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Synthesis of polymer based copper (II) complex and its analytical behaviour

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The aim of this work was the synthesis and sorption studies of polymer based copper (II) complex. The synthesized polymer, viz; polyacryloyl salicylaldehyde (PAS) and Ethylenediamine polyacryloyl salicylaldehyde (EDPAS) were used for preparing the polymer-Copper (II) metal complex at neutral medium with stirring time of 2-5 hrs. The obtained complexes are characterized by using IR technique. Batch adsorption process is used to estimate the amount of copper ion on the polymer surface. This is confirmed by various parameters such as pH, temperature and conduct time. The adsorption data were explained and to get better insight into the mechanism of adsorption process.

Keyword: Polymer, Copper, Sorption, pH and FTIR.

1. Introduction

Copper in trace amount is important industrially as a toxicant and biological nonessential and as an occupational hazard ^[1]. Recent discoveries in coordination metal complexes show that the economic potentialities and advantages are more if the coordination compounds are made heterogeneous rather homogeneous ^[2]. Polymer metal complexes are a class of compounds belongs to the polymer group. High molecular weight PMCs is work, as storage houses for solar energies while the low molecular weight complexes do not. PMCs play a vital role in the fields of nuclear chemistry, metal ion separation ^[3, 4], organic synthesis ^[5, 6], waste water treatment ^[7, 8], pollution control ^[9], industrial process ^[10], hydro methodology ^[11-13]. Polymer drug groups ^[14] and trace metal field ^[15]. A PMC is a coordination complex between a ligand on the polymer and metal ion. The polymeric ligand can be obtained by the polymerization of monomers containing coordinating sites or by the chemical reaction between a polymer and a low molecular weight compound having

coordinating ability. The adequate characterization of chemical changes occurring on polymer supports is a problem in the field of polymer support chemistry. The important and useful techniques for characterization of polymers are TG analysis and infrared spectroscopy. The functional group analysis can be done by ordinary chemical methods. In this study, poly acryloyl chloride was utilized as the raw materials for the preparation of PAS and EDPAS, Which were used to synthesis of polymer copper metal complex by chemical method. The uptake capacity of copper ion on the polymer matrix was evaluated. The effect of conduct time, solution pH and temperature on batch adsorption studies were discussed in details.

2. Experimental

2.1 Preparation of polymer backbone (poly acryloyl chloride)

In a four necked reaction kettle, 10 ml of acryloyl chloride was taken and maintained at 0-5 °C in an ice-salt mixture bath. When the temperature is maintained

at 5 °C, then added 1 gm of benzyl peroxide, which was taken in 20 mL of chlorobenzene. When the addition of benzyl peroxide is over with continuous stirring with the temperature of the bath was raised to 70 ± 2 °C. In this temperature range the system was maintained with constant stirring for four hours. After four hours, the system is fitted off and evaporated to dryness in desiccators overnight. The white powder, which obtained is poly-acryloyl chloride PAC and reserved for further experimentation. The FTIR spectroscopy of polymers was measured by using FTIR model; Nexus 690.

2.2 Preparation of polymer metal complexes

Table 1: Characterization of Polymer Copper (II) complex.

Polymer System	Metal Ion	Condition			Colour of the polymer - metal
		Temperature	pH	Stirring time (h)	
PAS	Cu(II)	R.T	7	2	Violet
EDPAS	Cu(II)	R.T	7	5	Violet

Solution of a large number of reagents and complexing agents were prepared from their analar grade [16].

2.3 Cu(II) Standard solution

A 100 mL of stock solution of divalent copper was prepared by dissolving 0.03929mg of AR crystallize copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (Merck) in doubly distilled de-ionized water. Aliquots of this solution were standardized by EDTA titration using Sulfon black-T as indicator. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water and when required.

2.4 EDTA Solution

100mL stock solution of EDTA (0.01% w/v) was prepared by dissolving 10mg of A.C.S. grade ($\geq 99\%$) of disodium dihydrogen ethylenediaminetetraacetate dihydrate in (100 mL) de-ionized water.

2.5. Potassium Permanganate Solution

A 1% potassium permanganate Solution (Merck) was prepared by dissolving in de-ionized water. Aliquots of this solution were standardized with oxalic acid. Sodium azide solution (2.5% w/v) (purity $>99\%$) was also used.

2 g of the polymers PAS and EDPAS were added to the 250 mL round bottom flask 25 mL 0.1 M metal ion solution was taken. Optimum conditions were maintained by addition of suitable buffers, temperature and stirring time, etc., maintained optimum conditions were discussed and stirred vigorously for 2 to 3 hours, depending upon the polymer and metal ion. After the stirring was over the metal ion absorbed polymers were filtered and kept in desiccator for drying and characterized through IR spectral studies. The prepared polymer metal complexes were presented in table 1.

2.6 Tartrate Solution

A 100mL stock solution of tartrate (0.01% w/v) was prepared by dissolving 10mg of A.C.S grade (99%) potassium sodium tartrate tetrahydrate in (100mL) de-ionized water.

2.7 Aqueous Ammonia Solution

A 100 mL solution of aqueous ammonia was prepared by diluting 10mL concentrated NH_4OH (28–30%, A.C.S grade) to 100 mL with deionized water. The solution was stored in polypropylene bottle.

3. Results and Discussion

3.1 Characterization of Polymer-Cu(II) complex

The prepared polymers were subjected to identify the functional groups $-\text{CHO}$ in the case of PAS and $>\text{C}=\text{N}$ moiety in the case of EDPAS was confirmed through the respective chemical tests and found positive results. Similar observation has been reported by Schurz and Dyer [17, 18]. The IR spectra of polyacryloyl chloride and polyacryloyl salicylaldehyde are shown in figure.1 and 2. In figure. 2. a sharp signal which is observed at 709 cm^{-1} due to $>\text{C}=\text{O}-\text{Cl}$ group is disappeared in the present spectra indicating the introduction of phenolic $-\text{OH}$ of the salicylaldehyde and acid chloride of the poly acryloyl chloride. Hence almost all polyacryloyl chloride units might have been substituted with those of salicylaldehyde. Further a doublet around 1115 cm^{-1}

and 1161cm^{-1} is observed which is not present in the PAC spectrum, which is due to C-O-C moiety. A broad and sharp signal which is observed in the present spectra about 1739cm^{-1} may be due to $-\text{CHO}$ moiety of the salicylaldehyde. A sharp signal at 1452cm^{-1} and another small signal at 1563cm^{-1} is due to C=C of the poly vinyl vibrations. A broad signal, which is available at 3348cm^{-1} may be due to the intermediate hydrogen bonding units which are present at least in lower units.

Similarly the preparation of EDPAS polymer which has the very sharp signal at 1559cm^{-1} was observed in both ED treated polymer and semicarbazone treated polymer observed may be due to $>\text{C}=\text{N}$ moiety. The intermolecular hydrogen bonded signal in PAS is slightly disturbed as shift to 3419cm^{-1} in ED treated polymer and almost at same position in semicarbazone treated polymer. These changes may be due to conversion of some of the salicylaldehyde units into its derivatives. Hence, it is assumed that the ethylene diamine treated polymer and semicarbazone treated polymers are believed to be present as shown in figure.3.

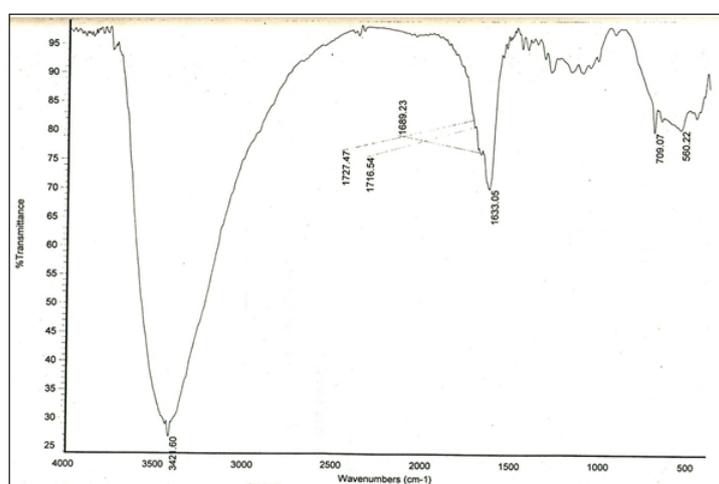


Fig 1: IR Spectra of poly acryloyl chloride

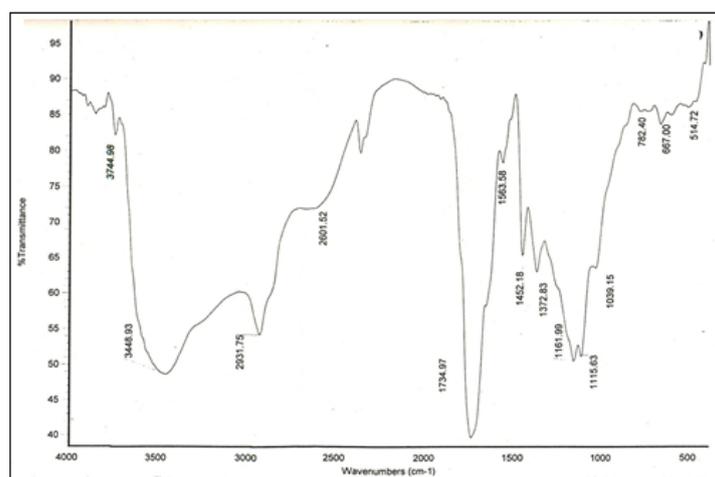


Fig 2: IR Spectra of poly acryloyl salicylaldehyde (PAS)

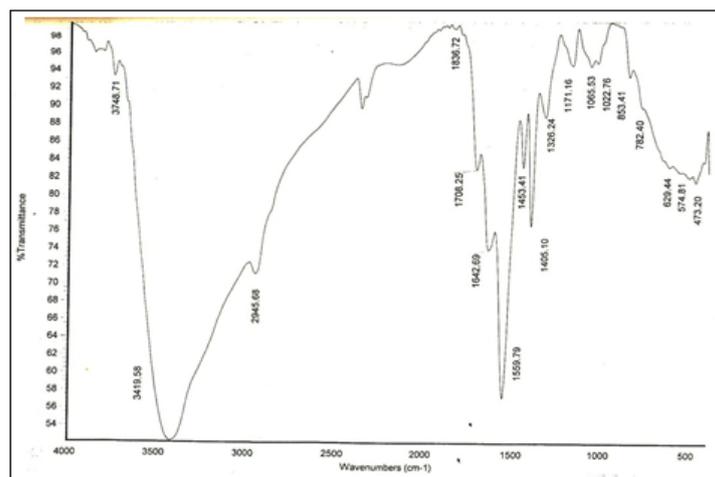


Fig 3: IR Spectra of ED-PAS polymer

The Cu(II) content in polymer-metal complex is estimated by using analytical procedure. In PAS-Cu(II) systems, the Cu(II) content is 0.03 g and 0.05 g for EDPAS-Cu(II) complex. The percentage of Copper (II) content in the polymer matrix is 7% and 11% for PAS and EDPAS respectively. This is confirmed by the IR spectra of PAS-Cu(II) complex and EDPAS-Cu(II) complex. IR spectra of PAS-Cu(II) complex shows comparing the unmetallated and metallated polymer spectra reveals that C=N group which is represented by the 1554 cm^{-1} absorption is completely removed in metallated spectra and hence it is being concluded the bond is

C=N group of the polymer. It is shown in the figure.4. The IR spectra of figure. 5. explains that the EDPAS-Cu(II) complex shows significant absorption which are described as follows. A very sharp signal which is observed at 1559 cm^{-1} are assigned to C=N of the polymer which splits into two signals out of which one is shifted to lower value of 1514 cm^{-1} and the other to the higher frequency side of 1564 cm^{-1} . These two signals were absent in the unmetallated polymer. Hence the C=N group present in the polymer is undergoing a change and hence participated in the metal ion bounding.

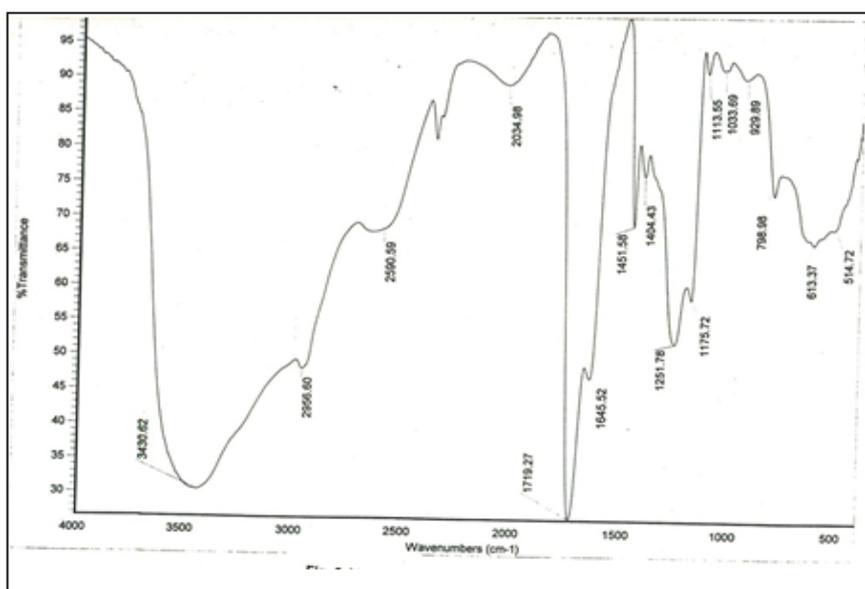


Fig 4: IR Spectra of PAS – Cu(II) metal complex

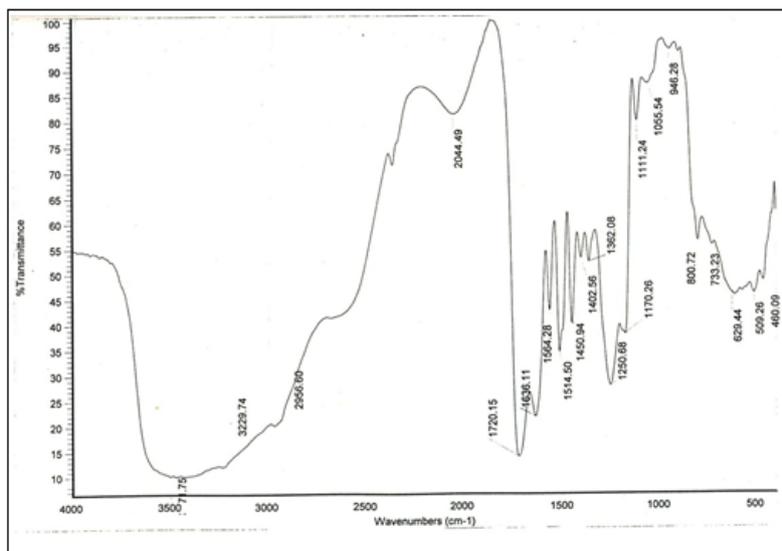


Fig 5: IR Spectra of EDPAS – Cu(II) metal complex

The analytical applications of the polymers are optimization of condition for the maximum uptake of metal ions are well discussed by batch method.

3.2 Effect of pH

To see the effect of different pH we have taken 0.5ppm Cu(II) solution. Of the various pH studied, hydrochloric acid was found to be the best acid for the system. The effective concentration of the metal ions was calculated up to 30 min. The metal up take by the polymer is calculated after finding the difference in metal ion concentration used and formed. The values are given in the table. 2.

Table 2: Effect of pH on metal ion Cu(II)

S. No	Polymer	% of metal ion uptake						
		pH						
		4	5	6	7	8	9	10
1	PAS	5	8	15	14	20	20	8
2	EDPAS	4	9	12	15	18	16	9

From the above studies it is show that the entire polymer show a metal up take of 15% in related pH and maximum at pH 9. Hence a metal basic pH favours the maximum metal uptakes.

3.3 Effect of temperature

About 25 mL of 0.1 M metal solution is taken in a reagent bottle about 15 mL of buffer at which maximum metal uptake is found and heated to 40 °C on a water bath. Some more systems were maintained at 25, 30, 35 and 40 °C for half an hour with

occasional shaking after the addition of 5 g of polymer. Each system is filtered off and estimated for metal ion concentration and the results are presented in table. 3.

Table 3: Effect of temperature on metal ion uptake by the polymer

S. No	Polymer	% of metal ion uptake at different temperature (°C)*			
		25	30	35	40
1	PAS	15.0	18.0	25.0	23.0
2	EDPAS	17.0	17.0	23.0	22.0

From the observations it can be shown that all the polymers studied were have a maximum uptake around 35 °C and on either side there is decrease in the efficiency the metal ion uptake.

3.4 Effect of contact time

To these system polymers of 5 g of each was added and shaken for different periods of time intervals (30, 60, 90, 120 min) each reagent bottle is removed from the shaker and immediately filled off and metal ion content was estimated and the results are presented in table. 4. From the results it can be concluded that for the maximum uptake of the metal ions a contact period of 90 minutes is sufficient and after that period there is no significant uptake of metal ion is expected.

Table 4: Effect of contact time for maximum uptake of metal ions

S. No	Polymers	Contact time (in minutes) and maximum uptake of metal ion (%)			
		Time (in minutes)			
		30	60	90	120
1	PAS	15	22	42	40
2	EDPAS	18	32	44	45

4. Conclusion

Acryloyl chloride is polymerized to polyacryloyl chloride using benzyl peroxide as initiators. Poly acryloyl chloride is treated with salicylaldehyde to get polyacryloxy salicylaldehyde and also for EDPAS. Poly-acryloxy salicylaldehyde is condensed with ethylene diamine and semicarbazide hydrochloride to get derivatives of aldehyde. The polymers are characterized by FTIR analysis. Polymers have been used and polymer metal complexes have been prepared using Cu(II) ion and characterized. Application of these polymers for metal ion uptake is studied and optimum conditions are fixed. Responsibility of the polymer is studied in batch study.

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