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Der Pharma Chemica, 2012, 4 (2):791-799
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Preparation, Characterization and Chelating Ion-exchange Properties of copolymer Resin Derived from 2,4-Dihydroxy Benzoic acid, Ethylene Diamine and Formaldehyde

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ABSTRACT

Copolymer resin (2,4-DHBEDF) has been synthesized by the condensation polymerization of 2,4-dihydroxybenzoic acid and ethylene diamine with formaldehyde in the presence of acid catalyst, was proved to be selective chelation ion-exchange resin for certain heavy metals. The chelating ion-exchange properties of these copolymer was studied for Fe(III), Cu(II), Ni(II), Co(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 involving 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 ion-exchange capacity of metal ions has also been determined experimentally and compared 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 spectra, nuclear magnetic resonance spectra and C¹³ NMR spectra. The physico-chemical and spectral methods were used to elucidate the structures of 2,4-DHBEDF resin. The morphology of the copolymer was studied by scanning electron microscopy; showing amorphous nature of the resins therefore can be used as a selective ion-exchanger for certain metal ions.

Key words: Polycondensation, Resins, Degree of Polymerization, Structure, Ion-exchanger.

INTRODUCTION

Many research works has been carried out on the preparation and characterization of urea containing copolymers. Copolymer is found very useful application as adhesive, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins [1-5]. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions [6-7]. Chelating ion-exchange properties of the resin involving poly[(2,4- dihydroxybenzophenone) butylene] and its polychelates with transition metals are reported [8]. A new chelating sorbent for metal ion extraction under saline conditions has also been studied [9]. Poly (2- hydroxy-4 acryloyloxybenzophenone) resin [10] and resin functionalized with dithiooxamide [11] are found to be chelation ion exchangers. Copolymers involving 2-hydroxyethylmethacrylate and 2-methacryloyl-amidocysteine [12], polyacrylonitrile beads and 2-amino-2-thiazoline [13] and 4-hydroxy acetophenone-biuret-formaldehyde [14] are reported for their ion-exchange characteristics. The purpose of present study, is to explore the adsorption behavior of five metal ions Fe²⁺, Cu²⁺, Ni²⁺, Co²⁺ and Pb²⁺ on the newly synthesized copolymer resin 2,4-DHBEDF 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. The copolymer resin under investigations are 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 polymers is their capability to recover metal ions from waste solution. Hence the chelating ion exchange property of the 2,4-DHBEDF 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, precipitation 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 [15-16].

The present study deals with the synthesis and characterization of 2,4-DHBEDF copolymer resin by spectral methods for the first time. The synthesized copolymer was characterized by elemental analysis, UV-VIS, FT-IR, ^1H NMR, ^{13}C NMR, intrinsic viscosity and number average molecular weight. One of the important applications of chelating and functional polymer is their capability to recover metal ions from waste solutions. Hence, the chelation ion-exchange property of the 2,4-DHBEDF copolymer resin was also reported for specific metal ions. Some commercially available ion-exchange resins are given in Table 1.

MATERIALS AND METHODS

All the reagents and chemicals were of the analytical grade

Preparation of 2,4-DHBEDF copolymer resin

A mixture of 2,4-dihydroxybenzoic acid (0.1 mol), ethylene diamine (0.1 mol), formaldehyde (0.2 mol) and 2M HCl (200ml) was taken in a round bottom flask, fitted with water condenser and heated in on oil bath at $126 \pm 2^\circ\text{C}$ for 5 hrs with occasional shaking. The resinous solid product obtained was immediately remove from the flask as soon as reaction period was over and then purified.

The solid resinous product obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of mortar and pestle. The powdered sample was washed many times with boiling water to remove unreacted monomers. The air dried powdered then extracted with diethyl ether and then with petroleum ether to remove 2,4-dihydroxy benzoic acid-formaldehyde copolymer which might be present along with 2,4-DHBEDF copolymer resin. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The resulting polymer sample was filtered, washed several time with boiling water, dried in air, powdered and kept in vacuum over silica gel.

Characterization of the copolymer

The copolymer resin was subject to micro analysis for C, H and N on Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weights \overline{M}_n were determined by conductometric titration in DMSO using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 gm of terpolymer was made. Inspection of such a plot revealed that there were several breaks in the plot. From this plot the first break and the last break were noted. The calculation of \overline{M}_n by this method is based on the following consideration [17-18] : (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, (\overline{DP}) the average molecular weight have to be determined.

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

$$\overline{M}_n = \overline{DP} \times \text{molecular weight of the repeating unit}$$

The intrinsic viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30°C. Intrinsic viscosity (η) was calculated by the Huggin's eq.(1) [19] and Kraemer's eq.(2) [20].

$$\ln \eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \text{----- (1)}$$

$$\ln \eta_r/C = [\eta] - K_2 [\eta]^2 C \text{----- (2)}$$

Electronic absorption spectra of the copolymers in DMSO were recorded with a double beam spectrophotometer fitted with an automatic pen chart recorder on thermosensitive paper in the range of 200 – 850 nm.

Infrared spectra of 2,4-DHBEDF copolymer resin was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of 4000 – 500 cm^{-1} at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR and C^{13} NMR spectra were recorded with Bruker Adanve – II 400 NMR spectrophotometer using DMSO- d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications, which is shown in Figure 5. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur (M.S.).

Ion-exchange properties

The ion-exchange properties of the 2,4-DHBEDF copolymer resin was determined by the batch equilibrium method [21]. We studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the copolymer and solutions.

Determination of metal uptake in the presence of electrolytes of different concentrations

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 using either 0.1 M HNO_3 or 0.1 M NaOH . The suspension was stirred for 24 h at 30°C. To this suspension 2 ml of 0.1 M solution of the metal ion was added and pH was adjusted to the required value. The mixture was again stirred at 30°C for 24 h. 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 (ethylenediamine tetraacetic 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 [22-23]. Metal ion, its pH range, buffer and indicator used and colour change are given in **Table 3**. The metal ion uptake can be determined as:

$$\text{Metal ion adsorbed (uptake) by resin} = (X - Y) Z \text{ mmol/g}$$

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

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 the Rate of Metal Ion Uptake as a Function of Time

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 described above were carried out, in which the metal ion taken up by the chelating resins was determined from time to time at 30°C (in the presence of 25 ml of 1 M NaNO_3 solution). It was assumed that, under the given conditions, the state of equilibrium was established within 24 h [24]. The rate of metal uptake is expressed as percentage 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:

$$\text{Metal ion taken up at different times (\%)} = \text{Metal ion adsorbed} / \text{Metal ion adsorbed at equilibrium} \times 100$$

The percent amount of metal ions taken up at different times is defined as: Percentage of metal ion adsorbed after 1 h = $(100X) / Y$

Where X is mg of metal ion adsorbed after 1 h and Y is mg of metal ion adsorbed after 25 h. 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 0.1 M metal nitrate solution of Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺ and Pb²⁺.

Evaluation of the Distribution of Metal Ions at Different pH Solutions

The distribution of each of the seven metal ions i.e., Cu(II), Ni(II), Co(II), Pb(II) and Fe(III) between the polymer phase and the aqueous phase was determined at 30°C and in the presence of 1 M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio, D, is defined by the following relationship [25-26]...

$$D = \frac{\{\text{Wt. (in mg) of metal ions taken up by 1 gm of terpolymer}\}}{\{\text{Wt. (in mg) of metal ions present in 1 ml of terpolymer}\}}$$

RESULTS AND DISCUSSION

The resin sample was dark brown in colour, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, and pyridine and concentrated H₂SO₄. The resins synthesized do not show sharp melting point but undergo decomposition 420-425°K. These resins were analyzed for carbon, hydrogen, and nitrogen content. The composition of copolymer obtained on the basis of the elemental analysis data was found to be in good correlation, which is presented in Table 1.

The molecular weight (\overline{M}_n) of the copolymer was determined by nonaqueous conductometric titration in DMSO against KOH in a 50% (v/v) DMSO/alcohol mixture using 100mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100g of copolymer was made. The number average molecular weight (\overline{M}_n) could be obtained by multiplying the \overline{DP} by the formula weight of the repeating unit.

Table 1. Elemental analysis data, molecular weight determination and viscometric data of 2,4-DHBEDF copolymer resin

Copolymer	Elemental analysis (%)			Molecular Weight	Intrinsic Viscosity [η]
	C	H	N		
	Calc. (Found)	Calc. (Found)	Calc. (Found)		
2,4-DHBEDF	55.78 (55.46)	5.80 (5.88)	11.60 (11.76)	5803.68	0.8942

Viscometric measurements were carried out in DMSO at 30°C. All resins showed normal behaviors. The intrinsic viscosity was determined by the Huggin's [27] eq. (1) and Kraemer's [28], eq. (2) are noted.. In accordance with the above relations, the plots of η_{sp}/c and against C were linear giving as slopes K₁ and K₂ respectively. The Intercept on the axis of viscosity function gave the (η) value in both the plots. The values of (η) obtained from both relations were in good agreement with each other. The values of Huggin's and Kraemer's constant K₁ (0.28) and K₂ (0.26) were determined from the slope of the graph and satisfy the condition of the relation K₁ + K₂ = 0.54 favorably [30-31]. It was observed that terpolymer having higher average molecular weight (Mn) shows a higher value of intrinsic viscosity [32].

Electronic Spectra

The UV-visible spectra of all 2,4-DHBEDF copolymer resin is shown in Figure 1. UV-visible spectra of purified resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min⁻¹ and at a chart speed of 5 cm min⁻¹. The perused of the UV-visible spectra of copolymers should almost similar nature. The spectra of these copolymers exhibit two absorption maxima in the region 248.50 and 282.50 nm. These observed positions of the absorption bands indicate the presence of hydroxy group, which is in conjugation with the aromatic nucleus. 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 presence of phenolic hydroxyl group (auxochromes) is responsible for hyperehromic shift i.e. Σ_{max} higher values [32-33]. This observation is in good agreement with the proposed most probable structures of this copolymer resin

Infrared Spectra

The IR spectra of 2,4-DHBEDF copolymer resins revealed that copolymer give a broad band appear in the region $3450 - 3250 \text{ cm}^{-1}$ may be assigned to the stretching vibration of the phenolic hydroxyl groups exhibiting intermolecular hydrogen bonding [34]. The sharp band displayed at $1630 - 1680 \text{ cm}^{-1}$ may be due to the bending vibration of $>\text{COOH}$ group. The band obtained at $\sim 1533 \text{ cm}^{-1}$ suggest the presence of $>\text{NH}$ (amido) group. A band appear in the reason of $1250 - 1340 \text{ cm}^{-1}$ show the presence of methylene bridges ($>\text{CH}_2$) in the polymer chain [35]. 1,2,3,4 and 5 pentasubstitution of aromatic ring is recognized from the bands appearing at $\sim 557.9 \text{ cm}^{-1}$

Nuclear Magnetic Resonance Spectroscopy

^1H NMR spectra of 2,4-DHBEDF copolymer resin show a weak multiplicity signals (unsymmetrical pattern) in the region 7.77 to 7.88 (δ) ppm may be due to the aromatic protons. The weak multiply signals appearing at 6.62 – 6.75 (δ)ppm may be due to the amido $-\text{CH}_2-\text{NH}-$ linkage [36-37]. A signal appeared in the region 4.07 – 4.98 (δ) ppm may be due to proton of methelenic bridges ($\text{Ar}-\text{CH}_2-$) of polymer chain. The signal in the range of 8.26 – 8.32 (δ) ppm is attributed to phenolic $-\text{OH}$ proton. A weak signal in the range of 3.2(δ) ppm exhibits the present of $\text{Ar}-\text{COOH}$ group.

^{13}C Nuclear Magnetic Resonance Spectroscopy

The peaks appeared at 122.14, 128.71, 129.49, 132.88 and 154.94 ppm may be corresponded to carbons present in aromatic benzoic acid ring [38]. The peak appeared at 163.11 ppm of may be corresponding to ethylene group of ethylene diamine moiety. The medium peak appeared at 116.33 ppm may be confirmed the presence of $-\text{C}-\text{NH}$ group of copolymer resin. The peak appeared at 66.56 ppm may be due to the presence of $-\text{C}-\text{OH}$ group in aromatic benzoic acid group. The peaks appeared at 39.91 to 40.27 ppm may be due to the $-\text{CH}_2-$ bridge in copolymer resin. All these peaks confirmed that the 2,4-DHBEDF copolymer resin must have linear structure.

Scanning electron microscopy (SEM)

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.1 for 2,4-DHBEDF. It gives the information of surface topography and defect in the structure. The resin appeared to be dark brown in colour. The morphology of polymer resin shows

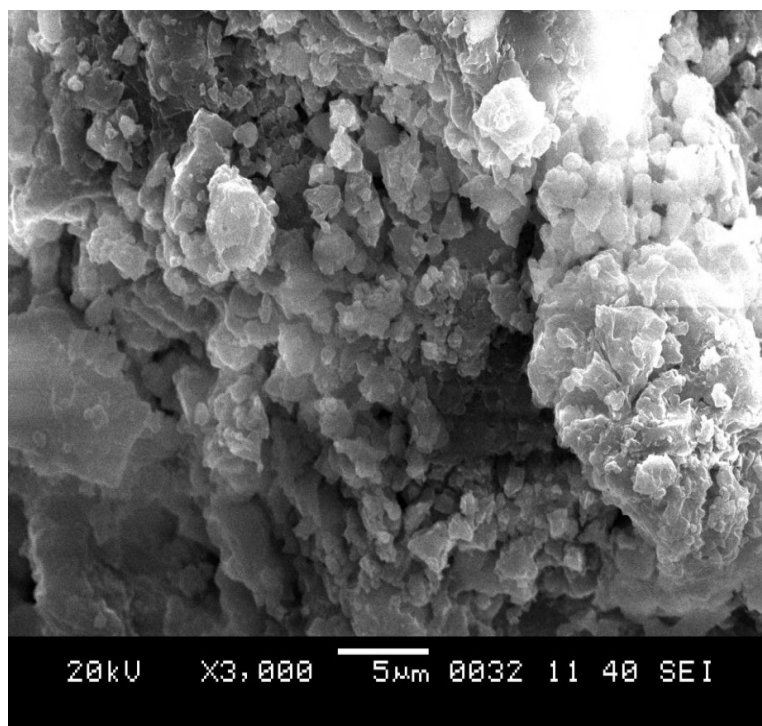


Fig.1. SEM Micrograph of 2,4-DHBEDF copolymer resin

spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 2,4-DHBEDF 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. Thus by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin [39-40], the 2,4-DHBEDF copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

Ion-exchange properties

Batch equilibrium technique developed by Gregor *et al.* and DeGeiso *et al.* was used to study of ion exchange property of 2,4-DHBEDF copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 2,4-DHBEDF is presented in Table 2, 3 and 4. Five metal ions Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{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 [28, 29, 30]. The details of experimental procedure are given below.

Table 2. Evaluation of the effect of different electrolytes on the uptake of several metal ions by 2,4-DHBEDF copolymer resin

Metal ion	Electrolyte (mol./l)	pH	Weight of metal ion (in mg. ⁻¹) taken up in the presence of different electrolytes			
			NaClO ₄	NaCl	NaNO ₃	Na ₂ SO ₄
Fe^{3+}	0.01	2.5	0.13	0.16	0.17	0.73
	0.05		0.15	0.24	0.29	0.67
	0.10		0.32	0.37	0.48	0.54
	0.50		0.64	0.68	0.69	0.49
	1.00		0.73	0.76	0.79	0.46
Cu^{2+}	0.01	4.5	0.08	0.09	0.09	0.58
	0.05		0.12	0.14	0.15	0.49
	0.10		0.22	0.21	0.20	0.41
	0.50		0.34	0.57	0.34	0.31
	1.00		0.58	0.66	0.49	0.20
Co^{2+}	0.01	5.0	0.06	0.09	0.19	0.40
	0.05		0.10	0.12	0.27	0.30
	0.10		0.20	0.27	0.42	0.20
	0.50		0.58	0.62	0.63	0.16
	1.00		0.67	0.71	0.70	0.09
Ni^{2+}	0.01	4.5	0.01	0.02	0.01	0.46
	0.05		0.02	0.07	0.001	0.35
	0.10		0.08	0.12	0.003	0.27
	0.50		0.27	0.20	0.005	0.23
	1.00		0.48	0.33	0.007	0.14
Pb^{2+}	0.01	6.0	0.13	0.20	0.37	1.62
	0.05		0.20	0.2	0.56	1.22
	0.10		0.38	0.77	0.93	0.89
	0.50		1.27	1.91	1.50	0.61
	1.00		2.01	2.25	1.83	0.42

[M(NO₃)₂] = 0.1 mol./lit.; Volume of metal ion solution = 2 ml.; Volume of electrolyte solution: 25 ml.; Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

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

We examined the effect of NO_3^- , Cl^- , SO_4^{2-} and ClO_4^- 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 Table 2, which shows that the amount of metal ions taken up by a given amount of terpolymer 2,4-DHBEDF 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(III), Cu(II) and Pb(II) ions increasing with increasing concentration of electrolytes. Whereas in the presence of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolytes [28]. Above 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.

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 3. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Table 3 shows the results of rate of uptake of metal ion on 2,4-DHBEDF 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 data's of Table 3 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(III) ions required about 3 hrs for the establishment of the equilibrium, whereas Cu(II) and Pb(II) ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe(III) >> Pb(II) > Cu(II) for the copolymer [36, 41, 42].

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.

Table.3.Comparison of the rates of metal (M) ion uptake by 2,4-DHBEDF copolymer resin

Metal ion	% of metal ion uptake at different time (hrs.)					
	1	2	3	4	5	6
Fe ³⁺	57.5	75	99.5	-	-	-
Cu ²⁺	8.2	15.4	25	33	45	49.5
Co ²⁺	50	62.5	76.5	85	87.5	90.5
Ni ²⁺	2	10	22	30.5	36.5	40.5
Pb ²⁺	40	51	61	74	78	85

[M(NO₃)₂] = 0.1 mol./lit.; Volume of metal ion solution = 2 ml.; Volume of electrolyte solution: 25 ml.;
Weight of resin = 25 mg.; Time = 24 hrs, at room temperature.

Metal ion uptake = (amount of metal ion absorbed x 100)/ amount of metal ion absorbed at equilibrium.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table 4. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymer resin 2,4-DHBEDF increase with increasing pH of the medium [22, 28, 31, 43-44]. 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 (Table 4). The selectivity of Fe(III) ion is more for the 2,4-DHBEDF polymer 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 Fe(III) > Cu(II) > Pb(II) [31]. Thus the result of such type of study is helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [22, 29]. The lowering in the distribution ratios of Fe(III) was found to be small hence, efficient separation could be achieved.

Table.4.Distribution ratio (D) of various metal ion as a function of the pH by 2,4-DHBEDF copolymer resin.

Metal ion	Distribution ratio of metal ion at different pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe ³⁺	100.2	120.26	139.03	4865.6	-	-	-	-	-	-
Cu ²⁺	-	-	-	38.09	42.79	61.77	72.72	96.29	133.33	184.62
Co ²⁺	-	-	-	52.20	87.12	122.75	344.72	1527.34	1278.6	1688.9
Ni ²⁺	-	-	-	27.30	39.009	62.136	80.52	72.72	108.64	306.42
Pb ²⁺	-	-	-	67.36	82.05	130.59	378.95	684.06	1527.3	2874.1

D = Weight (mg.) of metal ion taken up by 1 gm. of terpolymer/ Weight (mg.) of metal ions present in 1 ml. of solution.
[M (NO₃)₂] = 0.1 mol. /lit.; Volume = 2 ml. Volume of electrolyte solution: 25 ml. Weight of resin = 25 mg. Time = 24 hrs (equilibrium state), at room temperature.

CONCLUSION

2, 4-DHBEDF copolymer resin was prepared from 2, 4-dihydroxy benzoic acid and ethylene diamine and formaldehyde in presence of acid catalyst by condensation polymerization technique. The semi crystalline nature of

the 2,4-DHBEDF copolymer resin were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+} , Cu^{2+} , Pb^{2+} , Co^{2+} and Ni^{2+} ions. Since 2,4-DHBEDF copolymer contain phenolic (-OH) group and amino (-NH₂), it play a key role in the ion exchange phenomenon, because of it higher tendency of capturing metal ions. Thus 2,4-DHBEDF copolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. Due to considerable differences in the uptake capacities at different pH and media of electrolyte, and the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to separate particular metal ions from their admixtures by this technique. The copolymer shows higher selectivity for Fe^{3+} , Cu^{2+} than for Pb^{2+} , Co^{2+} and Ni^{2+} ions

Acknowledgement

Authors are thankful to the Director, Laxminarayan Institute of Technology, Nagpur, India, for providing the necessary laboratory facilities and also thankful to SAIF, Punjab University, Chandigarh for carrying out spectral analysis. One of the author W. B. Gurnule thanks to University Grant Commission, New Delhi for financial assistance.

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