Ion Exchange Properties of Resins Derived from *p*-Hydroxybenzaldehyde, Resorcinol and Formaldehyde

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Received 17 January 2009; Revised 1 July 2009; Accepted 1 September 2009

Abstract: The terpolymeric resins were prepared by base catalyzed polycondensation of *p*-hydroxybenzaldehyde, resorcinol and formaldehyde. Resin obtained by molar monomer composition, *p*-hydroxybenzaldehyde: resorcinol: formaldehyde as 1:1:3 was abbreviated as PHBRF-I and that prepared by 1:2:4 composition was abbreviated as PHBRF-II. These resins were characterized by physicochemical methods such as elemental analysis, UV-Vis, IR and NMR. ion-exchange study was carried out with Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} & Cd^{2+} by batch equilibrium method. The rate of metal ion uptake by PHBRF-II terpolymeric resin was higher than that of PHBRF-I. Effect of pH and electrolytes under specified condition were also studied. The terpolymeric resins show high selectivity for Cu^{2+} , Zn^{2+} and Co^{2+} as compared to Ni^{2+} , Pb^{2+} and Cd^{2+} .

Keywords: Terpolymeric resin, Batch equilibrium method, Effect of electrolyte.

Introduction

Polymeric chelating ion exchange materials open a wide hope of opportunities in industrial, environmental and biological application owing to their metal ion-exchange selectivity and low cost of production and easy regeneration^{1,2}. Incorporation functional group into the polymeric matrix is of great interest in connection with trace concentration of heavy metal ions. Various phenolics formaldehyde co-polymers have been reported to have satisfactory ion exchange properties^{3,4}. Recently, Pal *et al*^{5,6} reported the ion exchange properties of salicylic acid, dithiobiuret / dithioxamide trioxane tercopolymers and reported selectivity metal ion uptake over wide range of pH and found that resin show high selectivity for fast

and low for Pb^{2+} and Hg^{2+} . Many workers⁷ synthesized polystyrene based chelating with 1-nitroso-2-naphthol as functional group and studied the chelating ion exchange properties. Chelation ion exchange resin obtained by polycondensation of salicylaldehyde, biuret and trioxane has been reported⁸. Manavalan *et al*⁹ synthesized *p*-hydroxybenzoic acid-thiourea-formaldehyde resin and studied ion exchange properties. Banerjee *et al*¹⁰ functionalized amberlite IRC-50 resin by 8-aminoquinoline group. The resin was found to be very useful for preconcentration and separation of copper and zinc. Shah *et al*^{11,12} reported the ion exchange properties of anthranilic acid-resorcinol-formaldehyde and 8-hydroxyquinoline-catechol-fomaldehyde terpolymeric resins. The synthesis and ion exchange properties of resin derived from *p*-hydroxyacetophenone; hexamine and formaldehyde were previously reported¹³. The present paper deals with synthesis and comparative ion exchange study of newly synthesized resin obtained by base catalyzed polycondensation of *p*-hydroxybenzaldehyde, resorcinol and formaldehyde (PHBRF-I & PHBRF-II). The tentative structures terpolymeric resins are given below.

Experimental

All chemicals used were of A.R. or Chemically pure grade.

Synthesis of resins

PHBRF-I was prepared by condensing *p*-hydroxybenzaldehyde (0.1 M), resorcinol (0.1 M) and formaldehyde (0.3 M) was refluxed in presence of 1M NaOH (100 mL) in an oil bath at 122-125 °C for 6.0 h. Similarly PHBRF-II was prepared by using *p*-hydroxybenzaldehyde (0.1 M), resorcinol (0.2 M) and formaldehyde (0.4 M). Buff red colored products were precipitated by treating it with 1:1 HCl. The products were washed several times with hot water to remove unreacted reactants and finally squeezed with ether to remove if any *p*-hydroxybenzaldehyde-formaldehyde co-polymer which might be formed along with PHBRF tercopolymer. The products were further purified by dissolving in 10% NaOH and reprecipitated with 1:1 HCl. Finally the products were washed several times with hot water (deionised, 0.3 $\mu\text{S cm}^{-1}$ conductivity). PHBRF-I and PHBRF-II were found to be 78% & 72%. The products were dried in vacuum desiccator. The dried products were grinded and sieved in 300 mesh sieve. The synthetic details are summarized in Table 1

Table 1. Synthetic details.

Resins	<i>p</i> -Hydroxy-acetophenone	Hexamine	Formaldehyde	Catalyst 0.2 M HCl	React. Temp. °C	Time, h	Yield, %
PHBRF-I	0.1 M	0.1 M	0.3 M	100 mL	120 ± 2	6.00	78
PHBRF-II	0.1 M	0.2 M	0.4 M	100 mL	120 ± 3	5.00	72

Procedure for determination of the effect of electrolyte on metal uptake

The resin sample (25 mg) was suspended in electrolyte solution of required concentration (25 mL) for 24 h. The pH of solution was to 6.0 using 0.1 M HNO₃ or 0.1 M NaOH. To this solution 2 mL of 0.1 M metal nitrate solution added at room temperature and pH was adjusted to required value. The mixture was stirred again at room temperature for 24 h and filtered. Solids were washed and washings were quantitatively combined with filtrate. The metal content was determined by direct EDTA titration. The amount of metal exchanged was determined from the difference between blank and reading in actual experiment. The amounts of metal ion in mg per g of resin were calculated in presence of NaNO₃, NaCl, and Na₂SO₃ and Na₂SO₄ electrolyte for metal ions Cu²⁺, Zn²⁺, Ni²⁺, Co²⁺, Pb²⁺ and Cd²⁺.

Procedure for evaluation of rate of metal ion uptake

In order to determine optimum time required to reach the equilibrium the experiments were performed as above but here metal ion uptake was estimated as a function of time in h in presence of 1 M NaNO₃ solution (25 mL). It was assumed that the equilibrium state was established within 24 h. The rate of metal uptake was expressed in percent uptake related to state of equilibrium.

$$\% \text{ Metal uptake} = \frac{\text{mg of metal sorbed in given time}}{\text{mg of metal sorbed in 24 h}} \times 100$$

Procedure to study effect of pH on metal uptake

The resin sample 25 mg was allowed to swell for 24 h in 1 M NaNO₃ solution. The pH was adjusted to required value as above. 2 mL of 0.1 M metal nitrate solution was added. The pH was maintained again and stirred for 24 h. Metal was estimated by EDTA titration to determine the distribution K_D value between polymer phase and solution phase. The K_D value was calculated by formula,

$$K_D = \frac{\text{mg of metal exchanged per gm of resin}}{\text{mg of metal present in 1 mL of solution}}$$

Results and Discussion

The elemental analysis of PHBRF resins was carried out in SAIF, Chandigarh the data are represented in Table 2.

Table 2. Elemental analysis of PHBRF resin.

Resin	% C		% H		% O		Molecular formula of repeat unit
	Calc	Found	Calc.	Found	Calc.	Found	
PHBRF-I	71.11	70.77	5.18	5.30	23.71	23.38	C ₁₆ H ₁₄ O ₄
PHBRF-II	70.41	69.84	5.10	5.13	24.49	24.26	C ₂₃ H ₂₀ O ₆

Electronic absorption spectra of PHBRF- resin

Electronic spectra of all PHBRF resin samples were recorded in DMF solvent in region 250-750 nm. The spectra are shown in Figure 1. It can be seen from the spectra that, the absorption bands do not show shifting pronouncedly toward either shorter or longer wavelength with increase in the composition of either *p*-hydroxybenzaldehyde or resorcinol relative to each other. Moreover the absorption spectra of PHBRF-II show hyperchromic effect with increase in number of –OH group in repeating unit of PHBRF-II resins as compared to PHBRF-I at higher λ. These absorptions clearly indicate the presence of carbonyl group. The mentioned absorption are attributed to n-π* transition. In addition to these, bands due to π-π* transition are also observed toward shorter wave length. The observations of spectra are summarized in Table 3

Figure 1. Electronic Spectra of PHBRF resins.

Table 3. Characteristic absorption bands and related transitions.

Resin	Wavelength, nm range for $n-\pi^*$ transition	Wavelength, nm range for $\pi-\pi^*$ transition	Group
PHBRF-I	450	300	$>C=O$
PHBRF-II	450	320	$>C=O$

Infrared spectra

Infra red spectra of all PHBRF terpolymeric resins are shown in Figure 2 and characteristics IR data are listed in Table 4. It can be seen from spectra of PHBRF resins that show nearly same IR spectra. The broad band at $3200-3450\text{ cm}^{-1}$ was assigned to H-bonded $-OH$ group. The characteristic two bands at 2940 and 2840 cm^{-1} was assigned to $-CH$ stretch in $-CHO$ group. Bands at 1600 , 1500 and around $1440-1460\text{ cm}^{-1}$ was due to aromatic rings. The strong band at 1680 cm^{-1} clearly indicate presence of carbonyl group ($>C=O$) in aldehydes. The medium band at 1380 cm^{-1} assigned to $-CH_2-$ bridges linking two resorcinol moieties. This band is absent in IR spectra of PHBRF-I clearly support the assigned structure of PHBRF-I resin shown above. The characteristics band at 1280 cm^{-1} was assigned to $-CH_2-$ bridges between *p*-hydroxybenzaldehyde and resorcinol moieties. The characteristics medium bands around 1220 and 1080 cm^{-1} indicate the presence of 1, 2, 3, 5-tetrasubstituted aromatic rings. Moreover the bands at 840 cm^{-1} were assigned to 1, 2, 3, 4- tetra substituted aromatic rings.

Table 4. Characteristic IR data of PHBRF resin¹⁴⁻¹⁶.

PHBRF -I, cm^{-1}	PHBRF- II, cm^{-1}	Assignments
3200-3450 (b)	3200-3450 (b)	H-bonded $-OH$ (Phenolic)
2940, 2840 (w)	2940, 2840 (w)	$-CHO$
1680 (s)	1680 (s)	$-C=O$ str. (aldehydes)
1500, 1600 1440 (m)	1508,1600 1440 (m)	Aromatic ring
-----	1380 (m)	Res- CH_2 -Res moiety, (Res = Resorcinol)
1280 (m)	1280 (m)	PHB- CH_2 -Res moiety, (PHB = <i>p</i> -Hydroxybenzaldehyde)
1180, 1100 (m)	1220, 1080 (m)	1,2,3,5-Tetra substituted benzene ring
840 (w)	840 (w)	1,2,3,4-Tetra substituted benzene ring

Figure 2. IR spectra of PHBRF resins.

Ion exchange properties

The data from the Table 5 reveals that rate of metal ion uptake of PHBRF- I is higher for Cu^{2+} and lowest for Pb^{2+} . Rate of metal ion uptake show the order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+}$. PHBRF-II is more selective for Zn^{2+} . PHBRF-II has comparatively higher exchange rate than PHBRF-I. The lower rate of Cd^{2+} and Pb^{2+} may be due to comparatively larger size of the ions and steric effect. Effect of electrolyte on ion exchange is summarized in Table 6. The inspection of data reveals that the amount of metal uptake in presence of NaNO_3 is larger than NaCl , Na_2SO_4 and Na_2SO_3 . It is interesting to note that resin PHBRF do not exchange Pb^{2+} and Cd^{2+} in presence of Na_2SO_3 and Na_2SO_4 . For the metal ions such as Cu^{2+} , Zn^{2+} , Ni^{2+} , and the exchange capacity increases with increase in the concentration of NO_3^- and Cl^- . Whereas it decreases with increase in concentration of SO_3^{2-} and SO_4^{2-} . The effect of pH on distribution ratios of metal ion between resin and solution phase can be explained by revealing the data given in Table 7. The study was carried out in the limit of higher pH in order to prevent hydrolysis of metal ions. K_D values in general found to follow the order PHBRF-II > PHBRF-I. K_D values of metal ions were found to increase with increase in pH. The lower distribution ratios of Pb^{2+} may be attributed to steric effect and low stability constant *i.e.* weak ligand stabilization energy of metal complexes.

The possible order of ion exchange for divalent ions is $\text{Pb} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$. In present study, PHBRF- I and PHBRF-II show the order of K_D values $\text{Pb}^{2+} < \text{Cd}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$ and $\text{Cd}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+}$ respectively at pH 6.0. At pH 3.0, PHBRF-I show the order $\text{Co}^{2+} < \text{Pb}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$ and for PHBRF- II the order of K_D values is $\text{Cd}^{2+} < \text{Pb}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+}$. The result of the study obviously is helpful in the separation of metal ions. For example the separation of Co^{2+} and Zn^{2+} can be achieved using PHBRF-I at optimum pH 3.0. Similarly for efficient separation of Zn^{2+} and Pb^{2+} the optimum pH is 6.0.

Table 5. Percent rate of metal ion uptake.

M^{2+}	Time, H	PHBRF-I	PHBRF-II	M^{2+}	Time, h	PHBRF-I	PHBRF-II
Cu^{2+}	1	42.34	53.17	Cd^{2+}	1	48.26	54.37
	2	54.62	68.46		2	55.25	59.37
	3	68.25	74.36		3	61.18	68.11
	4	74.39	85.32		4	72.38	78.29
	5	88.73	92.35		5	79.55	82.93
	6	96.33	98.05		6	82.34	88.25
	7	~	~		7	87.06	93.45

Contd...

Zn ²⁺	1	19.29	24.18	Ni ²⁺	1	29.53	48.11
	2	54.76	59.91		2	59.46	75.43
	3	69.04	70.46		3	68.47	81.34
	4	70.56	78.73		4	77.16	86.41
	5	74.57	84.64		5	85.24	90.47
	6	84.21	91.56		6	91.28	96.35
	7	~	~		7	~	~
Pb ²⁺	1	42.18	48.41	Co ²⁺	1	35.63	47.5
	2	57.44	64.23		2	48.17	53.21
	3	65.34	75.43		3	62.33	68.33
	4	71.15	81.35		4	78.24	82.46
	5	79.35	84.44		5	85.46	88.17
	6	81.11	85.29		6	90.72	94.67
	7	84.24	88.26		7	□	□

Mt (NO₃) = 0.1 M, 2 mL, Electrolyte = NaNO₃ 1 M 25 mL, Equilibrium state = 24 h,

Wt. of resin = 25 mg, Temp. = Room Temp., Error = ± 5 %.

Table 6. Amount of metal ion exchanged (mg) per gram of resin.

Metal ion	Conc. Resin	NaNO ₃		NaCl		Na ₂ SO ₃		Na ₂ SO ₄	
		PHBRF-I	PHBRF-II	PHBRF-I	PHBRF-II	PHBRF-I	PHBRF-II	PHBRF-I	PHBRF-II
Cu ²⁺	0.0125	52.37	86.34	45.21	78.15	82.64	104.79	90.76	94.43
	0.025	113.55	104.35	98.46	125.48	69.44	80.12	74.33	84.26
	0.5	142.38	165.75	114.35	136.11	42.58	67.26	64.54	79.77
	1	154.32	178.25	134.26	174.34	34.26	47.35	58.43	68.14
Zn ²⁺	0.0125	84.25	113.4	63.47	88.76	105.94	112.85	115.36	128.34
	0.025	117.65	174.88	98.41	144.38	87.42	90.06	78.14	90.42
	0.5	124.43	193.4	133.22	175.37	59.45	68.32	68.36	74.55
	1	181.22	224.27	174.41	206.47	38.41	33.14	53.24	68.96
Pb ²⁺	0.0125	66.28	94.63	55.73	83.14	NOE	NOE	NOE	NOE
	0.025	122.04	286.34	94.89	123.84	NOE	NOE	NOE	NOE
	0.5	203.47	412.87	128.33	145.53	NOE	NOE	NOE	NOE
	1	322.48	589.33	152.74	189.25	NOE	NOE	NOE	NOE
Ni ²⁺	0.0125	54.98	87.26	46.25	59.15	98.152	129.24	80.74	105.4
	0.025	75.65	124.75	61.854	78.69	84.36	97.23	76.12	94.25
	0.5	96.34	165.37	85.31	94.63	56.47	78.14	53.67	81.37
	1	127.3	180.24	115.47	124.3	36.44	55.25	34.75	59.46
Co ²⁺	0.0125	64.25	94.65	52.34	84.22	74.12	98.27	85.14	115.24
	0.025	85.74	145.85	66.48	124.88	55.26	67.14	60.54	91.24
	0.5	117.35	184.23	87.41	153.47	34.22	55.42	49.13	75.63
	1	134.52	207.14	116.14	174.32	27.52	42.11	34.15	55.24
Cd ²⁺	0.0125	124.89	142.47	68.43	114.75	NOE	NOE	NOE	NOE
	0.025	165.47	178.25	123.62	173.12	NOE	NOE	NOE	NOE
	0.5	204.74	215.45	147.22	204.42	NOE	NOE	NOE	NOE
	1	225.15	239.35	174.54	244.18	NOE	NOE	NOE	NOE

Mt (NO₃) = 0.1M, 2 mL, Electrolyte = 1M 25 mL, Equilibrium state = 24 h, Wt. of resin = 25 mg.

Temp = Room temp. NOE = No exchange.

Table 7. Distribution K_D values of different metal ions as a function of pH.

M^{2+}	pH	PHBRF-I	PHBRF-II	M^{2+}	pH	PHBRF-I	PHBRF-II
Cu^{2+}	3	187.36	256.48	Cd^{2+}	3	126.35	184.7
	3.5	216.75	293.45		3.5	153.46	204.92
	4	256.48	315.41		4	184.69	256.28
	4.5	298.16	398.44		4.5	217.36	298.53
	5	348.33	453.37		5	241.14	321.45
	5.5	398.25	502.48		5.5	297.36	342.57
Zn^{2+}	6	435.93	540.04		6	334.02	362.73
	3	265.26	387.53	Ni^{2+}	3	116.34	236.42
	3.5	289.34	418.4		3.5	184.75	298.15
	4	378.15	478.25		4	203.43	386.24
	4.5	398.44	502.48		4.5	287.55	478.37
	5	468.26	566.24		5	312.41	546.77
	5.5	496.35	587.06		5.5	354.28	596.36
Pb^{2+}	6	530.03	750.44		6	371.98	623.06
	3	84.33	166.45	Co^{2+}	3	67.46	206.7
	3.5	124.45	215.63		3.5	134.55	287.59
	4	145.78	262.47		4	197.36	358.27
	4.5	165.28	334.67		4.5	214.76	464.87
	5	185.54	445.09		5	286.35	512.64
	5.5	228.44	548.26		5.5	305.47	668.73
	6	241.53	551.65		6	399.54	784.44

$Mt(NO_3) = 0.1\text{ M}$, 2 mL, Electrolyte = $NaNO_3$ 1 M 25 mL, Equilibrium state = 24 h,
Wt. of resin = 25 mg, Temp = Room temp.

Conclusions

The elemental analysis, UV-Vis spectra, IR spectra and ion exchange properties support to the tentative structure of PHBRF resins shown above. The study of ion exchange data in general, show the order PHBRF-I < PHBRF-II that conclude the fact that the chelating ion exchange properties depend upon the number of active site (No. of – OH group) present on polymeric matrix. The rate of metal ion uptake found to increase in order PHBRF-I < PHBRF-II. The electrolyte Na_2SO_3 and Na_2SO_4 are not suitable for ion exchange as compared to $NaNO_3$ and NaCl. The resins PHBRF-I can be used to separate Co^{2+} - Zn^{2+} and Zn^{2+} - Pb^{2+} at pH 3.0 and at pH 6.0 respectively. Similarly PHBRF-II show high selectivity for Zn^{2+} and Co^{2+} at pH 3.0 and 6.0 respectively. However the terpolymeric resins show high selectivity for Cu^{2+} , Zn^{2+} and Co^{2+} as compared to Ni^{2+} , Pb^{2+} and Cd^{2+} .

Acknowledgement

One of the authors is thankful to UGC Delhi for granting fellowship under FIP and Principal, Arts, commerce and Science College, Arvi Dist- Wardha.. We are also grateful to Director and R.H. Limsey, Head, Dept. of Chemistry, Institute of Science, Nagpur for providing available facilities at the centre and to Dr. R. S. Bhavsar and Dr. R. B. Kharat for continuous encouragement. We are thankful to Director & Avtar Singh, SAIF, Punjab University, for analyzing the samples.

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