

**ICEWEST-2015 [05th - 06th Feb 2015]****International Conference on Energy, Water and
Environmental Science & Technology****PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai-600 005, India****Metal Uptake Properties of Chelating Azo Polymeric Resin:
Synthesis, Characterization and Biological Properties****R. Keerthiga¹, S. Vijayalakshmi¹ and T. Kaliyappan*****Department of Chemistry, Pondicherry Engineering College, Pondicherry. India**

Abstract: The monomer of ((meth)acryloyloxybis(2-hydroxy benzaldehydephenylenediimine)) azo polymer were prepared by reacting (meth)acryloyl chloride with azo compound derived from diamine Schiff base and diazonium salt of 4-aminophenol. The monomer was polymerized in DMF at 70°C using benzoyl peroxide as free radical initiator. Polymer metal complex was obtained in DMF solution of polymer with aqueous solution of metal ions. The polymer and the polymer metal complex was characterized by elemental analysis and spectral studies. The IR spectral data of these complexes suggest that the metals are coordinated through nitrogen of the azo group and the oxygen of the phenolic -OH group. The electronic spectra and magnetic moments of the polychelates shows that octahedral and square planar structure for Ni(II) and Cu(II) complexes respectively. X-ray diffraction studies revealed that polychelates are highly crystalline. The thermal and electrical properties, catalytic activity, structure property relationships are discussed. Further the synthesized polymer was used for metal uptake studies from waste water, which is one of the effective waste water treatment strategy.

Keywords – Polychelates, Azo-Schiff base metal uptake property, Polycondensation, Polymeric Schiff base.

Introduction

The recent research in application of Schiff bases and its chelating properties has greatly contributed to the field of co-ordination chemistry. The combination of organic synthesis with co-ordination chemistry has made a revolution in field of optical data storage, metallurgy, pharmaceutical, catalysis, heavy metal ion absorption, selective electrode, analytical application and clinical studies. The polymeric Azo Schiff base containing C=N, C=O, N=N proven to shape a flexible and versatile chelating properties with di, tri and multidentate ligands Thus polymeric Schiff bases have wide application in environmental safety technologies like treatment of radioactive materials, removal of chromium from tannery waste, waste water treatment, absorption of heavy metal ions etc. The azo moiety of polymeric Schiff bases containing both C=N and N=N groups shows wide range of biological activities like anti tumor, anti cancerous, anti bacterial, anti fungicidal and anti-inflammatory properties¹⁻⁴.

As a part of digital revolution the azo Schiff base containing C=N shows important application in optical displays, optical storage data, metal-azo dyes are used in(digital versatile disc-recordable) DVD-R as

coating layer and various digital component. Thus polymeric Schiff bases are proven to have wide range of application in various inter disciplinary sciences and technology. In continuation to the era of research of Schiff bases this article deals with synthesis, characterization, metal uptake property of chelating azo-schiff base polymer resins⁸⁻¹³.

Experimental

Ethanol and N,N-dimethylformamide were distilled before use. The materials salicylaldehyde, Phenyl enediamine, 4-aminophenol (Analytical grade) were purchased from sigma Aldrich and Merck were used directly without further processing

Synthesis of Schiff base [Bis(2-hydroxyl benzaldehyde)phenylenediimine]

The Schiff base was synthesized by reacting 2.5g of phenylenediamine dissolved in ethanol with 1.8ml of salicylaldehyde in presence of anhydrous sodium acetate. After 20 mins of refluxing the light yellow precipitate was filtered and recrystallized with ethanol.

Synthesis of Azo-Schiff base [4-hydroxyazobenzene [bis(2-hydroxyl benzaldehyde) phenylenediimine]]

The diazonium salt was synthesized by reacting 4-aminophenol with sodium nitrite in presence of HCl at -5°C. The azo Schiff base was synthesized by coupling the diazonium salt with bis(2-hydroxylbenzaldehyde) phenylenediimine at -5°C. The pH was adjusted to 7 using 2M NaOH and the mixture was refluxed for about 1hr. The precipitate was filtered and dried

Synthesis of Monomer

The monomer was synthesized by reacting 4-hydroxyazobenzene[bis(2-hydroxylbenzaldehyde) phenylenediimine (4-HAB₂-HBE) 2.7g with 3.2ml of methylacryloylchloride in presence of 2-butanone with pinch of hydroquinone. The mixture was refluxed for about 4 hrs at -5°C.

Synthesis of Polymer.

The monomer of methylacryloyl 4-hydroxyazobenzene[bis(2-hydroxylbenzaldehyde)phenylenediimine was polymerized in DMF at 70°C using benzoyl peroxide as free radical initiator for about 24 hrs

Synthesis of Metal chelates

The metal chelates of Cu (II), Ni (II) were prepared in room temperature in an neutral medium. Poly(4-HAB₂-HBE-MA)Cu (II)/Ni (II) were prepared by dissolving Poly(4-HAB₂-HBE-MA) in DMF(30ml). An aqueous solution of Copper (II) acetate (0.74g) dissolved in distilled water(20ml) was added to polymer solution drop wise by constant stirring, pH of the solution was adjusted to 7 by dilute ammonium hydroxide. The mixture was digested in water bath for 2hrs and filtered, washed with hot water and dried.

Determination of metal uptake at different pH

The polymer is treated with aqueous solution of Cu(II) and Ni(II) of known concentration. The pH of the solution was adjusted to the desired value using either 0.1M HCl or 0.1M NaOH. This suspension is agitated for 24h over a magnetic stirrer. The precipitated complexes were filtered off and were washed thoroughly with demineralized water. The filtrate along with the washings were collected and quantitative determination of metal ion concentration was done by standard titration method for Cu(II) and dimethyl glyoxime method for Ni(II).

Determination of metal uptake at different electrolytes concentration

The polymer sample (20 mg in 25 ml) dissolved in DMF was added in an electrolytic solution (NaCl/Na₂SO₄, 25 ml) of a known concentration. The pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NH₃ solutions. The solution was stirred for 24 h at ambient temperature. To this solution, 10 ml of a 0.1 M solution of metal ion Cu(II)/Ni(II) was added, and the pH was adjusted to the required value. The mixture was again stirred at 25 °C for 24 h and filtered. The solid was washed, and the metal-ion content was determined by standard titrimetric method for Cu(II) and by the dimethyl glyoxime method for Ni(II). The amount of the metal-ion uptake by the polymer was calculated from the difference between a blank experiment

and the reading in the actual experiments. The experiments were performed in the presence of several electrolytes with Cu(II) and Ni(II) ions.

Results and discussion

Characterization of the polymer and its metal complexes

The novel Poly (4-HAB₂-HBP-MA) was synthesized from 4-hydroxyazobenzene[bis(2-hydroxyl benzaldehyde) phenylenediimine with methylacryloylchloride in presence of 2-butanone with pinch of hydroquinone. Polymer metal complexes were obtained from a DMF solution and an aqueous solution of the metal ions Cu(II) and Ni(II) in the presence of few drops of ammonia solution. The polymer Poly(4-HAB₂-HBE-MA) was soluble in DMF, DMSO, chloroform, and insoluble in common organic solvents such as benzene, toluene, methanol, and water. The polychelates were insoluble in all the common organic solvents but sparingly soluble in chloroform. All the polymer metal complexes were colored compounds¹⁶.

The IR spectra of Poly(4-HAB₂-HBE-MA) and its metal complexes were shown in(Figure. 1. The polymer showed a broad absorption band appeared in the region 3100- 3600cm⁻¹ may be assigned to phenolic hydroxyl(-OH) stretching vibration. The vibration of the azo group (-N=N-) of free ligand was observed at 1625cm⁻¹. The strong band at 1600cm⁻¹ may be ascribed to ketonic groups (C=O). The medium intensity band at 1200cm⁻¹ in the spectrum of the polymer is due to hydrogen bonded ring system of the ligand. The presence of sharp and strong band at 3200-3550cm⁻¹ indicates the presence of C=N bridge. In Polychelates this band seems to be merged with very broad band of phenolic hydroxyl group. The absorption bands at 550-650 and 450-600cm⁻¹ are ascribed to the formation of M-O and M-N bands respectively¹⁷ which further supports the coordination of the azo nitrogen and the phenolic oxygen.

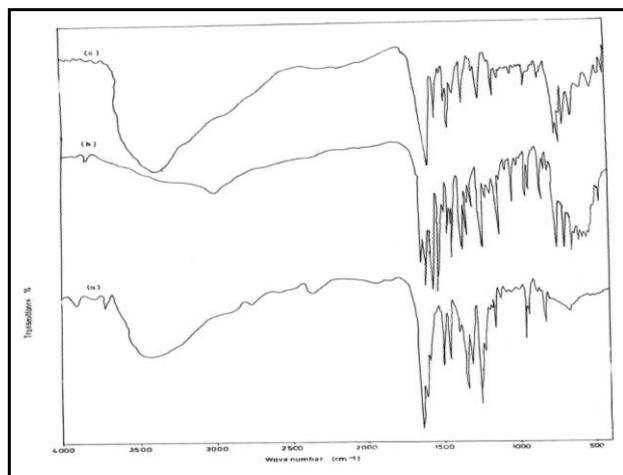


Figure. 1 IR spectra of Poly(4-HAB₂-HBP-MA) (a), Poly(4-HAB₂-HBP-MA) Cu(II)(b) and Poly(4-HAB₂-HBP-MA) -Ni(II)(c)

The ¹H-NMR spectrum of Poly(4-HAB₂-HBE-MA) showed a resonance signal at 9.0ppm, which may have been due to phenolic -OH protons. The resonance signals due to aromatic protons appeared as broad multiplets in the region 6.9 - 7.2ppm. The signals in the region 7.3-7.7 ppm are attributed to protons of -NH bridge. The resonance signals at 1.2- 3.5 ppm due to methylene and methine protons. As the polychelates were not soluble in common organic solvents, the ¹H-NMR spectra of the polychelates were not reported.

The X-ray diffractogram of Poly(4-HAB₂-HBE-MA) and its Cu(II)/Ni(II) complexes are shown in (Figure. 2). The X-ray diffraction of Poly(4-HAB₂-HBE-MA) indicated that resin is amorphous, whereas its polychelates exhibited a number of reflection planes. This was assignable to a significant increase in crystallinity of the resin on coordination to the metal ion. The crystallinity of polychelates may not be due to ordering in polymer induced during metal chelates anchoring, more so, since anchoring of metals to the polymer would imply inter chain cross-linking between polymeric chains, which should further reduce rather than enhance any such ordering¹⁹. The appearance of crystallinity in polychelates may be due to the inherent crystalline nature of the metallic compounds Scheme 2.

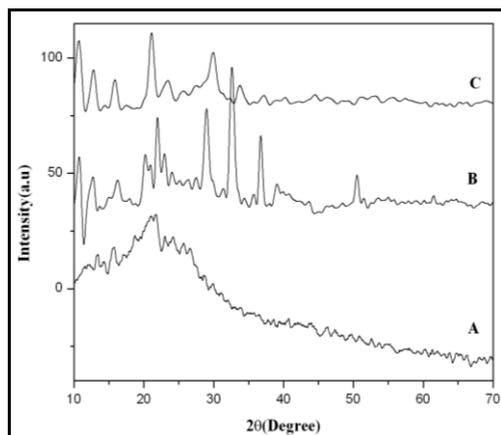
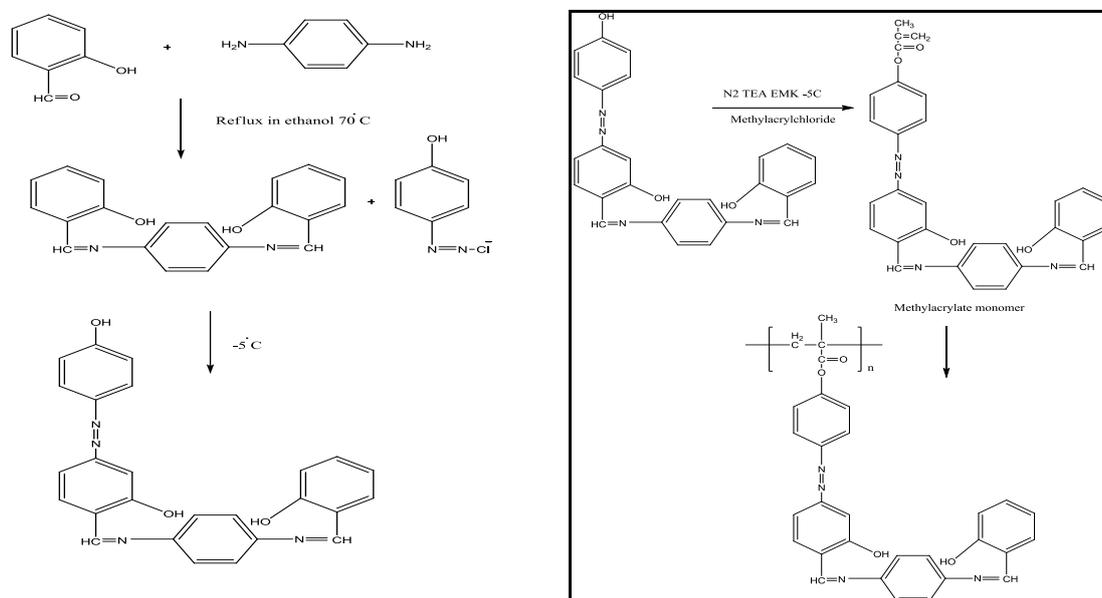
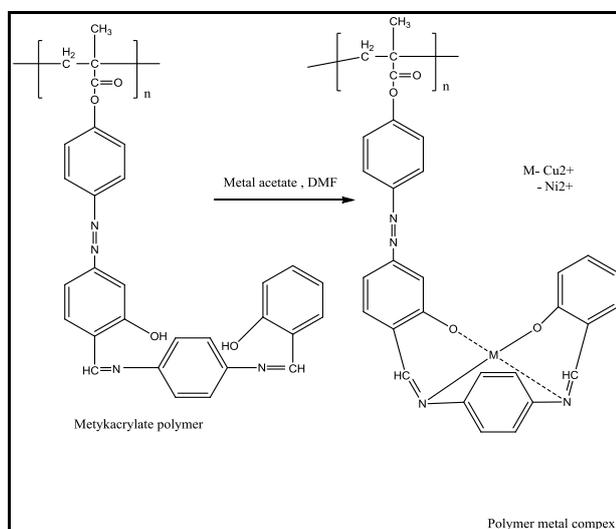


Figure. 2 X-ray diffractogram of Poly(4-HAB₂-HBP-MA)(a), Poly(4-HAB₂-HBP-MA) Cu(II)(b) and Poly(4-HAB₂-HBP-MA) -Ni(II)(c)

Scheme 1



Scheme 2.



The glass transition temperature of Poly(4-HAB₂-HBE-MA), Poly(4-HAB₂-HBE-MA -Cu(II) and Poly(4-HAB₂-HBE-MA -Ni(II)chelates were found to be 365, 565 and 410 °C, respectively. The difference in transition may have been due to the cross linking during complexation. Thermograms of the chelating polymer and its Cu(II) and Ni(II) complexes in the temperature range of 70-900°C are shown in Fig. 3. The

decomposition corresponding to 12, 8 and 6% for the polymer and Ni(II) and Cu(II) polychelates were observed in the temperature range 70-160 °C which is attributed to the moisture or solvent entrapped in the molecule. The weight loss in the temperature range 170-450°C was probably due to the degradation of the main chain [nearly 75% for the polymer, 62% for Ni(II) and 50% for Cu(II)]. In the case of polychelates, a stable metallic oxide is formed as the final decomposition product [18]. This behavior clearly indicated that the macromolecular azo group in this study, which provided O₂ donor sites, exhibited a greater affinity toward Cu(II) than toward the Ni(II) ion; this coordination prevented the splitting of hydroxyl molecules and ketone groups²⁰⁻²³. Also, the metal ions providing a coordination crosslinking between polymer chains increased the thermal stability, as shown in Scheme (1) In the case of polychelates, a stable metallic oxide is formed as the final decomposition product²⁴. This behaviour clearly indicated that the macromolecular azo in this study, which provided NO donor sites, exhibited a greater affinity toward Cu(II) than toward the Ni(II) ion; this coordination prevented the splitting of azo and hydroxyl molecules²⁵. Also, the metal ions providing a coordination crosslinking between polymer chains increased the thermal stability. The IR, ¹H-NMR, and XRD studies confirmed that the chelation of the metal ions have possibly occurred between two groups from different polymeric chains, as shown in Scheme 2.

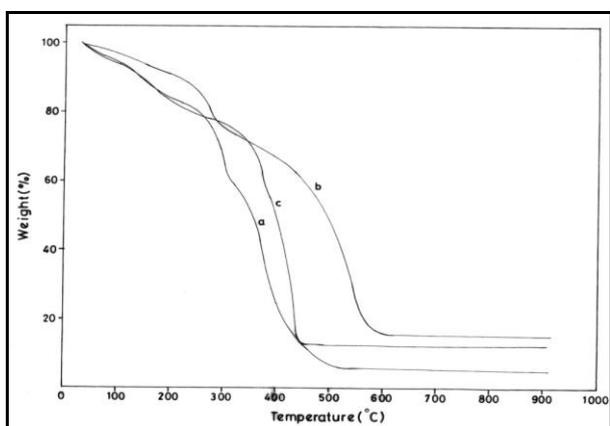


Figure. 3 TGA curves of Poly(4-HAB₂-HBP-MA) (a), Poly(4-HAB₂-HBP-MA) Cu(II)(b) and Poly(4-HAB₂-HBP-MA) -Ni(II) (c)

Effect of pH on metal ion uptake properties

The effect of pH on the metal binding affinity of the chelating agents on polymeric materials is a very important parameter. Ionization of the chelating ligand and the stability of the metal-ligand complexes vary when changing the pH. The effect of pH on transition metal ion uptake for Poly(4-HAB₂-HBE-MA) was examined for Cu(II) and Ni(II) ions in aqueous solutions under non-competitive conditions as a function of pH with a adsorption time of 24h. The results of four experiments of adsorption of metal ions for varying pH values are shown in (Figure 4). Both divalent metal ions examined in this study show the same behavior. Metal hydroxides were precipitated at pH>7 for Cu(II) and at pH>8 for Ni(II). The extent of adsorption of Ni(II) as compared to Cu(II) was significantly low. The metal uptake was seen to significantly increase with increasing pH²⁶. This was ascribed to the ease of coordination of the -OH group at higher pH and also enhanced basicity of the -N=N- nitrogen which get protonated in the acidic conditions.

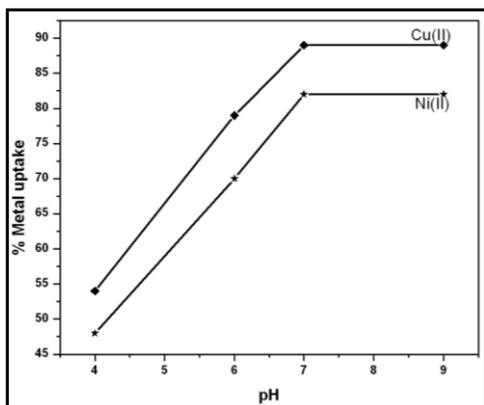


Figure. 4 Metal ion uptake behaviour of Poly(4-HAB₂-HBP-MA) resin at different pH

Influence of electrolytes on metal ion uptake properties

Table 1 reveals that the amount of metal ions taken up from a given amount of a polymer depends on the nature and concentration of the electrolyte present in the solution. In the presence of chloride and sulfate ions the uptake of Cu(II) and Ni(II) ions increase with an increasing concentration of the electrolyte. This observation can be explained on the basis of the stability constants of the complexes which Cu(II) and Ni(II) ions form with these anions²⁷. The above trend was observed increase in metal binding affinity under different electrolytes may be due to the nature of the ligand group in the repeat unit of the polymer.

Table 1 Percentage Metal Uptake of Poly(4-HAB₂-HBP-MA) with different electrolytes

Metal Ion	pH	Electrolyte (mol L ⁻¹)	Percentage of the metal ion taken up in the presence of	
			NaCl	Na ₂ SO ₄
Cu ²⁺	3	0.01	67	43
		0.05	72	57
		0.1	83	63
	5	0.01	71	66.7
		0.05	79	70
		0.1	87.4	79
	7	0.01	84	79
		0.05	89	84
		0.1	93.3	91.8
Ni ²⁺	3	0.01	74	41
		0.05	80	57
		0.1	82	66
	5	0.01	76	67
		0.05	84	74
		0.1	86.2	82
	7	0.01	77.6	74
		0.05	86	81.4
		0.1	91.2	89

Resin regeneration and recyclability

Regeneration of the adsorbed metal ions from the Poly(4-HAB₂-HBE-MA) resin was studied in the batchwise system. The polymeric metal complexes were placed in a desorption medium containing 7MHCl, and the amount of metal ions released was determined. The desorption ratio for the metal ions used in this study were calculated using the equation²⁸⁻²⁹.

$$\text{Desorption ratio \%} = \frac{\text{Amount of metal ions released}}{\text{Amount of metal ions adsorbed on resin}} \times 100$$

More than 95% of the adsorbed metal ions were removed using a 7MHCl solution. The reproducibility of the aforementioned results was established by the sequence being repeated four times with the same polymeric resin for each of the metal ions (Figure 5). The adsorption capacities for the metal ions on Poly(4-HAB₂-HBE-MA) did not change noticeably during the repeated adsorption–desorption operations, this revealed the good recyclability and stability of the polymer under acidic conditions.

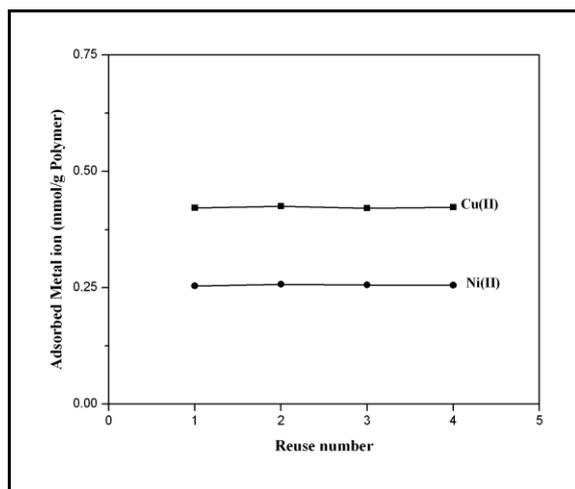


Figure. 5Regeneration of Poly(4-HAB₂-HBP-MA) Cu(II) and Poly(4-HAB₂-HBP-MA)- Ni(II)with an initial metal- ion concentration of 100 ppm for the adsorption of pH 5 at 25°C with 0.02 g of polymer at an initial volume of 100 ml.

Conclusions

In the present work, a novel polyfunctional resin Poly(4-HAB₂-HBE-MA) was synthesized and characterized by various analytical techniques. These complexes have been characterized and were assigned a metal to ligand ratio of 1:2. The thermal stability of the ligand and polychelates is in the order polychelates > ligand. Poly(4-HAB₂-HBE-MA) resin has a good binding potential for the divalent metal ions over a wide pH range (5-9). The polymer has high regeneration ability as high as 95% without any loss in its sorption behaviors. Finally, the results revealed that, the azo based ligand can be effectively used for the removal of heavy metal ions from water and wastewater.

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