

Research Article

Novel Polychelates of Trivalent La, Pr, Nd, Sm, Gd, Tb and Dy. Lanthanides with Phenol Based Resin and Application of Resin as an Ion Exchanger

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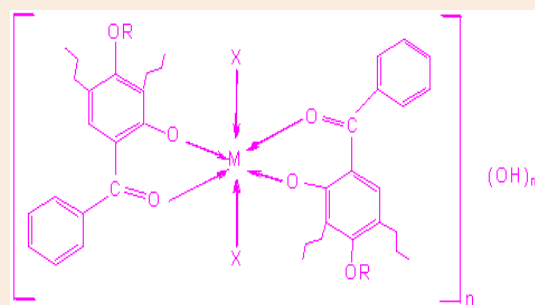
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Abstract

Synthesis of monomer 2,4-dihydroxy Benzophenone (DHBP) was carried out from resorcinol. The resins poly [(2,4-dihydroxy Benzophenone) ethylene], was synthesized using DHBP with ethane diol. Synthesised resin was used to prepare polychelates of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III), Monomer, resin and polychelates were characterized using modern analytical methods. The application of resin is also studied as an ion-exchanger for above mentioned Ln(III) metal ions at different Concentration of electrolyte, p^H and Time. It is found that the resin is found effective and efficient as an ion exchanger.

Keywords: Monomer, Resin, Polychelates, Lanthanides



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Introduction

Mineral processing and metal finishing industries produce large amount of effluents containing chromium, zinc, cadmium, copper, nickel and other toxic elements [1]. Metal ions are non-biodegradable in nature, therefore, their intake at certain level is toxic [2]. Copper is both vital and toxic for many biological system [3]. The increasing stringent environmental regulations and enforcement of discharge limits require effective decontamination and purification method. From an analytical point of view, it is known that solid retains analysts. The analyst are eluted from the sorbent using a suitable eluent. Preconcentration method is widely accepted technique for monitoring low concentration of metal ions.

Numerous method have been described for its effective separation and preconcentration; procedures based on ion exchange [4, 5], solvent extraction [6-8] and solid phase extraction (SPE) [9-13] are amongst them. Chelate-forming selected resins [14-17] have found numerous applications for separation and monitoring heavy metals, including lanthanides from aqueous solution [18-20]. The use of chelating resins for separation or removal method of choice is due to its high separation efficiency, good reproducibility of retention parameters and simplicity [21-24]. Considerable efforts have been made for improvement, economical and optimization of the chelating properties of ion-exchange resins [25-26]. Chelating ion exchange resins have specific chelating groups which are extensively useful in separation and preconcentration of metal ions [27-30]. Vernon [31] has summarized the desirable properties of a chelating polymer which includes: high capacity and appropriate selectivity. Polymeric resins which process chelating properties are found to be more selectivity. Polymeric resins which posses chelating properties are found to be more selective by nature [32, 33] as compared to other conventional techniques [34, 35] to remove metal ions. The

solid phase extraction method using molecular imprinted polymers is the most useful method for separation and preconcentration of trace metals [36, 37]. Molecular imprinting is a methodology for the introduction of selective recognition sites into highly cross-linked polymeric matrices via the template-directed assembly of functionalized monomers into a polymer network [38-40].

The chelate forming polymeric ligands characterized by reactive functional group containing O, N, S and P donor atoms and capable of coordinating to different metal ions, have been extensively studied [41-47]. Chelate forming polymers having multidentate coordination sites are known to form complexes with metal ions readily [48-50]. In a polymer matrix, they are expected to show affinity and selectivity towards the metal ion at an appropriate p^H . This led us to synthesized chelating resins, have affinity for the metal ions at appropriate p^H [51-54].

The phenolic resins are playing vital role in construction, automobile, electrical and appliance industries [55-57].

Experimental

Materials and Methods:

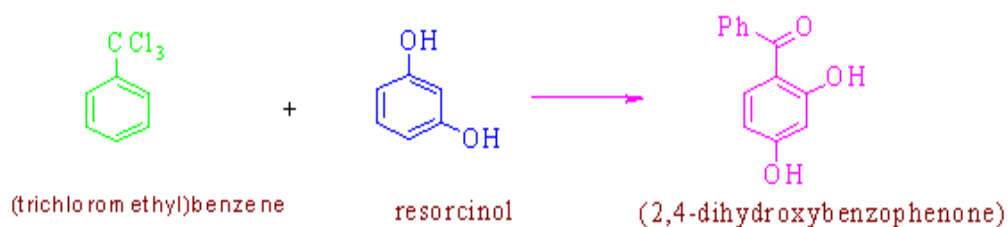
All the chemicals were used of AR grade and their solution were prepared in double distilled water &/or solvents. Hydrated acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium were used in the preparation of the polychelates.

Their characterization have been determined using VPO, NMR, UV-Visible, Electronic spectra and batch equilibrium technique was used for the ion exchange study. Ion exchange study was carried out using different electrolytes, varying various factors such as Time and p^H .

Synthesis of 2,4-Dihydroxy Benzophenone (DHBP)

In a round bottom flask Benzotrichloride (19.55 gm, 0.1 mol) and resorcinol (11 gm, 0.1 mol) were placed. The aqueous methanol (30%, 140 mL) was added slowly with stirring to the reaction mixture.

Then the resulting solution was refluxed at 85°C temp. for 5 hrs with constant stirring. Then the reaction mixture was allowed to cool and separated product at the bottom was collected by filtration. Than it was washed with hot water to remove unreacted resorcinol to give pale yellow needles of 2,4-dihydroxy benzophenone (DHBP) (Scheme 1).



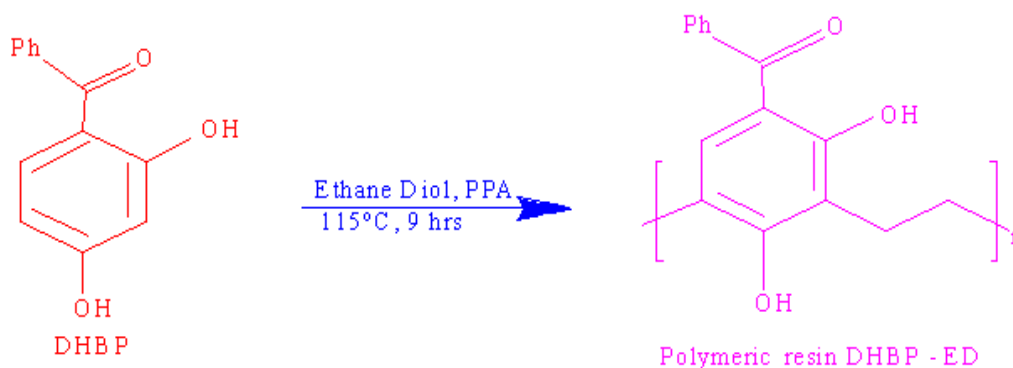
Scheme 1 Synthesis of 2,4-dihydroxy benzophenone

Synthesis of Resins:

Polycondensation of 2,4 dihydroxy benzophenone with Ethane Diol

To a well stirred and ice-cooled mixture of 2,4 dihydroxy benzophenone (12.84 gm, 0.06 mol) and ethane diol (3.35mL, 0.06 mol), polyphosphoric acid (PPA) (20gm) was added slowly with stirring as a catalyst (Scheme 2). The

reaction mixture was cooled and left at room temperature and condensed an oil bath at 115°C for 9 hrs. The reaction mixture was then cooled, poured on crushed ice and left overnight. A brown solid was separated acid and monomer. The synthesized resin was further purified by reprecipitation from dimethyl formamide (DMF) with water for three times and dried at 60°C temperature. The purified resin was reddish brown in color. D.P. > 265°C, Yield 42.80%.

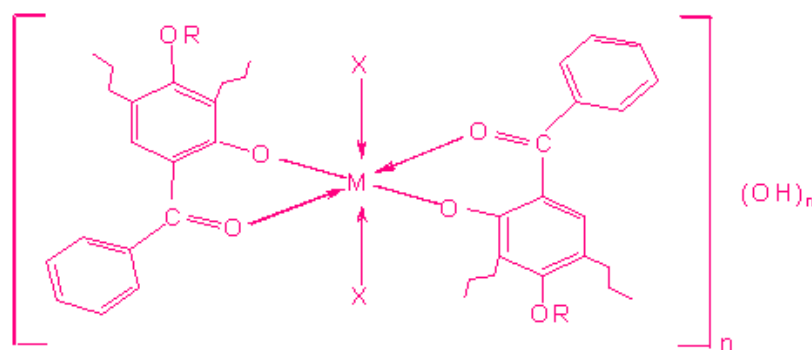


Scheme 2 Synthesis of DHBP-ED resin

Synthesis of Polychelates

The polymeric ligands DHBP-ED was used to synthesize polychelates of Ln(III) ions. Following general procedure has been established and used for several trials for the synthesis of polychelates from polymeric ligands. Hydrated acetates of lanthanum, Praseodymium, Neodymium, Samarium, Gadolinium, Terbium and Dysprosium were used for the synthesis of the polychelates.

A dried polymeric ligand (0.01 mol) was dissolved in DMSO (50 mL). The metal acetate (0.005 mol) was also dissolved in DMSO (25 mL). The hot and clear solution of the metal acetate was added to the hot and clear solution of polymeric ligand with constant stirring. A dark colored product precipitated out immediately. The suspension was digested on a water bath for two hours and then filtered. The solid was washed with cold DMSO to remove unreacted metal acetate. Finally, the polychelate formed was washed with acetone and dried at 60°C for 24 hrs. The proposed geometry of the polychelate is given in **scheme 3**.



Scheme 3. proposed geometry of polychelates
M = La^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Dy^{III}
X = H₂O R = H

Results and Discussion

Resin and polychelates were characterized using modern analytical methods. Their IR, NMR, Average molecular weight, UV visible spectra found same as reported earlier [58].

Table 1 Analytical data of the DHBP-ED resin and its Polychelates

Compound	Formula weight of Repeating unit	% Found (Calculated)			μ_{eff} (B.M)
		M	C	H	
(DHBP-ED) _n [C ₁₅ H ₁₂ O ₃] _n	240	---	75.00 (74.98)	5.00 (5.03)	---
{[La(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ La] _n	670	20.90 (20.71)	53.91 (53.74)	4.02 (4.05)	Diamagnetic
{[Pr(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Pr] _n	672	21.00 (20.95)	53.51 (53.58)	4.03 (4.04)	3.66
{[Nd(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Nd] _n	675	21.22 (21.34)	53.41 (53.32)	4.00 (4.02)	3.63
{[Sm(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Sm] _n	681	22.03 (22.05)	52.93 (52.84)	3.95 (3.99)	1.72
{[Gd(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Gd] _n	682	22.03 (22.05)	52.94 (52.84)	3.96 (3.99)	7.88
{[Tb(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Tb] _n	690	23.10 (23.01)	52.30 (52.18)	3.90 (3.94)	9.46
{[Dy(DHBP-ED) ₂ (H ₂ O) ₂].OH} _n [C ₃₀ H ₂₇ O ₉ Dy] _n	694	23.35 (23.41)	52.00 (51.91)	3.95 (3.92)	10.63

DHBP-ED = poly [(2,4-dihydroxybenzophenone)ethylene

Poly [(2,4- dihydroxy benzophenone) ethylene] resin - (DHBP-ED)

¹H NMR (DMSO – d₆): δ = 12.02 (s, phenolic OH, ortho to (Ar-Co)), 3.92 (q, 2H –Oet, para to (Ar-CO)), 3.35 (t, 2H, bridge), 3.17 (t, 2H, bridge), 7.23 – 7.66 (6H, Ar-H).

IR(KBr): 3200-3400 (-OH stretching), 2950-2980 (-CH₂ Stretching), 2735 (Intra mol. H-), 1635±10 (>C=O), 1590, 1560, 1525, 1495, (-C=C-), 1345 (-OH), 1280±10 (Ar-O-R), 995, 860 ± 10, 700 (Ph ring) cm⁻¹.

Vapor pressure Osmometry (VPO) / Experimental Details (VPO)

An average molecular weight of the resin was determine using the technique and experimental process carried out same as earlier [59]. As indicated above, estimation of (n) [60-63] by VPO comprises of two experiments (i) experiments for known solute (polystyrene) to determine VPO constant 'K' and (ii) experiments for unknown solute (resin).

Estimation of VPO constant K

Four diluted solutions of polystyrene with known concentration prepared in DMF. The concentrations were 5.56, 11.12, 16.68 and 22.25 gm. mol⁻¹ in DMF. The VPO [64-66] experiment was carried out by following the details prescribed in the instrument manual (Knauer Germany, Vapor Pressure Osmometer). The bridge out put SD (In

millivolts) which is ultimately proportional to the vapor pressure lowering is measured for each experiment. The plot was found to be linear passing through the origin. The slope of the plot was measured and K was calculated. The details are shown in the table. The value of VPO constant was found to be 1.15×10^4 mV.kg.mol⁻¹.

Estimation of (n) of resins

Dilute solutions of resins samples were prepared. Four concentrations were prepared, and they were about 2.21, 4.42, 6.63 and 8.84 gm.mol⁻¹ in DMF the VPO experiment was carried out with each concentration and corresponding bridge output reading in SD (millivolts) was noted. Then a plot of SD Vs C was drawn. The plot was found to be linear and passing through the origin. The slope of the plot was determined. From the value of the slope and the VPO constant K (1.15×10^4), the value of (n) of the resin samples was estimated. The details of concentration, bridge output SD, Slope and (n) calculation of the resins DHBP-ED, presented in table 2.

Table 2 Molecular Weight Determination of Resins by VPO Method

Resin	Conc. Gm.mol ⁻¹	S.D. Millivolts	Slope of Plot	$\bar{M}_n = K/\text{slope}$ g.mol ⁻¹
DHBP-ED	2.21	22.00	9.39	1124
	4.48	43.00		
	6.63	65.00		
	8.84	85.00		
	2.21	21.00		

Visible Spectra of Resins

Polymers carrying the reactive functional groups are significant in a variety of uses. Amongst these materials which are ultraviolet absorbing groups attached to the polymer chain [64]. In recent years polyolefin films have been made more stable to atmospheric degradation by incorporating polymerizable 2-hydroxy benzophenone in the main chain [65].

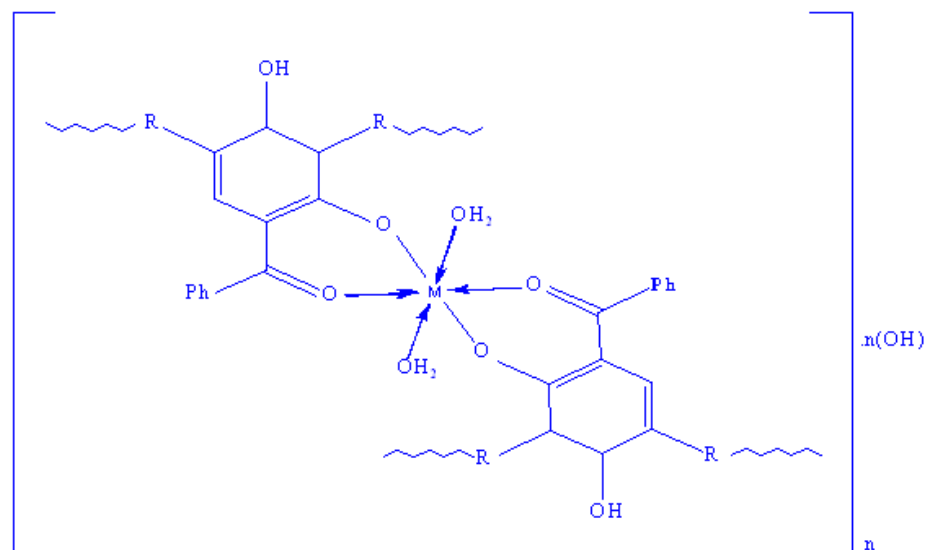
Backer [66] had prepared 2-hydroxy-4-acryloxy benzophenone, 2-hydroxy-4-methacryloxybenzophenone and several other similar polymerizable UV-absorbers and had copolymerized them with ethylene to give polymeric and had copolymerized them with ethylene to give polymeric UV-absorbers. He found that polyethylene (PE) films (0.1mm) stabilized with 2-hydroxy-4-methacryloxybenzophenone (incorporated as comonomer) were much resistant to weathering than films stabilized by blending in additives.[67] Narang [68] reported that repeated toluene extract of a copolymer 2-hydroxy-4-methacryloxybenzophenone and ethylene did not remove any of the UV stabilizers and the polymer showed no evidence of exudation on long-term exposure.

The UV spectra of DHBP [69] and its polymeric resins (DHBP-ED, DHBP-1,2 PD, DHBP-1,3 BD and DHBP-1,4 BD) shows bands at 289 and 390 nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition [70]. By proper selection of copolymer, useful UV-absorbing polymers with varying amount of UV-absorbing groups (DHBP) can be synthesized. DHBP has intermediate thermal properties and hence can remain in a blend resins during various applications and can also protect the resins from UV light.

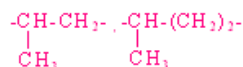
UV Visible Spectra of Polychalates

The data indicates the energy of $f-f$ transitions in polychelates is slightly reduced compared to the corresponding aquo ions either because of the slight covalent interaction of the “4 f ” orbitals with vacant ligand orbitals leading to some delocalization with consequent reduction in interelectronic repulsion [64] or by increased nuclear shielding of the orbitals due to slight covalent ligand-metal electron drift compared to the aquo ions of the lanthanides. The $f-f$ transition bands of the polychelates show weak perturbation and increased intensity due to complex formation, presumably due to the nephelauxetic effect [65].

The electronic spectra of all the polychelates exhibit the addition of two spectral bands in the resin 289-295 and 390-420 nm. The first band occurs in the spectra of polymeric ligand (resin).



Where, R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$



M = La^{III} , Pr^{III} , Nd^{III} , Sm^{III} , Gd^{III} , Tb^{III} , Dy^{III}

Scheme 4. Synthesized different lanthanide Metal complexes

The chelating behaviour of synthesized phenolic benzophenone based resins for lanthanide metal ions (La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+}) was determined by batch equilibrium technique. The fine resin powder sample was dried in vacuum at $60^\circ C$ for 24 hrs and was then used for the ion-exchange study. Duplicate experiments involving 0.50 gm of dry, 300 mesh size resin samples were equilibrated with 15.0 mL of acetate-acetic acid buffer solution of pH 7.0 ionic strength of 0.10 M (using sodium perchlorate) for 2 hrs. To this mixture, 2.0 mL of 0.1 M metal ion solution was added. After being shaken for 24 hrs at $30^\circ C$, the mixture was filtered and metal content remaining in the filtrate was determined by complexometric titration using standard Na_2EDTA solution and xylenol orange as an indicator [66]. Ion-exchange study was carried out using three experimental variables:

1. p^H of the aqueous medium,
2. Electrolyte and its ionic strength and
3. Shaking time

Among these three variables, two were kept constant and only one was change at a time to evaluate its effect on metal uptake capacity of the resins. The details of the experimental procedure are as given below.

Influence of an Electrolyte on Uptake of Metal

In order to study the influence of nature of the electrolyte and its concentration on the amount of metal ions taken up by the samples, the experiments were carried out as follows. All experiments were carried out with 50 mg of the resin under specified conditions as fixed pH and in presence of various concentrations of electrolytes under study. The 50 mg of the resin sample was stirred in each of the following four solutions for 24 hrs.

Set	:	I	II	III	IV
Concentration	:	0.05 M	0.10 M	0.50 M	1.00 M

0.1 M solution of metal ion (2 mL) was added to each of the above solutions. The pH of the mixed solution was adjusted to the given value by adding required amount of aqueous acid or alkali. After 24 hrs the content of each filtrate and washings were collected. The metal ion in solution was estimated with complexometric method using standard Na₂EDTA.

A separated blank experiment was carried out in absence of an electrolyte using same amount of resin and metal ion. Instead of electrolyte distilled water was used to swell the resin. The difference in the amount of metal ion in the residual solution of blank and actual experiment represent the excess metal ion which has been taken up by the given chelating resin due to the presence of give electrolyte of known concentration. Such experiments were carried out using NaCl, NaNO₃, Na₂SO₄ and NaClO₄. The details are given in the table 3.

Effect of the p^H of the Medium on metal Binding Capacity

The effect of p^H on the metal binding capacity of the resins was estimated at room temperature in the presence of 1.0M NaNO₃ solution as an electrolyte.

The resin sample (50 mgs) was suspended in the electrolyte solution and pH of the suspension was adjusted to required value by addition of either 0.1M HNO₃ or 0.1M NaOH solution. To this, metal solution (0.1M metal nitrate, 2mL) was added and pH of the medium adjusted to the desired value. The content was mechanically stirred for 24 hrs, filtrated and washed with distilled water. The filtrate and the washings were collected in a conical flask and the unabsorbed metal was estimated by back titration with standard Na₂EDTA solution using suitable indicator. A separate blank experiment (without adding resin sample) was also carried out in the same manner. From the difference between the sample and blank, the amount of metal adsorbed by the resin was calculated and expressed in terms of milli-equivalent per gram of the resin (meq.g⁻¹). The above experiment was performed at p^H = 3.0, 4.0, 4.5, 5.0, 5.5 and 6.0. Results are presented in table 4-5.

Evaluation of Distribution Ratio (K_D) of Metal Ions over the Wide Range of p^H

The distribution of each of the metal ions La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, Tb³⁺ and Dy³⁺ between the resin phase (solid) and aqueous phase (liquid) was estimated at appropriate pH, using 1.0M NaNO₃ solution. The 50 mg of the resin was stirred in 1.0M NaNO₃ (40mL) at 3 p^H for 24 hrs. To the swelled resin, 2mL, 0.1M metal nitrate solution was added. The p^H was adjusted to the required value. The experiments were carried out from 3.0, 4.0, 4.5, 5.0, 5.5 and 6.0 p^H. After 24 hrs mixture was filtered; the filtrate and washings were collected. The amount of metal ion which remained in the aqueous phase was estimated. The original metal ion concentration is known, and the metal ion adsorbed by the resin was estimated. The distribution ratio 'K_D' is calculated from the following equation; and presented in table 6.

$$K_D = \frac{\text{Amount of metal ion adsorbed by resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution}}{\text{Weight of resin}}$$

Evaluation of the rate of Metal Uptake

To determine the time required to reach the state of equilibrium under given experimental condition, series of experiments have been carried out, in which metal taken up by chelating resin was estimated from time to time. It is assumed that 25°C and under given conditions, the state of equilibrium is established in 24 hrs. The rate of metal uptake is expressed as a percentage of the attainment of the state of equilibrium. If “X” gm of metal ions were adsorbed after one hour and “Y” mg of metal ions are adsorbed at equilibrium i.e. after 24 hrs $X \times 100/Y$ would be the measure of percentage of equilibrium attained after one hour.

The resin sample was swelled by keeping it in contact with the electrolyte at the required p^H . 50 mg resin sample was stirred in 50 mL of 1.0 M $NaNO_3$ for 24 hrs then 2 ml of 0.1M metal solutions was added and required p^H was adjusted with HNO_3 / $NaOH$ solution, then such experiment were carried out varying the contact period viz. 1,2,3,4,5,6,7 up to 24 hrs, respectively. After the reaction time was over, the solid was filtered and washed with distilled water. The filtrate and washings were collected and estimated for the metal ions and data are presented in table 7-8.

Comparative study of Ion Exchange resins

Ion-exchange study was carried out with seven metal ions under limited variables and experimental conditions. For a comparative study, study was carried out strictly under similar conditions with DHBP-ED. From the study, the behavior of the synthesized polymers as a chelating ion-exchanger with respect to experimental variables is as follows;

Effect of Electrolyte and its Concentration on the Metal Binding Capacity

The results of the effect of the nature and concentration of an electrolyte on the amount of various metal ions adsorbed by the resins from their solution at room temperature are shown in **table 3**. From these data it is revealed that amount of metal ion taken up by the given amount of resin sample depends upon the nature as well as concentration of electrolyte employed for the study. It is also observed that amount of La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} uptake by resin is increasing with increase in concentration of NO_3^- , ClO_4^- and Cl^- and decreases with an increase in concentration of SO_4^{2-} .

It is also observed that in presence NO_3^- , ClO_4^- and Cl^- ions, good results are obtained from all metal ions while SO_4^{2-} ion is not found suitable for maintaining high ionic strength of solution in ion-exchange study. The Cl^- ion has a tendency to form a strong complex with many metal ions [67]. In the ion-exchange study all the relevant experiments were carried out using $NaNO_3$ as electrolyte to maintain constant ionic strength of the solution. The overall observation of the result shows that on an average, the metal ion adsorption by the resin is much better in presence of 1.0M $NaNO_3$ Solution.

Effect of p^H on the Metal Binding Capacity

The equilibrium also depends on the p^H of the aqueous medium to a great extent. The study of influence of p^H of the aqueous medium on the metal uptake capacity of resin was carried out in presence of constant amount of 1.0M $NaNO_3$ solution at various p^H value between 3.0 to 6.0 for La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} metal ions.

Typical p^H -binding capacity profile for the resin indicates that, at lower p^H values ($< p^H$ 6) protonation of chelating groups takes place, complexation with available ligands is reduced and hence percentage uptake decreases. At higher p^H values ($> p^H$ 6) deprotonation of coordination resin takes place and hence, the absence of the competition between metal ions and protons for lone pair electrons is observed. Thus, the percentage of metal ions uptake increases through the formation of stable polymer- metal complexes [68]. It is found that the relative amount

of metal ion uptake by the resin increases with increasing pH of the medium [69-71]. The maximum uptakes metal ion occurs at pH=6.0.

Evaluation of Distribution Ration (K_D) of Metal Ions over the wide Range of p^H

The effects of p^H on the amount of metal ions distributed between two phases. The results shows that the amount of metal ions taken up by the resins at equilibrium increases with increase in the p^H of the medium. The ion-exchange study is helpful in selecting the optimum p^H for a selective uptake of a particular metal ion from a mixture of different ions. For all the metal ions, time required for the uptake by all the resins does not differ much from each other. This is also true for the time required to reach the state of equilibrium for any given metal ions. It is found that the relative amount of distribution ratio increases with increasing p^H of the medium.

Rate of Metal uptake as a Function of Time

In the present study, it was assumed that, under the prescribed experimental condition the state of equilibrium is established within 24 hrs. The result of the rate of metal uptake by the resin is a function of time. It is expressed in terms of % of metal ions adsorbed by the resin after regular time intervals with respect to 100% adsorption after 24 hrs i.e. in the state of equilibrium. The rate of metal ion adsorption by resin was determined for various metal ions to establish the shortest time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. The term "rate" refers to the speed of change in the concentration of metal ion in the aqueous solution which is in contact with resin. Thus, the uptake of metal ion by the resins increases with increase in initial metal ion concentration and reaches a plateau at higher concentration [72-73]. The uptake of metal ions by the resin involves either chelation or ion-exchange [74-77] or both. The result show that as the time increases the uptake of metal ions also increases and also the time taken for the uptake of different ion at the given stage depend on the nature of the metal ion and chelating resin samples.

Table 3 Effect of Electrolyte Concentration on Metal Ion Adsorption Capacity of DHBP-ED Resin

Metal ions	Electrolyte (Mol. lit ⁻¹)	Metal ion uptake (meq.g ⁻¹) in presence of electrolyte			
		NaNO ₃	NaCl	Na ₂ SO ₄	NaClO ₄
La ³⁺	0.05	0.57	0.49	0.53	0.55
	0.10	0.69	0.66	0.45	0.63
	0.50	0.77	0.73	0.36	0.75
	1.00	0.81	0.79	0.29	0.81
Pr ³⁺	0.05	0.53	0.49	0.51	0.56
	0.10	0.65	0.67	0.43	0.65
	0.50	0.75	0.75	0.32	0.77
	1.00	0.79	0.81	0.28	0.82
Nd ³⁺	0.05	0.58	0.49	0.52	0.56
	0.10	0.65	0.66	0.44	0.66
	0.50	0.82	0.77	0.34	0.76
	1.00	0.87	0.84	0.29	0.79
Sm ³⁺	0.05	0.60	0.50	0.53	0.57
	0.10	0.69	0.67	0.44	0.67
	0.50	0.80	0.76	0.34	0.77
	1.00	0.88	0.85	0.30	0.82
	0.05	0.55	0.50	0.52	0.58

Gd ³⁺	0.10	0.65	0.64	0.44	0.69
	0.50	0.80	0.75	0.35	0.79
	1.00	0.86	0.87	0.31	0.84
Tb ³⁺	0.05	0.60	0.51	0.52	0.59
	0.10	0.67	0.65	0.43	0.68
	0.50	0.79	0.76	0.32	0.79
Dy ³⁺	1.00	0.89	0.88	0.30	0.85
	0.05	0.58	0.53	0.52	0.59
	0.10	0.69	0.69	0.44	0.70
	0.50	0.78	0.77	0.34	0.81
	1.00	0.89	0.89	0.33	0.88

Table 4 Effect of p^H on metal ions uptake capacity of DHBP-ED resin Blank reading = 20.92

Metal ions	Metal Ion uptake pH of the medium					
	3.0	4.0	4.5	5.0	5.5	6.0
La ³⁺	18.42	18.02	17.67	17.32	16.99	16.67
Pr ³⁺	18.57	18.27	17.87	17.52	17.17	16.77
Nd ³⁺	18.82	18.47	18.17	17.77	17.42	17.02
Sm ³⁺	18.52	18.22	17.92	17.52	17.22	16.92
Gd ³⁺	18.37	17.97	17.67	17.37	17.12	16.82
Tb ³⁺	18.67	18.47	18.17	17.72	17.42	16.97
Dy ³⁺	18.32	17.97	17.52	17.17	16.87	16.62

Table 5 Effect of p^H on metal ions uptake capacity of DHBP-ED resin

Metal ions	Metal Ion uptake (meq.g ⁻¹) pH of the medium					
	3.0	4.0	4.5	5.0	5.5	6.0
La ³⁺	0.50	0.58	0.65	0.72	0.79	0.85
Pr ³⁺	0.47	0.53	0.61	0.68	0.75	0.83
Nd ³⁺	0.42	0.49	0.55	0.63	0.70	0.78
Sm ³⁺	0.48	0.54	0.60	0.68	0.74	0.80
Gd ³⁺	0.51	0.59	0.65	0.71	0.76	0.82
Tb ³⁺	0.45	0.47	0.55	0.64	0.70	0.79
Dy ³⁺	0.52	0.59	0.68	0.75	0.81	0.86

Table 6 Distribution Ratio K_D on metal ion uptake by DHBP-ED resin

Metal ions	Distribution Ratio K _D					
	3.0	4.0	4.5	5.0	5.5	6.0
La ³⁺	114.00	135.78	154.49	174.59	195.52	214.15
Pr ³⁺	106.30	121.83	143.36	163.01	183.45	207.87
Nd ³⁺	93.73	111.42	127.13	148.90	168.77	192.47
Sm ³⁺	108.85	124.47	140.62	163.01	180.48	198.58
Gd ³⁺	116.60	137.88	154.49	171.67	186.44	204.75
Tb ³⁺	101.23	111.42	127.32	151.69	188.77	195.52
Dy ³⁺	119.21	137.89	163.01	183.45	201.65	217.32

Table 7 Effect of Time on ions uptake capacity of DHBP-ED resin Blank reading = 20.92 ml

Metal ions	Time in hours*						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
La ³⁺	19.17	18.74	18.33	18.01	17.65	17.30	16.87
Pr ³⁺	19.37	18.99	18.19	18.24	17.84	17.48	17.05
Nd ³⁺	19.28	18.96	18.60	18.30	17.94	17.58	17.23
Sm ³⁺	19.33	19.00	18.64	18.27	17.89	17.59	17.23
Gd ³⁺	19.19	18.80	18.46	18.10	17.64	17.33	17.01
Tb ³⁺	19.33	18.95	18.59	18.26	17.87	17.58	17.22
Dy ³⁺	19.24	18.93	18.46	18.10	17.65	17.38	16.97

Table 8 Effect of Time on metal ions uptake capacity of DHBP-ED resin

Metal ions	% attainment in equilibrium Time in hours*						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
La ³⁺	41.17	51.07	60.71	68.33	76.79	85.05	95.11
Pr ³⁺	37.27	46.38	56.71	64.49	74.11	82.68	93.05
Nd ³⁺	41.81	50.25	59.39	67.07	76.32	85.55	94.39
Sm ³⁺	39.65	47.97	56.91	66.05	75.61	83.25	92.09
Gd ³⁺	42.18	51.51	59.92	68.72	79.81	87.39	95.25
Tb ³⁺	40.13	49.81	58.92	67.11	77.01	84.36	93.44
Dy ³⁺	38.99	46.12	57.31	65.47	76.02	82.23	91.68

Conclusion

It is found that the efficiency of the resin is dependent on nature and concentration of electrolyte used. In addition to this the other factors such as p^H and time also play an important role in exchange of ions. In this case optimum $p^H = 6$ and time is dependent upon nature of metal ion, resin and polychelate.

It is revealed from this study 2,4-dihydroxy-ethane diol resin acts as an efficient and effective ion exchanger for Lanthanides(III) metal ions.

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