REMOVAL OF TOXIC METAL IONS USING ION-BINDING COPOLYMER RESIN BY BATCH EQUILIBRIUM TECHNIQUE

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ABSTRACT

Copolymer resin has been synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in 4:1:5 ratio in the presence of acetic acid as catalyst at $126 \pm 2°C$ for 5 hours was proved to be a selective chelating ion-exchange copolymer for certain metal ions. On the basis of their elemental analysis composition of 8-HQ5-SASF-IV has been determined and conductometric titration in non-aqueous medium method has been used for determination of the number average molecular weight of this copolymer. The viscosity measurements in dimethylsulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. This newly synthesized 8-HQ5-SASF-IV copolymer resin was characterized by electronic spectra, FTIR spectra, ^1H 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^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+} ions over the pH range, 2.5 to 6.5 and in media of various ionic strengths. The order of metal ion uptake at higher concentrations by the 8-HQ5-SASF-IV terpolymer at lower pH is $Cu^{2+} > Ni^{2+} > Fe^{3+}$. At higher pH level, the metal ion (Zn^{2+}, Co^{2+} and Pb^{2+}) uptake decreases while the concentration increases. Therefore the order of metal ion uptake at lower concentration is $Zn^{2+} > Co^{2+} > Pb^{2+}$. The amount of Pb^{2+} metal ion uptake by the 8-HQ5-SASF-IV terpolymer was very lower compared to all the other metal ions, because of the bigger hydrated size of Pb^{2+} ion.

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

I.   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. Polymers used as ion-exchange resins 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 in 4:1:5 ratio. The purpose of present study, is to explore the adsorption behavior of eight metal ions Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} Hg^{2+} and Pb^{2+} on the newly synthesized copolymer resins 8-HQ5-SASF-IV at different pH values, different concentrations of different electrolytes and at different shaking time intervals. On the basis of affinity differences the adsorption behavior of these metal ions towards the chelating resins as functions of pH, electrolyte concentrations and shaking time.

II.   MATERIAL AND METHOD

2.1 Synthesis of 8-HQ5-SASF-IV copolymer resin

The 8-HQ5-SASF-IV copolymer resin was prepared by the condensation polymerization of 8-hydroxyquinoline 5-sulphonic acid (0.4 mol) and semicarbazide (0.1 mol) with formaldehyde (0.5 mol) in acetic acid medium at 126 ± 2 °C in an oil bath for 5 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-HQ5-SASF-IV 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 82.48% and the melting point is between 572-575 ºK. The purified copolymer resin was used for further characterization.

Ion-exchange properties

The ion-exchange properties of the 8-HQ5-SASF-IV 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.

 In known concentration of an electrolyte solution (25 ml) the copolymer sample (25 mg)   was suspended . The pH of the suspension was adjusted to the required value by using either 0.1 N HCl or 0.1 N NaOH and stirred for a period of 24 hrs at 25ºC. 2 ml of a 0.1 M solution of metal ion was added into this suspension and the pH was adjusted to the required value. This mixture was again stirred at 25ºC for 24 hrs and filtered [9, 10]. 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 [11]. The experiment was repeated in the presence of other three electrolyte such as $NaCl$, $NaClO_4$ and Na_2SO_4.

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 25ºC (in the presence of 25 ml of 1 M $NaNO_3$ 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 at different time 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.

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

The distribution of each one of the eight metal ions i.e. Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} Hg^{2+} and Pb^{2+} between the polymer phase and the aqueous phase was determined at 25ºC and in the presence of a 1M $NaNO_3$ solution.

The experiments were carried out from 3.5 to 6.5 pH for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. In case of Fe^{3+} the study was carried out from 2.5 to 4.0 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. If the original metal ion concentration is known, the metal ion adsorbed by the resin can be calculated. 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.

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

III. 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_2SO_4. The resin synthesized do not show sharp melting point but undergo decomposition 572-575 ºK. Based on the analytical data, the empirical formula of the copolymer resin is found to be $C_{42}H_{33}O_{17}N_3S_4$, which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen and

sulfur content. C = 51.48% (Cal) and 51.85 % (F), H=(3.37)% (Cal) and 3.78 % (F), N =4.29 %(Cal), and 4.26 % (F), S= (13.07)% (Cal) and 13.54 %(F). The number average molecular weight ($\overline{\text{M n}}$) could be obtained by multiplying the $\overline{\text{DP}}$ by the $_{\text{formula}}$ weight of the repeating unit [12, 13]. The calculated molecular weight for 8-HQ5-SASF-IV resin is 979.

Viscometric measurement was carried out in DMSO at 32ºC. 8-HQ5-SASF-IV resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's eq. (2) and Kraemer's, eq. (3) which is 1.98 and -1.52 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_1 and K_2 (0.46) respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots [14, 15]. The values of (η) obtained from both relations were in good agreement with each other.

UV-visible spectra of 8-HQ5-SASF-IV resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min^{-1}. The spectra of these copolymers exhibit two absorption maxima in the region 280 nm and 320 nm. The observed positions of the absorption bands with different intensities indicate the more intense band 260 nm is due to ($\pi \rightarrow \pi^*$) allowed transition which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromophore groups like >C=C, >C=N, >C=O and –SO_3H groups are in conjugation with an aromatic nucleus (quinoline ring) and the less intense band at 320 nm may be due to (n$\rightarrow \pi^*$) forbidden transition in >C=N –SO_3H, and   –OH groups [16−18]. 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. 250 nm and 320 nm may be due to combined effect of conjugation (due to chromophore) 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 [19]. i.e. higher $\in_{max}$ [20] . The $\in_{max}$ value gradually increases in the order 8-HQ5-SASF-I < 8-HQ5-SASF -II < 8-HQ5-SASF -III < 8-HQ5-SASF -IV. This increasing order of $\in_{max}$ values may be due to introduction of more and more chromophores and auxochromes (phenolic - OH group) in the repeat unit of the copolymer resins [21].

The IR spectrum of 8-HQ5-SASF-IV copolymer resin is presented in Fig. 1 [22-23]. A broad absorption band appeared in the region 3440-3300 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding. The presence of sharp and strong band at 3398 cm^{-1} indicates the presence of –NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

A band appeared at 2917.14 cm^{-1} is assigned to aromatic ring (-CH) stretching modes The 2, 5, 6, 8 substitution of aromatic ring is confirmed from the sharp, medium/weak bands appearing at 1027, 1083, 1201, and 1295 cm^{-1}, respectively [24, 25]. A weak band appeared at 2847.67 cm^{-1} is attributed to –CH_2 group present in the terpolymer ligand. The band appeared in the region of 1373.55 cm^{-1} to 1373.84 cm^{-1} is attributed to –CH_2 -bending (twisting and wagging) mode of vibrations. The band appeared at 1625.88 cm^{-1} is assigned to –C=O amide (I) stretching vibration. stretching mode and a strong band at 1525 cm^{-1} is attributed to C=N stretching of quinoline ring.
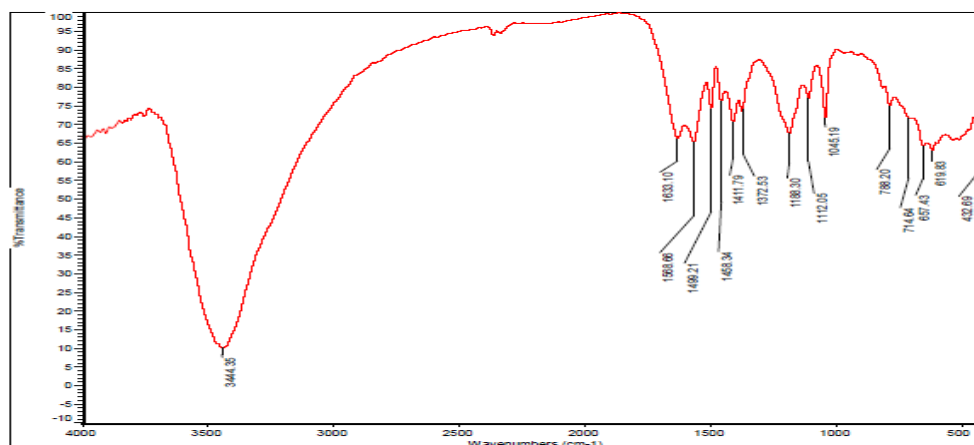
Fig. 1. FTIR Spectra of 8-HQ5-SASF-IV Copolymer Resin

The NMR spectrum (Fig. 2) of 8-HQ5-SASF-IV polymer was scanned in DMSO-d_6 solvent. In the spectrum of ligand, the resonance signal appeared in the range at 9.04 (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 [26, 27]. The signals in the region 7.44 (δ) ppm are attributed to protons of –NH bridge present in the ligand structure and the signals appeared in the range of 4.67 ppm are assigned to methylene protons of Ar-CH2-N moiety [28]. The weak multiplate signals (unsymmetrical pattern) in the region of 8.97 (δ) ppm may be attributed to aromatic proton (Ar-H). [29, 30]. The signals in the range of 9.99(δ) ppm are attributed to proton of -SO_3H groups.
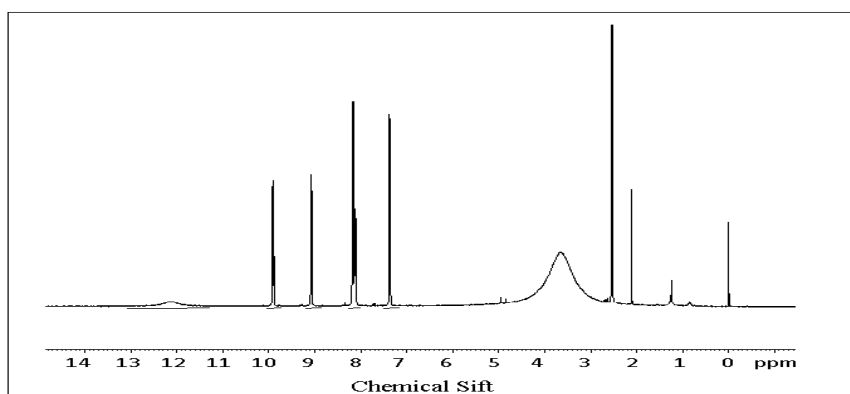

Fig. 2. Proton NMR spectrum of 8-HQ5-SASF-IV copolymer resin

IV.   Scanning electron micrographs

The surface features of the materials has been studied by surface analysis which is great useful for understanding . The morphology of the 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 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-

HQ5-SASF-IV copolymer resin sample. Spherulites the amorphous region shows secondary structural feature such as corrugations and having deep pits. But the corrugation in the surface area with deep pits shows the amorphous nature of the terpolymers. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and spherulite structure having deep pits represent the transition between crystalline and amorphous. 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 [31, 32], the 8-HQ5-SASF-IV copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.
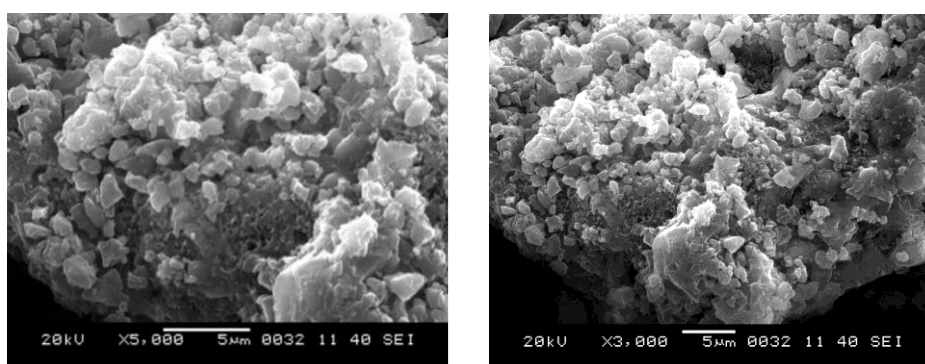

Fig.3. (a) and (b) SEM of 8-HQ5-SASF-IV Copolymer resin

V. 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 [33, 34, 35].

8-HQ5-SASF-IV 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 at 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-HQ5-SASF-IV copolymer was studied with these three variables by keeping two variable constant at each time.

Polymer + metal ion solution + shaking → polymer – metal ion chelate

(Metal uptake capacity of polymer depends on stability of polymer – metal ion chelate)

Batch equilibrium technique developed by Gregor et al. and De Geiso et al. was used to study of ion exchange property of 8-HQ5-SASF-IV copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 8-HQ5-SASF-IV is presented in table 1, 2, 3. 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 evaluable its effect on metal uptake capacity of the polymer [20, 22, 36].

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

The various concentrations of NO_3^-, Cl^-, SO_4^{2-} and ClO_4^- effected on the equilibrium of metal resin interaction at 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^{3+}, Cu^{2+}, Zn^{2+} and Pb^{2+} 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 [35]. NO_3^-, Cl^-, and ClO_4^- ions form weak complex with the above metal ions, while SO_4^{-2} 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.

$M(NO_3)_2$] =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; Pb(II)=6.0

Table 1. Uptake of several metal ions by 8-HQ5-SASF-IV copolymer resin at three different concentration of electrolyte solution $NaNO_3$, NaCl, $NaClO_4$, Na_2SO_4

Metal Ion	Electrolyte Concentration (mole/lit)	Weight of metal ion (mg)taken up in presence of[b]			
		$NaNO_3$	NaCl	$NaClO_4$	Na_2SO_4
Cu^{2+}	0.1	4.17	3.94	3.86	2.74
	0.5	4.53	4.24	4.03	2.49
	1	4.97	4.75	4.35	2.04
NI^{2+}	0.1	4.08	3.94	3.42	2.46
	0.5	4.42	4.11	3.81	1.44

	1	4.83	0.35	4.32	1.02
Co^{2+}	0.1	3.28	2.81	2.78	1.71
	0.5	2.94	2.39	2.54	1.39
	1	1.96	1.79	0.71	0.98
Zn^{2+}	0.1	3.30	3.22	2.95	1.86
	0.5	3.09	2.93	2.78	1.44
	1	2.92	2.74	2.62	1.16
Pb^{2+}	0.1	2.82	2.45	2.13	0.62
	0.5	2.36	2.21	1.79	0.38
	1	1.91	1.54	1.36	0.20
Fe^{2+}	0.1	4.16	3.86	3.82	2.72
	0.5	4.47	4.36	3.98	2.14
	1	4.88	4.66	4.38	1.79

b. **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 table 2. When shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Table 2 shows the results of rate of uptake of metal ion on 8-HQ5-SASF-IV 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^{3+} ions required about 3 hrs for the establishment of the equilibrium, whereas Cu^{2+}, Zn^{2+} and Pb^{2+} ions required about 6 hrs. Thus the rate of metal ions uptake follows the order $Fe^{3+} > Cu^{2+} > Hg^{2+} \approx Pb^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+}$ for the 8-HQ5-SASF-IV copolymer [35].

Table 2. Comparison of the rate of metal ion uptake by 8-HQ5-SASF-IV copolymer resin

Metal Ion	Metal Ion Uptake (%)						
	1	2	3	4	5	6	7
Fe^{2+}	58	67	80	92	96	-	-
Cu^{2+}	60	69	83	88	97	-	-
Ni^{2+}	56	68	81	80	93	-	-
Zn^{2+}	48	58	70	76	82	95	-
Co^{2+}	37	46	68	72	82	94	-
Pb^{2+}	42	47	63	78	80	85	96

a = $M_t (NO_3)_2$ = 0.1 mol/lit, V = 2 ml, $NaNO_3$ = 1.0 mol/l, V = 25 ml, room   temperature

c. Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ 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 table 3. 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. 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 Fe^{3+} ion is more for the 8-HQ5-SASF-IV copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 2.5 to 6.5 is found to be Fe(III) > Cu(II) > Ni(II) > Zn(II) > Co(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 [32, 35]. For example, the result suggests the optimum pH 3.5 for the separation of Fe^{3+} and Zn^{2+} with distribution ratio 'D' is 226.63 and 22.45 respectively using the 8-HQ5-SASF-IV copolymer resin as ion exchange. Similarly for the separation of Fe^{3+} at the optimum pH is 2.5 with distribution ratio is 114.45 for 8-HQ5-SASF-IV copolymer. The lowering in the distribution ratios of 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 Fe(III) > Cu(II) > Ni(II) > Zn(II) > Co(II) > Pb(II).

Table 3. Distribution ration (D) of various metal ions as function of different pH by 8-HQ5-SASF-IV Copolymer resin

Metal Ion	PH						
	2.5	3	3.5	4	5	6	6.5
Fe^{2+}	114.45	160.34	226.63	353.06	-	-	-
Cu^{2+}	-	-	45.61	92.04	163.16	286.36	365.41
Ni^{2+}	-	-	32.76	84.48	148.32	274.64	323.32
Zn^{2+}	-	-	22.45	72.32	138.54	256.76	286.22
Co^{2+}	-	-	24.15	66.53	117.46	218.06	270.38
Pb^{2+}	-	-	20.16	60.86	98.18	208.44	236.2

VI. 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-HQ5-SASF-IV 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 Fe^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} Co^{2+} and Pb^{2+} ions. This study of ion-exchange reveals that 8-HQ5-SASF-IV 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 polluted air, for the purification of industrial waste solution and for the purpose of purification and desalination of water.

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