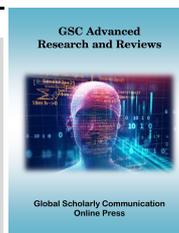


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(RESEARCH ARTICLE)



Synthesis, characterization and chelating properties of tannin-8-hydroxy quinoline - formaldehyde polymer

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Abstract

Tannin obtained from Eucalyptus plant, condensed with formaldehyde and then 8-hydroxy quinoline. The so called obtained polymer designated as TFQ was used for metal chelate formation. Thus Transition metal chelates of TFQ with Zn^{+2} , Co^{+2} , Cu^{+2} , Ni^{+2} and Mn^{+2} metal ions were prepared. The ligand TFQ and its all five metal chelates were characterized by nitrogen content, IR, UV-Visible spectral studies, magnetic moments and thermogravimetry. The antimicrobial activity of all the samples has also been monitored against common microbes.

Keywords: Tannin; 8-hydroxy Quinoline; Metal Chelates; Spectral Study; Thermogravimetry and Magnetic Moments.

1. Introduction

Considered research has targeted on natural materials like Tannin, to develop biobased materials [1-3]. Tannin is common material extracting from plants which contain high amount of polyphenols [4,5] its common structure is as follows

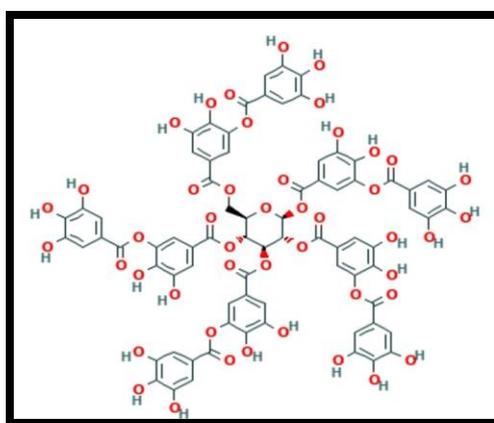


Figure 1 Structure of Tannin

Tannin is pivotal materials for various industries like leather, textile, coating, cosmetic etc. Recently the Tannin based copolymer resins are reported [5].

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Having phenolic group and tendency to condense with formaldehyde, the present authors thought to explore the field to metal chelating resin based on Tannin. Thus the present communication comprises the synthesis of Tannin-formaldehyde-8-hydroxy quinoline (TFQ) copolymer and study of its chelating properties. The work is scanned in scheme - 1.

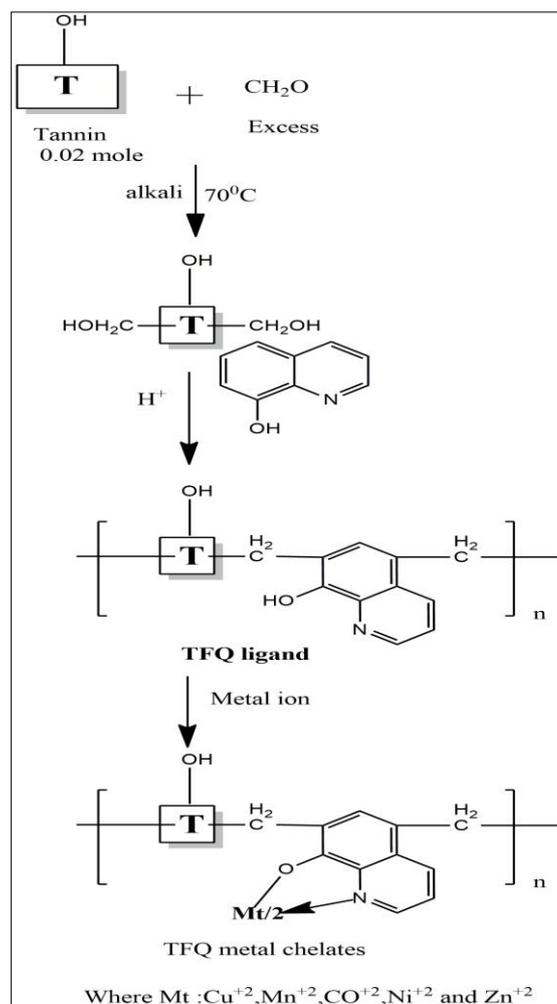


Figure 2 Scheme of the synthesis of Tannin-formaldehyde-8-hydroxy quinoline

2. Material

Tannin was extracted from *Eucalyptus* bark and leaves. It was used as dry form. All other chemicals were used as analytical pure grade.

2.1. Measurements

Nitrogen content of all the samples was determined on colman analyzer. The infrared spectra (FT-IR) were recorded in the range 4000-400cm⁻¹ with a Perkin Elmer spectrum GX spectrophotometer (FT-IR) instrument using KBr pallets. The metal content of polymeric chelates was carried out by EDTA titration method as reported in literature [6]. Magnetic moment of all polymeric chelates determined at room temperature using Gouy method reported in literature [18]. The reflectance spectra of all polymeric metal chelates were recorded on Backman spectrophotometer. TG Analysis of polymeric chelates was determined on Du Pont 950 thermogravimetric analyzer at 10°K per minutes [7, 8].

2.2. Synthesis of Tannin-Formaldehyde-8-hydroxy Quinoline copolymer (TFQ)

In a round bottom flask Tannin powder (34g, 0.02 mole) and formaldehyde (37% w/v) solution in 1% aqueous NaOH solution (200 ml) was heated on boiling water bath. The resultant resinous mass was neutralized by dil. HCl. To this resin solution 8-hydroxy quinoline (54.5g, 0.5 mole) in dil. HCl was added and reflux for 3hrs. The dark brown mass was

obtained. The mass was neutralized by aq. ammonia. The product was filtered, washed and air dried. Yield was 85%. It was soluble in DMF and DMSO solvent. It did not melt upto 300°C.

[The Tannin: 8-hydroxy quinoline ratio taken at unimolar hydroxy group]

2.3. Synthesis of Polymeric Chelates of TFQ

The polymeric metal chelates viz. Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Zn²⁺ of TFQ ligand was synthesized as follow:

Polymeric TFQ ligand solution (0.01 mole) was prepared using 20% formic acid and further warm for 10 min on water bath. Then warm metal salt solution (0.01 mole) prepared in 50% aqueous formic acid was added gradually to above prepared solution with constant stirring. The resulting product was made alkaline using dil. NH₃ solution till the polymeric metal chelate formed. It was further heated on water bath for complete coagulation. The ppts were filtered, washed with DMF and air dried. The synthesized polymeric chelates were designated as M(II) TFQ. The characterization of all polymeric chelates was displayed in Table -1.

3. Results and discussion

TFQ was obtained in form of pale dark brown powder and soluble in DMF and DMSO. N and metal content analyses results of TFQ and their metal chelates are provided in Table-1 which consistent with the predicted structure as shown in above Scheme-1. The polymeric chelates of TFQ ligand with various metals such viz. Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and Zn²⁺ were also obtained with good yield.

Table 1 Elemental analyses of TFQ and its metal chelates

Designation of sample	Elemental analyses (%)			
	N		M ²⁺	
	Cal.	Found	Cal.	Found
TF	-	-	-	-
TFQ	3.41	3.37	-	-
Cu ²⁺ +TFQ	3.17	3.14	7.19	7.20
Ni ²⁺ +TFQ	3.19	3.13	6.68	6.60
Co ²⁺ +TFQ	3.19	3.15	6.71	6.65
Mn ²⁺ +TFQ	3.20	3.12	6.28	6.22
Zn ²⁺ +TFQ	3.16	3.14	7.39	7.35

IR spectra of synthesized TFQ ligand show a broad band in the range 3350-3385 cm⁻¹ due to OH stretching of Tannin and 8-hydroxy quinoline derivative which confirms presence of 8-HQ nucleus. Also the characteristics bands were found at 1445, 1426, 1514 and 1610 cm⁻¹ further supports here presence of 8-hydroxy quinoline derivative. The aliphatic C-O of ether group was found at 1070 and 1167 cm⁻¹ while weak bands at 2720 and 2832 cm⁻¹ attributes to aliphatic -CH₂ groups. Also other typical bands 8-quinolinol was found at their respective positions as reported earlier [6]. The IR spectra of metal chelates resemble each other with only difference found in bands of metal-ligand bonding.

The comparison of IR spectrum of ligand and their metal chelates has not shown any characteristic because there are number of hydroxyl groups present in Tannin. So the interpretation at complexation is not rectified. However it is fact the metal content confirm the chelation. Also the formation of M-O bonds was confirms by bands found at 1100 cm⁻¹ due to C-O-M stretching frequency [9]. Another band is shifted to lower frequency (about 20-30 cm⁻¹) than found in its parent ligand.

The diffuse electronic spectrum of Cu²⁺ chelates shows two broad bands around 14120 and 23758 cm⁻¹. The first band may be due to a ²T_{1g} → ²F_g transition, while the second band may be due to charge transfer. The band along with magnetic moment value found at 1.85 BM suggests a distorted octahedral structure for the Cu²⁺ metal chelates [8]. As the spectrum of the metal chelate of Ni²⁺ show two distinct bands at 15165 and 23574 cm⁻¹ are assigned as ³A_{1g} → ³T_{1g(F)}, and ³A_{1g} →

${}^3T_{1g}(P)$ transitions, respectively suggested the octahedral environment for Ni²⁺ ion and further supported by magnetic moment value found at 3.15 BM [10]. The Co²⁺ metal chelate shows two absorption bands at 22556 and 15235 cm⁻¹, which can be assigned ${}^4T_{1g} \rightarrow {}^2T_{2g}$, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions, respectively. The found reflectance bands and the magnetic moment value i.e. 4.12 BM indicate an octahedral geometry for Co²⁺ metal chelate [11]. The spectrum of Mn²⁺ polymeric chelate consist two bands at 18028 cm⁻¹ and 24870 cm⁻¹ may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g(G)}$ and ${}^6A_{1g} \rightarrow {}^4A_{2g(G)}$ transitions, respectively. The high intensity of the bands and magnetic moment value at 5.02 BM suggests the octahedral geometry for Mn²⁺ chelate [12]. The magnetic moment values revealed paramagnetic nature for all metal chelates except the Zn²⁺ chelate which is diamagnetic in nature.

The TG analyses of TFQ and polymeric chelates were carried out to study the thermal behavior. The all results are displayed in Table-2. Examination of these results shows the single step degradation in the temperature range of 300-400°C while 400-500 °C the wt. loss is found almost around 90% for the TFQ ligand. Similarly the single step degradation was in the temperature range of 300-400°C while 550°C the wt. loss is found almost around 90% for the TFQ. The decomposing rate in all polymeric metal chelates were found initially low up to 200°C and then increases to maximum at the range 400-500 C. The thermal stability order of polymeric chelates is as follows: Cu²⁺-TFQ > Co²⁺-TFQ > Mn²⁺-TFQ > Ni²⁺-TFQ > Zn²⁺-TFQ.

Table 2 TGA analyses TFQ and its metal chelates

Sample	% Wt. loss at Temp(°C)					
	100	200	300	400	500	600
TFQ	2	5	20	38	70	78
Cu ²⁺ TFQ	4	7	12	35	68	74
Ni ²⁺ TFQ	5	8	14	39	72	78
Co ²⁺ TFQ	7	10	15	45	86	90
Mn ²⁺ TFQ	5	10	14	48	80	87
Zn ²⁺ TFQ	7	12	18	65	92	95

Antifungal activity of all the samples was monitored against various fungi, following the method reported in literature [13]. The examination of antifungal shown in Table-3 suggests that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among the all synthesized polymeric chelates Cu²⁺ chelate found more toxic against fungi [14].

Table 3 Antifungal activity of TFQ and its metal chelates

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	<i>Asperginus niger</i>	<i>Botrydeplaia thiobromine</i>	<i>Nigrospora Sp.</i>	<i>Rhisopus Nigricans</i>
TFQ	66	81	73	74
Cu ²⁺ TFQ	86	90	91	85
Ni ²⁺ TFQ	68	84	87	88
Co ²⁺ TFQ	78	86	78	81
Mn ²⁺ TFQ	76	87	81	78
Zn ²⁺ TFQ	74	91	86	76

4. Conclusion

Tannin is good monomer for polymerization with formaldehyde. Tannin was copolymer with formaldehyde and 8-hydroxy quinoline (a chelating agent). The copolymer was designated as TFQ then its various transition metal chelating

were prepared and characterized. The chelates are thermally stable and have good antifungal activity. Overall the TFQ resin can be good metal precipitant and is could be used for extraction of metals from ores.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors have no conflict of interest.

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