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Synthesis of resin VI: Salicylic acid, diaminobenzoic acid and formaldehyde resin and its ion exchange properties

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ABSTRACT

The resin salicylic acid-diaminobenzoicacid-formaldehyde (SDBF) has been synthesized by the condensation of salicylicacid and diaminobenzoicacid with formaldehyde in the presence of hydrochloricacid as catalyst. Resin was characterized by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV- Visible spectral studies. The number average molecular weight of the resin was determined by non-aqueous conductometric titration. Chelation ion exchange properties have also been studied for various metal ions employing a batch equilibrium method. It was employed to study the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the polymer sample and a solution containing the metal ion. The study was approved out over wide pH range and in media of various ionic strengths. The resin depicted advanced selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+}ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

Key words*:* Resin, Condensation, Chelation, Batch equilibrium, Metal ion uptake

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INTRODUCTION

Resins exhibits better thermal and electrical properties than those of phenol-formaldehyde type copolymer. These resins can be used as high energy materials, ion exchangers, semiconductors, bonding agent/additives, molding material, fungicides in plant and living tissues, biosensors and controlled release devices for pharmaceuticals.[1-5]. Now a day's renewed interest has been evidenced in the context of obtaining materials with high temperature resistance and ion exchangers. Patel and Lad [6] reported the novel resins: poly (keto-amine-ureas) and studied the glass reinforcement of such resin- epoxy systems. Michael and coworkers have reported the synthesis, structural and thermal degradation of a polymer derived from salicylic acid, guanidine and formaldehyde [7].Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resin were studied by Gurnule and coworkers [8]. Ion exchange resin derived from semicarbazone and oximes of 2-hydroxy acetophenone-substituted benzoic acid - formaldehyde studied by Nayak et.al. [9-10].Chelation ion exchange resins derived from 2-hydroxy-4-methoxyacetophenone and thiourea with trioxane was investigated by Pancholi et. al.[11]. Patel[12-13] reported the ion exchange properties of resacetophenone (2, 4 dihydroxy acetophenone) -formaldehyde and resacetophenone oxime-formaldehyde resins. In our laboratory, extensive research work was carried out on synthesis and characterization of resins and their ion exchange properties [14-17]. However, the literature studies have revealed that no resins has been synthesized using the monomers salicylic acid, diaminobenzoiczcid and formaldehyde. Thus in the present communication we account synthesis, characterization and ion exchange properties of a SDBF resin.

MATERIALS AND METHODS

2.1 Chemicals

All Chemicals were AR grade or chemically pure grade. Salicylic Acid, Diaminobenzoicacid were purchased from Aldrich Chemical Co., USA while Formaldehyde from RANKEM, Ranbaxy, India, DMF and DMSO (HPLC grade) were used.

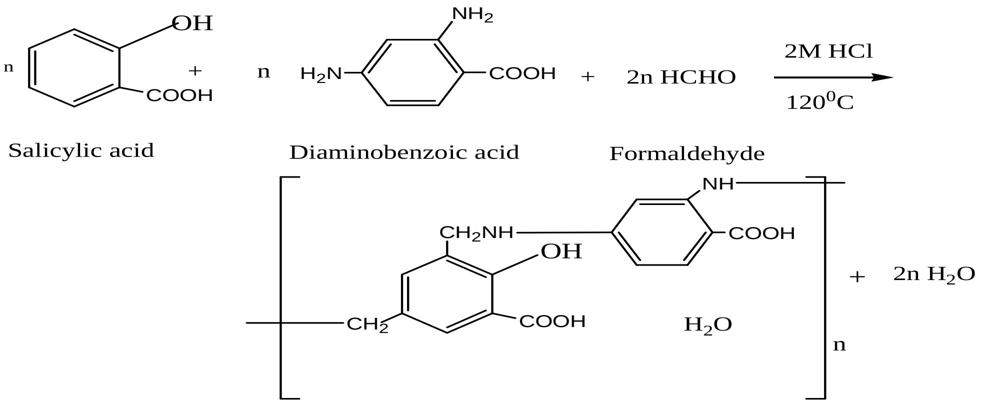
2.2 Instruments used

The elemental analysis of resin for C, H and N were analyzed on Carlo Erber Elemental Analyzer Fourier Transform. Infrared spectra in the region 400-4000cm^{-1} were recorded on a Perkin-Elmer with KBr pellets. The electronic spectrum of the terpolymer was recorded in dimethylformamide (DMF) at room temperature with a UV-240 Shimadzu double beam spectrophotometer. The NMR was scanned at 300MHz with dueterated dimethylsulfoxide (DMSO) solvent at RSIC, Chandigarh.

2.3 Synthesis of SDBF Resin

2.3.1 Condensation of Salicylicacid(S) and Diaminobenzoicacid (DB) with Formaldehyde (F):

A mixture of salicylicacid, diaminobenzoicacid, formaldehyde and 2M hydrochloric acid was taken in a round bottom flask fitted with water condenser and heated in an oil bath at 120^{0}C for 6 hours with occasional shaking. The temperature of electrically heated oil bath was controlled with the help of dimmer stat .The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified. The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agated mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air-dried powder was extracted with diethyl ether and then petroleum ether was used to remove salicylicacid diaminobenzoicacid copolymer, which might be present along with SDBF resin. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipeted by gradual drop wise addition of 1:1 (v/v) hydrochloric acid with constant and rapid stirring to avoid lump formation [14-16, 22,23]. The SDBF resin so obtained was filtered, washed several times with hot water and dried (yield=17g; mp=282^{0}C).Analytical data for $C_{16}H_{14}N_2O_5 \cdot H_2O$ as per numerical calculations and experimental evidence are mentioned below respectively. Theoretically calculated C=57.83%, H=4.81%, N=8.43%. Experimentally found C=57.38 %, H=5.11%, N=8.12%.



SDBF Resin

2.4. Ion exchange properties

The purified SDBF resin sample was finely powdered and used in all experiments carried out in the ion exchange study.

2.4.1 Determination of Metal ion uptake in the presence of Electrolytes of Different Concentration

25mg of the finely powdered resin was suspended in an electrolyte solution (25ml) of known concentration. The pH of the solution was adjusted to required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for a period of 24hours at room temperature. To this suspension 2ml of 0.1M solution of electrolyte wasadded and the pH was adjusted to the required value. The mixture was again stirred at 25^0C for 24 hour and filtered. The polymer was washed and the filtrate and washings were combined and estimated for the metal ion content by titration against standard EDTA. A blank experiment was also carried out in the same manner without adding the polymer sample to estimate the metal ion content. The amount of metal ion taken up by the terpolymer in the presence of given electrolyte of known concentration was determined from the difference between the blank reading and the reading in the actual experimental [14-16, 22-27]. The experiment was repeated in the presence several electrolytes of known concentration seven different metal ions such as Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}. The results with seven different metal ions are reported in table 3.

2.4.2. Evaluation of the Rate of Metal Uptake

In order to determine the time required to reach the state of equilibrium under given experimental conditions series of experiments of the type described above were carried out, in which the metal ion uptake by the chelating resins was estimated from time to time at room temperature. It was assumed that under given conditions, the state of equilibrium is established in the 24 hrs. The rate of metal ion uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that in state of equilibrium as table 4 [14-16, 22-27].

2.4.3. Evaluation of distribution of metal ions at different pH values

The distribution of each of the metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} between the resin phase and aqueous phase was estimated at 25^0C using 1M $NaNO_3$ solution. The experiments were carried out as described above and the pH value. The distribution ratio "D" was determined by the following equation [14-16, 22-27]:

The results are presented in table 5.

RESULTS AND DISCUSSION

The terpolymer resin was soluble in DMF and DMSO; however it is insoluble in common organic solvents. The composition of the polymeric unit was assigned on the basis of a detailed study of the elemental analysis of the polymer, ultraviolet-visible (UV-Visible), IR and NMR spectral studies.

3.1. Characterization of resin

3.1.1.Determination of molecular weight by conductometric titration

The molecular weight (Mn) of the resin was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50mg of sample. A plot (Fig.1) of the specific conductance against the milieqvivalents of potassium hydroxide required for neutralization of 100g of terpolymer was made. Inspection of such a plot revealed the breaks in the plot. The first break at 270 miliequivalent of base and the last break at 2250 miliequivalent of base were noted. The calculations of (Mn) by this method is based on the following considerations [14-16, 18]: (1) the first break corresponds to neutralization by the more acidic phenolic hydroxy group of all the repeating units; (2) The break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized. On the basis of the average degree of polymerization (DP) is given by the following relation.

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

The number average molecular weight (Mn) is 2875, which is obtained by multiplying the DP by the formula weight of the repeating unit [14-16, 18].

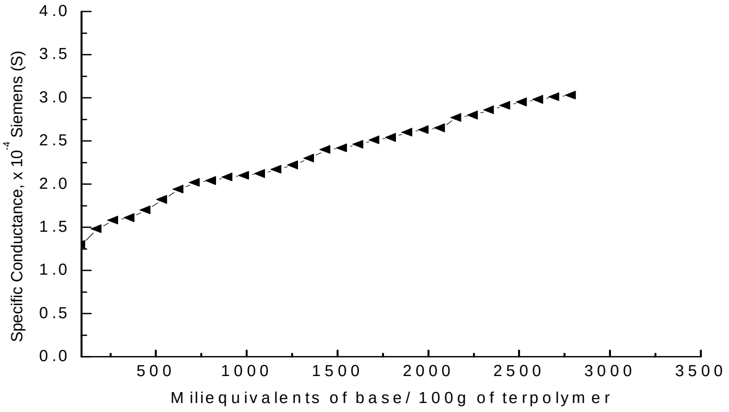


Figure 1: Conductometric titration curve of SDBF resin

3.1.2.UV-Visible studies

The electronic spectrum of the SDBF resin is shown in figure 2. The spectrum depicted two characteristic bands in the region of 270 nm and 380 nm. The band at 270nm indicates the presence of a carbonyl (>C=O) group containing a carbon oxygen double bond in conjugation with an aromatic nucleus and was characteristic of a $\pi \rightarrow \pi^*$ transition while the latter band may be due to $n \rightarrow \pi^*$ electronic transition. The additional shift of absorption to the longer wavelength region i.e. is bathochromic shift from the basic value (237nm and 320nm, respectively) may be due to conjugation effect and phenolic hydroxyl group (auxochrome) is more effective for hyperchromic effect.[14-16, 18].

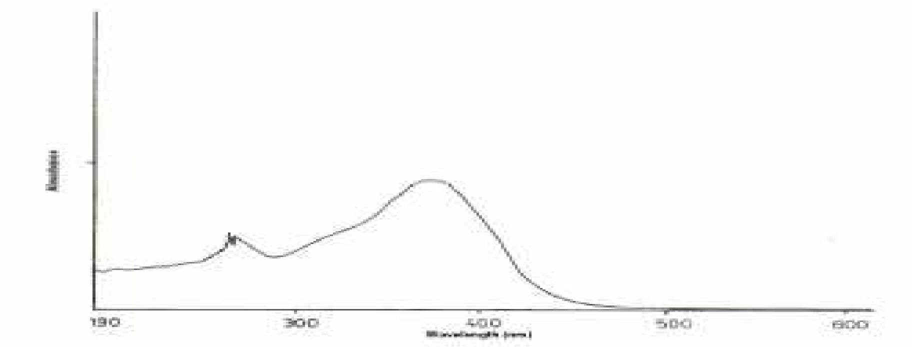


Figure 2: Electronic spectrum of SDBF resin

3.1.3Infra Red Studies

The IR spectrum of the newly synthesized Salicylicacid, diaminobenzoicacid, formaldehyde resin is depicted in fig 3 and IR values are mentioned in table 1. A broad band appeared at 3400.3 cm-1 [14-17,19,20] might be due to the stretching vibrations of phenolic hydroxyl group exhibiting intermolecular hydrogen bonding which exists between -OH groups of different polymer chains. The band observed at 2925.1 cm-1 may be due to the stretching vibrations of –NH (imide) [14-17, 19, 20]. The inflections around 1288.1 cm-1 and 765.2 cm-1 suggest the presence of wagging,rocking vibrations of methylene (-CH2-) bridges in polymeric chains [14-17,19,20]. The broad band at 1591.9 cm-1 may be due to the stretching vibrations of >C=O [14-17,19,20].The broad bands at 688.5 and 619.5 cm-1 are due to –NH wagging and deformation out of plane vibrations in terpolymer resin respectively [14-17,19,20]. The band at 1342.2 cm^{-1} may be due to phenolic >C-O stretching modes of vibration [14-17, 19, 20]. The bands present at 907 cm-1to1173.6 cm-1suggests that the aromatic ring is 1, 2, 3, 5-tetrasubstituted [14-17, 19, 20].

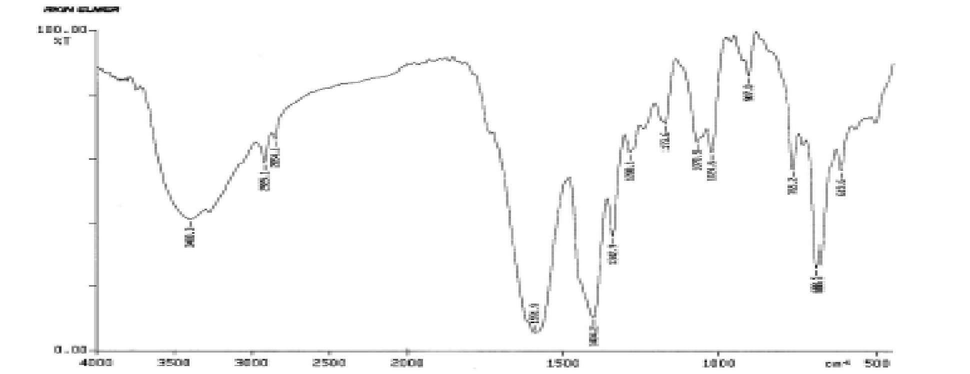


Figure 3: Infrared spectrum of SDBF resin

Table 1.IR Spectral data of SDBF resin

Assignment	Observed band Frequency (cm^{-1})	Expected **band** Frequency (cm^{-1})
Phenolic -OH	3400.3	3500-3000
-NH stretch	2925.1	3500-2800
>C=O stretching	1591.9	1680-1630
Phenolic C-O	1342.2	1410-1310
Methylene bridge (-CH$_2$) mode		
Wagging	1288.1	1300-1200
Rock	765.2	775
1,2,3,5- substitution on aromatic ring	907-1173.6	900-1200
Tetra substitution benzene ring	830	~830
N-H wagging	688.5	650-800
N-H deformation out of plane	619.5	800-600

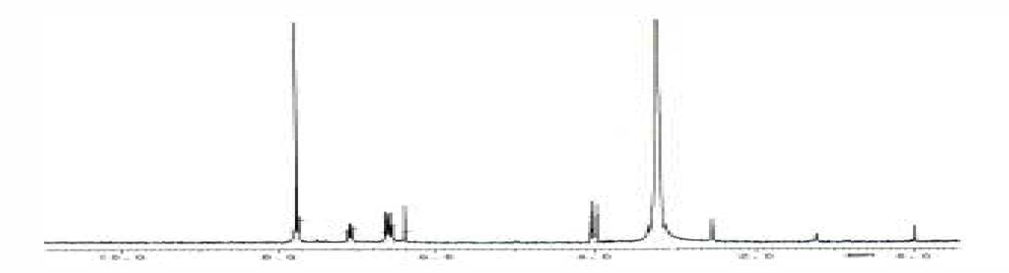


Figure 4: NMR spectrum of SDBFresin

Table 2. ^{1}H-NMR spectral data of SDBF resin

Nature of proton	Chemical Shift,δ (ppm)	Expected Chemical Shift,δ (ppm)
Aromatic (Ar-H)	7.7	7.3-8.8
Phenolic (Ar-OH)	7.9	7.5-12
Carboxylic (Ar-COOH)	7.4	7.41
-NH bridging	6.7	5.0-8.5
Ar-CH$_2$-N moiety	3.9	2.5-4.5

3.1.4. NMR studies

The NMR spectrum of the SDBF resin shown in figure 4 exhibits signals in the region of 7.7 δ (ppm), which may have been due to the proton of the aromatic ring (Ar-H), and the signals in the region 7.9 δ (ppm) may have been due to the phenolic-OH proton in hydrogen bonding (Ar-OH) [14-22]. The signals displayed at 7.4 δ (ppm) may have been due to the carboxylic proton of Ar-COOH [14-22]. The presence of a broad signal around 6.7 δ (ppm) may have been due to the presence of –NH bridges [14-22]. A methylene proton Ar-CH2-N moiety was inferred by the appearance of a weak singlet signal at 3.9 δ (ppm) [14-22]. The spectral data is as tabulated in table 2.

3.2. Ion-exchanging properties

To ascertain the selectivity of SDBF, we have studied the influence of various electrolytes, the rate of metal uptake and the distribution of metal ions between the resin and solution. The results of the batch equilibrium study carried out with resin sample SDBF are presented in tables 3, 4 and 5.

3.2.1.Effect of Electrolyte on Metal Uptake

The data presented in table 3 reveals that the amount of metal ions taken up for a given amount of resin sample depends on the nature and concentration of electrolyte present in the solution. In presence of chloride and nitrate ions, the amount of Fe^{3+} Cu^{2+}, and Ni^{2+} ions taken up by the terpolymer sample increases while in presence of sulphate ions the amount of above mentioned ions taken up by the resin samples decreases with increasing concentration of electrolyte. Moreover, The amount of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions taken up by the terpolymer samples decreases with increasing concentration of the chloride, nitrate and sulphate ions. This may be explained on the basis of stability constant of the complexes with Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal cations [14-16, 22-25].

Table 3. Evaluation of the effect of different electrolytes on the uptake of several metal ions of SDBF resin

Metal ion	Electrolyte Conc. (mole/lit)	Weight of metal ion (mg) taken up in presence of		
		$NaNO_3$	NaCl	Na_2SO_4
Fe^{3+}	0.01	1.99	1.93	2.63
	0.05	2.14	2.09	2.53
	0.1	2.31	2.23	2.21
	0.5	2.69	2.54	2.06
	1	2.84	2.71	1.91
Cu^{2+}	0.01	0.76	0.68	1.55
	0.05	0.96	0.89	1.45
	0.1	1.22	1.13	1.14
	0.5	1.51	1.42	0.86
	1	1.74	1.62	0.66
Ni^{2+}	0.01	1.03	0.93	1.84
	0.05	1.12	1.01	1.52
	0.1	1.31	1.19	1.06
	0.5	1.64	1.56	0.89
	1	2.04	1.96	0.68
Co^{2+}	0.01	1.89	1.85	1.83
	0.05	1.61	1.59	1.51
	0.1	1.26	1.19	1.16
	0.5	1.12	1.09	1.05
	1	1.01	0.98	0.91
Zn^{2+}	0.01	1.46	1.43	1.39
	0.05	1.34	1.32	1.32
	0.1	1.12	0.98	1.02
	0.5	0.92	0.84	0.76
	1	0.84	0.79	0.70
Cd^{2+}	0.01	1.41	1.27	1.33
	0.05	1.30	1.14	1.06
	0.1	1.07	0.97	0.79
	0.5	0.99	0.81	0.71
	1	0.83	0.72	0.56
Pb^{2+}	0.01	1.40	1.14	0.99
	0.05	1.15	0.89	0.75
	0.1	0.98	0.72	0.63
	0.5	0.84	0.69	0.49
	1	0.77	0.51	0.24

^{a}[$M(NO_3)_2$=0.1 mol/l; Volume = 2ml; Volume of electrolyte solution: 25 ml; time: 24 h ; room temperature

3.2.2. Rates of metal uptake

The rates of metal adsorption by the SDBF resin have been measured for Fe^{3+}, Cu^{2+}, Ni^{2+} Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions, in order to know the equilibrium time required. The term "rates" refers merely change in the concentration of metal ion in the aqueous solution, which is in contact with given terpolymer resins. The experimental results which are given in table 4, shows that the time taken for the uptake of the metal ions at a given stage depends on the nature of the metal ion under the given conditions. As the size of the metal ion increases time taken for the uptake metal ion also increases. The experimental results indicate that Fe^{3+} ions required less time of 4 hours for the establishment of equilibrium. Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, ion required 5 hours while Cd^{2+} and Pb^{2+} ions required about 6 hour reaching for the establishment of equilibrium. It is further revealed that the rates of metal ion uptake follow the order: $Fe^{3+} > Cu^{2+}$ - Ni^{2+} - Co^{2+} - $Zn^{2+} > Cd^{2+}$ - Pb^{2+} for all the terpolymers [14-16, 22-25].

Table 4. Comparison of the rates of metal ion uptake of SDBF resin

Metal ions	Percentage of the metal ion uptake^{b} at different times (h)						
	0.5	1	2	3	4	5	6
Fe^{3+}	63	75	81	91	98	-	-
Cu^{2+}	38	49	68	80	91	97	-
Ni^{2+}	23	34	53	71	81	96	-
Co^{2+}	18	33	48	64	80	95	-
Zn^{2+}	16	23	37	63	79	95	-
Cd^{2+}	15	30	61	72	80	89	98
Pb^{2+}	14	26	37	69	78	89	96

$^{b}[M^{+}(NO_3)_2]=0.1$ mole/l, Volume=2,$NaNO_3=0.1$mol/l,Volume of electrolyte solution=25ml, time=24hr (equilibrium state), room temperature.

$$^{b}\text{Metal ion uptake} = \frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$$

3.2.3. Evaluation of distribution coefficient of the metal ions over wide pH range

The results of the effect of pH on the amount of metal ion distributed between two phases are incorporated in table 5. Examination of the data indicates that the relative amount of metal ions taken up by the resin samples at equilibrium increases with increasing pH of the medium [14-16, 22-25]. The study was carried out only up to pH=6.5 in order to prevent hydrolysis of the metal ions at higher pH. Perusal of data given in table 5 the selectivity of resin samples for $Fe^{3+}$is higher than that of other metal ions. The lower distribution ratio of Fe^{3+} due to sterric hindrance imposed by polymer matrix [22-25]. Among the other metal ions Cu^{2+} and Ni^{2+} ions taken up more selectively by terpolymer resin. The other metal ions Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}have distribution ratio, 'D' over the pH range of 4 to 6.5. This could be attributed to the low stability constant i.e. the weak ligand stabilization energy of the metal complexes [14-16, 22-25]. The possible order of selectivity of a cation-exchange resin for divalent metal ions is [14-16, 22-25]: Pd>Cu>Ni>Co>Zn>Cd>Fe>Mn>Mg. Comparison of the values of distribution coefficients of a given metal ion for all the four molar ratio of terpolymer reveals that there is no much difference in the values. Thus in the present study the observed order of distribution ratio of metal ions measured in the range of 1.5 to 6.5 pH was found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$.

Earlier workers have also suggested this order of selectivity for a salicylic acid containing polymer.

Table 5. Distribution ratio D^{a} of the metal ion as a function of the pH^{b} of SDBF resin

Metal ion	Distribution ratio of the metal ion at different pH								
	1.5	2.0	2.5	3.0	4.0	4.5	5.0	6.0	6.5
Fe^{3+}	217.4	292.6	598.4	-	-	-	-	-	-
Cu^{2+}	-	-	-	114.6	204.1	397.8	595	981.9	1171.4
Ni^{2+}	-	-	-	93.1	114.5	158.1	234.4	403.3	859.6
Co^{2+}		-	-	68.2	87.3	98.6	145.2	224.9	386.3
Zn^{2+}	-	-	-	38.9	53.6	81.4	142	231.6	361.3
Cd^{2+}	-	-	-	31.8	50.2	74.3	114.4	185.3	298.5
Pb^{2+}	-	-	-	29.6	49.8	68.7	127.4	173.3	276.4

$^{a}[M^{+}(NO_3)_2]=0.1$ mole/l, Volume = 2, $NaNO_3$ = 0.1mol/l,Volume of electrolyte solution=25ml, time=24hr (equilibrium state),Room temperature.

$$^{a}D = \frac{\text{Weight of metal ions taken up by 1g of resin}}{\text{Weight of metal ions present in 1ml of solution}}$$

CONCLUSION

[1] It is selective chelating ion-exchange resin for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions.
[2] These resin showed a higher selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+} ions as compared to Zn^{2+}, Cd^{2+} and Pb^{2+} ions.
[3] The polymer showed higher selectivity for Fe^{3+} at pH 2.5 as compared to other metal ions.

[4] The results of ion exchange study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of a different metal ion.
[5] Thus resin can be useful in water treatment and pollution control.

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