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## Ln(III) Polychelates of Phenolic Resin: Synthesis, Characterization and Ion Exchange Applications of Propane 1,3-Diol Resin

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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 propane 1,3-diol synthesized resin has been utilized 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, Polychelate, Lanthanides

### INTRODUCTION

Polymer-metal complexes have been attracting interest in many scientific and technological fields in recent years. Currently some coordination polymers have been prepared from cyclic and non-cyclic polymers containing unresolved functional groups those act as a chelating group [1]. Chelate-forming polymers [2-4] have found widespread separation and monitor lanthanides containing of heavy metals [5], from aqueous solutions; they shows significant applications in pollution control [6], bioinorganic industry, water refining and selective removal of excess materials [7-9], preconcentration [10], hydrometallurgy [11]. Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930 [12,13]. Amine groups to form anion exchangers were developed [13].

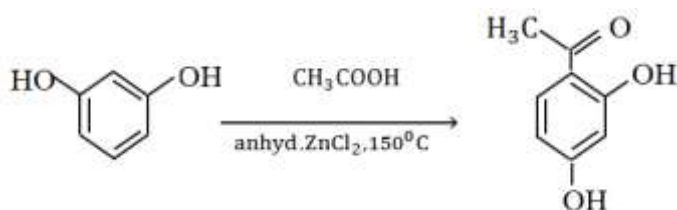
### MATERIAL AND METHODS

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 Vapor Pressure Osmometry (VPO), Nuclear Magnetic Resonance (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.

### RESULTS AND DISCUSSION

#### Synthesis of monomer 2,4-Dihydroxy Acetophenone (DHAP)

Freshly fused and powdered zinc chloride (16.5 g, 0.27 mol) was dissolved in glacial acetic acid (16 ml) by heating in a beaker on a sand bath. Dry resorcinol (11 g 0.1 mol) was added with stirring to the mixture 140°C at the solution was heated and kept for 20 min at 150°C. Dilute hydrochloric acid (1:1, 50 ml) was added to the mixture and then the solution was cooled at 5°C. The separates yellow product was filtered, 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. is 142-148°C Scheme 1.

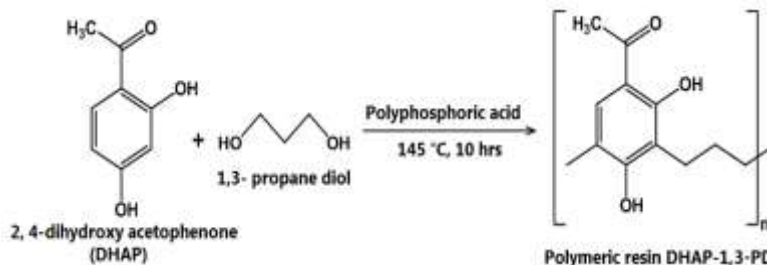


Scheme 1: Synthesis of 2,4-dihydroxy acetophenone

### Synthesis of resins

#### Synthesis of DHAP-1,3 PD

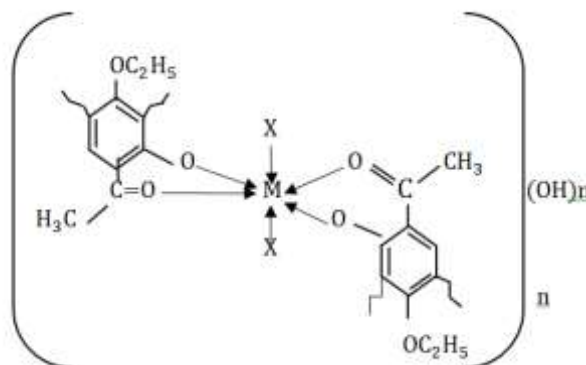
Polyphosphoric acid (20 g) was added slowly with constant stirring to the ice cooled mixture of DHAP (9.12 g, 0.06 mol) and 1,3-PD (4.34 ml, 0.06 mol). Then the mixture was kept at room temperature for 30 min and heated in oil bath at 147°C for 9 h. Then mixture was cooled and crushed in kept for night. Now by filter product was collected remove unreacted acid by alcohol. Synthesized resin was solvable in dimethyl sulfoxide. The polymer was brown in colour with decomposition point > 270°C and yield 7.51 g (82.42%) (Scheme 2).



Scheme 2: Synthesis of resin DHAP-1,3-PD

#### Synthesis of polychelates

Hydrated acetates of La, Pr, Nd, Sm, Gd and Tb, were used in the preparation of the polychelates. The hot solution of the lanthanum acetate (1.72 g, 0.005 mol) added it to constant stirring in the solution of polymeric ligand (0.01 mol). Brown-black colored yield was separated. Then it was digested on a water bath for 3 h then after it was filtered. Then washed with Dimethyl Sulfoxide (DMSO) for removal of unreacted metal acetate. At last, the polychelate made and washed with acetone and dried at 50°C for 20 h. Same procedure was applied for the synthesis of all mentioned hydrated acetates polychelates. All the polychelates are found soluble in Dimethyl fluoride (DMF) and DMSO. The yield obtained 60-80% Scheme 3.



Scheme 3: Proposed structure of polychelate

Where, M=La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III), X= H<sub>2</sub>O

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.

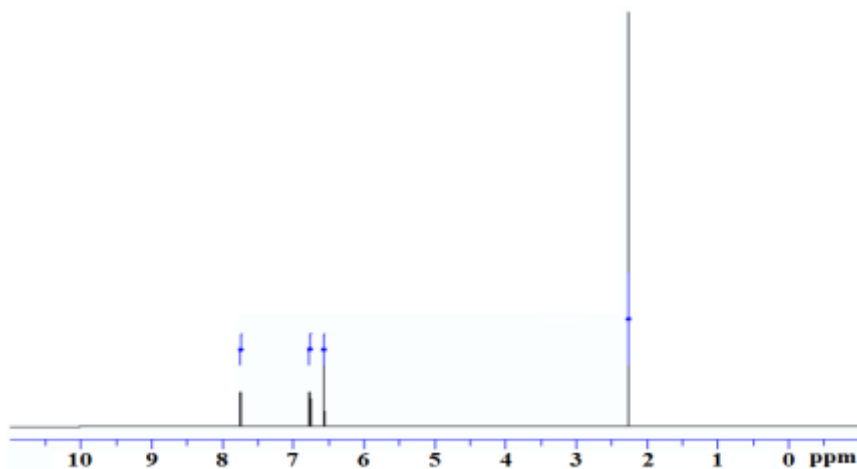
Table 1: Analytical Data of Polymeric Ligand DHAP- 1,3-PD and its polychelates

Compound	Formula weight of repeating unit	Yield g (%)	(% Found (Calculated))			$\mu_{\text{eff}}$ (B.M.)
			M	C	H	
(DHAP-1,3-PD) <sub>n</sub> (C <sub>16</sub> H <sub>14</sub> O <sub>3</sub> ) <sub>n</sub>	254	7.51 (82.42)	---	75.49 (75.57)	5.49 (5.55)	---
([La(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> La] <sub>n</sub>	698	0.92 (72.85)	19.81 (19.88)	54.95 (55.03)	4.42 (4.47)	DM
([Pr(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Pr] <sub>n</sub>	700	0.90 (71.27)	20.06 (20.11)	54.82 (54.87)	4.40 (4.46)	3.71
([Nd(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Nd] <sub>n</sub>	703	0.88 (69.91)	20.39 (20.49)	54.56 (54.61)	4.37 (4.44)	3.63
([Sm(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Sm] <sub>n</sub>	710	0.87 (68.66)	21.07 (21.18)	54.08 (54.14)	4.32 (4.40)	1.71
([Gd(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Gd] <sub>n</sub>	717	0.93 (73.81)	21.88 (21.94)	53.59 (53.62)	4.30 (4.36)	7.89
([Tb(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Tb] <sub>n</sub>	718	0.95 (75.11)	22.04 (22.12)	53.43 (53.49)	4.28 (4.35)	9.50
([Dy(DHAP-1,3-PD) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](OH)) <sub>n</sub> [C <sub>32</sub> H <sub>31</sub> O <sub>9</sub> Dy] <sub>n</sub>	722	0.96 (76.32)	22.43 (22.50)	53.17 (53.23)	4.25 (4.33)	10.55

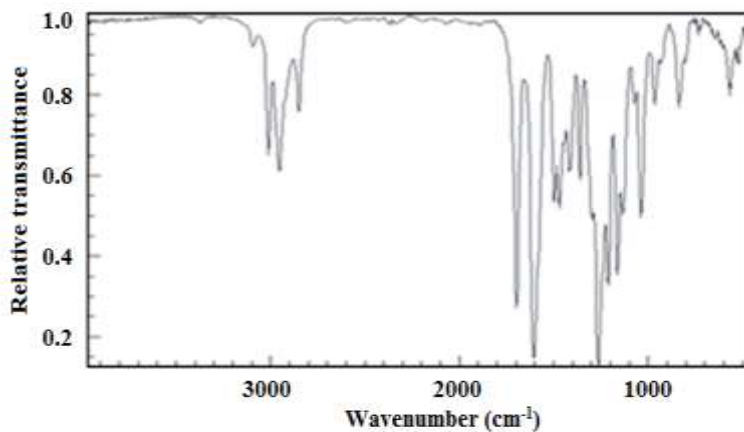
DHAP-1, 3-PD=poly [(2-hydroxy-4-ethoxyacetophenone)1,3-propylene]

**Monomer of DHAP**

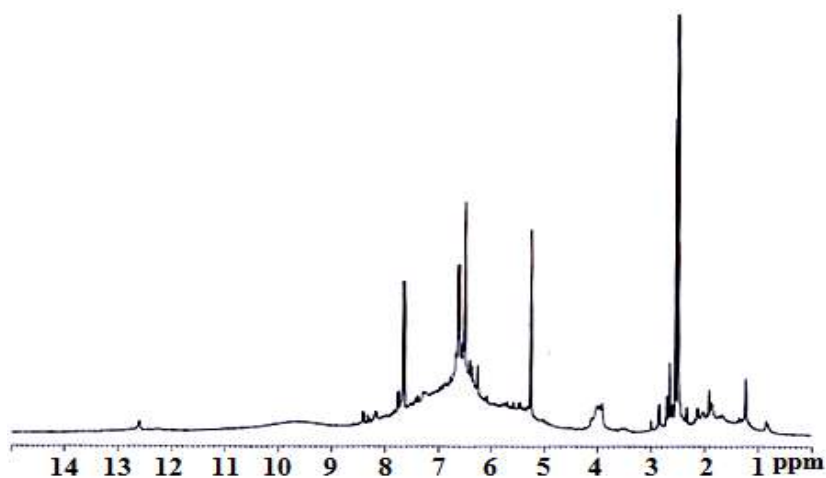
$^1\text{H-NMR}$  (DMSO- $d_6$ ):  $\delta=12.75$  (s, phenolic OH, ortho to  $(\text{CH}_3\text{-CO})$ ),  $6.55$  (s, phenolic OH, para to  $(\text{CH}_3\text{-CO})$ ),  $2.57$  (s, 3H,  $(\text{CH}_3\text{-CO})$ ),  $6.44$  (m, 2H, Ar-H),  $7.62$  (d, 1H, Ar-H).



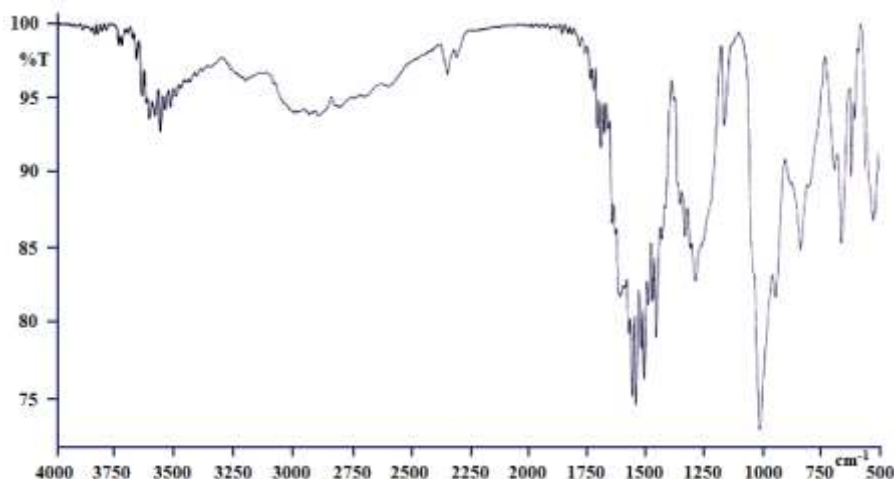
IR (KBr): 3200-3400 (-OH stretching), 2734 (Intra mol. H Bond), 1589 ( $> \text{C=O}$ ), 1563, 1521, 1492 ( $-\text{C}=\text{C}-$ ), 1345 (-OH), 1266 (Ar-O-R), 890, 690 (Ph ring)  $\text{cm}^{-1}$

**Poly[(2,4-dihydroxy acetophenone)1,3-propylene]resin (DHAP-1,3-PD)**

$^1\text{H-NMR}$  (DMSO- $d_6$ ):  $\delta=12.12$  (s, phenolic OH, ortho to  $(\text{CH}_3\text{-CO})$ ),  $6.14$  (s, phenolic OH, para to  $(\text{CH}_3\text{-CO})$ ),  $1.65$  (m, 2H, bridge),  $2.15$  (t, 2H, bridge),  $2.65$  (t, 2H, bridge),  $2.93$  (s, 3H,  $(\text{CH}_3\text{CO})$ ),  $6.51$  (1H, Ar-H).



IR (KBr): 3200-3400 (-OH stretching), 2950-2880 ( $-\text{CH}_2$  stretching), 2730 (Intra molecular H Bond),  $1610 \pm 10$  ( $> \text{C=O}$ ), 1560, 1525, 1490 ( $-\text{C}=\text{C}-$ aromatic), 1385 (-OH),  $1230 \pm 10$  (Ar-O-R), 1120, 890, 680 (Ph ring)  $\text{cm}^{-1}$ .



### Vapor Pressure Osmometry (VPO)

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 of DMF. VPO experiment was carried out with each concentration and the corresponding bridge output reading in millivolt was noted and a plot of millivolts 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 VPO [14] method are presented in Table 2.

Table 2: Molecular weight determination of resins by VPO method

Resins	Concentration (g/kg)	Millivolts	Slope of plot	$\overline{M}_n = K/\text{Slope g/mol}$
HEAP-1,3-PD	2.21	23.0	10.40	1105
	4.42	47.0		
	6.63	69.0		
	8.84	92.0		

$K = \text{polystyrene constant} = 1.15 \times 10^{-4}$

### 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-1,3-PD) shows one band each at 281 and 395 nm, due to the  $n-\pi^*$  and  $\pi-\pi^*$  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 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 of two spectral bands in the resin 278(14-293 nm and 449-460 nm). The band is assigned to the transition of the type  $\pi-\pi_1^*$  and  $\pi-\pi_2^*$  [15]. Then next band is allocated to the polymeric ligand (resins)  $\rightarrow \text{Ln(III)}$  transitions of all the polychelates. The electronic spectra of Pr(III),  $f^3$ , polychelates were exhibits absorption at different frequencies.

### 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 g 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  $\text{Na}_2\text{EDTA}$  [17,18] solution and xylenol orange as an indicator.

(a) To examine the effect of different electrolytes on metal ion uptake, tests were for fixed contact time of one day at 30°C and pH below 6 using different  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$  electrolytes at different concentrations. (b) Same test were also carried out in the pH range 3.0 and 6.0 for a secure interaction time of 24 h of 0.1 M. (c) The selectivity of resins for lanthanides (III) metal ions was inspected under comparable experimental settings where the secure time was varied from 2 to whole day at 30°C.

### Effect of an electrolyte concentration on metal-ion uptake

The result metal ion uptake by resin at room temperature. The electrolytes  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$  at different dilution of 0.05, 0.1, 0.5 and 1.0 mol.lit<sup>-1</sup>, at pH=5.6 for a secure interaction time of 24 h. The results of lanthanides (III) metal ions are presented in Different Table 3 given below. These results reveals that, the extent of  $\text{Ln}^{3+}$  ions uptake by resin rises with rise in the dilution of  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$  and declines

with a rise in concentration of  $\text{SO}_4^{2-}$ . Therefore, the influence of  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$  is less, on the position of metal chelates at equilibrium state that does  $\text{SO}_4^{2-}$ . The effect of pH on the amount of metal ions distributed between two phases can be explained by the results shown in Table 4.

#### The rate metal-ion uptake as a function of contact time

In the technique, a 0.4 mg of dry 250 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 1-24 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.

**Table 3: Effect of different electrolytes and its concentration on metal ions adsorption by DHAP-1,3-PD resin**

Metal ions	Electrolyte (mol.Lit <sup>-1</sup> )	Metal ion uptake (meq. g <sup>-1</sup> ) in presence of electrolyte			
		NaNO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaClO <sub>4</sub>
La <sup>3+</sup>	0.05	0.32	0.29	0.62	0.32
	0.10	0.45	0.41	0.51	0.46
	0.50	0.57	0.58	0.39	0.59
	1.00	0.71	0.71	0.27	0.72
Pr <sup>3+</sup>	0.05	0.33	0.34	0.58	0.34
	0.10	0.44	0.47	0.49	0.48
	0.50	0.56	0.62	0.38	0.62
	1.00	0.69	0.77	0.26	0.74
Nd <sup>3+</sup>	0.05	0.37	0.31	0.59	0.33
	0.10	0.51	0.44	0.46	0.49
	0.50	0.67	0.61	0.35	0.61
	1.00	0.78	0.72	0.26	0.72
Sm <sup>3+</sup>	0.05	0.34	0.33	0.60	0.34
	0.10	0.49	0.45	0.49	0.45
	0.50	0.64	0.59	0.37	0.56
	1.00	0.79	0.71	0.28	0.70
Gd <sup>3+</sup>	0.05	0.31	0.37	0.57	0.28
	0.10	0.45	0.49	0.45	0.39
	0.50	0.61	0.63	0.34	0.52
	1.00	0.74	0.79	0.25	0.65
Tb <sup>3+</sup>	0.05	0.32	0.32	0.56	0.33
	0.10	0.44	0.46	0.46	0.47
	0.50	0.60	0.62	0.35	0.59
	1.00	0.72	0.74	0.27	0.71
Dy <sup>3+</sup>	0.05	0.30	0.28	0.58	0.31
	0.10	0.43	0.39	0.47	0.43
	0.50	0.57	0.52	0.33	0.58
	1.00	0.70	0.69	0.25	0.69

**Table 4: Distribution ratio K<sub>D</sub> on metal ion uptake by DHAP-1,3-PD resin**

Metal ions	Distribution ratio K <sub>D</sub>					
	pH 3.0	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0
La <sup>3+</sup>	102.50	115.75	137.74	152.01	172.71	191.41
Pr <sup>3+</sup>	89.61	102.50	118.44	140.57	163.73	181.84
Nd <sup>3+</sup>	121.15	134.94	154.92	172.71	191.14	213.52
Sm <sup>3+</sup>	115.75	123.88	143.40	160.78	178.78	194.28
Gd <sup>3+</sup>	118.44	137.74	154.92	175.73	184.92	200.61
Tb <sup>3+</sup>	115.28	132.15	148.13	166.71	184.92	203.81
Dy <sup>3+</sup>	121.15	137.74	150.14	172.71	181.84	207.02

**Table 5: Effect of time on metal ions uptake capacity of DHAP-1,3-PD resin**

Metal ions	% attainment in equilibrium, Time (h)						
	1.0 h	2.0 h	3.0 h	4.0 h	5.0 h	6.0 h	7.0 h
La <sup>3+</sup>	38.19	48.17	56.92	63.31	74.88	83.76	91.08
Pr <sup>3+</sup>	40.95	51.05	59.95	67.25	75.11	84.03	92.37
Nd <sup>3+</sup>	42.19	49.88	55.75	64.67	76.71	86.15	93.57
Sm <sup>3+</sup>	43.02	51.19	59.93	68.82	79.09	87.48	94.13
Gd <sup>3+</sup>	38.99	48.45	56.76	66.39	78.01	86.37	93.09
Tb <sup>3+</sup>	40.12	49.79	58.11	68.76	76.95	85.29	92.14
Dy <sup>3+</sup>	39.92	46.97	59.63	67.24	77.31	85.11	91.45

### CONCLUSION

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

### ACKNOWLEDGEMENT

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