



SYNTHESIS, CHARACTERIZATION AND ION-EXCHANGING PROPERTIES OF NOVEL ION-EXCHANGE RESIN PART-III

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ABSTRACT

The polyamine (PA) was prepared by condensation of 1,4-bis(chloromethyl) benzene and benzidine. The PA was then treated with cyanuric chloride at 0°C followed by reaction with 5-amino-8-Hydroxyquinoline in THF in conc. NaOH (PH 9-10) at room temperature for 8 hrs. The resultant polymer designated as polyamine-s-triazine-5-amino-8-Hydroxyquinoline (PATHQ) was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PATHQ sample was monitored for its chelating and ion-exchanging properties. The polymeric metal chelates of PATHQ with Cu²⁺, Zn²⁺, Mn²⁺, Ni²⁺, UO₂²⁺ and Co²⁺ metal ions were prepared and characterised by metal:ligand ratio, IR and reflectance studies, magnetic properties, thermogravimetry and microbicidal activity. Batch equilibration method has been adopted, for evaluation of ion-exchange properties.

Key words Polyamines, s-triazine, 5-amino-8-Hydroxyquinoline, polymeric metal Chelates, and magnetic properties, IR spectra, ion-exchange properties, Batch equilibrium method, thermogravimetry.

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INTRODUCTION

The effluents from mines and metal industries set up the serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit¹⁻³. The contents of this metal can be reduced by treatment of lime, but result is not satisfactorily. Thus ion-exchange technique has been proved very useful in this context. The ion-exchange resin can be used for metal extraction from ore, analytical reagent, and separation of metal ion and deionization of water⁴⁻¹⁰. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer¹¹⁻¹². The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem¹¹⁻¹². The aim of the present work is to prepare and study the novel ion-exchange resin. Thus we reported recently the novel ion-exchange resin^{13,14}. In continuation of this work^{13,14} the present paper comprises the synthesis of novel ion-exchange resin containing a well known metal complexing agent and 8-hydroxyquinoline and its i.e. chelating and ion-exchanging properties measurements. The synthetic route is shown below

EXPERIMENTAL

Materials: All the chemicals used were of either pure or analytical grade.

Synthesis of polyamines (PA) and PA-triazine (PAT) resin were prepared by method reported in an earlier communication¹³⁻¹⁵. 5-Amino-hydroxyl quinoline was prepared by method reported by method reported in literature¹⁶.

Synthesis of PAT-5-Amino-8-Hydroxy quinoline (PATHQ)

To a mixture of PAT polymer (0.01 mole) and 5-Amino-8-Hydroxy quinoline (0.02 mole) in THF (100 ml), Conc. NaOH was added with maintaining pH 9-10 of the mixture was heated upto 60°C gently for 5 minute and it was stirred at room temperature for 8 hrs. The resulted gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 90%. It did not melt up to 300°C and insoluble in water and common organic solvents.

Synthesis of polymeric chelates

The polymeric metal chelates of PATHQ were synthesized by reaction of PATHQ with corresponding metal acetates. The detail procedure is as follows-

A dried PATHQ polymer (0.01 mole) was dispersed in 200 ml aqueous solution of 20% aqueous formic acid and warmed on a water bath for 10 minutes. To this dispersed solution a warm solution of metal acetate (0.01 mole) in 50% aqueous formic acid solution was added drop wise with constant stirring. The reaction mixture as made alkaline with dilute ammonia solution in order to coagulate polymeric chelates. The resultant contents were further digested on water bath for an hour. Finally the solid polymer chelates were filtered off Washed with hot water followed by acetone. DMF and dried in air. The polymer chelates of PATHQ with Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , UO_2^{2+} and Zn^{2+} transition metal ions.

Measurements

Elemental analyses for C,H and N content were carried out on TF 1101 elemental analyzer (Italy). IR spectra of polymer ligand and their metal chelates were scanned on a NICOLET 760 DR FTIR spectrophotometer in KBr phase. The metal content of polychelates was performed by decomposing a weighed amount of each polymer chelate followed by EDTA titration as reported in literature¹⁷. Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using Mercury tetrathiocyanato cobaltate (II) $\text{Hg} [\text{Co} (\text{NCS})_4]$ as a calibrant. The diffuse reflectance spectra of all the solid polychelates were recorded on a Beckman DK-2A spectrophotometer with solid reflectance attachments. MgO was employed as the reference attachments. MgO was employed as the reference compound. Thermal behaviour of these metal chelates was studied by TGA performed on thermogravimetric analyzer.

The batch equilibration method was adopted for the ion-exchanging properties^{18,19}. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and distribution of various metal ions of different PH values were carried out following the details of the procedures described earlier^{18,19}.

RESULTS AND DISCUSSION

The polymer sample PATHQ was in form of dark brown powder and insoluble in common organic solvents. It swells up to some extent in conc. NaOH solution. It did not melt up to 300°C. The elemental contents in Table-1 are consistent with the predicted structure. The IR spectrum comprises the bands due to secondly NH (3400 cm^{-1}), methylated group ($2930, 2850, 1430 \text{ cm}^{-1}$), s-triazine and aromatic 8HQ moieties ($3030, 1500, 1600 \text{ cm}^{-1}$). The TGA of PATHQ contains single step degradation. The degradation starts from 280°C, loss rapidly between 300 to 500 and almost lost 85% at 650°C.

Characterization of Polymeric Chelates

The polymeric chelates of PATHQ with different metal ions such as Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} UO_2^{2+} and Zn^{2+} vary in color from dark green to brown. They generally resemble each other. Comparison of IR spectra of the parent ligand with their polymer chelates has revealed certain characteristics differences as mentioned below.

One of the significant differences to be expected between IR spectrum of parent ligand and its metal chelates is the absence of a broad band in the region of $3370\text{-}3450 \text{ cm}^{-1}$ due to O-H stretching vibration frequencies in IR spectrum of polymer chelates as the oxygen of this O-H of parent ligand has formed a bond with the metal ion. However this band has explicable by the fact that water molecules might have strongly absorbed to the chelates during the formation.

Another noticeable difference is that the bands due to C=N stretching vibration of 8-quinolionol at 1606 cm^{-1} in IR spectrum of PATHQ has assigned to implane O-H deformation and this is shifted towards higher frequency in the spectra of polymer chelates indication the formation of metal-oxygen bonds²⁰⁻²². This has been further confirmed by a weak band at 1100 cm^{-1} . Corresponding to C-O-M stretching frequency²⁰⁻²². All these characteristic features of IR suggest the general structure of polymer chelates as shown in Scheme 1.

Examination of data about metal content in each polymer chelates (Table- 1 and 2) has revealed a 1:1 metal: ligand stoichiometry in all the polychelates. Magnetic moment (μ_{eff}) data of polymer chelates given in Table I has reveals that all metal chelates like Cu^{2+} , Ni^{2+} and Co^{2+} are paramagnetic, while that of Zn^{2+} is diamagnetic in nature. The electronic spectral data assignments are shown in Table-3. The electronic spectra of PATHQ with Cu^{+2} ions show two broad bands at 14950 and 23529 cm^{-1} due to ${}^2T_{1g} \rightarrow {}^2E_g$

transition and charge transfer spectra respectively suggesting a distorted octahedral structure for PATHQ polymer chelates. The PEAQ with Ni²⁺ and Co²⁺ ion polychelates give two absorption bands respectively at 14925, 24096 cm⁻¹ and 14925, 22471 cm⁻¹ corresponding to ⁴T_g → ²T_{1g}, ⁴T_{1g} → ⁴T_{1g}(P) transition. Thus, absorption band of diffuse reflectance spectral and the values of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the Ni²⁺, and Co²⁺ polychelates. The spectra of polychelates of Mn²⁺ ion show two weak bands at 17241 cm⁻¹ and 25031 cm⁻¹ assigned to the transition ⁶A_{1g} → ⁴T_{2g} (4G) and ⁶T_{1g} → ⁴T_{1g}(4G) respectively and assigned an octahedral structure for PATHQ chelates. As the spectrum of the Zn²⁺ chelates is not well resolved it is not interpreted but its μ_{eff} value reveals its diamagnetic nature as expected. The TGA data (TG thermograms not shown) of all polymeric chelates are shown in Table-2. The TGA data as thermograms reveals that the rate of decomposition of all polymeric chelates is initially low up to 200°C temperature and rapidly increases to maximum in the range 400-500 °C. This might be due to accelerated catalytically by *insitu* formation of metal oxide of thermal stability of all these polychelates is quite similar.

Ion-Exchange properties

The examination of data presented in Table-2 reveals that the amount of metal ions taken up by a given amount of the PATHQ polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe³⁺, Cu²⁺ and UO₂²⁺ ions taken up by the polymer sample increase with the increase in concentration of ions taken up by the polymer sample increase with the increase in concentration of ions like chloride, chlorate and nitrate but decrease with the increase in concentration of the sulfate ions. The amounts of the remaining three metal ions Co²⁺, Mn²⁺, and Zn²⁺, taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

Rate of metal uptake

The rates of metal absorption by the PATHQ sample were measured for Fe³⁺, UO₂²⁺, Cu²⁺ and Mn²⁺ ions presence of 1 M NaHCO₃ to know the time required to reach the stage of equilibrium. All experiments were carried out at pH 3. The examination of the results presented in Tab.3 Shows that UO₂²⁺ and Fe³⁺ ions required slightly more than three hours for the establishment of equilibrium and Cu²⁺ and Mn²⁺ ions required about five h for the purpose. In the experiments with solution containing UO₂²⁺ and Fe³⁺ ions, more than 70% of equilibrium was established in the first h. This reveals that the rate of uptake of metal ions follows the order UO₂²⁺, Fe³⁺ > Cu²⁺ > Mn²⁺. The rates of uptake of Zn²⁺ and Co²⁺ ions have been found to be very low at pH 3. Hence the values are no reported.

Distribution ratio of metal ions at different pH values

The results described in Tab.4 reveal that the amount of metal ions taken up by the polymer sample PATHQ at equilibrium increases with the increase in pH. The selectivity of the polymer sample UO₂²⁺ and Fe³⁺ ions are higher than that for each of the remaining metal ions. The distribution ratio for Fe³⁺ ions is lower than that for UO₂²⁺ by about 1800 units at pH 3. The lower values of the distribution ratio for Fe³⁺ ions requires its attachment with proper sites on three different polymer chains and that of the UO₂²⁺ ion requires such an attachment with sites on two polymer chains. Among the remaining metal ions, Cu²⁺ has a high value of distribution ration at pH 6 while the other three mental ions Co²⁺, Zn²⁺, and Mn²⁺ have a low distribution ration over a pH range from 4 to 6. Further work in the direction of wide range at such polymers and their ion exchanging properties are under progress.

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Table-1: Elemental analyses of polymeric metal Chelates of PATHQ and their metal chelates

Sample Designation	Elemental Analysis					Elemental Analysis					
	N%		M%		μ _{eff}	%Weight loss at different temperature °C					
	Cal.	Found	Cal.	Found	B.M						
PATHQ	21.10	21.0	-----	----	-----	200	300	400	500	600	700

PATH (Cu ²⁺) 2H ₂ O	18.83	18.7	7.17	7.1	1.78	0.8	1.4	15	53	69	84
PATHQ(Ni ²⁺) 2H ₂ O	18.91	18.8	6.75	6.8	3.00	1.0	8.1	23	56	72	93
PATHQ(UO ₂ ²⁺) 2H ₂ O	15.34	15.4	24.38	24.3	D	1.8	10.9	28	59	77	92
PATHQ(CO ²⁺) 2H ₂ O	18.94	18.8	6.65	6.6	4.03	1.6	9.8	23	65	71	96
PATHQ(Mn ²⁺) 2H ₂ O	19.02	19.0	6.22	6.3	4.68	1.6	11	24	63	76	97
PATHQ (Zn ²⁺) 2H ₂ O	18.81	18.9	7.27	7.2	D	0.9	9	17	58	67	90

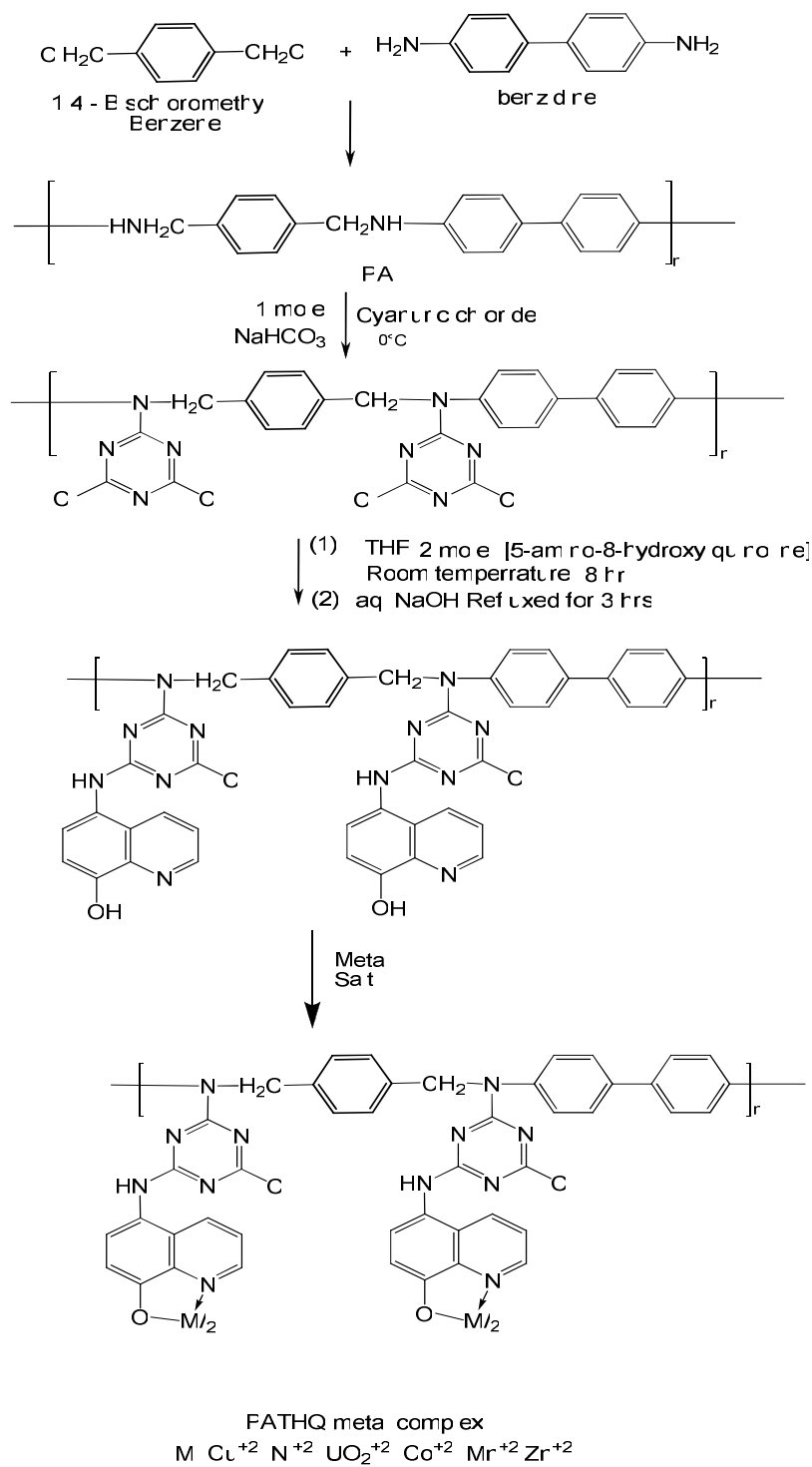
OH groups: 4 per repeat unit.
 IR features: 3400 (-NH-), 3600-2200 cm⁻¹ (-OH-)
 1604, 1500, 3050 cm⁻¹ (aromatic), 1520, 1260, 860 (S-triazine)
 2930, 2850, 1430 cm⁻¹ (-CH₂)

Table-2: Evaluation of the influence of different electrolytes in the uptake of several metal ions
 ([Mt (NO₃)₂] = 0.1 mole · l⁻¹)^a

Metal ions	PH	[Electrolyte] (mole · l ⁻¹)	Adsorption of mmol. · 10 ¹ of the metal ion on PATHQ polymer ^b .			
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄
Cu ²⁺	5.5	0.01	0.07	0.05	0.11	0.26
		0.05	0.15	0.07	0.13	0.24
		0.1	0.11	0.12	0.14	0.23
		0.5	0.24	0.14	0.18	0.21
		1.0	0.40	0.18	0.23	0.17
Fe ³⁺	2.75	0.01	0.08	0.10	0.01	0.18
		0.05	0.18	0.12	0.02	0.04
		0.1	0.21	0.13	0.05	0.06
		1.0	0.31	0.21	0.21	0.04
UO ₂ ²⁺	4.0	0.01	0.15	0.12	0.11	0.20
		0.05	0.19	0.14	0.13	0.21
		0.1	0.14	0.23	0.17	0.24
		0.5	0.22	0.43	0.20	0.17
		1.0	0.53	0.42	0.23	0.18
Co ²⁺	5.5	0.01	0.11	0.13	0.07	0.04
		0.05	0.10	0.12	0.10	0.05
		0.1	0.03	0.13	0.07	0.04
		0.5	0.02	0.04	0.05	0.03
		1.0	0.01	0.01	0.02	0.01
Mn ²⁺	5.5	0.01	0.18	0.22	0.20	0.14
		0.05	0.15	0.20	0.16	0.10
		0.1	0.13	0.17	0.19	0.06
		0.5	0.10	0.16	0.18	0.02
		1.0	0.08	0.17	0.13	0.01
Zn ²⁺	5.5	0.01	0.10	0.05	0.07	0.11
		0.05	0.10	0.04	0.06	0.02
		0.1	0.08	0.06	0.02	0.05
		0.5	0.02	0.03	0.01	0.01
		1.0	0.01	0.01	0.01	0.01
Ni ²⁺	5.5	0.01	0.06	0.10	0.01	0.16
		0.1	0.19	0.13	0.01	0.02
		0.5	0.20	0.12	0.05	0.05
		1.0	0.31	0.20	0.20	0.03

a. Volume of electrolyte solution 40 ml, time 24h, volume of metal ion solution 1ml,

temp. 25 °C
b. Wt. of PATS polymer 25 mg.



Scheme-1

Table-3: Comparison of the rates of metal (Mt) ion uptake ^a

Time (h)	Attainment of equilibrium state ^b			
	Fe ³⁺	UO ₂ ²⁺	Cu ²⁺	Mn ²⁺
0.5	62.5	31.2	33.7	21.7
1	71.1	65.1	51.5	46.1
2	87.3	83.4	63.9	62.5
3	91.2	91.1	74.3	76.3
4	90.4	95.7	83.5	83.5
5	---	---	89.1	85.5
6	---	---	93.6	91.5
7	---	---	92.1	97.2

- a. [Mt(NO₃)₂] = 0.1 mole · l⁻¹, volume 1 ml, [NaNO₃] = 1 mol · l⁻¹, volume 40 ml
pH = 3, temp 25° C, wt of PATS polymer 25 mg.
b. Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

Table-4: Distribution ratios, D, of different metal ions as a function of the pH

pH	Distribution ratio ^a of metal ions ^b					
	Cu ²⁺	Fe ³⁺	UO ₂ ²⁺	Co ²⁺	Mn ²⁺	Zn ²⁺
1.5	-----	-----	247	----	-----	-----
1.75	126	123	423	----	-----	-----
2.0	164	162	513	---	----	----
2.5	441	446	542	---	----	----
3.0	949	943	2783	----	----	----
4.0	---	---	----	2	72	75
5.0	----	----	----	75	134	135
6.0	---	---	----	333	255	253

^ammol of metal ions taken up by 1 g of polymer / mmol of ions present in 1 ml of solution
[Mt(NO₃)₂] = 0.1 mol/l, Volume = 1ml, wt. of polymer = 25mg, [NaNO₃] = 1mol.l, volume = 44ml, temp. = 25° C, time = 24hr (equilibrium state).
^bError +/- 5%

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