CHELATING ION-EXCHANGE PROPERTIES OF TERPOLYMER RESINS DERIVED FROM P-HYDROXYACETOPHENONE, QUINHYDRONE AND MELAMINE

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Abstract

The terpolymeric resins abbreviated as PAQM-I, PAQM-II and PAQM-III was synthesized by polycondensation of p-Hydroxyacetophenone, Quinhydrone and Melamine in 1:1:1, 1:3:1 and 1:4:2 molar proportions respectively, in presence of Poly-Phosphoric acid (PPA). The resins were characterized by various physico-chemical methods such as elemental analysis, IR, 1H-NMR, UV-Vis and non-aqueous conductometric titrations. Chelating ion- exchange properties of PAQM-I, PAQM-II and PAQM-III terpolymer were studied for Cu2+, Mg2+, Pb2+ and Bi3+ by batch equilibrium method. PAQM resins are more selective Cu2+> Mg2+> Pb2+. However, with varying pH the ion exchange selectivity was found to change with varying pH. Therefore the resin can be used for selective separation of metals at particular pH.

Key Words: Polycondensation, Ion-exchange, Polymerization, Rate of metal ion uptake.

Introduction

Coagulants are those substances which are capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about. Alum has been traditionally used as a coagulant in water treatment for over hundred years. It is commonly available, relatively inexpensive and has long been recognized as a successful compound for removal of colour and turbidity from water supplies. However, more recently attention has been directed to alternative coagulants in water treatment in efforts to reduce residual aluminium in finished water, minimize sludge production[1,2] and eliminates post precipitation of aluminium residues in the distribution systems [3,4]. Alum is conventional coagulant against which performance of other coagulant is generally compared. The Poly Aluminium Chloride is an effective coagulant for removal of organic matter [5,6,7,8] fluorides[9,10,11] and heavy metals from waters of different alkalinities. Ion exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. 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. In spite of its advanced stage of development, various aspects of ion exchange technology have been studied in many countries to improve its efficiency and economy in its application to radioactive waste management. The synthetic resins are used primarily for purifying water, but now various applications including separating out some elements [1-6].

Copolymer resins (8-HQSABF) were synthesized by the condensation of 8-hydroxyquinoline-5-sulphonic acid and biuret with formaldehyde in the presence of hydrochloric acid as catalyst, proved to be selective chelation ion exchange copolymer resins for certain metals such as Cu^{2+}, Cd^{2+}, Co^{2+} and Zn^{2+} ions by batch equilibrium method. 8-HQSABF resins showed a higher selectivity for Cu^{2+} ions than for Cd^{2+}, Co^{2+} and Zn^{2+} ions. Hence on the basis of above studies 8-HQSABF resins may be used as semiconductors, surface coating, ion-exchangers, and materials for rechargeable battery cell in various electronic industries, plastic materials, elastomers and in boilers plants [7]. Masram et al studied ion exchange properties of pHPDF for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions employing a batch equilibrium method. The terpolymer showed higher selectivity for Fe^{3+}, Cu^{2+} and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions [8].

Pancholi *et al* studied ion exchange properties of a 2-hydroxy-4-Methoxyacetophenone-Thiourea-Trioxane polymer proved to be a selective chelating ion exchange polymer for Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+} and UO_2^{2+} ions by a batch equilibrium method. The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed a higher selectivity for Cu^{2+}, Fe^{2+} and UO_2^{2+} ions than for Mn^{2+}, Co^{2+} and Zn^{2+} ions [9].

Terpolymer resin (BPEDF-2) was synthesized by the condensation of 2, 2'-biphenol ethylenediamine with formaldehyde in 2:1:3 proportion in the presence of 2M HCl as a catalyst. The concentration of different toxic metal like As (III) has increased which can be removed by ion exchange method [10]. Rahandale studied chelating ion-exchange properties of 2, 4-HABF-IV for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions [11]. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake. The polymer showed highest selectivity for Fe^{3+}, Cu^{2+} ions than for Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions.

Janardanan *et al* studied ion exchange kinetics of Pb^{2+}, Cu^{2+}, Cd^{2+} and Mn^{2+} ions on thermally stable bimetallic ion exchange material [12].

The present communication deals with the systematic study of synthesis and ion- exchange properties of PAQM-I, PAQM-II and PAQM-III terpolymer resin derived from p-Hydroxyacetophenone, Quinhydrone and Melamine by the batch equilibrium method.

Materials:

All chemicals were AR grade or chemically pure grade, p-hydroxyacetophenone, Quinhydrone, melamine, glycerol and polyphosphoric acids were from s. d. fine chemicals, India.

Synthesis of resins derived from p-Hydroxyacetophenone, Quinhydrone, Melamine (PAQM)

The PAQM-I terpolymer resin was synthesized by polycondensation of a mixture of p-hydroxyacetophenone (0.1M), quinhydrone(0.1M) and melamine(0.1M) in the presence polyphosphoric acid (PPA, 20gm) in an oil bath at 120^0C for 8 Hrs with intermittent shaking. To well-stirred and ice-cooled mixture of p-hydroxyacetophenone (0.1M), quinhydrone (0.1M) and melamine (0.1M) in the presence polyphosphoric acid (PPA, 20gm) was added with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 30 minutes and heated in an oil bath at 120^0C for 8 Hrs the reaction mixture was then cooled, poured on crushed ice and left over night. A dark brown product was separated out [13 - 17].

The product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The product was again washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove copolymer which might be produced along with a terpolymer. It was further purified by dissolving in DMSO then filtered and reprecipitated by gradual drop wise addition of distilled water with constant and rapid stirring in order to avoid the lump formation. The purified PAQM-I product so obtained by filtration, washed with hot water, dried, powdered and kept in vacuum desiccators over silica gel. Yield was found to be 68%. The synthetic details are given in table1.

Similarly PAQM-II terpolymeric resin was prepared with varying molar proportion 1:3:1 of reacting monomers at 120°C for 8 Hrs, in the presence of polyphosphoric acid as catalyst and purified as above method. Yield was found to be 72%.

Similarly PAQM-III terpolymeric resin was prepared with varying molar proportion 1:4:2 of reacting monomers at 120°C for 8 Hrs, in the presence of polyphosphoric acid as catalyst and purified as above method. Yield was found to be 75%.

Reaction schemes of PAQM-I, PAQM-II and PAQM-III are shown in figure 1, 2 and 3 respectively. Table1 show that the synthesis details of PAQM terpolymer resins.
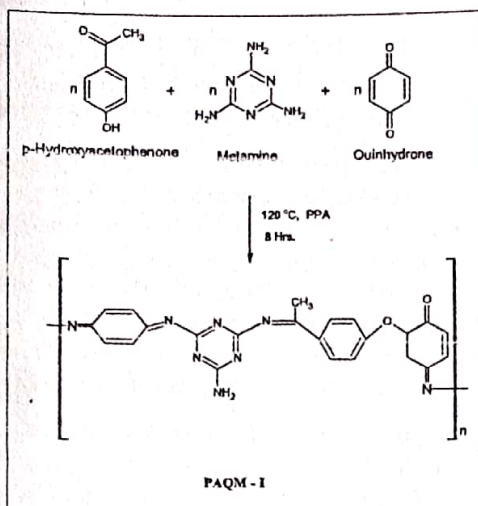
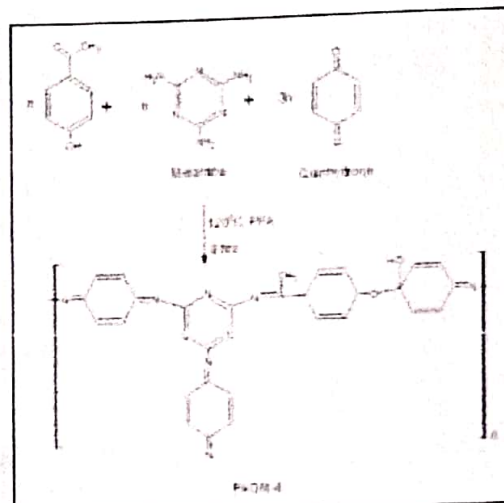Figure 1: Reaction scheme of PAQM-I Terpolymer resin
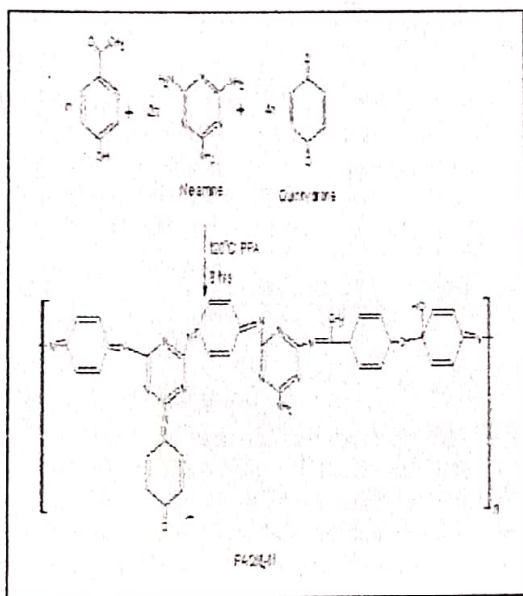

Figure 2: Reaction Scheme of PAQM-II terpolymer resin

Figure 3: Reaction Scheme of PAQM-III terpolymer resin

Table1: The synthesis details of PAQM terpolymer resins

Terpolymer resins	PAQM-I	PAQM-II	PAQM-III
p-Hydroxyacetophenone	0.1M	0.1M	0.1M
Quinhydrone	0.1M	0.3M	0.4M
Melamine	0.1M	0.1M	0.2M
Catalyst(polyphosphoric acid)	20 g	20 g	20 g
Reflux temperature±2°C	120	120	120
Time(Hrs)	8.0	8.0	8.0
Yield (%)	68	72	75
Color of synthesized resins	Dark brown	Dark brown	Dark brown

Ion exchange experimental procedures:

The ion exchange properties of PAQM resin, using batch equilibrium method, were studiedand results of samples PAQM-I , PAQM-II and PAQM-III are shown in table to2 for four metal ions under the given experimental condition.

1.Procedure to Study the Influence of Different Electrolyte on Metal Uptake:
25 mg of pure finely powered resin sample was suspended in electrolyte solution (25 ml) of previously known concentration. The pH of suspension was adjusted to desired value by 0.1 M HNO_3 or NaOH solution. The resin was swollen for 24 Hrs along with constant stirring at room temperature. To this suspension 5 ml of metal nitrate solution was added and pH of the solution was adjusted to required value. The mixture was again stirred for 24 Hrs. At room temperature and filtered the residue was washed several times. The washings were quantitatively collected with filtrate. The amount of metal ion taken up by polymeric resin was estimated from the difference between observation obtained from blank and experimental system. The same procedure was repeated for different electrolyte with different concentrations thereof. The experiment was carried out for four metal ions such as Cu^{2+}, Mg^{2+}, Pb^{2+} and Bi^{3+} [18-19].

2. Procedure to Evaluate the Rate of Metal Uptake
The optimum time required to reach the state of equilibrium under the given set of condition was estimated using series of experiments described by using 25 ml 0.25 M $NaNO_3$ solution instead of different electrolyte solution wherein the metal ions were spectrophotometrically estimated as a function of time in hours. The evaluation of rate of metal uptake based on the assumption that under experimental condition the state of equilibrium would be established within 24 Hrs [20-21]. The rate of metal uptake expressed in percent metal uptake was estimated for a given time related to this state of equilibrium.

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

3. Procedure for Evaluation of Distribution of Metal Ion (K_D) as a Function of pH
The distribution of metal ions at required pH was estimated between resin phase and liquid phase. The metal ion was estimated at appropriate pH. The pH was adjusted time to time by 0.1 M HNO_3 and 0.1 M NaOH. 25 mg of resin sample was stirred with 25 ml of 0.25 M $NaNO_3$ solution for 24 Hrs and then 5 ml of metal solution was added. The experiments were carried out in pH range 4.0 to 7.0. The distribution ratio K_D was determined by following equation [22-25],

$$K_D = \frac{mg \, of \, metal \, exchange \, per \, gm \, of \, resin}{mg \, of \, metal \, present \, in \, 1 \, ml \, of \, solution}$$

Result and discussion

a)   Influence of electrolyte on metal uptake.
The influences of NO_3^-, NO_2^-, Cl^- and SO_4^{2-} at various concentrations on equilibrium state of metal- resin interaction were studied [25]. The amount of metal ion taken up by polymeric samples depends upon nature and concentration of electrolyte solution. The amount of metal ion taken up by resin decreases with increase in concentration of NO_3^-, NO_2^-, Cl^- and SO_4^{2-} anions. I had seen no exchange of ion in Pb^{2+} in Na_2SO_4. This may be explained on the basis of common ion effect.

Table-2 Amount of metal ion exchanged (mg) per g of resin

Metal ion	Electrolyte Conc. Resin	NaNO₃			NaNO₂			NaCl			Na₂SO₄		
		PAQM-I	PAQM-II	PAQM-III	PAQM-I	PAQM-II	PAQM-III	PAQM-I	PAQM-II	PAQM-III	PAQM-I	PAQM-II	PAQM-III
Cu^{2+}	0.25	55.12	43.47	34.95	40.13	41.24	42.08	43.75	47.50	50.45	37.50	36.25	45.00
	0.5	51.23	46.04	41.95	36.16	30.12	25.96	35.50	41.25	47.50	30.25	31.25	36.25
	0.75	43.26	36.07	28.88	37.54	36.02	35.01	35.00	39.75	46.25	30.23	38.75	40.25
Mg^{2+}	0.25	40.94	38.40	34.85	33.73	35.36	36.86	25.91	34.53	39.22	36.52	39.09	40.34
	0.5	59.37	52.15	50.76	49.28	47.57	49.15	49.98	42.28	37.60	36.90	40.55	46.20
	0.75	52.18	51.04	29.16	43.75	45.40	45.68	51.28	47.37	41.13	41.36	42.48	44.43
Pb^{2+}	0.25	54.17	52.11	45.06	42.98	43.94	46.75	40.63	43.34	46.08	NOE	NOE	NOE
	0.5	43.21	35.00	32.38	39.88	39.56	46.00	41.51	49.11	46.79	NOE	NOE	NOE
	0.75	50.55	48.98	45.73	40.48	46.07	43.95	37.24	40.13	40.53	NOE	NOE	NOE
Bi^{3+}	0.25	56.38	47.01	44.08	38.15	45.95	48.57	39.12	34.81	32.71	27.03	25.09	30.55

| 0.5 | 22.79 | 17.76 | 15.82 | 25.01 | 28.96 | 29.38 | 23.94 | 31.46 | 39.53 | 29.12 | 28.91 | 35.79 |
| 0.75 | 32.42 | 27.61 | 24.33 | 32.58 | 27.24 | 36.80 | 30.25 | 30.65 | 35.64 | 26.12 | 27.31 | 30.15 |

b) Rate of metal uptake

The dependence of rate of metal ion uptake on nature of metal ion is shown in figures 4, 5 and 6. The rates of absorption of four metal ions on resins were determined in order to establish the shortest period of time to reach the equilibrium. The data revealed that the optimum time required to reach equilibrium is 7.0 Hrs for all metal ions except Pb^{2+}. It was also found that rate of metal ion increases as the time passes with increase in the time. However it becomes to nearer to 100% around 7 Hrs except Pb^{2+} ion for the Pb^{2+} the minimum time required to achieve equilibrium 6 Hrs. So overall minimum time required to reach equilibrium is selected as 7 Hrs.
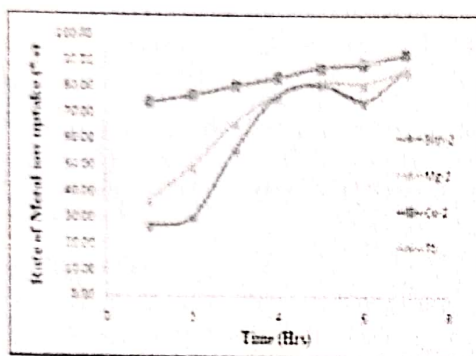

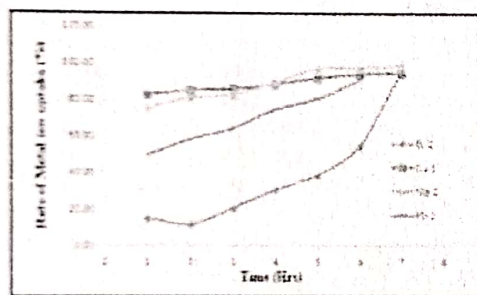Figure 4:- Rate of metal ion uptake of PAQM-I terpolymer resin

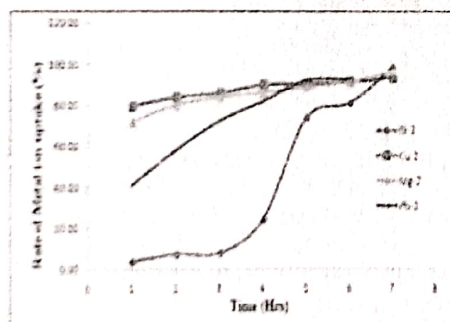Figure 5:- Rate of metal ion uptake of PAQM-II terpolymer resin

Figure 6:- Rate of metal ion uptake of PAQM-III terpolymer resin

K_D for PAQM				
Metal Ions	pH	PAQM-I	PAQM-II	PAQM-III
Cu^{2+}	4	254.45	407.04	422.62
	4.5	39.33	266.68	255.71
	5	391.8	755.31	783.44
	5.5	100.33	79.56	100.33
	6	136.46		268.61
	6.5	387.46	151.32	775.55
	7	460.76	408.99	526.98
Mg^{2+}	4	113.01	88.02	280.38
	4.5	522.50	560.89	580.23
	5	813.00	668.76	243.38
	5.5	417.64	421.66	726.00
	6	99.31	461.61	254.56
	6.5	10.45	80.61	495.55
	7	424.34	537.69	420.35
Pb^{2+}	4	167.83	329.07	387.93
	4.5	57.12	62.23	347.94
	5	62.95	394.88	166.72
	5.5	222.26	62.10	199.52
	6	107.59	235.92	317.73
	6.5	331.66	140.22	74.42
	7	411.20	665.32	504.38
Bi^{3+}	4	265.84	191.69	348.30
	4.5	142.26	54.99	40.77
	5	439.57	699.60	59.44
	5.5	170.62	193.29	111.95
	6	274.04	96.18	267.31
	6.5	7.64	76.57	722.20
	7	350.91	111.87	342.82

Table 3- Distribution K_D values of different metal ions as a function of pH

c) Distribution of metal ions as a function of pH

The data of distribution (K_D) of various metal ions as a function of pH is represented in table 3 revealed that the relative amount of metal ions taken up by PAQM resin increases with increase in Proportion of resin at the same pH. Distribution ratio values in general found to follow the order, PAQM-III > PAQM-II > PAQM-I. As the proportion of quinhydrone increase K_D value increases. At pH 5 in PAQM-I, PAQM-II and PAQM-III resins show the order of distribution ratio values decreases as Mg^{2+} > Bi^{3+} > Cu^{2+} > Pb^{2+}, Cu^{2+} > Bi^{3+} > Mg^{2+} > Pb^{2+} and Cu^{2+} > Mg^{2+} > Pb^{2+} > Bi^{3+} respectively. In PAQM-II, the order of distribution ratio value was found to be Mg^{2+} > Cu^{2+} > Pb^{2+} > Bi^{3+} at pH 6 and in PAQM-III, ratio was found to be Cu^{2+} > Bi^{3+} > Mg^{2+} > Pb^{2+}. K_D values for the metal ions were found to be very sensitive to pH. Lot of fluctuations was observed in the K_D values with respect to pH. However, in case of PAQM-I, pH 4 and 6 for Bi^{3+}, pH 4.5, 5 and 5.5 for Mg^{2+} and at pH 6.5, 7 for Cu^{2+} are found to be more selective. In case of PAQM-II, pH 4, 5, 6.5 for Cu^{2+}, pH 4.5, 5.5, 6 for Mg^{2+}, pH 7 for Pb^{2+} are found to be more selective. In case of PAQM-III, at pH 4, 5, 6.5 and 7 for Cu^{2+}, at pH 4.5, 5.5 for Mg^{2+}, at pH 6 for Pb^{2+} are more selective. PAQM resins are more selective Cu^{2+} > Mg^{2+} > Pb^{2+}.

Conclusion

Among the electrolytes such as $NaNO_3$, NaCl, $NaNO_2$ and $NaSO_4$, the $NaNO_3$ is found to be more suitable electrolyte supporting to the metal ion exchange of metal ion under study by all new synthesized resins. But in case Pb^{2+} ions in Na_2SO_4, there is no exchange of ions. As above all PAQM resins are more selective for Cu^{2+} > Mg^{2+} > Pb^{2+}. The ion exchange data support to the assigned structure of resins as shown in figure 1, 2 and 3.

Acknowledgements

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