chemically pure grade and are procured from the market.

Synthesis of 8-HQ5-SAOF –III copolymer resin

The 8-HQ5-SAOF–III copolymer resin was prepared by condensing 8-hydroxyquinoline5-sulphonic acid (7.29, 0.3 mol) and oxamide (0.88gm, 0.1mol) with formaldehyde (14 ml of 37% solution, 0.4 mol) in the presence of 2M HCl (200ml) as a catalyst at 140ºC in an oil bath for 6 hrs with occasional shaking to ensure thorough mixing. The solid resinous product obtained was removed immediately from the flask. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. Then it was extracted with diethyl ether to remove excess of 8-hydroxyquinoline5-sulphonic acid -formaldehyde copolymer which might be present along with 8-HQ5-SAOF –III copolymer resin. The purified copolymer resin was finely ground and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 80%.The proposed structure of 8-HQ5-SAOF –III copolymer resin has been assigned in Fig.1.

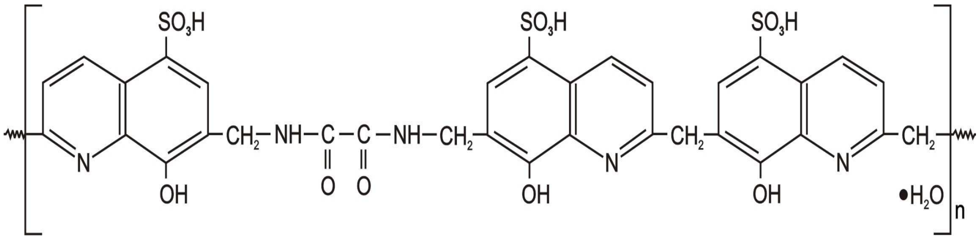


Fig.1. Structure of representative 8-HQ5-SAOF-III copolymer resin

Characterization of the copolymers

Electron absorption spectrum of copolymer resin in DMSO (spectroscopic grade) was recorded on shimadzu double beam spectrophotometer in the range of 200 to 850 nm**,** Infra-red spectra of 8-HQ5-SAOF–III copolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000-400 cm^{-1}**,** Nuclear Magnetic Resonance (NMR) spectra of newly synthesized copolymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d$_6$ at sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. SEM has been scanned by FEI-Philips XL-30 electron microscope.

Ion-exchange properties

The ion-exchange property of the 8-HQ5-SAOF –III copolymer resin was determined by the batch equilibrium method [14,15].

Determination of metal uptake in the presence of various electrolytes and different concentration

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for 24 hrs at 30ºC. To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 30ºC for 24 hrs. The polymer was then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylene diamine tetra-acetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes [14, 15]. Metal ion, its pH range, buffer used, indicator used and colour change are given in Table 1. The metal ion uptake can be determined as,

Metal ion adsorbed (uptake) by resin = (X-Y) Z millimols / gm.

Where,
‘Z’ ml is the difference between actual experimental reading and blank reading.
‘X’ mg is metal ion in the 2ml 0.1M metal nitrate solution before uptake.
‘Y’ mg is metal ion in the 2ml 0.1M metal nitrate solution after uptake.

Table 1 Data of experimental procedure for direct EDTA titration

Metal Ion	pH range	Buffer used	Indicator used	Colour change
Fe(III)	2-3	Dil.HNO_3/dil.NaOH	Variamine blue	Blue-Yellow
Cu(II)	9-10	Dil.HNO_3/dil.NaOH	Fast sulphone black	Purple-Green
Ni(II)	7-10	Aq.NH_3/NH_4Cl	Murexite	Yellow-Violet
Co(II)	6	Hexamine	Xylenol orange	Red-Yellow
Zn(II)	10	Aq.NH_3/NH_4Cl	Salochrom black	Wine Red-Blue
Cd(II)	5	Hexamine	Xylenol orange	Red-Yellow
Pb(II)	6	Hexamine	Xylenol orange	Red-Yellow

By using this equation the uptake of various metal ions by resin can be calculated and expressed in terms of millimols per gram of the copolymer.

Estimation of rate of metal ion uptake as function of time

In order to estimate the time require to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 30ºC (in the presence of 25ml of 1M $NaNO_3$ solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 hrs [15]. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium and it can be defined by the following relationship.

The percent amount of metal ions taken up at different time is defined as.

$$\text{Percentage of amount of metal ion taken up at different time} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

Percentage of metal ion adsorbed after 1 hr = (100X) / Y

Where,
'X' mg of metal ion adsorbed after 1 hr and 'Y' mg of metal ion is adsorbed after 25 hrs, then by Using this expression, the amount of metal adsorbed by polymer after specific time intervals was calculated and expressed in terms of percentage metal ion adsorbed. This experiment was performed using 0.1M metal nitrate solution of Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+},Cd^{2+} and Pb^{2+}.

Evaluation of the distribution of metal ions at different pH
The distribution of each one of the seven metal ions i.e., Cu (II), Ni (II), Co (II), Zn (II), Cd (II), Pb (II), and Fe (II) between the polymer phase and the aqueous phase was determined at 30^0C and in the presence of 1M $NaNO_3$ solution. The experiments were carried out as described above at different pH values. The distribution ratio, D, is defined by the following relationship [16].

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

$$\text{Metal ion adsorbed (uptake) by the resin} = \left(\frac{ZX}{Y}\right)\frac{2}{0.025}$$

Where,
'Z'= is the difference between actual experiment reading and blank reading,
'C' = gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,
'Y' = gm of metal ion in 2ml of metal nitrate solution after uptake.

RESULTS AND DISCUSSION

The 8-HQ5-SAOF –III copolymer resin was found to be yellow in colour. The copolymer is soluble in DMF, DMSO and is insoluble in almost all other organic solvents.

Electronic Spectra
The UV–visible spectra (Fig. 3) of the 8-HQ5-SAOF –III copolymer sample in pure DMSO was 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}. The 8-HQ5-SAOF –III copolymer sample displayed two characteristic broad bands at 240-260 nm and 310-330 nm. Both of these bands seem to be merged with each other because of their very broad nature. These observed position for the absorption bands indicate the presence of a carbonyl (C=O; ketonic) group having a carbon–oxygen double which is in conjugation with -NH group**.** The former band (more intense) can be accounted for by $n\rightarrow\pi^*$ transition while the latter band (less intense) may be due to a $\pi\rightarrow\pi^*$ transition [13]. The bathochromic shift (shift towards longer wave length) from the basic values of the >C=O group viz. 320 and 240 nm, respectively may be due to the combined effect of conjugation of >C=O and NH groups and phenolic hydroxyl group (auxochrome) and quinoline ring [17].

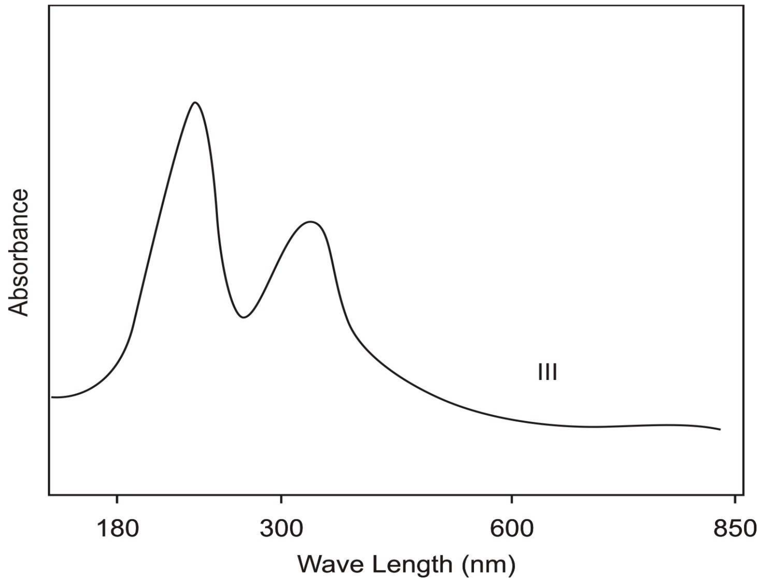


Fig.3. Electronic absorption spectra of 8-HQ5-SAOF-III copolymer resin

Infrared Spectra

Infrared spectra of the 8-HQ5-SAOF –III copolymer resin is shown in Fig.4 and IR spectral data are tabulated in Table 4. Very broad band appeared in the region 3506cm^{-1} may be assigned to the stretching vibration of phenolic –OH groups exhibiting intermolecular hydrogen bonding between -OH and >C=O and NH group of amide [18]. The bands obtained at 1385 cm^{-1} suggest the presence of methylene (-CH_2-) bridges. A sharp strong peak at 1552 cm^{-1} may be ascribed to aromatic skeletal ring breathing modes. The 1,2,3,5 tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium/weak absorption bands appeared at 957, 1072 and 1141cm^{-1} respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3110 cm^{-1} which seems to be merged with very broad band of phenolic hydroxy group.

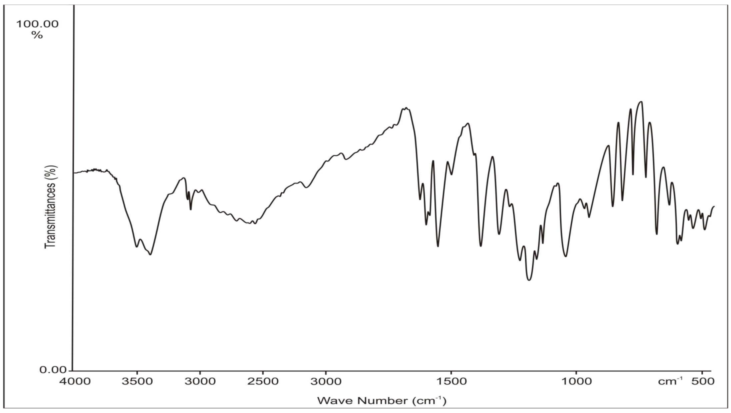


Fig.4. Infrared spectra of 8-HQ5-SAOF-III copolymer resin

Table 4 IR Frequencies of 8-HQ5-SAOF-III copolymer Resin

Observed band frequencies (cm^{-1}) 8-HQ5-SAOF-III	Assignment	Expected band frequencies (cm^{-1})
3506(b,st)	-OH phenolic intermolecular hydrogen bonding	3750-3200
3398(b,st)	>NH stretching (amide/imide)	3400-3100
3102(m)	Aryl C-H stretching	3200-3000
3081(sh)	=C-H stretching	3000-3150
2567(m)	-C-H stretching of CH_2 group	2800-2500
1652(sh,st)	>C=O stretch (oxamide moiety)	1750-1600
1552(sh,st)	Aromatic ring (substituted)	1600-1500
1557(sh,st)	-NH bending of secondary amide	1570-1450
1413(m,sh)	SO_3H stretching	1410
1385(sh,st)	-CH_2- bridge	1390-1370
1312(sh,st)	-CH_2 bending (wagging & twisting)	1370-1280
1303(m)	-CH_2- plane bending	1300-1250
857(sh)	Tetrasubtituted aromatic ring	830
957(m) 1072(m) 1141(m)	1,2,3,5 substitution in aromatic ring	950 1058 1125

sh=sharp; b=broad; st= strong; m= medium; w=weak

Nuclear Magnetic Resonance spectra

The NMR spectrum of the copolymer was scanned in DMSO-d_6. The spectrum is given in Fig.5. The spectral data are given in Table 5. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [19]. The medium singlet at 2.53-2.59 (δ) ppm may be due to the methylene proton of Ar-CH_2 bridge. The singlet obtained in the region of 8.97 (δ) ppm may be due to the methylene proton of Ar-CH_2-N moiety. The signals in the region 7.45 (δ) ppm are attributed to protons and –NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region at 6.94 (δ) ppm may be due to terminal methylene group. The signals in the range at 9.04 (δ) ppm may be due to phenolic hydroxy protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding on -OH group [20]. The signals in the range at 10.00 (δ) ppm may be due to SO_3H protons.

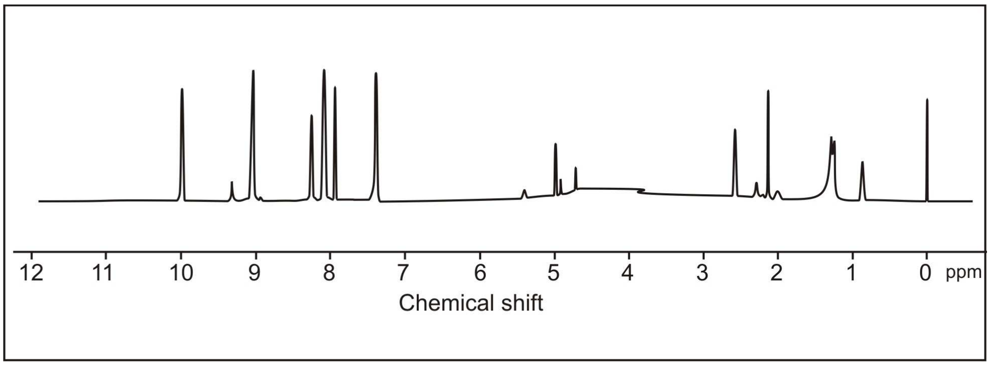


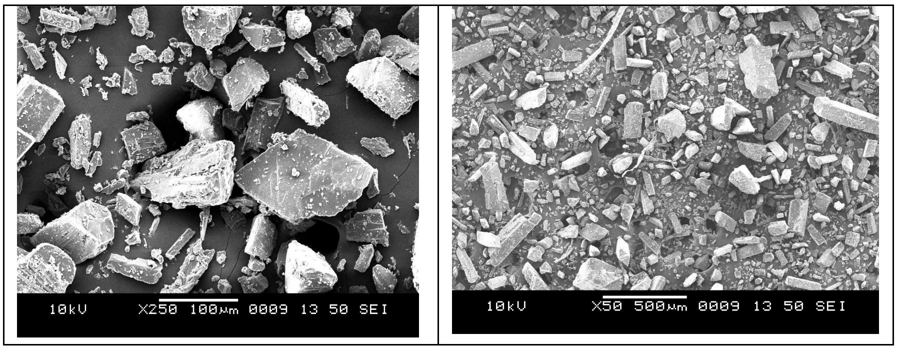
Fig.5. Nuclear magnetic resonance spectra of 8-HQ5-SAOF-III copolymer resin

Table 5 ^{1}H NMR Spectral Data of 8-HQ5-SAOF-III copolymer resin

Observed Chemical Shift	**Nature of proton assigned**	**Expected chemical shift (δ) ppm**
4.66	Methylene proton of Ar-CH_2-N moiety	3.00 to 3.5
7.45	Proton of – NH bridge	5.00 to 8.00
8.97	Aromatic proton (Ar-H)	6.2 to 8.5
9.04	Proton of phenolic – OH involved intramolecular hydrogen bonding	8.00 to 10.00
10.00	Proton of SO_3H group	9 to 10

Scanning Electron Microscopy (SEM)

Figure 6 shows the scanning electron microscopy (SEM) [20] micrographs of the pure 8-HQ5-SAOF –III copolymer sample at 1500X and 3000X magnification. The morphology of resin exhibits growth of crystals from polymers solution corresponding to the most prominent organisation in polymers on a large scale such as in size of few millimeters spherulites. The morphology of resin shows a fringed micelle model of the crystalline-amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer**.** The micrograph of pure sample shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structure but during condensation polymerization of some crystalline structure lost into amorphous nature.



(A) **(B)**

Fig.6 SEM of 8-HQ5-SAOF-III copolymer resin

On the basis of the nature and reactive position of the monomers, elemental analysis UV-visible, IR, NMR spectral studies and taking into consideration the linear structure of other phenol -formaldehyde and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for 8-HQ5-SAOF –III copolymer resin, has been shown in Fig. 1.The morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin [20], the 8-HQ5-SAOF –III copolymer resin is more amorphous in nature, hence, higher metal ion exchange capacity.

Ion-exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al were used to study ion exchange properties of 8-HQ5-SAOF –III copolymer resin. The results of the batch equilibrium study carried out with the copolymer 8-HQ5-SAOF –III is presented in Fig.6-11. Seven metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution were used. The experiments were repeated for six times and the mean standard deviations were calculated at different concentrations, shaking times and pH of the solutions and have been found to be as follows.

At different concentrations

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	0.48	0.73	0.95	0.38	0.72	0.69	0.86

At different shaking times

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	17.23	17.26	18.43	19.44	19.37	26.44	24.97

At different pH of the solutions

Metal ions	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Standard Mean deviation	453.76	425.41	214.80	156.25	63.49	79.18	92.82

The ion exchange study was carried out using three experimental variables : a) Electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium, Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymers similar to the earlier co-workers [21]. The details of experimental procedure are given below.

Effect of electrolyte and its ionic strength on metal uptake

We examined the influence of NO_3^- and SO_4^{2-} at various concentrations on the equilibrium of metal-resin interaction. Fig.7-8 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. But 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 ion chelates + Polymer - metal ion chelates

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. But 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.

In the presence of nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte [21,22]. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions increase with decreasing concentration of the sulphate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions [21]. 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 –III copolymer resin is found to be higher when comparing to the other polymeric resins [22, 23].

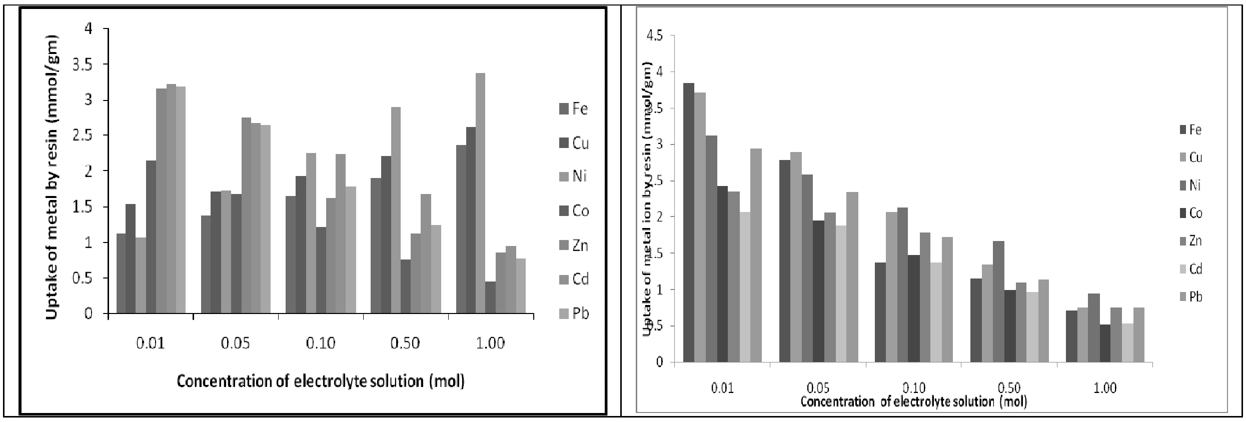


Fig.7& 8 Uptake of several metal ions by 8-HQ5-SAOF-III copolymer resin at five different concentrations of electrolyte NaNO3 solution

Estimation of the rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried to while operating as close to equilibrium conditions as possible. As shaking time increases the polymer gets more time for adsorption, hence uptake increases on the increasing in the time**.** Fig.9 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 3hrs for the establishment of the equilibrium, whereas Cu (II), Ni (II), Co (II) and Zn (II) ions required about 5 or 6 hrs [7, 8]. Thus the rate of metal ions uptake follows the order Cu (II) > Ni (II) > Co (II) ≈ Zn (II) > Cd (II) > Pb (II) for all of the copolymers [23, 24]. The rate of metal uptake may depend upon hydrated redii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Cd(II), the rate of uptake is in the comparable that of Pb (II) because of difference in 'd' orbital.

Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by Figure 10. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the 8-HQ5-SAOF –III copolymer increases with increasing pH of the medium [24, 25**]**.The magnitude of increase, however, is different for different metal cation. The study was carried from pH 2.5 to 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, since Fe^{3+} forms octahedral complex with electrolyte ligand, showing crowding effect (sterric 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 stability of chelates with particular metal ion. The data of distribution ratio show a random trend in certain cases [26]. This may be due to the amphoteric nature of the 8-HQ5-SAOF –III resin.

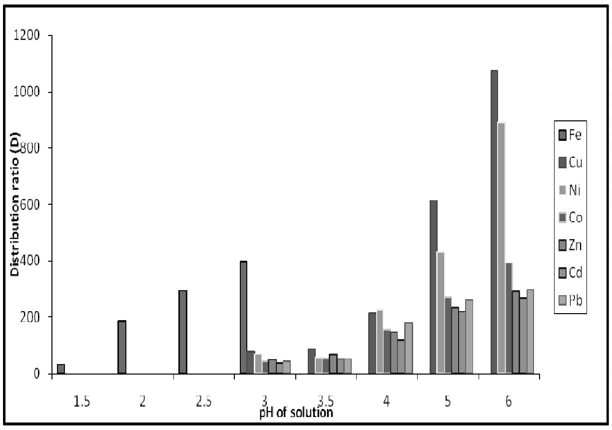


Fig.9 Comparison of the rate of metal ion uptake by 8-HQ5-SAOF-III copolymer resin

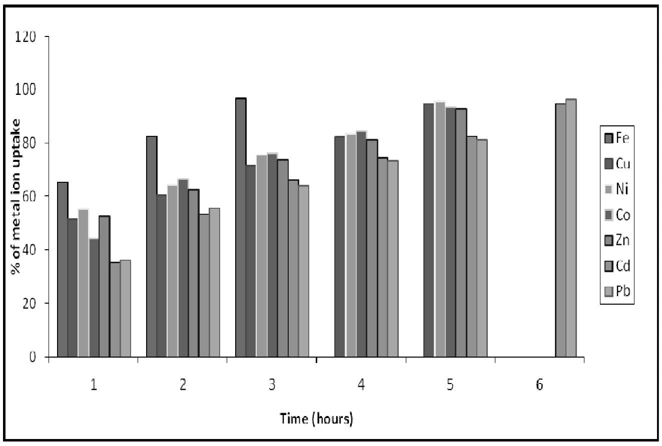


Fig.9. Comparison of the rate of metal ion uptake by 8-HQ5-SAOF-III copolymer resin at different pH

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 sterric influence of the methyl group and hydroxyl group in 8-HQ5-SAOF –III 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 to 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 to 6.0 then other ions which form rather weak complex. While at pH 3 the copolymer has more selectivity of Fe^{3+} ions. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Cd (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 [26]. For example, the result suggests the optimum pH 6.0, for the separation of Co (II) and Ni (II) with distribution ratio 'D' at 415.4 and 854.4 respectively using the p-COF copolymer resin as ion-exchanger. Similarly, for the separation of Cu (II) and Fe (III) the optimum pH is 3, at which the distribution ratio 'D' for Cu (II) is 66.1 and that for Fe (III) are 341.5. The lowering in the distribution of Fe (III) was found to be small and, hence, efficient separation could be achieved [24, 25, 26].

The strength of ion exchange capacities of various resins can be studied by comparing their ion exchange capacities. The ion exchange capacity (IEC) is a fundamental and important quantity for the characterization of any ion exchange material. It is defined as the amount of ion that undergoes exchange in a definite amount of material, under specified experimental conditions. The ion exchange capacity of 8-HQ5-SAOF –III copolymer has been calculated, which was found to be 4.3 mmol g^{-1} which indicates that 8-HQ5-SAOF –III copolymer resin is better ion exchanger than commercial phenolic and some polystyrene commercial ion exchangers.

For the strongly acidic cation exchange resin such as cross linked polystyrene sulphonic acid resins, the ion exchange capacity is virtually independent of the pH of the solutions. For weak acid cation exchangers, such as those containing carboxylate group, ionizations, occurs only in alkaline solution. Similarly weakly basic cation exchanger does not work above pH-9.

CONCLUSION

A copolymer 8-HQ5-SAOF–III based on the condensation reaction of 8-hydroxyquinoline5-sulphonic acid and oxamide with formaldehyde in the presence of acid catalyst was prepared. 8-HQ5-SAOF –III is a selective chelating ion-exchange copolymer resin for certain metals. The copolymer resin 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. The uptake of some metal ions by the resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the copolymer resin were pH dependent. From the results of distribution coefficients, it can be observed that Cu (II) has higher value of distribution ratio. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture.

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REFERENCES

[1] H. Treavor, C. Boyer Philip, *Water Research*, **40**(**2007**)2865-2876.
[2] B. Shah, A. Shah, N. Patel, *Iran Polym J*, **17**(**2008**)3-17.
[3] P.S. Lingala, L.J. Paliwal, H.D. Juneja, *Proc Nat Acad Sci Ind*, **71**(**2001**)205- 212.
[4] W.B. Gurnule, H.D. Juneja, L.J. Paliwal, *Ultra Sci* **13**(**2001**)333-339.
[5] P.K. Rahangdale, W.B. Gurnule, L.J. Paliwal, R.B. Kharat, *React Funct Polym*, **55**(**2003**)255-265,
[6] V.D. Mane, N.J. Wahane, W.B. Gurnule, *J Appl Polym Sci*, **111**(**2009**)3039.
[7] S.S. Rahangdale, Zade A.B., W.B. Gurnule, *J. Appl Polym Sci*, **108**(**2008**)747-756.
[8] M.V. Tarase, A.B. Zade, W.B. Gurnule, *J Appl Polym Sci*, **108**(**2008**)738-746.
[9] B.A. Boto, L Pawlowski, Waste Water Treatment by Ion Exchange, Chapman & Hall, New York, (**1987**).
[10] D.C. Sherrington, P. Hoge, Syntheses and Separations using Functional Polymers, John Wiley, ichester, (**1988**).
[11] D. Feng, C. Aldrich, H. Tan H, *Minerals Engineering*,**13**(**2001**)623-642,
[12] B.A. Shah, A.V. Shah, B.N. Bhandari, *Asia J hem*, **13**(**2001**)1305-1308.
[13] P.K. Roy, A.S. Rawat, V. Choudhary, P.K. Rai, *J.Appl Polym Sci*, **94**(**2004**)1771-1779.
[14] M.M. Jadhao, L.J. Paliwal, N.S. Bhave, *J App Polym Sci*, **96**(**2005**)1606- 1610.
[15] R.H. Gupta, A.B. Zade, W.B. Gurnule, *J. Appl. Polym*, **109**(**2008**)3315-3320.
[16] S.A. Patel, B.S. Shah, R.M. Patel, P.M. Patel, *Iran Polym J*, **13**(**2004**)445-453.
[17] A.B. Shah, A.V. Shah, M.P. Shah, *Iran Polym J*, **15**(**2006**)809-819.
[18] P. E. P. Michel, J.M. Barbe, H.D. Juneja, L. J. Paliwal, *Europ Polym J*, **42**(**2007**)4995-5000.
[19] M.M. Patel, M.A. Kapadia, D.P. Patel, J.D. Joshi, *React Funct Polym*, **67**(**2007**)746-757.

[20] E. Suzuki, *J Microscopy*, **208**(**2002**)153-157.
[21] M.M. Jadhao, L.J. Paliwal, N.S. Bhave, *Ind J Chem*, **44**(**2005**)542.
[22] R. Manavalan, M.M. Patel, *Micromole. Chem*., **184**(**1983**)717-723.
[23] A. Burkanudeen, M. Karunakaran, *Orient J Chem*., **18**(**2002**)65-68.
[24] W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal, R.B. Kharat, *React Funct Polym*, **55**(**2003**)255-268.
[25] MM Jadhao, Physicochemical studies of some biphenyl terpolymer, Ph D Thesis, Department of Chemistry; RTM Nagpur University Nagpur, (**2005**).
[26] R.N. Singru, A.B. Zade, W.B. Gurnule, *J App Polym Sci*, **116**(**2010**)3356-3366.