



## Removal of Toxic Metal Ions Using Ion-Binding Copolymer Resin by Batch Equilibrium Technique

Jyotsana Khobragade<sup>1</sup> and W. B. Gurnule<sup>2\*</sup>

<sup>1</sup>Dept of Chemistry, Gurunanak Science College, Ballarpur

<sup>2</sup>Dept of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur -440024, Maharashtra, India

E-mail: jdranteke@rediffmail.com, wbgurnule@gmail.com

### Abstract

Copolymer resin has been synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in the presence of acid catalyst at 122 °C was proved to be a selective chelating ion-exchange copolymer for certain metal ions. A copolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non-aqueous medium. The viscosity measurements in dimethylsulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by electronic spectra, FTIR spectra, <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra. The surface morphology of the copolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature. Ion-exchange properties of this resin was studied by batch equilibrium method for Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. The resin shows a higher selectivity for Fe<sup>3+</sup> ion over any other ions.

**Keywords:** Resin, Copolymer; Degree of polymerization; Polycondensation; Ion-exchange; Synthesis.

### Introduction

The treatment of industry wastes has been a strong concern as it continues to grow day by day. One category of such industrial pollutants includes heavy metals, often contained in the wastewater. When released into the environment, these metals can cause severe damage to the human body, including accumulative poison, brain damage, and cancer [1-3]. Several processes were accessible for heavy metal removal, including chemical precipitation, membrane, and retention technique [4-6]. An effective technique to separate the selective metal ions from wastes was greatly found to be ion-exchange process. Ion-exchange resins are polymers that can reversibly interchange the counter ions. The resins are organized into two main types depending upon the charge of the counter ions with which they can exchange. The cationic exchangers contain the negatively ionizable group which is capable of interchanging the positively charged or cationic counter ion. The anionic exchange resin interchanges the negatively charged or anionic counter ion due to the existence of the positively ionizable group. Polymeric resin was synthesized and reported for its ion-exchange characteristics [7].

However no work seems to have been carried out on synthesis and chelation ion-exchange studies of the terpolymer resins synthesized from 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde. The purpose of present study, is to explore the adsorption behavior of eight metal ions Fe<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> on the newly synthesized copolymer resins 8-QSSF-II at different pH values, different concentrations of different electrolytes and at different shaking time

intervals. The adsorption behavior of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time.

### Material and Method

#### Synthesis of 8-QSSF-II copolymer resin

The 8-QSSF-II copolymer resin was prepared by the condensation polymerization of 8-hydroxyquinoline 5-sulphonic acid (0.2mol) and semicarbazide (0.1 mol) with formaldehyde (0.3 mol) in hydrochloric acid medium at 122 ± 2 °C in an oil bath for 4 hrs. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of 8-hydroxyquinoline 5-sulphonic acid - formaldehyde copolymer, which might be present along with the 8-QSSF-II copolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 89% and the melting point is between 410-430°K. The sieved resin was used for further characterization.

#### Ion-exchange properties

The ion-exchange properties of the 8-QSSF-II copolymer resin was determined by the batch equilibrium method. We studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the copolymer and solutions.

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 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 hrs at 25°C. To this suspension was added 2 ml of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 hrs and filtered [21, 22]. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA. 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 [23]. The experiment was

repeated in the presence of other three electrolyte such as NaCl, NaClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>.

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type describe above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 25°C (in the presence of 25 ml of 1 M NaNO<sub>3</sub> solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 hrs. the rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain related to that at the state of equilibrium.

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

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

The distribution of each one of the eight metal ions i.e. Fe<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO<sub>3</sub> solution.

The experiments were carried out from 1.5 to 6 pH for Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>. In case of Fe<sup>3+</sup> the study was carried out from 1.5 to 3.0 pH. After 24 hrs the mixture was filtered, the filtrates and washing were collected. Amount of the metal ion which remained in the aqueous phase was estimated by back titration with standard EDTA solution using appropriate indicator. Similarly blank experiment was carried out without adding polymer sample. The amount of metal adsorbed by the polymer was calculated from the difference between sample and blank reading. The original metal ion concentration is known and the metal ion adsorbed by the polymers was estimated. The distribution ratio 'D' is calculated from the following equation-

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

If we consider

'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.

$$\text{Metal ion adsorbed [uptake] by the resin} = \frac{ZX}{Y} \frac{2}{0.025} = \left( \frac{ZX}{Y} \right) 133.33$$

### Results and Discussion

The resin sample was light brown in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, pyridine and concentrated H<sub>2</sub>SO<sub>4</sub>. The resin synthesized do not show sharp melting point but undergo decomposition 410-430°K. Based on the analytical data, the empirical formula of the copolymer resin is found to be C<sub>12</sub>H<sub>12</sub>N<sub>4</sub> SO<sub>5</sub>, which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen content. C =44.44% (Cal) and 44.15% (F), H=3.70% (Cal) and 3.48% (F), N =17.28%(Cal), and 17.75% (F), O= 24.69% (Cal) and 26.23%(F). The number average molecular weight (

$\overline{M}_n$ ) could be obtained by multiplying the  $\overline{DP}$  by the formula weight of the repeating unit [24, 25]. The calculated molecular weight for 8-QSSF-II resin is 58329.

Viscometric measurement was carried out in DMSO at 30°C. 8-QSSF-II resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's eq. (2) and Kraemer's, eq. (3) which is 0.29 and 0.27 respectively. In accordance with the above relations, the plot of  $\eta_{sp}/c$  and  $\eta_{rel}/c$  against C was linear giving as slopes K<sub>1</sub> and K<sub>2</sub> (0.56) respectively. The intercept on the axis of viscosity function gave the ( $\eta$ ) value in both the plots [26, 27]. The values of ( $\eta$ ) obtained from both relations were in good agreement with each other.

UV-visible spectra of 8-QSSF-II resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min<sup>-1</sup>. The spectra of these copolymers exhibit two absorption maxima in the region 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus [28, 29]. The appearance of former band (more intense) can be accounted for  $\pi \rightarrow \pi^*$  transition while the later band (less intense) may be due to  $n \rightarrow \pi^*$  electronic transition. The shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic effect i.e.  $\epsilon_{max}$  higher values.

The IR spectrum of 8-QSSF-II copolymer resin is presented in Fig. 1 and IR data are specified

in Table 2. [30-31]. A broad absorption band appeared in the region 3440-3300 cm<sup>-1</sup> may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding. The peak at 1370-1250 cm<sup>-1</sup> (-CH<sub>2</sub> plane bending), indicate the presence of methylene (-CH<sub>2</sub>) group and 1357-1349 cm<sup>-1</sup> methylene bridge in copolymer chain. The bands appeared at 1441 cm<sup>-1</sup> (Aryl C-H stretching) and 950-1125 cm<sup>-1</sup> (substituted aromatic ring) may be ascribed to aromatic ring. The band at 600-800 cm<sup>-1</sup> indicates the presence of tetra substituted aromatic ring. 1,2,3,5 substitution in aromatic ring was confirmed by the bands appeared at  $\sim$  950, 1058, 1125. The band of -NH stretching (3200-3000 cm<sup>-1</sup>) seems to be merged with very broad band of phenolic hydroxyl group.

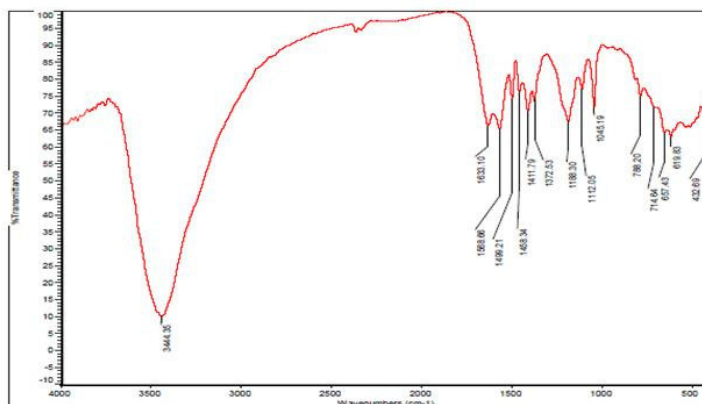


Fig. 1. FTIR Spectra of 8-QSSF-II Copolymer Resin

The NMR spectrum (Fig. 2) of 8-QSSF-II polymer was scanned in DMSO-d<sub>6</sub> solvent. The chemical shift (ppm) observed is assigned on the basis of data available in literature [32,33]. The singlet obtained in the region 3.88 - 3.95 (ppm) may be due to the methylene proton of Ar-CH<sub>2</sub>-moiety. The weak multiple signals (unsymmetrical pattern) in the region of 8.23-8.18 (ppm) may be

attributed to aromatic proton (Ar-H). The signals in the range at 9.12 to 9.15 (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 [34.35]. The signals in the range of 9.96 – 9.93 (ppm) are attributed to proton of -SO<sub>3</sub>H groups.

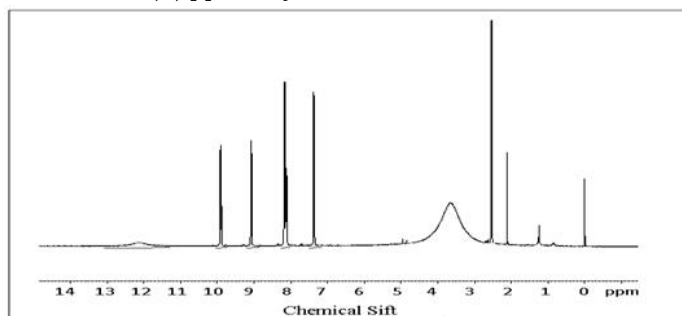


Fig. 2. Proton NMR spectrum of 8-QSSF-II copolymer resin

**Scanning electron micrographs**

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron micrographs at different magnification, which is shown in Fig. 3(a) and 3(b). It gives the information of surface topology and defect in the structure. The resin appeared to be dark drawn in colour. The morphology of polymer resin shown spherule and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 8-QSSF-II copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But

the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits, which is shown Fig.3 (a,b.). Due to the deep pits, resin exhibits higher exchange capacity for  $Pb^{2+}$  ions (as well as other many metal ions). This could be the reason of bigger nitrated  $Pd^{2+}$  ions, which can easily penetrate in to the deep pits. Thus by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature. When compare to the other resin [35, 36], the 8-QSSF-II copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

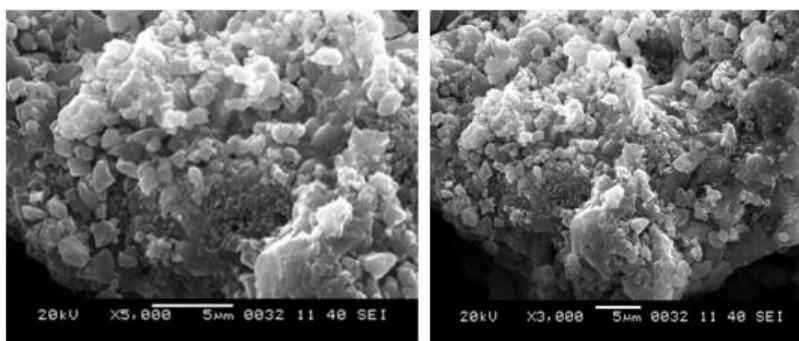


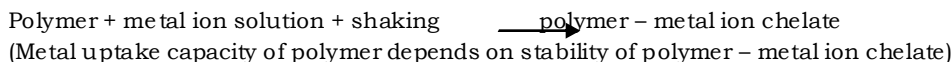
Fig.3. (a) and (b) SEM of 8-QSSF-II Copolymer resin

**Ion-exchange properties**

With a view to ascertain the selectivity of the studied the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the copolymer and solution containing the metal ions, by using batch equilibrium method [37,38]. Data of experimental procedure for direct EDTA titration is presented in Table 4. The structure of polychelate of copolymer resin has been given in Fig.6.

The 8-QSSF-II copolymer shows that the group -OH and -NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating behavior. When polymer is suspended in metal ion solution, the chelating tendency of copolymer forms the cyclic complex with

the metal ion, which absorbs the metal ion from solution to surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known as metal uptake of polymer. Due to metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ion, is also known as selectivity of polymer towards the uptake of metal ion. The metal uptake of copolymer depends on three variables, concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of 8-QSSF-II copolymer was studied with these three variables by keeping two variable constant at each time.



Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of 8-QSSF-II copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 8-QSSF-II is presented in

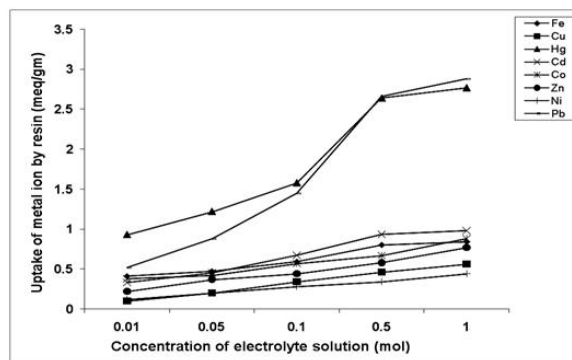
Fig. 7-12. eight metal ions  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength (b)

shaking time and (c) pH of the aqueous medium. Among three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymer [20, 22, 36].

**Effect of electrolytes and their concentration on the metal ion uptake capacity**

We examined the effect of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and ClO<sub>4</sub><sup>-</sup> at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in [Fig.4-8], which shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte [39]. Above NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> ions form weak complex with the above metal ions, while SO<sub>4</sub><sup>2-</sup> form stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the

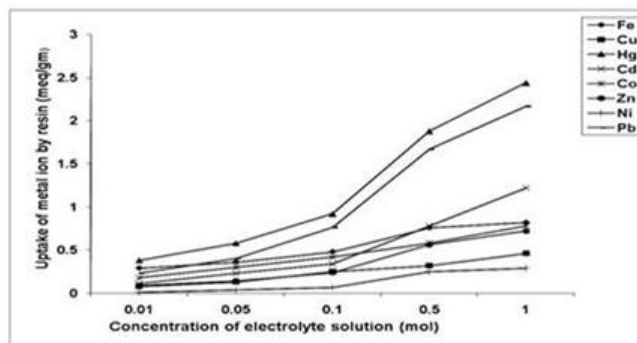
complexes with those metal ions and nature of ligands.



M(NO<sub>3</sub>)<sub>2</sub>=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III)=2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)= 6.0; Pb(II)=6.0

Fig. 4. Uptake of several metal ions by 8-QSSF-II copolymer resin at five different concentration of electrolyte solution NaNO<sub>3</sub>



M(NO<sub>3</sub>)<sub>2</sub>=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III)=2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)= 6.0; Pb(II)=6.0

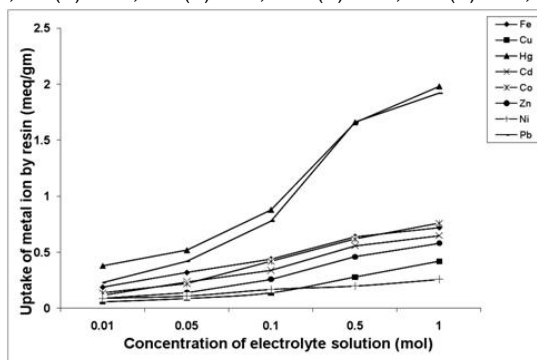
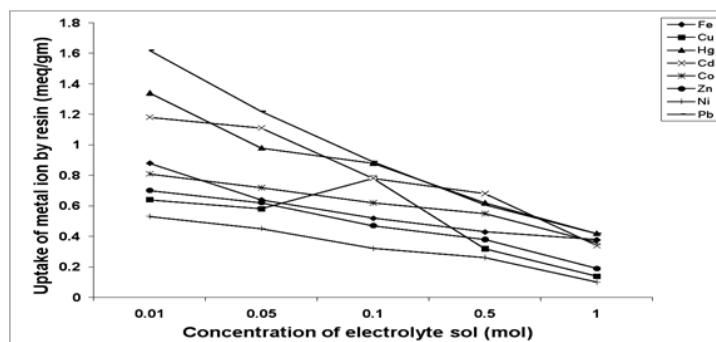


Fig. 5. Uptake of several metal ions by 8-QSSF-II copolymer resin at five different concentration of electrolyte solution NaCl

M(NO<sub>3</sub>)<sub>2</sub>=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III)=2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)= 6.0; Pb(II)=6.0

Fig. 6. Uptake of several metal ions by 8-QSSF-II copolymer resin at five different concentration of electrolyte solution NaClO<sub>4</sub>



M(NO<sub>3</sub>)<sub>2</sub>=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III)=2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)= 6.0; Pb(II)=6.0

Fig. 7. Uptake of several metal ions by 8-QSSF-II copolymer resin at five different concentration of electrolyte solution Na<sub>2</sub>SO<sub>4</sub>

**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 out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different, which is given in Fig 11. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Fig.11 shows the results of rate of uptake of metal ion on 8-QSSF copolymer resin. The rate

refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe<sup>3+</sup> ions required about 3 hrs for the establishment of the equilibrium, whereas Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe<sup>3+</sup> > Cu<sup>2+</sup> > Hg<sup>2+</sup> ≈ Pb<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Cd<sup>2+</sup> > Co<sup>2+</sup> for the 8-QSSF copolymer [40].

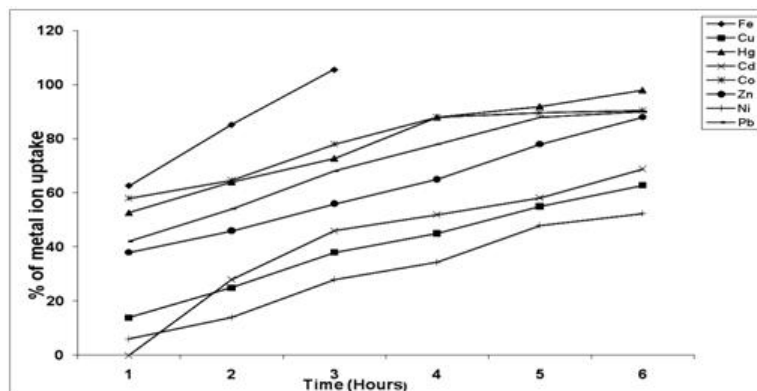


Fig. 8 Comparison of the rate of metal ion uptake by 8-QSSF-II copolymer resin

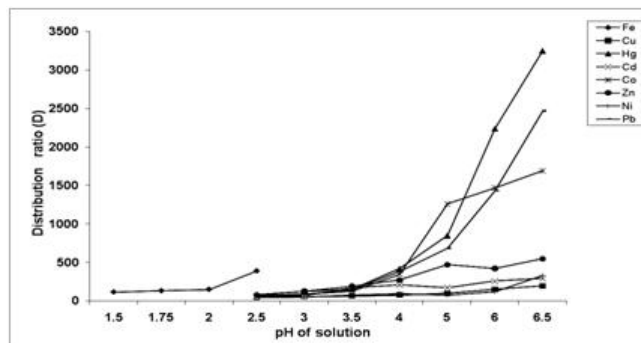
**Distribution ratios of metal ions at different pH**

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H<sup>+</sup> ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in [Fig.12]. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymers increase with increasing pH of the medium [40]. The magnitude of increase, however,

is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of  $\text{Fe}^{3+}$  ion is more for the 8-QSSF-II copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$  [38]. 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 [32, 36]. For example, the

result suggests the optimum pH 2.5 for the separation of  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  with distribution ratio 'D' is 460 and 665 respectively using the 8-QSSF-II copolymer resin as ion exchange. Similarly for the separation of  $\text{Fe}^{3+}$  at the optimum pH is 2.5 with distribution ratio is 480.2 for 8-QSSF-II copolymer. The lowering in the distribution ratios of  $\text{Fe}^{3+}$  was found to be small hence, efficient separation could be achieved. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be  $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+}$ .



**Figure 9.** Distribution ration (D) of various metal ions as function of different pH by by 8-QSSF-II Copolymer resin

### Conclusions

Copolymer resin was prepared from 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in acetic acid medium by condensation technique. The amorphous nature of the 8-QSSF-II copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for trivalent and divalent metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  ions. This study of ion-exchange reveals that 8-QSSF-II copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

### References

- Hoai N. T., Yoo D. K.; Kim D. (2010):** J. Hazard. Mater., 173 Pp 462-467.
- Devi M., Fingermann M. (1995):** Bull. Environ. Contam. Toxicol. 55, Pp746-750.
- Rivas B. L., Pooley S. A. Maturana H. A. Villegas S, (2001):** Macromol. Chem. Phys. 202, Pp443-447.
- Angelova N., Manolova N. Rashkov I., (1995):** Eur polym J, 31 (8), Pp 741-753.
- Manolova N., Ignalova M., Rashkov I., (1998) :** Eur polym J, 34(8), 1133-1140.

- Patel S. A., Shah B. S., Patel R. M., Patel P. M., (2004):** Iran Polym J, 13, Pp 445-453.
- Zalloum R. M., Mubarak S. M., (2008):** J Appl Polym Sci, 109 Pp 3180-3184.
- Roy P. K., Rawat S. S., Rai P. K., (2004):** J Appl Polym Sci, 94, Pp 1771-1779.
- Rivas B L., Pereira E D., Gallegos P., Geckeler K E., (2002):** Polym Adv Technol, 13, Pp 1000-1005
- Gurnule W. B., Juneja H. D., Paliwal L. J., (2002):** React Funct Polym, 50, Pp 95-100.
- Gurnule W. B., Rahangdale P. K., Paliwal L. J., Kharat R. B., (2003):** Synth React Inorg Met Org Chem, 33, Pp 1187-1205.
- Karunakaran M., Burkanudeen A, (2003):** Orient J Chem, 19, Pp 225-228.
- Burkanudeen A., Karunakaran M., (2002):** Orient J Chem, 18, Pp 65-68.
- Shah B. A., Shah A. V., Shah P. M., (2006):** Iran Polym J, 16, Pp 173-184.
- Shah B. A., Shah A. V., Bhandari B. N., (2008):** J. Iran. Chem. Soc, 5, Pp 25-22.
- Shah B. A., Shah A. V., Bhandari B. N., (2001):** Asian J Chem, 13, Pp 1305-1308.
- Gurnule W. B., Juneja H. D., Paliwal L. J (2003):** React and Funt Polym, 55, Pp 255-265.

- Gurnule W. B., Juneja H. D., Paliwal L. J., Kharat R. B., (2003):** J of Appl Polym Sci. 89, 787-790.
- Rahangdale S. S., Gurnule W. B., Zade A. B., (2008):** J. Appl. Polym. Sci, 56, Pp 747-756.
- Tarase M. V., Gurnule W. B., Zade A. B., (2010):** J Appl Polym Sci, 116, Pp 619-627.
- Mane V. D., Gurnule W. B., Zade A. B., (2009) :** J Appl Polym Sci, 111, Pp 3039-3049.
- Preuss A., Kunin R., (1956):** Proc. Inter. Conf. Peaceful Uses Atom. Energy-Geneva, 8.
- Denizli A., Garipean B., Karabakan A., Emir S., Patir S., (2003) :** Sep Pur Tech, 2, Pp 3-10.
- Shah B. A., Shah A. V., Shah P. M., (2006):** Iran Polym J, 15, Pp 809-819.
- Joshi J.D., Patel N. B., Patel S. D., (2006):** Iran Polym J, 15, Pp 219-226.
- Patle D. B., Gurnule W. B., (2014):** Desal. Water Treatment, Pp 1-10
- Katkamwar S. S., Gurnule W. B., Zade. A. B. (2009):** ; J Appl Polym Sci, 113, ,3330-3335.
- Singru R. N., Gurnule W. B., Zade A. B. (2008):** J Appl Polym Sci, 109, Pp 859-868.
- Rahangdale S. S., Gurnule W. B., Zade A. B., (2009):** E-Journal of Chemistry, 6(3), , Pp 835-843.
- Rahangdale S. S., Gurnule W. B., Zade A. B., (2009):** Indian J Chem. 48A, Pp 531- 535.
- Gupta R. H., Gurnule W. B., Zade A. B., (2008):** J. Appl. Polym. Sci, 109(5), 3315-3320.
- Patle D. B., Gurnule W. B., (2010):** Archives of Applied Science Research, 2 (1) Pp 261-276.
- Patle D. B., Gurnule W. B., (2010) :** Polymer Bulletin, 56, Pp 1-18.
- Singru R. N., Gurnule W. B., Zade A. B., (2010):** Iranian Polymer Journal. 19 (3), 169-175

