Synthesis, characterization and ion-exchanging properties of novel oligomeric azo dyes

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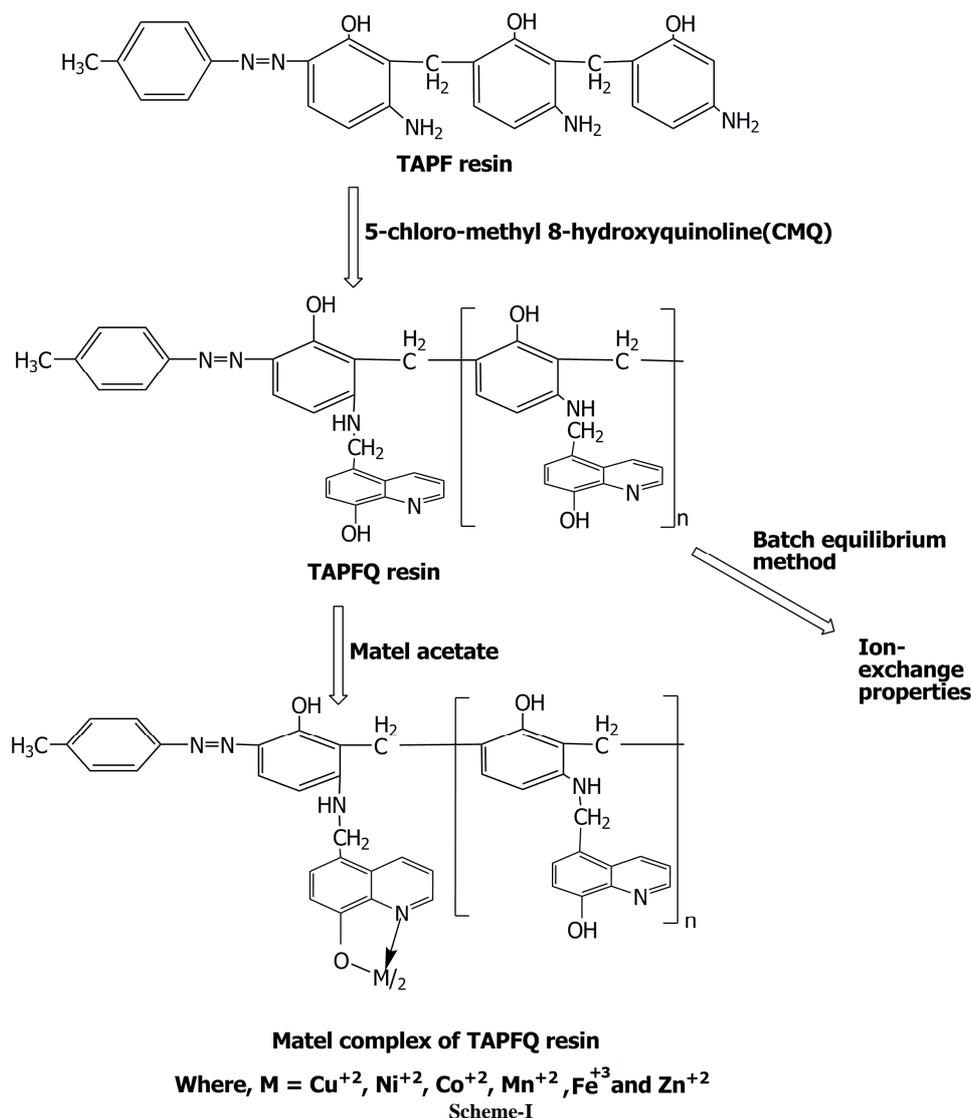[3]*Sheth L. H. Sci .College, Mansa, Gujarat*

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ABSTRACT

Diazotization of p-toluidine and coupling with 3-amino-phenol-Formaldehyde (APF) resin give oligomaric azo dye TAPF, based on 3-amino-phenol-Formaldehyde (APF) polymer. The TAPF was then treated with 5-chloro methyl-8-quinolinol hydrochloride in the presence of a THF in alkaline medium (pH 9-10) at room temperature for 7 hrs. The resultant oligomaric ligand designated as azo polyphenol-formaldehyde-5-chloromethyl-8-quinolinol (TAPFQ) was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The polymeric metal chelates of TAPFQ with Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Fe^{3+} and Co^{2+} metal ions were prepared and characterised by metal:ligand ratio, IR and reflectance studies, magnetic properties and thermogravimetry. The TAPFQ sample was also screened for its chelating and ion-exchanging properties. Batch equilibration method has been adopted for evolution of ion-exchange properties.

Key words: 3-amino-phenol-formaldehyde (APF) polymer, 5-chloromethyl-8-quinolinol, polymeric metal chelates, 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 limit.The ion-exchange resin are of organic polymera and play a pivotal role in various commodly application [1-3].The ion-exchange resin can be use for metal extraction from ore, analytical reagent, and separation of metal ion and deionization of water [4-10]. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer [11-12]. The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem [11-12]. The phenol-formaldyhyde type resins have also been reported as ion-exchange resine [13]. One of the resin 3-amino-phenol-Formaldehyde is reported for the purposes [14-15] but its modification into oligomeric ligand has not been reported.Thus, the aim of the present work to prepare and study the novel ion-exchange resin based on 3-amino phenol. The present paper comprises the studies on novel ion-exchange resin containing a well known metal complexing agent and 8-quinolinol. The synthetic route is shown below.

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Matel complex of TAPFQ resin

Where, M = Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Fe^{+3}and Zn^{+2}
Scheme-I

MATERIALS AND METHODS

Materials: All the chemicals used were of either pure or analytical grade.
Synthesis of 3-amino-phenol-Formaldehyde (APF) polymer was prepared by method repoted in literature [13]. The 5-chloromethyl-8-quinolinol hydrochloride (m.p. 280°C) was prepared by method reported in literature [16].

Synthesis of azo dyes based on 3-amino phenol-formadehyde (TAPF):
Preparation of azo coupling of aryl diazonium salts to phenol-formadehyde (TAPF): Diazonium salt of p-toluidine solution (0.1mole) was slowly added to an alkaline solution of 3-amino-Phenol-Formaldehyde polymer (APF) (0.1mole) at pH 8.5-9.0 and below 0-5°C. The resultant solution was stirred for 2.5 hrs.The dye was precipitated by lowering the pH to 6.0.The precipitated dye (TAPF) was filtered off, wash with water and air-dried. The yield of TAPF was 78% and m.p.174-175^{0}C (uncorrected). The predicted structure and formation of oligomeric ligand is shown in Scheme-1.

Synthesis of 6-(p-chlorophenyl) diazo-3-aminophenol-Formaldehyde-5-chloromethyl-8-quinolinol (TAPFQ): To a mixture of TAPF oligomeric (0.02 mole) and 5-chloromethyl-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

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was stirred at room temperature for 7 hrs. The resulted gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 83%. It did not melt up to 300°C and insoluble in water and common organic solvents.

Synthesis of oligomeric chelates:
The polymeric metal chelates of TAPFQ were synthesized by reaction of TAPFQ with corresponding metal acetates. The detail procedure is as follow.

A dried TAPFQ oligomer (0.02 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 (0.02 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 oligomeric 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 TAPFQ with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+} transition metal ions.

Measurments:
Elemental analyses for C, H and N content were carried out on TF 1101 elemental analyzer (Italy). IR spectra of oligomer 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 literature [17].

Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using Mercury tetrathiocyanato cobaltate (II) Hg[Co (NCS)$_4$] as a calibrant. The diffuse reflectance spectra of all the solid polychelates were recorded on a Backman 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 perfomed 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].

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RESULTS AND DISCUSSION

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The oligomer sample TAPFQ 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 300ºC. The elemental contents shown in Table-1 are consistents with the predicted structure. The IR spectrum of TAPFQ shows a broad band extending from 3400-3100 cm^{-1} with maxima at 3400, 3330 cm^{-1} attributed to –OH groupand NH$_2$ group. The weak bands at 2932 cm^{-1} and 2850 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of methylene groups (-CH$_2$-). The bands around at 1420, 1480, 1588 and 1600 cm^{-1} are due to 8-quinolinol moiety [20]. These features confirm the proposed structure of ligand TAPFQ. The TGA of TAPFQ contains single step degradation. The degradation starts from 280°C, loss rapidly between 300 to 500 and almost lost 87% at 650°C.

Characterization of Polymeric Chelates:
The polymeric chelates of TAPFQ with different metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+} vary in color from dark red 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 present at sharp 3400 cm^{-1} due to Sec. NH stretching vibration frequencies in IR spectrum of polymer chelates.However the band due to absence of as the oxygen O-H of parent ligand has not been predicated due to presence of already OH group of resin. However this band has explicable by the fact that water molecules might have strongly absorbed to the chelates during the formation.

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Table 1. Elemental analyses of polymeric metal Chelates of TAPFQ and their metal chelates.

Sample designation	Elemental Analysis					Elemental Analysis					
	N%		M%		μ_{eff}	%Weight loss at different temperature ºC					
	Cald	Found	Cald	Found	B.M						
TAPFQ	11.26	11.2	-----	----	------	200	300	400	500	600	700
TAPFQ (Cu^{2+})	10.90	10.8	3.25	3.2	1.77	9.5	12.6	28.5	50.4	65.5	81.3
TAPFQ (Ni^{2+})	10.92	10.9	3.00	2.9	2.96	8.4	17.9	23.4	54.5	68.4	90.4
TAPFQ (Co^{2+})	10.93	10.9	3.01	3.0	3.99	8.9	20.2	22.8	62.6	70.6	92.7
TAPFQ (Mn^{2+})	10.95	10.9	2.81	2.8	4.66	9.1	15.1	23.9	60.7	72.5	93.5
TAPFQ (Fe^{3+})	12.38	12.3	2.85	2.8	4.94	8.9	15.8	24.6	63.4	73.4	96.3
TAPFQ (Zn^{2+})	10.89	10.8	3.34	3.3	D	8.6	18.4	26.8	55.3	63.6	90.8

Another noticeable difference is that the bands due to C=N stretching vibration of 8-quinolinol at 1606 cm^{-1} in IR spectrum of TAPFQ has assigned to in plane O-H deformation and this is shifted towards higher frequency in the spectra of polymer chelates indication the formation of metal-oxygen bonds [21-23].This has been further confirmed by a weak band at 1100cm^{-1}. Corresponding to C-O-M stretching frequency [21-23]. All these characteristic features of IR suggest the general structure of polymer chelates as shown in Scheme I.

Examination of data about metal content in each polymer chelates (Table- I and II) has revealed 1:2 metal: ligand stoichiometry for divalent metal ions and 1:3 metal: ligand stoichiometry for Fe^{3+} 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 TAPFQ with Cu^{+2} ions show two broad bands at 14954 and 23532 cm^{-1} due to $2T_{1g} \rightarrow ^2E_g$ transition and charge transfer spectra respectively suggesting a distorted octahedral structure for TAPFQ polymer chelates. The TAPFQ with Ni^{2+} and Co^{+2} ion polychelates give two absorption bands respectively at 14928, 24099 cm^{-1} and 14928, 22474cm^{-1} corresponding to $^4T_g \rightarrow ^2T_{1g}$, $^4T_{1g} \rightarrow ^4T_{1g}(P)$ transition. Thus, absorption band of diffuse reflectance spectral and the values of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the Ni^{2+} and Co^{2+} poly chelates. The spectra of polychelates of Mn^{2+} ion show two weak bands at 17244 cm^{-1} and 25034 cm^{-1} assigned to the transition $^6A_{1g} \rightarrow ^4T_{2g}$ (4G) and $^6T_{1g} \rightarrow ^4T_{1g}(4G)$ respectively and assigned an octahedral structure for TAPFQ chelates. As the spectrum of the Zn^{2+} chelates is not well resolved it is not interpreted but its μeff 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 200ºC temperature and rapidly increases to maximum in the range 400-500ºC. 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 TAPFQ polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe^{3+} and Cu^{2+} 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 Co^{2+} , Mn^{2+} and Zn^{2+} taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

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 TAPFQ polymerᵇ.			
			NaClO₄	NaNO₃	NaCl	Na₂SO₄
Cu^{2+}	5.5	0.01	0.11	0.09	0.15	0.29
		0.05	0.22	0.12	0.17	0.28
		0.1	0.15	0.18	0.19	0.27
		0.5	0.30	0.20	0.22	0.24
		1.0	0.47	0.25	0.28	0.22
Fe^{3+}	2.75	0.01	0.09	0.14	0.04	0.15
		0.05	0.24	0.18	0.05	0.04
		0.1	0.26	0.16	0.08	0.08
		1.0	0.34	0.26	0.25	0.05

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Co^{2+}	5.5	0.01	0.16	0.17	0.09	0.07
		0.05	0.15	0.18	0.15	0.11
		0.1	0.08	0.17	0.10	0.08
		0.5	0.07	0.09	0.08	0.06
		1.0	0.03	0.04	0.06	0.03
Mn^{2+}	5.5	0.01	0.24	0.27	0.22	0.17
		0.05	0.21	0.24	0.19	0.15
		0.1	0.18	0.21	0.23	0.08
		0.5	0.15	0.22	0.18	0.09
		1.0	0.17	0.19	0.16	0.06
Zn^{2+}	5.5	0.01	0.14	0.10	0.09	0.15
		0.05	0.16	0.08	0.08	0.08
		0.1	0.12	0.07	0.05	0.11
		0.5	0.08	0.06	0.07	0.06
		1.0	0.07	0.04	0.04	0.04
Ni^{2+}	5.5	0.01	0.09	0.12	0.09	0.18
		0.1	0.21	0.15	0.07	0.09
		0.5	0.19	0.18	0.08	0.10
		1.0	0.32	0.24	0.28	0.05

a. Volume of electrolyte solution 40 ml, time 24h, volume of metal ion solution 1ml, temp. 25 ºC
b. Wt. of PATS polymer 25 mg.

Rate of metal uptake:

The rates of metal absorption by the TAPFQ sample were measured for Cu^{2+} and Mn^{2+} ions presence of 1 M $NaHCO_3$ 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 Table.3 shows that Fe^{3+} ions required slightly more than three hours for the establishment of equilibrium and Cu^{2+} and Mn^{2+} ions required about five hrs for the purpose. In the experiments with solution containing Fe^{3+} ion, more than 70% of equilibrium was established in the first hrs. This reveals that the rate of uptake of metal ions follows the order $Fe^{3+} > Cu^{2+} > Mn^{2+}$. The rates of uptake of Zn^{2+} and Co^{2+} ions have been found to be very low at pH 3. Hence the values are no reported.

Table 3. Comparison of the rates of metal (Mt) ion uptake [a]

Time (h)	Attainment of equilibrium state [b].		
	Fe^{3+}	Cu^{2+}	Mn^{2+}
0.5	62.8	35.2	22.4
1	71.9	51.9	46.9
2	88.9	63.8	62.7
3	91.8	75.0	76.7
4	90.8	84.2	84.5
5	---	89.7	85.9
6	---	94.5	92.5
7	---	93.7	97.9

a. [Mt (NO_3)_2] = 0.1 mole·l^-1, volume 1 ml [NaNO_3]=1 mol ·l^-1, volume 40 ml
pH = 3, temp 25º 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 rations, D, of different metal ions as a function of the pH

pH	Distribution ration[a] of metal ions[b]				
	Cu^{2+}	Fe^{3+}	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	-----	-----	----	-----	-----
1.75	132	134	----	-----	-----
2.0	167	169	---	----	----
2.5	452	456	---	----	----
3.0	951	955	----	----	----
4.0	---	---	8	79	81
5.0	----	----	86	142	143
6.0	---	---	340	263	266

a. mmol of metal ions taken up by 1 g of polymer/ mmol of ions present in 1 ml of solution
[Mt(NO_3)_2] = 0.1 mol l^-1, volume: 1 ml; wt. of polymer: 25 mg ; [NaNO_3] = 1 mol l^-1, volume: 44 ml; temp.: 25 0C, time 24 h (equilibrium state).
b. Error +/- 5%.

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Distribution ratio of metal ions at different pH values:

The results described in Table.4 reveal that the amount of metal ions taken up by the polymer sample TAPFQ at equilibrium increases with the increase in pH. The selectivity of the polymer sample Fe^{3+} ion are higher than that for each of the remaining metal ions. The lower values of the distribution ratio for Fe^{3+} ions requires its attachment with proper sites on three different polymer chains. Among the remaining metal ions, Cu^{2+} has a high value of distribution ration at pH 6 while the other three mental ions Co^{2+}, Zn^{2+} and Mn^{2+} 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.

CONCLUSION

In present communication we prepare novel ion-exchange resin based on 3-amino phenol i.e. TAPFQ. The novel ion-exchange resin containing a well known metal complexing agent and 8-quinolinol. The TAPFQ sample was shows good chelating and ion-exchanging properties. Batch equilibration method has been adopted for evolution of ion-exchange properties.

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