Analytical applications of 2,4-dihydroxyacetophenone-*p*-phenylenediamine-formaldehyde based resins

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ABSTRACT

The present paper reports the synthesis and ion exchange properties of resin. The resin(2,4DHAPDF) was synthesized by condensation 2,4 dihydroxy acetophenone (2,4 –DHA) and p-Phenylenediamine (PD)with formaldehyde (F) in the presence of catalyst HCl. Chelating ion exchange properties have been studied for heavy metal ions viz.Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+} by employing a batch equilibrium method. It was employed to study the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the polymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The overall rate of metal uptake follows the order: $Co^{+2} > Cd^{+2} > Pb^{+2} > Hg^{+2}$.

Key words*: 2,4-DHAPDF resin, Condensation, Chelating, Batch equilibrium, Metal ion uptake, Distribution Ratios.*
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INTRODUCTION

The heavy metal ion toxicity has increased substantially because of the use of metal ions as catalyst in various industries. Many methods such as electro deposition, co-precipitation and solid-liquid extraction have been developed for pre-concentration and removal of metal ions. However removal of the heavy metal ions by chelating ion-exchange resin using batch equilibrium method has gained rapid acceptance because of its wide variety of sorbent phases, high selectivity, high loading capacity and enhanced hydrophilicity [1-3].

Sykormmmma and Dubsky.[4] have prepared a selective ion-exchange resin by reacting a resacetophenone and anthranilic acid with formaldehyde. Various hydroxybenzoic acid-formaldehyde copolymers have been reported as being used as ion-exchangers [5]. Ion exchange resin derived from semicarbazone and oximes of 2-hydroxy acetophenone substituted benzoic acid- formaldehyde studied by Nayak et.al [6-8].

Kapadia et.al have studied the anions as well as cations exchange properties of resin derived from various derivatives like salicylic acid, anthanilic acid and hydroquinone towards various metal ions [9,10]. However, the literature studies have revealed that no resin has been synthesized using the monomers 2,4 Dihydroxyacetophenone, p-Phenylenediamine and Formaldehyde. Therefore in the present communication we report synthesis, characterization and analytical applications of a 2,4DHAPDF resin.

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MATERIALS AND METHODS

2.1 Materials:- Solvents like dimethyl formamide and dimethylsulphoxide were used after distillation. 2,4-Dihydroxyacetophenone p-Phenylene diamine, and Formaldehyde 37%) were purchased from market and are from Merck (Maharashtra, India). All other chemicals used were of chemically pure grade.

2.2 Synthesis of 2,4DHAPDF resin:-
The new terpolymeric resin, 2,4DHAPDF, was synthesized (Scheme 1) by condensing 2,4-Dihydroxy-acetophenone (0.1 mol) and p-Phenylene diamine (0.1 mol) with 37 % Formaldehyde (0.2 mol) in a molar ratio of 1:1:2 in the presence of 2 M HCl as a catalyst at $130\,^0C \pm 2\,^0C$ for 5h in an oil bath with occasional shaking to ensure thorough mixing. The temperature of electrically heated oil bath was controlled with the help of dimmer stat. The solid resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agated mortar and pestle. The powdered was washed many times with hot water to remove unreacted monomers. The air- dried powder was extracted with chloroform and petroleum ether was used to remove 2, 4 dihydroxy-acetophenone-p-phenylenediamine and other possible copolymers, which might be present along with 2,4DHAPDF resin. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipited by gradual drop wise addition of 1:1 (V/V) hydrochloric acid with constant and rapid stirring to avoid lump formation. The 2,4DHAPDF resin so obtained was filtered, washed several times with hot water and dried. (Yield = 82%, mp= $210\,^0C$)
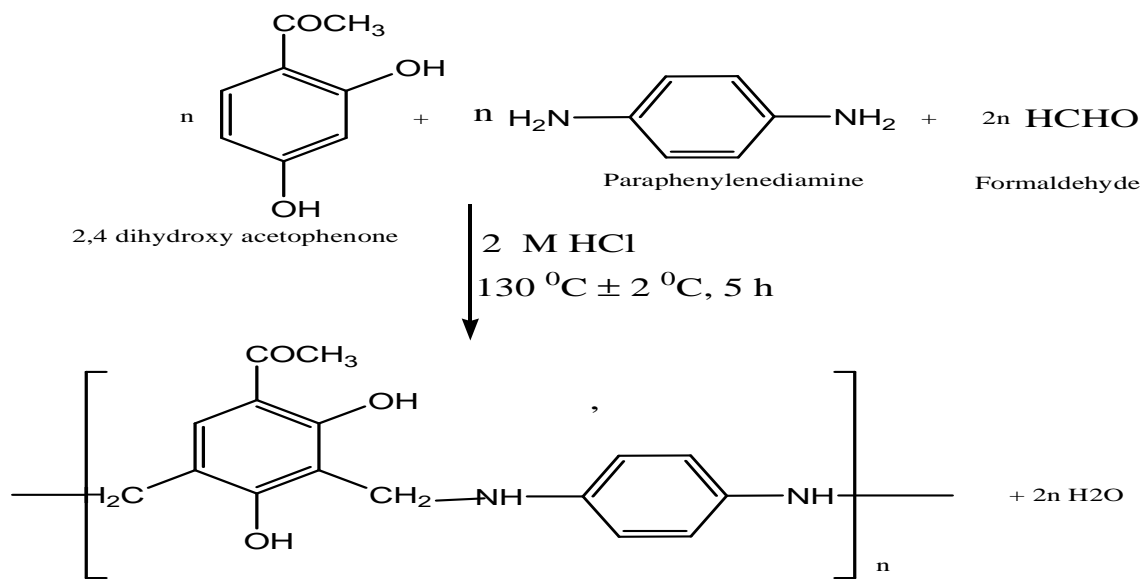
Scheme 1: Synthesis of 2,4DHAPDF resin

2.3 Removal of heavy metals:-
The purified 2,4DHAPDF resin sample was finely powdered and used in all experiments carried out in the ion exchange study.

2.3.1. Determination of effect of different electrolytes on Metal ion uptake:
The ion exchange properties of 2,4DHAPDF resin was determined by batch equilibrium method [11]. 25 mg of finely powdered resin was suspended in an electrolyte solution (25ml) of known concentration. The pH of the solution was adjusted to required value by using either 0.1M HCl or 0.1M NaOH. The suspension was stirred for a period of 24 hours at room temperature. To this suspension 2ml of 0.1M solution of metal was added and the pH was adjusted to the required value. The mixture was again stirred at $25\,^0C$ for 24 hour and filtered. The polymer was washed and the filtered and washing were combined and estimated for the metal ion content by titrating against

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standard ethylenediaminetetra acetic acid. A blank experiment was also carried out in the same manner without adding the polymer sample to estimate the metal ion content. The amount of metal ion taken up by the resin in the presence of given electrolyte of known concentration was determined from the difference between the blank reading and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes of known concentration with four different metal ions such as Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+}. The results with four different metal ions are reported in Table-1

2.3.2. Evaluation of the Rate of Metal Uptake:-
In order to estimate the time required to reach the state of equilibrium under given experimental conditions, a series of experiments of the type described above were carried out. The metal ion uptake by the chelating resins was estimated from time to time at room temperature at 25^0C. It was assumed that under given conditions, the state of equilibrium is established in the 24 hrs. The rate of metal ion uptake is expressed as percent of the amount of metal ion taken up after a certain time related to that in the state of equilibrium. (Table-2).

2.3.3 Evaluation of distribution of metal ion at different pH values:-
The distribution of each of the metal ion Co^{2+}, Hg^{2+}, Cd^{2+} and Pb^{2+} between the resin phase and aqueous phase was estimated at 25^0C using 1M $NaNO_3$ solution. The experiment was carried out as described above at different pH values. The results are presented in table-3

RESULTS AND DISCUSSION

With a view to ascertain the selectivity of the 2,4DHAPDF resin for the selected metal ions, we have studied the influence of various electrolytes on the selectivity of metal ion, the rate of metal uptake, and the distribution ratio of metal ions between the polymer and the solution containing the metal ions. From this study on four metal ions under limited variation in the experimental conditions, certain generalizations may be made about the behavior of the resin sample.

3.1. Effect of Different Electrolytes on Metal ion Uptake:-
The data obtained for resin with different electrolyte with various concentration it is revels that the amount of metal ion taken for a given amount of resin sample depend on the nature and concentration of electrolyte present in the solution. In presence of chloride and nitrates and sulphate ions, the amount of Hg^{+2}, Co^{+2}, Cd^{+2} and Pb^{+2} increases with decreasing concentration of chloride, nitrate and sulphate ions form with these anions [12,13]. This may be explained on the basis of the stability constants of the complexes with those metal ions. This type of trend also been observed by other investigators in related field [14-17].

Table 1 Evaluation of the effect of different electrolytes on the uptake of several metal ions of 2,4DHA-p-PDF resin

Metal ion	Electrolyte Conc. (mo/lit)	PH	Weight of metal ion (mg) taken up in presence of		
			$NaNO_3$	NaCl	Na_2SO_4
Pb^{2+}	0.01	5.5	2.06	1.48	-
	0.05		1.85	1.38	-
	0.1		1.68	1.04	-
	0.5		1.42	0.84	-
	1.0		0.50	0.56	-
Cd^{2+}	0.01	5.5	2.29	2.09	2.89
	0.05		1.89	1.60	2.50
	0.1		1.85	1.40	2.44
	0.5		1.21	1.16	1.22
	1.0		1.06	1.01	1.20
Co^{2+}	0.01	5.0	3.48	3.31	3.54
	0.05		3.24	2.96	3.07
	0.1		2.56	2.64	2.56
	0.5		1.82	1.62	1.81
	1.0		1.04	1.42	1.41
Hg^{2+}	0.01	6.0	0.83	0.73	-
	0.05		0.26	0.26	-
	0.1		0.18	0.22	-
	0.5		0.16	0.14	-
	1.0		0.09	0.04	-

[a]$[M^{n+}(NO_3)_2] = 0.1$ mol/L; volume = 2mL; volume of electrolyte solution = 25 mL; weight of resin= 25 mg; Time = 24 h; room temperature.

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Fig 1 Effect of sodium nitrate electrolyte on metal ion uptake by 2,4DHAPDF resin
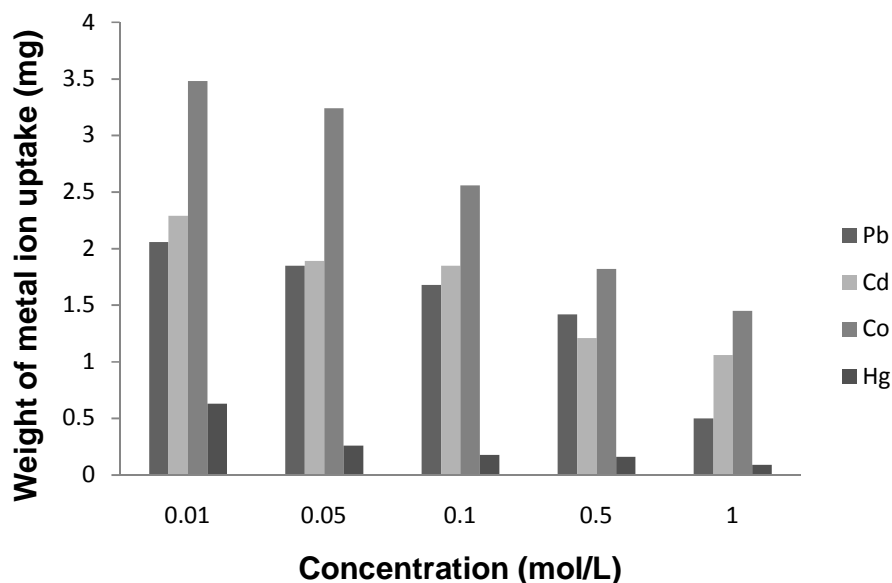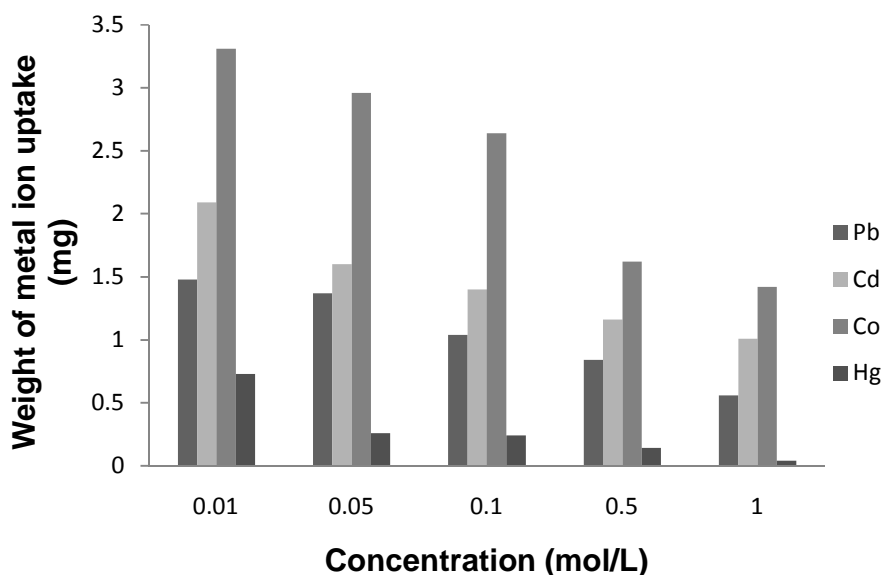

Fig 2 Effect of sodium chloride electrolyte on metal ion uptake by 2,4DHAPDF resin

3.2. Rate of metal uptake:

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out as close to equilibrium conditions as possible. Table-2 shows the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution that is in contact with the given polymer. The results show that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under the given conditions. The experimental results indicate that Co^{+2} required less time of 5 hours while Cd^{+2} and Pb^{+2} ions required about 6 hour for the establishment of equilibrium. Hg+2 required 7 hours for establishment of equilibrium. Thus, the rate of metal ion uptake follows the order of $Co^{+2} > Cd^{+2} > Pb^{+2} > Hg^{+2}$. This type of trend has also been observed by many investigators [18-20].

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Fig 3 Effect of sodium sulphate electrolyte on metal ion uptake by 2,4DHAPDF resin
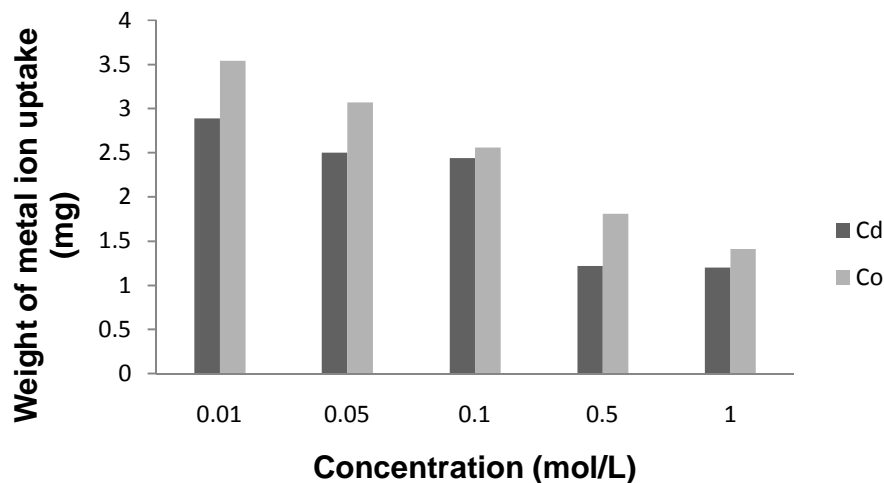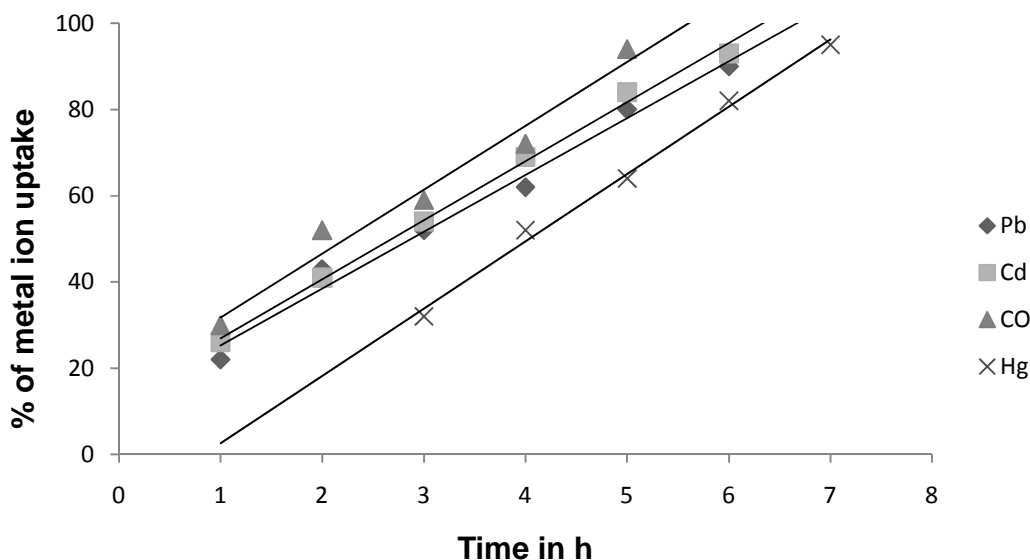

Table 2 Comparison of the rates of metal ion uptake of 2,4DHA-p-PDF resin

Metal ion	Percent of metal ion uptake at different time (h)						
	1h	2h	3h	4h	5h	6h	7h
Pb^{2+}	22	43	52	62	80	90	-
Cd^{2+}	26	41	54	69	84	93	-
Co^{2+}	30	52	59	72	94	-	-
Hg^{2+}	-	-	32	52	64	84	95

[a] $[M^{n+}(NO_3)_2]$ = 0.1 mol/L; volume = 2mL; volume of electrolyte solution = 25 mL; weight of resin= 25 mg;

Fig:4 The rates of metal ion uptake by 2,4DHAPDF resin

3.4. Distribution ratios of metal ions at different pH:
The results of the effect of pH on the amount of metal ion distributed between two phases are incorporated in table-3. The results indicate that the relative amount of metal ion taken up by the resin increases with increasing pH of the medium. The study was carried out only up to a definite pH value for the particular metal ion to prevent hydrolysis

163

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of the metal ion at higher: pH.[19] The observed order of distribution ratios of the metal ion measured in the pH range 3 to 6 is $Co^{+2} > Cd^{+2} > Pb^{+2} > Hg^{+2}$. The similar trend has also been observed by earlier investigators [16,21-23].

Table 3 Distribution ratio D of the metal ion as function of the PH of 2,4DHA-p-PDF 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
$Pb2^+$	-	-	-	33.4	40.0	88.0	104.5	110.5	118.0
Cd^{2+}	-	-	-	28.1	39.4	78.1	94.2	112.4	205.0
$Co2^+$	-	-	-	38.4	85.6	111.5	182.0	202.5	251.3
Hg^{2+}	-	-	-	-	-	12.9	24.0	42.5	114.0

$^{b}[M^{n+}(NO_3)_2] = 0.1 \ mol/L; \ volume = 2mL; \ NaNO_3 = 1.o \ mol/Lvolume = 25 \ mL; \ weight \ of \ resin = 25 \ mg; \ Time \ 24 \ h$

$$D \ = \ \frac{\text{Amount of metal on the resin}}{\text{Amount of metal in the solution}} \ X \ \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

The results of this type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture.

CONCLUSION

Resin based on condensation of 2,4-dihydroxyacetophenone and p-Phenylene diamine with formaldehyde in the presence of hydrochloric acid catalyst has been prepared. The results of an ion-exchange study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions. The resin showed higher selectivity for Co^{+2} andCd^{+2} than Pb^{+2} and Hg^{+2} ions.

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