



Synthesis, Characterization and Ion Exchange Applications of Resin of Ln (III) Polychelates

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ABSTRACT

Synthesis of monomer 2, 4-dihydroxy Acetophenone (DHAP) was carried out from resorcinol. The resins poly [(2, 4- di hydroxy Acetophenone) ethylene, was synthesized using DHAP with Butane1,4 diol. Synthesized resin was used to prepared 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.

Keywords: Monomer, resin, Polychelates, Lanthanides.

INTRODUCTION

Polymer-metal complexes have been attracting interest in many scientific and technological fields in recent years. Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups which act as a chelating group in binding polyvalent metal ions [1]. Chelate-forming polymers[2-4] have found widespread applications in the separation and monitoring of heavy metals, including lanthanides[5], from aqueous solutions; they shows significant applications in pollution control [6], bioinorganic industry, water purification and selective removal of waste materials in nuclear plants [7-9], preconcentration [10] , hydrometallurgy [11]. The chelates of phenols possess interesting microbial activities like growth inhibition and acceleration. Polymeric coordinating reagents are a novel type of substances possessing a combination of physical properties of a polymer and chemical properties of the attached reagent.

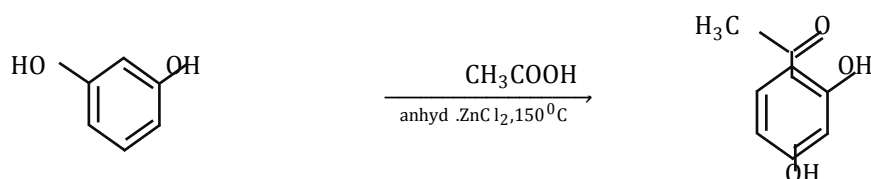
Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Many natural substances such as proteins, cellulose, living cells and soil particles exhibit ion exchange properties which play an important role in the way the function in nature. Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930 [12-13]. A few years later resins consisting of

polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed [13]. These two kinds of resin are still the most commonly used resins today.

MATERIALS AND METHODS

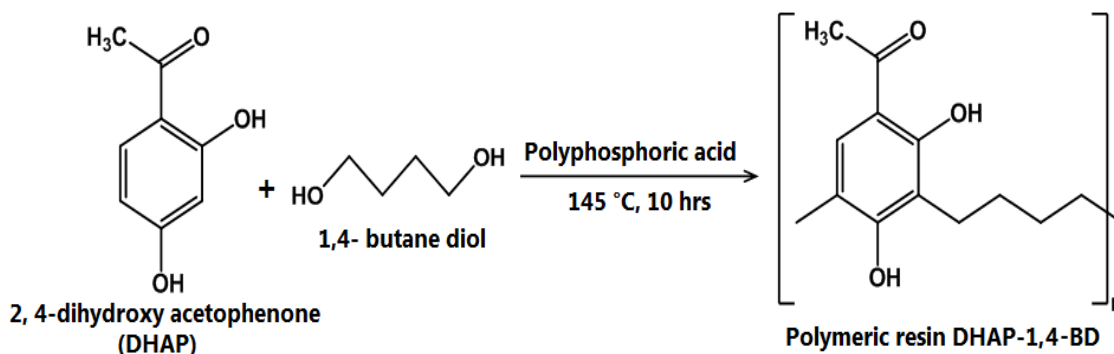
All the chemicals were used of AR grade and their solutions were prepared in double distilled water &/or solvents. Their characterization have been determined using VPO, NMR, UV-Visible, electronic spectra and batch equilibrium technique was used for the ion exchange study. Ion exchange study was carried out using different electrolytes, varying various factors such as Time and pH

Synthesis of Monomer 2, 4 - Dihydroxy Acetophenone (DHAP): Freshly fused and powdered zinc chloride (16.5 g, 0.27mol) was dissolved in glacial acetic acid (16 mL) by heating in a beaker on a sand bath. Dry resorcinol (11 g, 0.1mol) was added with stirring to the mixture at 140⁰C. The solution was heated until it just begins to boil and kept for 20 min at 150⁰C. Dilute hydrochloric acid (1:1, 50 mL) was added to the mixture and then the solution was cooled (5⁰C). The separates yellow product was filtered, was with dilute hydrochloric acid (1:3) and crystallized from hot water containing a little hydrochloric acid, the yield is 14 g (93%) and m.p.142 – 144⁰C.



Scheme 1. Synthesis of 2, 4 – di hydroxy Acetophenone (DHAP)

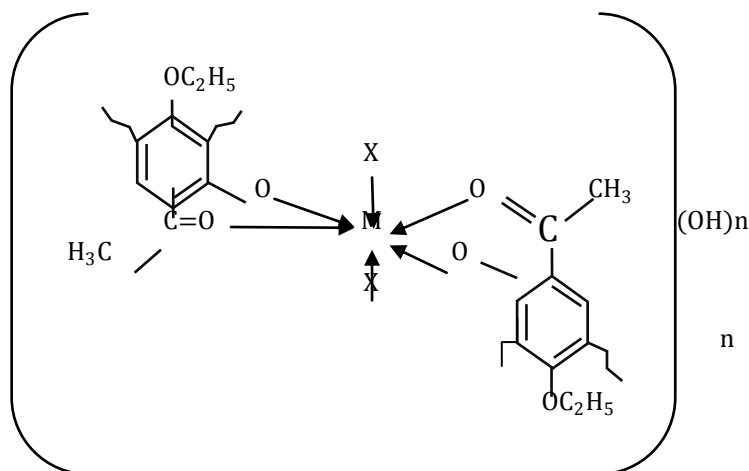
Synthesis of poly [(2, 4-dihydroxy Acetophenone) 1, 4- butylene] (DHAP-1, 4 BD) (Resins): Polycondensation of well stirred mixture of 2, 4- dihydroxy Acetophenone (9.12 g, 0.06 mol) and 1, 4 - butane diol (5.48 mL, 0.06 mol) in the presence of Polyphosphoric acid at catalyst at 145 °C was carried out for 10 h. The reaction mixture was then cooled, poured on crushed ice and left overnight. The product was collected by filtration and washed with cold water and methanol to remove unreacted acid and monomer. The synthesized resin was soluble in dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). The polymer was brown in colour with decomposition point >270 °C and yield 7.57 g (83.04 %) (Scheme 2)



Scheme 2. Synthesis of resin DHAP-1,4-BD

Synthesis of Polychelates: Hydrated acetates of lanthanum, praseodymium, neodymium, samarium, gadolinium, terbium, and dysprosium were used in the preparation of the polychelates. The hot and clear solution of the lanthanum acetate (1.72 g, 0.005 mol) was added with constant stirring to the hot and clear

solution of polymeric ligand (0.01 mol). A blackish-brown colored product separated out immediately. The suspension was digested on a water bath for 2h 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 h. A similar procedure was applied for the synthesis of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy (III) polychelates. All the polychelates are found soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The yield obtained was in the range of 60-80%.



Where, M=La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) X= H₂O

Scheme 3. Proposed structure of Polychelate

RESULTS AND DISCUSSION

Characterization of resin –(DHAP-ED) and their polychelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III), were carried out and the results are presented in table 1.

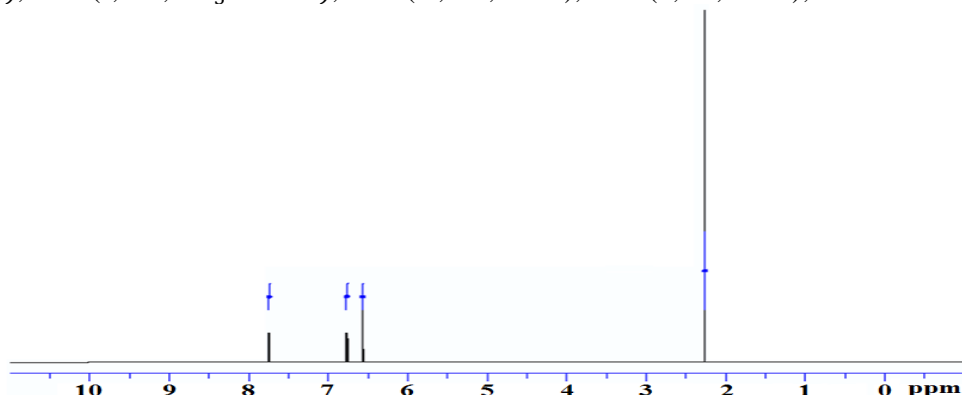
Table 1. Analytical Data of Polymeric Ligand DHAP- 1,4-BD and its polychelates

Compound	Formula weight of Repeating unit	Yield g(%)	(% Found (Calculated))			μ_{eff} (B.M.)
			M	C	H	
(DHAP-1,4-BD) _n (C ₁₇ H ₁₆ O ₃) _n	268	7.52 (82.51)	---	76.05 (76.10)	5.96 (6.01)	---
([La(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ La] _n	727	0.99 (74.11)	19.07 (19.11)	56.16 (56.21)	4.79 (4.86)	DM
([Pr(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Pr] _n	728	1.01 (75.10)	19.30 (19.34)	55.95 (56.05)	4.77 (4.84)	3.68
([Nd(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Nd] _n	732	0.95 (71.54)	19.64 (19.71)	55.7 (55.80)	4.75 (4.82)	3.57
([Sm(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Sm] _n	738	0.96 (72.24)	20.29 (20.37)	55.31 (55.33)	4.71 (4.78)	1.73
([Gd(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Gd] _n	745	0.97 (72.83)	21.04 (21.11)	54.74 (54.82)	4.69 (4.73)	7.81
([Tb(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Tb] _n	747	0.93 (69.97)	21.23 (21.29)	54.63 (54.70)	4.65 (4.72)	9.52
([Dy(DHAP-1,4-BD) ₂ (H ₂ O) ₂]OH) _n [C ₃₄ H ₃₅ O ₉ Dy] _n	750	0.94 (70.28)	21.60 (21.66)	54.38 (54.44)	4.62 (4.70)	10.53

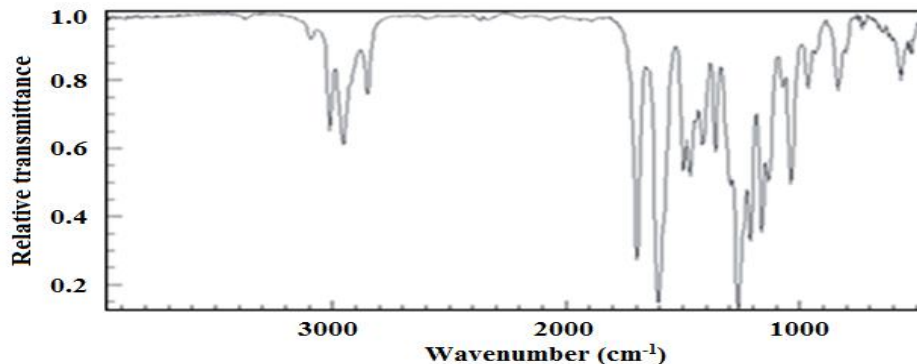
DHAP-1, 4-BD = poly [(2-hydroxy-4-ethoxyacetophenone) 1, 4-Butylene]

Monomer (DHAP)

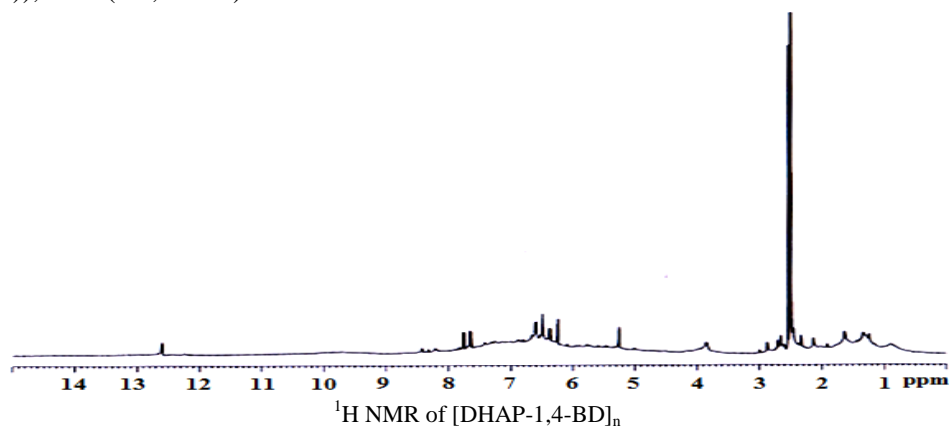
$^1\text{H NMR}$ (DMSO - d_6): δ 12.75 (s, phenolic OH, ortho to ($\text{CH}_3 - \text{CO}$)), 6.55 (s, phenolic OH, para to ($\text{CH}_3 - \text{CO}$)), 2.57 (s, 3H, $\text{CH}_3 - \text{CO}$), 6.44 (m, 2H, Ar-H), 7.62 (d, 1H, Ar-H);



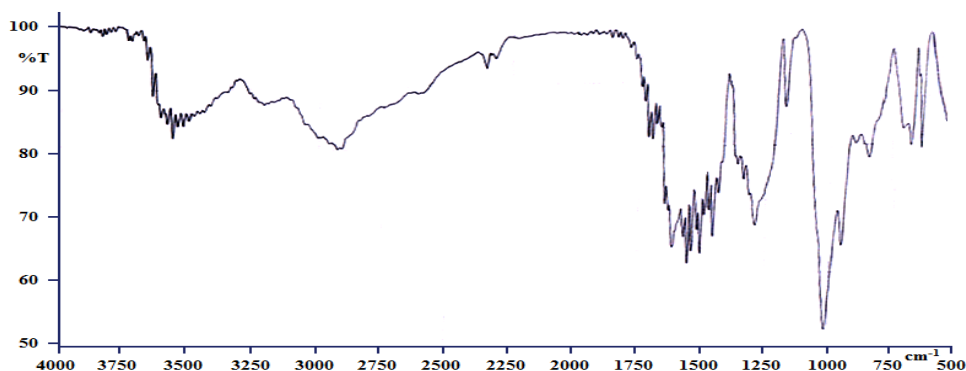
IR (KBr): 3200-3400(-OH stretching), 2734 (Intra mol. H Bond), 1589(>C=O), 1563, 1521, 1492 (-C=C-), 1345 (-OH), 1266 (Ar-O-R), 890, 690 (Ph ring) cm^{-1} ;

**Poly [(2,4-dihydroxyacetophenone)1,4- butylene] resin (DHAP-1,4-BD)**

$^1\text{H NMR}$ (DMSO - d_6): δ 12.75 (s, phenolic OH, ortho to ($\text{CH}_3 - \text{CO}$)), 5.80 (s, phenolic OH, para to ($\text{CH}_3 - \text{CO}$)), 1.75 (m, 2H, bridge), 2.05 (m, 2H, bridge), 2.35 (t, 2H, brigade), 2.63 (t, 2H, bridge). 2.91 (s, 3H, ($\text{CH}_3 - \text{CO}$)), 6.61 (1H, Ar-H).

**Poly [(2,4- dihydroxy acetophenone) 1,4- butylene] resin - (DHAP-1,4-BD)**

IR (KBr): 3200-3400(-OH stretching), 2950-2880 (- CH_2 stretching), 2730 (Intra molecular H Bond), 1610 \pm 10 (>C=O), 1560, 1525, 1490 (-C=C- aromatic), 1345 (-OH), 1260 \pm 10 (Ar-O-R), 1060, 890, 820, 520 (Ph ring) cm^{-1} .



Vapor Pressure Osmometry: The following procedure was used for the estimation of \overline{M}_n of the resins. Dilute solution of a polymer samples were prepared. The four concentrations were prepared and they were about 2.21, 4.42, 6.63, 8.84 g kg⁻¹ of DMF. VPO experiment was carried out with each concentration and the corresponding bridge output reading in millivolt was noted and a plot of millivolt Vs C drawn and found linear and passing through the origin. The slope of the plot was determined. From the value of the slope and the VPO constant K, the value \overline{M}_n of the polymer was estimated. The molecular weights of the resins determined by vapor pressure Osmometry [14] method are presented in table 2.

Table 2. Molecular weight determination of resins by Vapor Pressure Osmometry Method

Resins	Concentration g kg ⁻¹	Millivolts	Slope of Plot	$\overline{M}_n =$ K/Slope g mol ⁻¹
HEAP - 1,4 BD	2.21	22.0	9.95	1156
	4.42	45.0		
	6.63	66.0		
	8.84	88.0		

K = polystyrene constant = 1.15×10^4

UV-Visible Spectra of Resins: Polymers carrying the reactive functional groups are of value in a variety of uses, which have ultraviolet absorbing groups attached to the polymer chain. In recent years polyolefin films have been made more stable to atmospheric degradation by incorporating polymerizable 2-hydroxy benzophenone in the main chain. The UV spectrum of HEAP and its resins (DHAP-1,4 BD) shows one band each at 281 and 395 nm, due to the n- π^* and π - π^* transition. By proper selection of comonomer, useful UV-absorbing polymers with varying amount of UV- absorbing groups (HEPA) can be prepared. DHAP has intermediate thermal properties and hence can remain in a blend resins during various applications and can also protect the resins from UV light.

Electronic Spectra of Polychelates: The data indicates the energy of f-f transitions in the polychelates is slightly reduced compared to the corresponding aquo ions. This may be either because of the slight covalent interaction of the 4f orbitals with vacant ligand orbitals, leading to some delocalization with consequent reduction in inter-electronic repulsion or by increased nuclear shielding of the orbitals due to a slight covalent ligand-metal electron drift compared to the aquo ions of the lanthanides. The f-f transition bands of the polychelates showed weak perturbation and increased intensity was due to complex formation, presumably due to the Nephelauxetic effect. The electronic spectra of all the polychelates exhibit the addition if two spectral bands in the resin 278 - 293 nm and 449 - 460 nm. The first band occurs in the spectra of polymeric ligand (resins). The band is assigned to the transition of the type $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ [15]. The second band is assigned to the polymeric ligand (resins) \rightarrow Ln (III) transitions of all the polychelates. The La (III) polychelates were found diamagnetic in nature as expected for six coordinated octahedral geometry. The electronic spectra of Pr(III), f³, polychelates were exhibits absorption at 21,324, 20,865, 19,458 and 17,715 cm⁻¹, assigned to $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$, and $^3H_4 \rightarrow ^1D_2$,

transitions of Pr(III) in a octahedral environment, due to large crystal field with magnetic moment 3.71 B.M. The Nd(III) polychelates were paramagnetic as expected for f^4 system. Bands were obtained at 18,970, 17,645, 14,273 and 9,885 cm^{-1} for ${}^4I_{9/2} \rightarrow {}^2G_{9/2}$, ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^4I_{9/2} \rightarrow {}^2S_{3/2}$, and ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions of Nd(III) in octahedral geometry. In addition the bands at 23,168, 22,920 and 23,880 cm^{-1} for polychelates were assigned to ${}^4H_{5/2} \rightarrow {}^4F_{9/2}$, ${}^4H_{5/2} \rightarrow {}^6P_5$ and ${}^4H_{5/2} \rightarrow {}^4I_{11/2}$, transitions of Sm(III) in octahedral geometry due to large crystal field splitting and all the polychelates were paramagnetic in nature. The magnetic moment 1.73 B.M. is obtained as expected. The Gd(III) and Tb(III) polychelates were found paramagnetic in nature 7.89 B.M. and 9.50 B.M. as expected for six coordinated octahedral polychelates. The electronic spectra of Dy(III) f^{10} polychelates exhibits absorption at 27,750 cm^{-1} assigned to ${}^6H_{15/2} \rightarrow {}^6H_{13/2}$, transition of Dy(III) in octahedral geometry due to large crystal field splitting.

Ion-Exchange Study: The chelating characteristics of resin for lanthanide metal ions were investigated by the batch equilibrium technique [16]. 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 at ionic strength of 0.10 M (using sodium perchlorate) for 2 h. To this mixture, 2.0 mL of 0.1 M metal ion solution was added. After being shaken for 24 h at 30°C, the mixture was filtered and metal content remaining in the filtrate was determined by complexometric titration using standard Na_2EDTA [17] solution and xylenol orange as an indicator.

(a) To investigate the effect of different electrolytes on metal ion uptake, experiments were carried out with a fixed contact time of 24 h at 30°C and pH 5.6 using different NaNO_3 , NaCl , Na_2SO_4 and NaClO_4 electrolytes at different concentrations.

(b) Similar experiments were also carried out in the pH range 3.0 and 6.0 for a fixed contact time of 24 h at ionic strength of 0.1 M.

(c) The selectivity of resins for lanthanides (III) metal ions was examined under similar experimental conditions where the contact time was varied from 1 to 24 h at 30°C after being equilibrated with distilled water.

Effect of an Electrolyte concentration on Metal-Ion Uptake: The effect of nature and concentration of an electrolyte on the amount of metal ion uptake was investigated by determining the metal ion uptake by resin at room temperature. The electrolytes NaNO_3 , NaCl , Na_2SO_4 and NaClO_4 were used in four different concentrations of 0.05, 0.1, 0.5 and 1.0 mol. lit^{-1} , at pH=5.6 for a fixed contact time of 24 hours. The results of lanthanides (III) metal ions are presented in Different table given below. These results reveals that, the extent of Ln^{3+} ions uptake by resin increases with increase in the concentration of NO_3^- , ClO_4^- and Cl^- and decreases with an increase in concentration of SO_4^{2-} . This may be due to the higher charge and bigger size of the sulphate ion and other factors are also responsible for the behavior of SO_4^{2-} ion. Therefore, the influence of NO_3^- , ClO_4^- and Cl^- is less, on the position of metal chelates at equilibrium state that does SO_4^{2-} .

Effect of pH on Metal-Ion Uptake: The binding capacity of resins for lanthanide metal ions was studied in 1.0 M NaNO_3 (40mL) solution with the pH range of 3.0 to 6.0 under continuous shaking for a fixed contact time of 24 h at 30°C. Due to hydrolysis of metal ion at higher pH, the study was restricted up to maximum pH=6.0. The formation of metal hydroxide interfere the ion-exchange process. It is found that the relative amount of metal ion adsorbed by the resin increases with increasing pH of the medium. Thus maximum sorption of metal ion occurs at pH=6.0. The distribution ratio K_D of lanthanide metal ions between the resin phase (solid) and aqueous phase (liquid) is estimated at optimum, pH, using 1.0 M NaNO_3 solution. The experiments were carried out from 3.0 to 6.0 pH. Distribution ratio K_D (the concentration of metal ion in the adsorbed from on the resin phase divided by concentration of metal ion in solution phase) has been calculated using following equation

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

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results shown in table 4. It can be seen that the distribution ratio increases for lanthanide metal ions as the pH of the medium increases. It is found that the value of distribution ratio for given pH depends upon the nature of the polymeric ligand (resin).

The Rate Metal-Ion Uptake as a Function of Contact Time: In the technique, a 0.50 mg of dry 300 mesh sample of the resins was preconditioned by allowing the resin to equilibrate for 2 h with buffer solution at pH 6.0 before the sorption experiment. The sorption experiments were performed at 30°C under continuous shaking as a function of contact time 1 to 24 h. Results show that the uptake of metal ions increases with time until it reaches a steady state. It is assumed that at 25°C and under given conditions, the state of equilibrium is established in 24 h. The rate of metal ion uptake is expressed as percentage of the attainment at table 5. About 50% metal ion uptake was achieved after 2-3 h.

Table 3. Effect of different electrolytes and its concentration on metal ions adsorption by DHAP- 1,4- BD resin

Metal ions	Electrolyte (mole. 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	0.37	0.32	0.64	0.35
	0.10	0.49	0.44	0.51	0.47
	0.50	0.65	0.56	0.38	0.58
	1.00	0.81	0.72	0.27	0.71
Pr ³⁺	0.05	0.35	0.29	0.62	0.31
	0.10	0.46	0.37	0.51	0.42
	0.50	0.61	0.52	0.40	0.57
	1.00	0.74	0.66	0.29	0.70
Nd ³⁺	0.05	0.33	0.27	0.59	0.34
	0.10	0.44	0.43	0.45	0.47
	0.50	0.59	0.51	0.36	0.61
	1.00	0.73	0.69	0.27	0.71
Sm ³⁺	0.05	0.31	0.31	0.65	0.30
	0.10	0.46	0.42	0.51	0.43
	0.50	0.60	0.55	0.42	0.59
	1.00	0.73	0.75	0.29	0.72
Gd ³⁺	0.05	0.34	0.28	0.58	0.31
	0.10	0.47	0.40	0.44	0.45
	0.50	0.57	0.52	0.32	0.57
	1.00	0.69	0.68	0.21	0.69
Tb ³⁺	0.05	0.30	0.27	0.62	0.27
	0.10	0.44	0.41	0.50	0.41
	0.50	0.61	0.54	0.38	0.58
	1.00	0.78	0.71	0.37	0.71
Dy ³⁺	0.05	0.32	0.29	0.60	0.31
	0.10	0.45	0.39	0.49	0.44
	0.50	0.59	0.53	0.36	0.57
	1.00	0.72	0.69	0.29	0.69

Table 4. Distribution Ratio K_D on metal ion uptake by DHAP-1,4-BD resin

Metal ions	Distribution Ratio K_D					
	pH 3.0	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0
La ³⁺	124.73	141.55	153.09	173.95	192.03	211.82
Pr ³⁺	103.18	116.25	138.70	150.18	170.62	189.40
Nd ³⁺	116.53	127.49	144.41	156.01	167.90	186.27

Sm ³⁺	121.98	138.70	150.18	158.96	173.95	186.27
Gd ³⁺	101.24	105.82	121.98	138.70	150.18	167.90
Tb ³⁺	119.25	130.27	144.41	161.92	180.07	202.10
Dy ³⁺	100.56	116.53	135.87	150.18	164.90	183.16

Table 5. Effect of Time on metal ions uptake capacity of DHAP-1,4-BD resin

Metal ions	% attainment in equilibrium Time in hours*						
	1.0 h	2.0 h	3.0 h	4.0 h	5.0 h	6.0 h	7.0 h
La ³⁺	40.17	48.71	57.29	65.29	80.91	87.55	92.33
Pr ³⁺	39.17	46.01	58.16	65.24	78.77	86.25	93.30
Nd ³⁺	39.71	49.06	56.07	65.42	81.21	85.85	92.81
Sm ³⁺	42.13	51.75	60.91	68.63	77.75	84.17	92.19
Gd ³⁺	41.52	49.05	58.11	67.31	76.11	85.72	91.09
Tb ³⁺	38.71	46.18	57.62	68.20	77.01	85.11	92.91
Dy ³⁺	40.11	46.08	57.97	69.17	78.09	86.98	94.30

CONCLUSIONS

It is found that 2,4- dihydroxy Acetophenone –Ethane diol resin acts as an efficient and effective ion exchange for Ln(III) metal ions.

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