Original Article

Synthesis, Characterization And Chelating Properties Of Polymeric Azo Dye Based On 8-Hydroxyquinoline-Formaldehyde Polymer

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DOI: 10.47750/pnr.2022.13.S10.700

Abstract

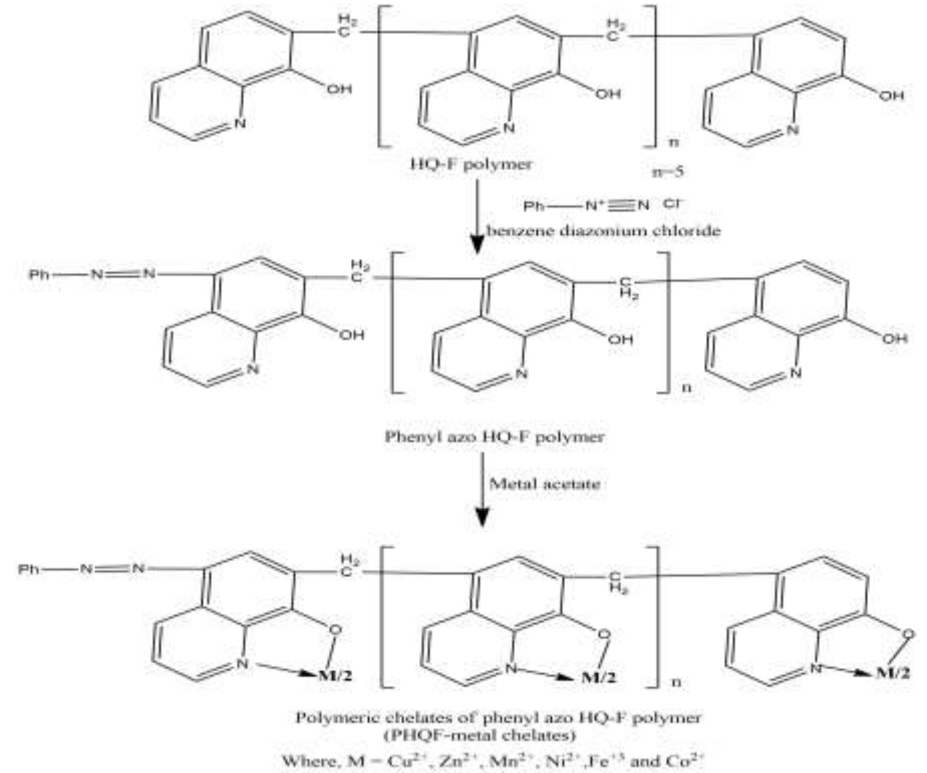
The polymeric phenyl azo 8-hydroxyquinoline-Formaldehyde (PHQ-F) was prepared by coupling of phenyl diazonium salt with 8-hydroxyquinoline-Formaldehyde (8HQ-F) polymer. The resultant polymeric ligand designated as PHQ-F was characterized by elemental analysis, IR spectral features and thermogravimetry. The polymeric metal chelates of PHQ-F with Cu^{2+}, Zn^{2+}, Mn^{2+}, $Ni^{2+}$$Fe^{+3}$ and Co^{2+} metal ions were synthesized and characterized by metal:ligand ratio, IR and reflectance studies, magnetic properties and thermogravimetry. The PHQ-F sample was also monitored for its chelating and metal ion-exchanging properties by batch equilibration method.

Key words: 8-hydroxyquinoline-Formaldehyde (8HQ-F) polymer, Diazotization, polymeric metal Chelates, IR spectra, ion-exchange properties, Batch equilibrium method, thermogravimetry and antimicrobial activity.

INTRODUCTION

8-hydroxy quinoline (HQ) is one of important heterocyclic derivatives due to its metal chelating behaviour [1]. HQ derivatives have high antibacterial activities [2-5]. Azo derivatives of HQ also play pivotal role as chelating agents of many metals [4-13]. But not applied for dying clothes. However, some of HQ azo dye has mordent dyeing application [14]. In addition HQ azo dyes have been found application in analytical chemistry [9-25].

The polymers derived from HQ and formaldehyde are reported very good metal chelates and ion-exchangers [26]. The Indian scientists have also good deal of work in this direction [27,28]. Good deal of work was carried out in the field of polymeric azo dye based on phenolic resins by Patel and his coworkers [29,30]. Looking to the phenolic properties and azo dye formation of HQ, the azo dyes based on 8-hydroxy quinoline - formaldehyde (HQF) polymer has not been studied either textile dyeing or metal chelating properties. Thus, the present authors thought interesting to undertake such study. Thus, the research design as present paper is shown in scheme.



EXPERIMENTAL

Materials: All the chemicals used were of either pure or analytical grade.
Synthesis of 8-hydroxyquinoline-Formaldehyde (HQ-F) polymer was prepared by method repoted in literature [26].

Synthesis of phenyl azo 8-hydroxyquinoline-Formaldehyde (PHQ-F) :

Phenyl diazonium salt solution (0.2mole) (prepared by diazotization of aniline) was slowly added to an alkaline solution of 8-hydroxyquinoline-Formaldehyde (HQ-F) (0.2mole) at pH 8.5-9.0 and below 0-5ºC. The resultant solution was stirred for 2hr. The dye was precipitated by lowering the pH to 6.0.The precipitated of PHQ-F was filtered off, wash with water and air-dried. The yield of PHQ-F was 67% and m.p. did not melt upto 300^0C (uncorrected). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Synthesis of polymeric chelates:

The polymeric metal chelates of PHQ-F were synthesized by reaction of PHQ-F with corresponding metal acetates. The detail procedure is as follow.

A dried PHQ-F 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 dark colored polymeric chelates were filtered off Washed with hot water followed by acetone. DMF and dried in air. Thus polymeric chelates of PHQ-F with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} transition metal ions were prepared.

Measurments

Elemental analyses for C,H and N content were carried out on TF 1101 elemental analyzer (Italy). Azo group was determined by Vogel's method [31]. Molecular weight of PHQF was determined by non-aqueous conductometric titration [29]. IR spectra of HQF ligand and its metal chelates were scanned on a NICOLET 760 DR FTIR spectrophotometer in KBr phase. The metal content of polymeric chelates was performed by decomposing a weighed amount of each polymeric chelate by mineral acid followed by EDTA titration as reported in literature [31].

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. Thermal behaviour of these metal chelates was studied by TGA perfomed on thermogravimetric analyzer.
The batch equilibration method was adopted for estimating ion-exchanging properties [32, 33]. The influence of different electrolytes on metal uptake by the HQF polymer. The effect of various common salts, kinetic absorption of metal ion on distribution of metal on HQF polymer was studied. 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 [32,33].

RESULTS AND DISCUSSION

The polymer sample PHQ-F 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 consistent with the predicted structure. More particularly the N% content is high than parent HQF. This may be due to presence of azo group. The IR spectrum of PHQ-F shows a broad band extending from 3400-3100 cm^{-1} with maxima at 3400,3330 cm^{-1} attributed to –OH group. The weak bands at 2935 $cm^{-1}$and 2850 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of methylene groups ($-CH_2-$). The weak band around 1407cm-1 may be assigned to Azo (-N=N-) group [34]. The bands around at 1425, 1480, 1580, and 1600 cm^{-1} are due to 8-hydroxyquinoline moiety [35]. These features confirm the proposed structure of ligand PHQ-F. The TGA of PHQ-F contains single step degradation. The degradation starts from 280°C, loss rapidly between 300 to 500 and almost lost 86% at 650°C.

Characterization of Polymeric Chelates:

The polymeric chelates of PHQ-F with different metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{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 PHQF with its polymer chelates has revealed certain characteristics differences as mentioned below.

One of the significant differences to be expected between IR spectrum of PHQF and its metal chelates is that the band due to –OH group is less broad in the spectra of polymeric chelates. This may due to metal chelation. 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 PHQ-F has assigned to implant O-H deformation and this is shifted towards higher frequency in the spectra of polymer chelates indication the formation of metal-oxygen bonds [36-38].This has been further confirmed by a weak band at 1100 cm^{-1}.Corresponding to C-O-M stretching frequency [36-38]. 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 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 PHQ-F with Cu^{+2} ions show two broad bands at 14955 and 23532 cm^{-1} due to $^2T1_g \rightarrow ^2E_g$ transition and charge transfer spectra respectively suggesting a distorted octahedral structure for PHQ-F polymer chelates. The PHQ-F with Ni^{2+} and Co^{+2} ion polychelates give two absorption bands respectively at 14925, 24099 cm^{-1} and 14925, 22470 cm^{-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+} polychelates. The spectra of polychelates of Mn^{2+} ion show two weak bands at 17245 cm^{-1} and 25030 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 PHQ-F 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 results of TGA data shows that the rate of decomposition of all polymeric chelates is initially low up to 200ºC temperature and rapidly increases to maximum in the range 400-500 ºC. This might be due to accelerated catalytically by `*in situ*` formation of metal oxide during thermal degradation of polymeric chelates.

Ion-Exchange properties

The estimated of data presented in Table-2 reveals that the amount of metal ions taken up by a given amount of the PHQ-F polymer depends upon the nature and concentration of the common salt 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 PHQF 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 PHQF 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 PHQ-F sample was measured for Fe^{3+},Cu^{2+} and Mn^{2+} ions in presence of 1 M $NaNO_3$ 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 hour for the purpose.

In the experiments with solution containing Fe^{3+} ions, 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 not been found due to low absorption at pH 3.

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 PHQ-F at equilibrium increases with the increase in pH. The selectivity of the polymer sample Fe^{3+} ions are higher than that for each of the remaining metal ions. 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.

Table-1 Elemental analyses of polymeric ligand and its metal chelates

Sample designation	Elemental Analysis					%Weight loss at different temperature ºC					
	N%		M%		μ_{eff}						
	Cald	Found	Cald	Found	B.M.	200	300	400	500	600	700
PHQ-F	13.36	13.3	-----	----	------	7.0	10.0	18.0	43.0	60.0	75.0
PHQ-F (Cu^{2+})	12.40	12.3	7.03	7.0	1.75	8.7	11.8	27.8	50.1	64.8	80
PHQ-F (Ni^{2+})	12.46	12.4	6.53	6.5	3.01	7.6	17.4	22.5	53.8	67.9	89
PHQ-F (Co^{2+})	12.46	12.4	6.56	6.5	4.02	8.4	19.6	22.2	62.0	70.0	90
PHQ-F (Mn^{2+})	12.51	12.5	6.14	6.1	4.66	8.5	14.5	23.1	59.9	71.9	91
PHQ-F (Fe^{3+})	12.50	12.4	6.23	6.2	4.94	8.6	15.1	24.5	63.0	73.1	95
PHQ-F (Zn^{2+})	12.37	12.3	7.22	7.2	D	8.1	17.8	26.6	54.7	63.3	90

Acid value : 1 –OH group/ repeating unit
OH group: 2-1 group/ polymeric chain
Azo group: 1020 (By aqueous conductometric titration)
Mol. Wt. : 3400-3330 cm^{-1} (-OH-)
IR features: 1600, 1580, 3040 cm^{-1} (aromatic), 2935, 2850, 1430 cm^{-1} ($-CH_2-$)
1405 cm^{-1} (-N=N-)

Table-2 Effect of common salts (i.e. electrolytes) on metal uptake by PHQF polymer

Metal ions	pH	[Electrolyte] (mole·l $^{-1}$)	metal uptake (mmol.·10^1)			
			$NaClO_4$	$NaNO_3$	NaCl	Na_2SO_4
Cu^{2+}	5.5	0.01	0.08	0.08	0.14	0.28
		0.05	0.17	0.11	0.16	0.27
		0.1	0.12	0.17	0.19	0.26
		0.5	0.27	0.19	0.21	0.24
		1.0	0.44	0.24	0.27	0.20
Fe^{3+}	2.75	0.01	0.07	0.12	0.06	0.18
		0.05	0.22	0.17	0.08	0.08
		0.1	0.24	0.15	0.09	0.10
		1.0	0.32	0.25	0.27	0.07
Co^{2+}	5.5	0.01	0.12	0.15	0.07	0.07
		0.05	0.10	0.16	0.13	0.10
		0.1	0.05	0.14	0.09	0.08
		0.5	0.04	0.09	0.07	0.06
		1.0	0.02	0.04	0.05	0.04
Mn^{2+}	5.5	0.01	0.20	0.26	0.21	0.16
		0.05	0.18	0.24	0.19	0.13
		0.1	0.15	0.20	0.22	0.07
		0.5	0.12	0.19	0.18	0.08
		1.0	0.14	0.17	0.15	0.05
Zn^{2+}	5.5	0.01	0.12	0.08	0.09	0.14
		0.05	0.14	0.06	0.08	0.07
		0.1	0.10	0.05	0.05	0.10
		0.5	0.06	0.04	0.07	0.06
		1.0	0.05	0.02	0.04	0.04
Ni^{2+}	5.5	0.01	0.07	0.12	0.09	0.17
		0.1	0.18	0.15	0.07	0.08
		0.5	0.16	0.18	0.08	0.09
		1.0	0.29	0.22	0.22	0.05

Common salt: 40 ml solution
Wt. of PHQF: 25mg
Metal ion solution: 1ml of 0.1M
Temp. : RT

Table-3 Rates of metal (Mt) ion uptake by PHQF polymer[a]

Time (h)	Attainment of equilibrium state %age metal uptake at equilibrium stage[b]		
	Fe^{3+}	Cu^{2+}	Mn^{2+}
0.5	62.4	34.9	21.9
1	71.5	51.5	46.5
2	88.7	63.4	62.9
3	91.3	74.6	76.3
4	90.4	83.9	83.9
5	---	89.5	85.8
6	---	94.0	91.9
7	---	93.3	97.5

a. Metal ion = 0.1 mole · l^{-1} ; 1 ml, $[NaNO_3]$=1 mol ·l^{-1}; 40 ml pH = 3, temp 25º C, wt of PHQ-F polymer 25 mg.
b. Considering the amount of metal at equilibrium stage at 100°C.

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+}	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	-----	-----	----	-----	-----
1.75	125	127	----	-----	-----
2.0	162	166	---	----	----
2.5	447	449	---	----	----
3.0	946	948	----	----	----
4.0	---	---	4	75	78
5.0	----	----	78	137	137
6.0	---	---	336	258	258

$$^{a}\ \frac{\text{mmol of metal ions taken up by 1 g of polymer}}{\text{mmol of ions present in 1 ml of solution}}$$

$[Mt(NO_3)_2]$ = 0.1 mol l^{-1}, volume: 1 ml; wt. of polymer: 25 mg ; $[NaNO_3]$ = 1 mol l^{-1}, volume: 44 ml; temp.: 25 ^{0}C, time 24 h (equilibrium state).
[b] Error +/- 5%.

ACKNOWLEDGEMENT:
The author thanks to --------- for providing research facility and encouragement.

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