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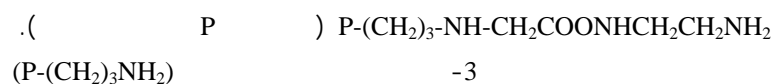
## PREPARATION OF IMMOBILIZED-POLYSILOXANE IMINO(2-AMINOETHYLACETAMIDE) AND ITS APPLICATION

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**Abstract:** A porous solid polysiloxane ligand system of the general formula  $\text{P}(\text{CH}_2)_3\text{NH}-\text{CH}_2\text{COONHCH}_2\text{CH}_2\text{NH}_2$ , (where P represents  $[\text{Si}-\text{O}]_n$  siloxane network) has been prepared by modification of the immobilized 3-aminopropylpolysiloxane,  $\text{P}(\text{CH}_2)_3\text{NH}_2$ , with ethyl chloroacetate followed by ethylenediamine. The new modified polysiloxane system exhibits good potential for uptake of metal ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ). This ligand system gives more stable complexes with metal ions than its parent 3-aminopropylpolysiloxane precursor. Thermogravimetric analyses of this ligand system and its copper complex show high stability at relatively high temperature.

**KEY WORDS:** Metal uptake, propylamine, ethyl chloroacetate ligand, ethylenediamine, polysiloxanes, immobilized-polysiloxane ligand systems.

### 1. Introduction

Recently, inorganic supports of silica based matrix bearing reactive organic sites have been the subject of considerable interest. These types are known as functionalized polysiloxanes which have been prepared either by the low temperature sol-gel process or by modification of pre-prepared

polysiloxane [1-14]. The sol-gel process involves hydrolysis and polycondensation of  $\text{Si}(\text{OEt})_4$  and the appropriate silane coupling agent  $(\text{RO})_3\text{SiX}$  where X represents a ligand containing functional group [1-9]. Modification methods were used to introduce the organic ligand containing functional groups when appropriate chelating silane agents are difficult to prepare [10-14]. These immobilized ligand systems have advantages, over organic polymers such as their high thermal, hydrolytic and mechanical stability in addition to lack of swelling in solvents [15-16]. These properties make important applications like; extraction, recovery and separation of metal cations from organic solvents [17-18] and aqueous solutions [1-14]. They were also used as stationary phases in chromatography [7,19] and as supported ligands for catalysis [8,20,21]. Many spectroscopic techniques such as solid state nuclear magnetic resonance (NMR), thermal analysis and photoelectron spectroscopy (XPS) have been employed to study the ligand-modified polysiloxane systems [22-30]. In this work a new immobilized-polysiloxane ligand system with a di-nitrogen chelating ligand was prepared and characterized. The immobilized ligand system was used for extraction of the metal ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) from aqueous solutions, and results show much promise for extraction, separation and preconcentration of metal ions.

## 2. Experimental

### 2.1. Reagents and Materials.

Tetraethylorthosilicate, 3-aminopropyltrimethoxysilane, ethyl chloroacetate and ethylene diamine were purchased from (MERCK) and used as received. Acetone, diethyl ether and methanol (spectroscopic grade) were also used as received. Metal ion solutions of appropriate concentration were prepared by dissolving the metal chloride (analytical grade) in distilled water. Various buffer solutions with pH values in the range of 3.5-6, were controlled using acetic acid/sodium acetate buffer solutions.

### 2.2. General Techniques.

Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument.

Thermogravimetric analysis was carried out using Mettler Toledo SW 7.01 analyzer.

The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer AAnalyst-100 spectrometer.

The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR, spectrometer using KBr disk in the range  $4000$  to  $400\text{ cm}^{-1}$ .

All pH measurements were obtained using HM-40V pH Meter.

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### 2.3. Preparations

#### 2.3.1. Preparation of 3-aminopropylpolysiloxane (P-A).

Aminopropylpolysiloxane was prepared as reported previously [1] by adding 3-aminopropyltrimethoxysilane (9.86 g, 0.05 mol) to a stirred solution of tetraethylorthosilicate (20.83 g, 0.1 mol) in 15 mL methanol and HCl (9.95 mL, 0.42 M). Gelation occurred within a few seconds. The product was left to stand for 12 hours then dried in vacuum oven at 90 °C. The material was crushed, sieved, washed successively with 50 mL portions of 0.025 M NaOH, water, methanol and diethyl ether and then dried in vacuum oven at 90 °C at 0.1 torr for 10 hours. The elemental analysis for the aminopolysiloxane is given in Table 1.

#### 2.3.2. Preparation of polysiloxane ethyl glycinate ligand system (P-G).

Ethyl glycinate ligand system was prepared as reported previously [5], where 3-aminopropylpolysiloxane (P-A) (3.0 g, 11.1 mmol) was refluxed for 12 hours with an excess (5 g, 40.8 mmol) of ethyl chloroacetate in toluene and a few drops of triethylamine. The solid product was filtered off, washed successively with 50 mL portions of 0.025 M NaOH, methanol and diethyl ether and then dried in vacuum oven at 90 °C for 12 hours. Elemental analysis for ethyl chloroacetate polysiloxane (P-G) is given in Table 1.

#### 2.3.3. Preparation of imino(2-aminoethylacetamide) ligand system (P-IAEA).

Ethyl glycinate polysiloxane (10.0 g, 29.2 mmol) was added to an excess of ethylenediamine (10.0 g, 167 mmol) in 50 mL toluene under nitrogen. The mixture was refluxed at 110 °C for 48 hours. The mixture was then cooled, and the solid product was filtered, washed successively with 50 mL portions of water, methanol and diethyl ether. The final product was dried at 90 °C in vacuum oven (0.1 torr) for 10 hours.

## 3. Results and Discussion.

### 3.1. Preparation of imino(2-aminoethylacetamide) ligand system (P-IAEA).

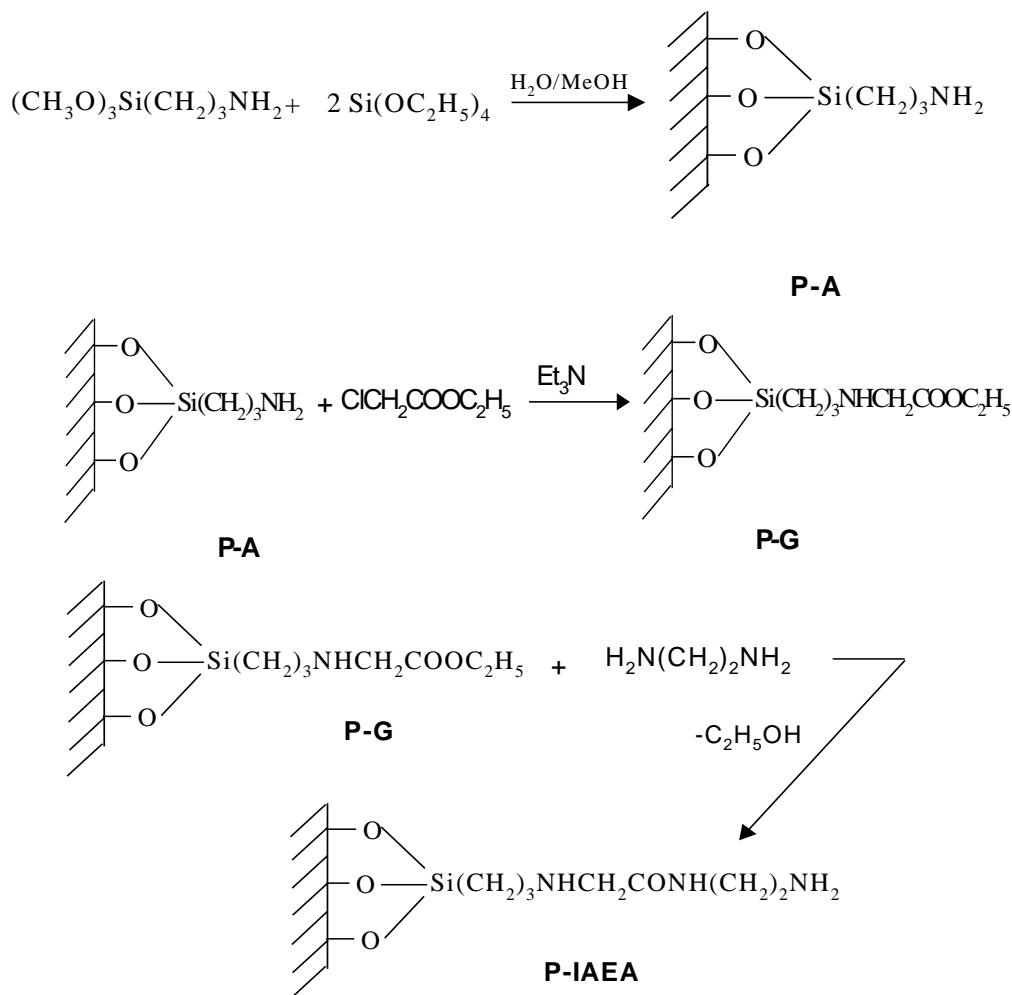
The imino(2-aminoethylacetamide) ligand system (P-IAEA) was prepared by a three-step synthesis based on previously prepared precursors (Scheme 1):

- 1- Preparation of 3-aminopropylpolysiloxane was prepared as previously reported[1], by hydrolytic polycondensation of 3-aminopropyltrimethoxysilane and tetraethylorthosilicate (TEOS) in the ratio of 1:2 (Scheme 1).

- 2- Preparation of polysiloxane ethyl glycinate ligand system (P-G) as previously reported [5] by the reaction of the 3-aminopropylpolysiloxane with excess ethyl chloroacetate in presence of triethylamine to facilitate removal of the generated HCl.
- 3- The new functionalized ligand system (P-IAEA) was achieved by direct reaction of P-G ligand system with ethylenediamine.

From elemental analysis, given in Table 1, it is obvious that the reaction between 3-aminopropylpolysiloxane and ethyl chloroacetate occurred. The carbon percentage increases and the nitrogen percentage decreases in case of P-G compared with the starting material (P-A). The lower carbon and higher nitrogen values are probably due to incomplete reaction of the amino groups with ethyl chloroacetate and the surface amino groups only were involved in the reaction. There is no evidence that more than one ethylacetate group may react with each nitrogen of the amino groups. This is clear by comparing the found and the expected elemental values of P-G. This can be attributed to steric hindrance.

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Scheme 1

### 3.2. FTIR Spectra.

The FTIR spectra of the immobilized 3-aminopropylpolysiloxane **P-A** and the modified forms **P-G** and **P-IAEA** ligand systems are given in FIG's 1a-c. The spectra show three characteristic absorption regions at  $3500\text{-}3000 \text{ cm}^{-1}$  due to  $\nu(\text{OH})$  or  $\nu(\text{NH}_2)$ ,  $1645\text{-}1560 \text{ cm}^{-1}$  due to  $\delta(\text{OH})$  or  $\delta(\text{NH}_2)$  and  $1200\text{-}900 \text{ cm}^{-1}$  due to  $\nu(\text{Si-O})$  respectively. The spectrum of the immobilized ligand **P-G** (FIG. 1b) shows strong band at  $1743 \text{ cm}^{-1}$  due to ester  $\nu(\text{C=O})$  stretching vibration. This confirms that the glycinate functionalized group is chemically bonded to the surface of the polysiloxane. The FTIR spectrum of **P-IAEA** ligand system (FIG. 1c) shows

a strong absorption at  $1637.7\text{ cm}^{-1}$  due to  $\nu(\text{N-C=O})$  vibration. The presence of the small band at  $1736.6\text{ cm}^{-1}$  after treatment of the ethyl glycinate polysiloxane system (P-G) with ethylenediamine shows that not all ethylacetate groups (-COOEt) are converted into the amide groups (N-C=O). This is due to steric hindrance.

### 3.3. Thermal Analysis.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) were examined for the imino(2-aminoethylacetamide) ligand system (P-IAEA) and its copper complex P-IAEA-Cu. The TGA and DTA were performed under nitrogen at temperature range  $20\text{ }^{\circ}\text{C} - 600\text{ }^{\circ}\text{C}$ .

FIG. 2a shows the thermogram of the immobilized (P-IAEA). Four peaks were observed. The first peak occurs at  $75\text{ }^{\circ}\text{C}$  where the ligand system lost 6.06 % of its initial weight. This is attributed to loss of physisorbed water and alcohol from the system pores [28-30]. The second peak at  $195\text{ }^{\circ}\text{C}$  corresponds to further loss of about 3.8 % weight of the polymer due to evaporation of internal alcohols and dehydroxylation of surface OH silica groups. The third broad peak at  $300\text{ }^{\circ}\text{C}$ , with a total loss of 17.5 %, is due to degradation of the organofunctional groups [28-30]. The fourth peak at  $430\text{ }^{\circ}\text{C}$ , where the system lost 4.7 % of its weight, is attributed to further condensation of hydroxyl groups left in the polymer forming siloxane bonds (dehydroxylation). The total lost found to be 32.7 %.

The thermogram of the immobilized (P-IAEA)-Cu ligand complex is given in FIG. 2b. Four main peaks were observed at  $85\text{ }^{\circ}\text{C}$  (7.3 % loss of weight),  $360\text{ }^{\circ}\text{C}$ - $405\text{ }^{\circ}\text{C}$  (9.6 % loss of weight) and  $545\text{ }^{\circ}\text{C}$  (9.11 % loss of weight). The ligand system shows a total loss of 26.3 % of its initial weight.

By comparing the thermogram of the P-IAEA free ligand with that of the P-IAEA-Cu complex (FIG's. 2a and 2b, respectively) one observes that there is a decrease in percentage loss of the initial weight at both the second and third peaks from about 21.0 % to 9.6 % respectively. It is also observed that the third broad peak at  $300\text{ }^{\circ}\text{C}$  of P-IAEA is shifted to higher temperature ( $350$ - $400\text{ }^{\circ}\text{C}$ ) in case of P-IAEA-Cu complex. The thermograms also show a total loss of 32.7 % of P-IAEA compared with 26.3 % of P-IAEA-Cu complex from their initial weights at the temperature range  $25$ - $600\text{ }^{\circ}\text{C}$ . These results provide evidence that these materials are thermally stable and the degradation of the functionalized ligand groups in the complex occurs at higher temperature than that of the free ligand system. This suggests that the immobilized ligand system became more thermally stable on complexation with metal ions.

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### 3.4 Metal uptake capacity:

The metal ion uptake capacity ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) was determined by shaking the functionalized ligand system P-IAEA with buffered solutions of the divalent metal ions. Measurements were carried out at various time intervals. The maximum metal uptake capacities by P-IAEA system as  $\text{mg M}^{2+}/\text{g ligand}$  at the optimum conditions are given in the following table:

Metal ion	$\text{Co}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$
Maximum Uptake ( $\text{mg M}^{2+}/\text{g Ligand}$ )	27.0	47.0	31.0	45.0

It is clear that uptake of metal ions increases in the order:

$$\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$$

#### 3.4.1. Effect of shaking time

Measurements of metal ions uptake by the ligand system P-IAEA were investigated at various time intervals. The uptake of copper ions versus time is given in FIG. 3. It is shown that the metal ion uptake increased as a function of shaking time and reached equilibrium after 48 hours where maximum uptake is obtained. Similar results were observed for the other metal ions.

#### 3.4.2. Effect of pH.

The effect of the pH value on the uptake of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions by P-IAEA is shown in FIG. 4. The results show an increase of metal ion uptake as the pH value is raised. The uptake reached its maximum at pH 5.5. Low uptake capacity occurs at lower pH values. This is probably due to protonation of amine nitrogens [31].

### Conclusion

The immobilized imino(2-aminoethylacetamide) ligand system was prepared by treatment the 3-aminopropylpolysiloxane with ethyl chloroacetate followed by ethylenediamine. Thermogravimetric analysis showed that this ligand system is thermally stable at elevated temperature. The FTIR confirmed the introduction of ethyl glycinate and ethylenediamine. This immobilized ligand system exhibits high potential for extraction of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  metal ions. Measurements of metal ion uptake by the chelating ligand system were carried out at various pH values using buffer solutions. The optimum pH value was in the range 5.5. This ligand system promises to be a good chelating solid system for water and waste water cleaning.

### Acknowledgements

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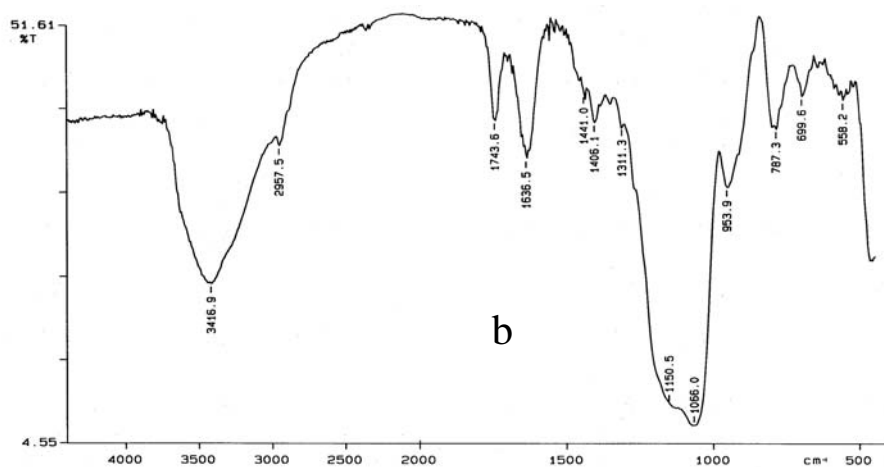
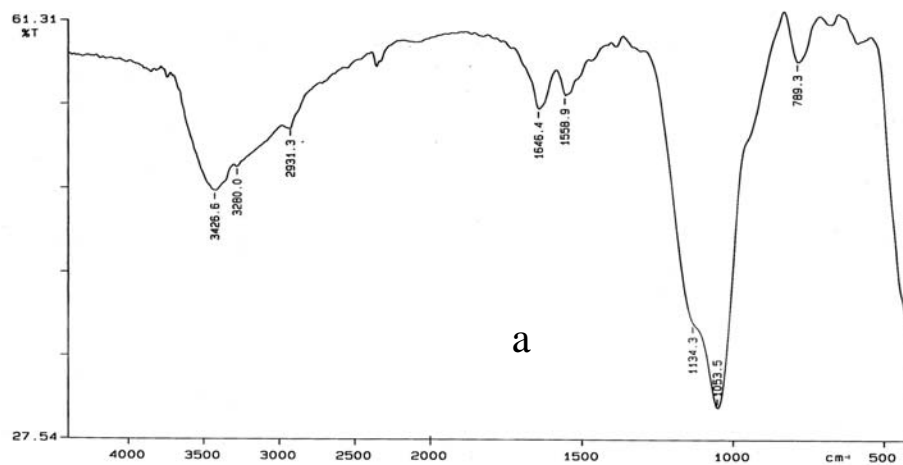
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**Table 1. Elemental Analysis Data for P-A and P-G**

Polysiloxane		%C	%H	%N	C/N
<b>P-A</b>	Expected	15.7	3.9	6.1	3.0
	Found	13.3	4.6	5.2	3.0
<b>P-G</b>	Expected	23.7	3.9	3.9	6.7
	Found	18.2	3.8	4.1	5.2

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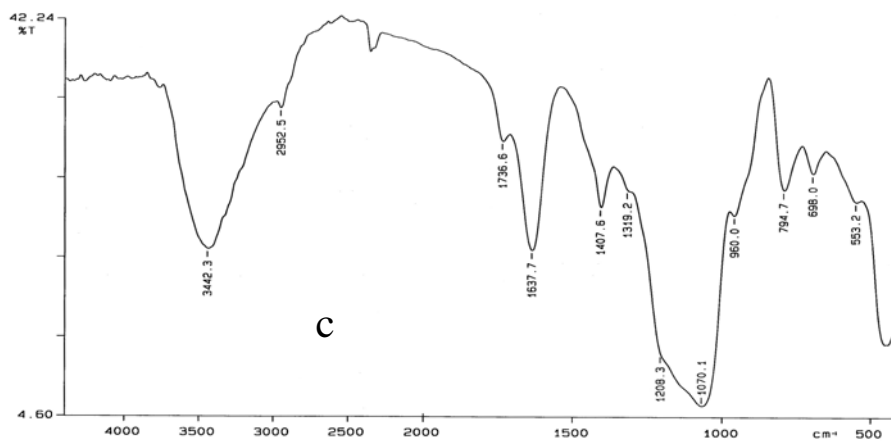
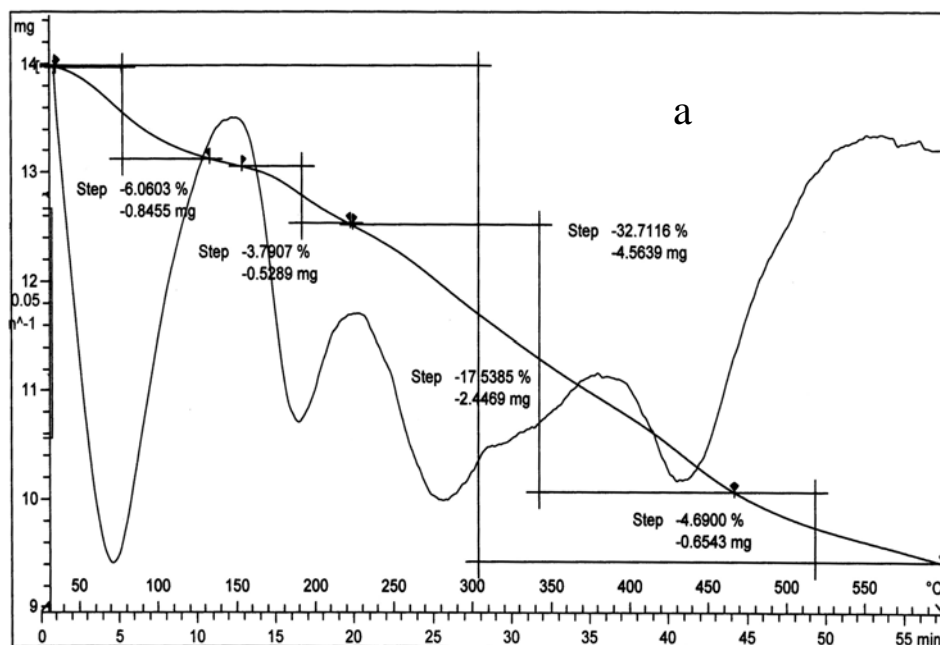


FIG. 1: FTIR Spectra of a) P-A, b) P-G, c) P-IAEA.



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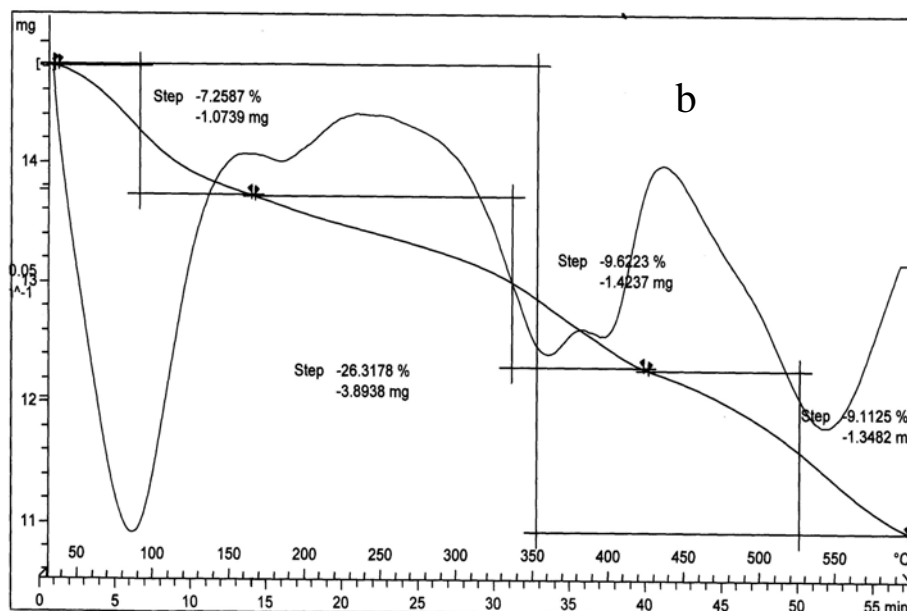


FIG. 2: Thermogravimetric analysis of a) P-G, b) P-G-Cu(II) complex.

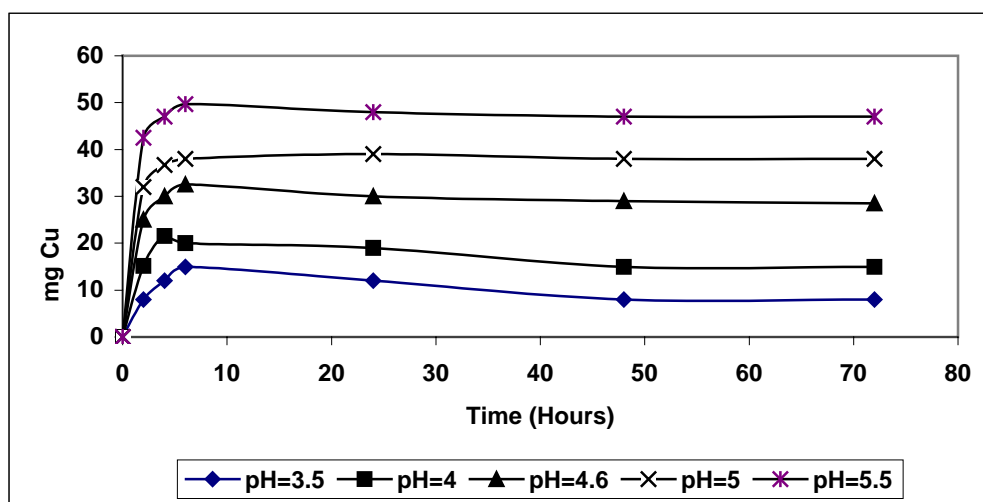


FIG. 3: Uptake of metal ions by P-IAEA versus time at various pH values.

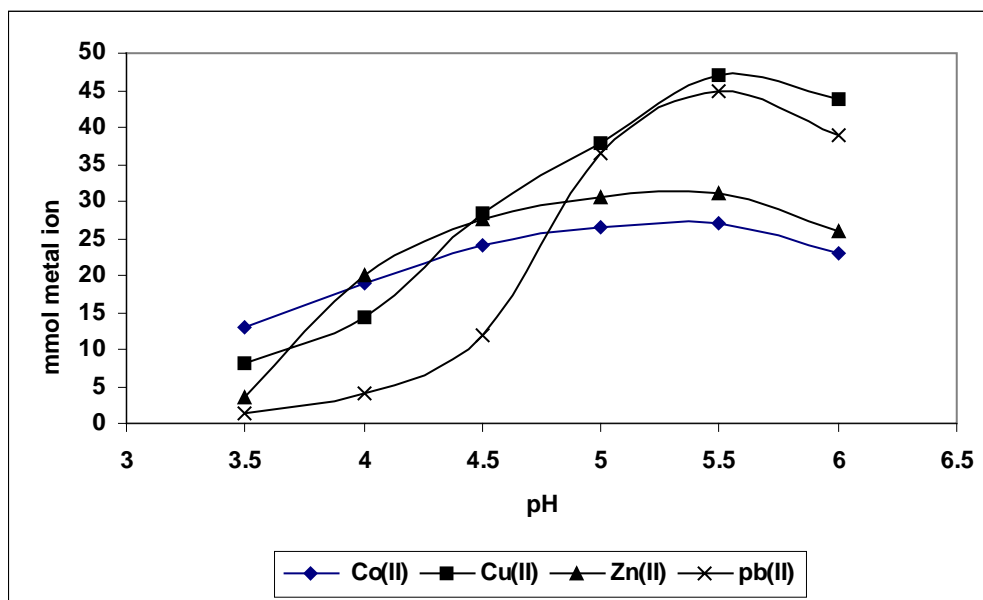


FIG. 4: Uptake of metal ions by P-IAEA versus pH values (72 hrs shaking time).