

Extraction of metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) using immobilized-polysiloxane iminobis(*n*-2-aminophenylacetamide) ligand system

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Abstract A new insoluble solid functionalized ligand system bearing chelating ligand group of the general formula $\text{P}-(\text{CH}_2)_3-\text{N}[\text{CH}_2\text{CONH}(\text{C}_6\text{H}_4)\text{NH}_2]_2$, where P represents $[\text{Si}-\text{O}]_n$ polysiloxane network, was prepared by the reaction of the immobilized diethyliminodiacetate polysiloxane ligand system, $\text{P}-(\text{CH}_2)_3\text{N}(\text{CH}_2\text{CO}_2\text{Et})_2$ with 1,2-diaminobenzene in toluene. ^{13}C CP-MAS NMR, XPS and FTIR results showed that most ethylacetate groups ($-\text{COOEt}$) were converted into the amide groups ($-\text{N}-\text{C}=\text{O}$). The new functionalized ligand system exhibits high capacity for extraction and removal of the metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with efficiency of 95–97% after recovery from its primary metal complexes. This functionalized ligand system formed 1:1 metal to ligand complexes.

Keywords Metal uptake · Iminodiacetic acid · Diethyliminodiacetate ligand · 1,2-diaminobenzene · Polysiloxanes · Polysiloxane-immobilized ligand systems

1 Introduction

The incorporation of chelating groups onto polysiloxane matrices may find applications such as extraction, recovery and separation of metal ions from aqueous solutions [1–5] and organic solvents [6, 7]. Further applications of these systems are their use in chromatography [8–10] and catalysis [11–13]. Investigations on polysiloxanes belong to one of materials research and development. One of the currently most widely used method for the preparation of the polysiloxane ligand systems is the sol gel process [1, 14]. This process involves hydrolysis and polycondensation reactions that lead to three dimensional crosslinking matrix. The technological importance of the sol-gel process arises from its simplicity. The chemical modification of pre-prepared polysiloxane precursors is widely used in the last years [2]. Many techniques have recently been applied to characterize their chemical structures and thermal properties including high-resolution solid state nuclear magnetic resonance (NMR) techniques [15–18], thermogravimetric analysis (TGA) [18–20], X-ray photoelectron spectroscopy (XPS) [2, 4, 21] and FT-IR spectroscopy [22, 23]. In the previous work, we reported the preparation of the immobilized iminobis(*N*-2-aminodiethylacetamide) ligand system and its application for metal uptake [2]. In this work a new modification of the diethyliminodiacetate polysiloxane was made with 1,2-diaminobenzene to produce the immobilized iminobis(*N*-2-aminophenylacetamide) polysiloxane ligand system to compare its metal uptake potential with the previously prepared immobilized iminobis(*N*-2-aminodiethylacetamide) ligand

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system. This new promising material was well characterized using variety of techniques including high-resolution solid state NMR, TGA, XPS and FT-IR analysis. This immobilized ligand exhibits high potential for extraction of metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) from aqueous solution.

2 Experimental

2.1 Reagents and materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, iminodiacetic acid and 1,2-diaminobenzene were purchased from Merck and used as received. Diethylether and methanol (spectroscopic grade) were used as received. Metal(II) solutions of the appropriate concentration were prepared by dissolving the metal(II) chloride (analar grade) in deionized water. pH (3.5–6) was controlled by using acetic acid/sodium acetate buffer solution.

2.2 General techniques

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

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo VG ESCALAB 250 instrument equipped with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV, 650 μm spot size). The samples were mounted onto double-sided adhesive tape. The pass energy was set at 150 and 40 eV for the survey and the narrow scans, respectively. Additional high resolution C1s and N1s regions were recorded using a pass energy of 10 eV. Charge compensation was achieved with a combination of electron and argon ion flood guns. The energy and emission current of the electrons were 4 eV and 0.35 mA respectively. For the argon gun, the energy and the emission current were 0 eV and 0.1 mA, respectively. The partial pressure for the argon flood gun was 2×10^{-8} mBar. These standard conditions of charge compensation resulted in a negative but perfectly uniform static charge. Data acquisition and processing were achieved with the Advantage software, version 2.2. Spectral calibration was determined by setting the main C1s component due to C–C/C–H bonds at 285 eV. The surface composition was determined using the manufacturer's sensitivity factors. The fractional concentration of a particular element A (% A) was computed using:

$$\%A = \frac{(I_A/S_A)}{\sum (I_n/S_n)} \times 100$$

where I_n and S_n are the integrated peak areas and the sensitivity factors, respectively.

^{13}C CP-MAS solid state NMR experiments were carried out at room temperature on a Bruker AVANCE 300 spectrometer at a frequency of 75.5 MHz (^{13}C) using a Bruker CP/MAS probe. Proton decoupling was always applied during acquisition. Solid samples were spun at 5 kHz using 7 mm ZrO_2 rotors.

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

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.

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

All ligand samples were shaken in aqueous metal ion solutions using an ELEIA-Multi Shaker.

2.3 Preparations

2.3.1 Preparation of 3-Iodopropyltrimethoxysilane

3-iodopropyltrimethoxysilane was prepared as previously described [5], where 3-chloropropyltrimethoxysilane was added dropwise with stirring to a solution of sodium iodide in dry acetone, at room temperature.

2.3.2 Preparation of 3-Iodopropylpolysiloxane (P-I)

Iodopropylpolysiloxane was prepared as previously reported [5] by adding 3-iodopropyltrimethoxysilane to a stirred solution of tetraethylorthosilicate in 1:2 molar ratio in the presence of HCl as a catalyst. The elemental analyses for the solid iodopolysiloxane material are given in Table 1.

2.3.3 Preparation of Polysiloxane-Immobilized Diethyliminodiacetate ligand system (P-DIDA)

The diethyliminodiacetate was first prepared as described before [9] by treating the iminodiacetic acid with absolute

Table 1 Elemental analysis data for the polysiloxane immobilized; iodopolysiloxane (P-I), diethyliminodiacetate (P-DIDA) and the modified form P-IAPA

Polysiloxane	Element	C%	H%	N%	I%	C/N
P-I	Expected	10.6	1.8	–	37.2	–
	Found	9.0	2.2	–	32.3	–
P-DIDA	Expected ^a	22.6	3.4	2.4	–	11.0
	Found	19.6	4.1	2.1	–	10.9
P-IAPA	Expected ^b	28.8	3.0	8.8	–	3.8
	Found	23.7	4.7	6.7	–	4.1

^aBased on results found for P-I.

^bBased on results found for P-DIDA assuming 100% reactions.

ethanol in presence of thionyl chloride. Functionalization of iodopolysiloxane with diethyliminodiacetate was carried out by adding diethyliminodiacetate to the iodopolysiloxane (P-I). The elemental analyses for the solid diethyliminodiacetate polysiloxane material are given in Table 1.

2.3.4 Preparation of Polysiloxane-Immobilized Iminobis(*N*-2-aminophenylacetamide) ligand system (P-IAPA)

10.0 g, of polysiloxane immobilized diethyliminodiacetate (P-DIDA) was refluxed with (10.0 g, 0.09 mol.) of 1,2-diaminobenzene, in presence of 50 cm³ toluene, at 110°C with stirring for 48 h under nitrogen. The mixture was cooled, and filtered, washed with successive 50 cm³ portions of water, methanol and diethyl ether. The final product was dried at 90°C in a vacuum oven (0.1 Torr) for 10 h. The elemental analyses are given in Table 1.

2.4 Metal uptake experiments

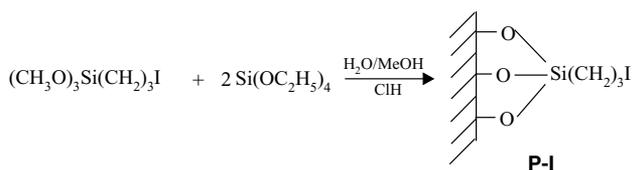
A 100 mg sample of the functionalized polysiloxane-immobilized ligand system, (P-IAPA) was shaken with 25 cm³ of 0.02 M aqueous solution of the appropriate metal ions (Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) using 100-cm³ polyethylene bottles. Determination of the metal ion concentration was carried out by allowing the insoluble complex to settle down, withdrawing an appropriate volume of the supernatant using a micropipette and then diluting to the linear range of the calibration curve for each metal. The metal ion uptake was calculated as mmole of Mⁿ⁺/g ligand. Each study was performed at least in a triplicate. Metal uptake was examined at different time intervals and pH values.

3 Results and discussion

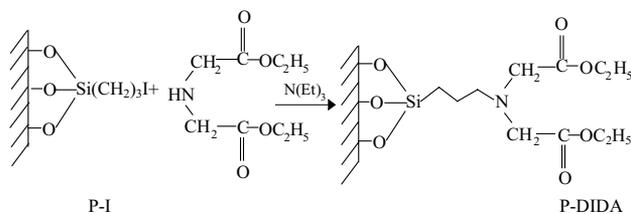
3.1 Preparation of Polysiloxane-Immobilized Iminobis(*N*-2-aminophenylacetamide) ligand system (P-IAPA)

This functionalized polysiloxane immobilized ligand system (P-IAPA) was prepared in three steps (Schemes 1–3)

1. Preparation of 3-iododopropylpolysiloxane (P-I) by hydrolysis and polycondensation of 3-



Scheme 1



Scheme 2

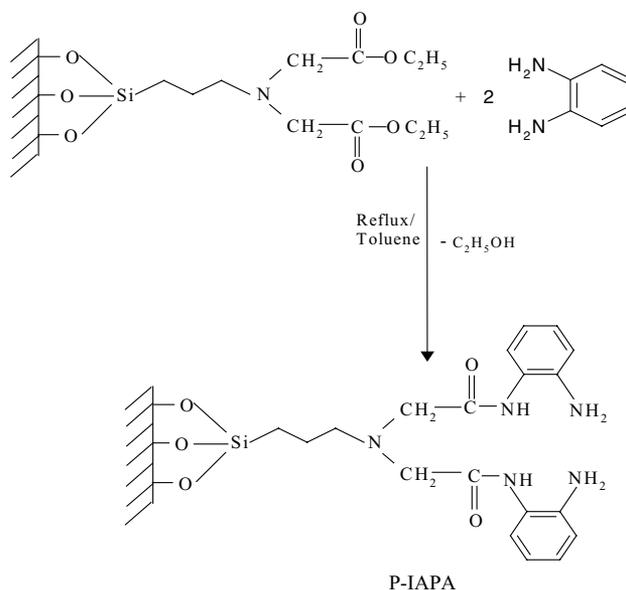
iodopropyltrimethoxysilane with tetraethoxysilane [5] (Scheme 1)

2. Preparation of polysiloxane-immobilized diethyliminodiacetate (P-DIDA) by the reaction of diethyliminodiacetate with 3-iodopropylpolysiloxane [9] (Scheme 2).
3. The new functionalized ligand system (P-IAPA) was prepared by the direct reaction of P-DIDA ligand system with 1,2-diaminobenzene (Scheme 3).

The introduction of 1,2-diaminobenzene into the polysiloxane system was evident from the increase of carbon and nitrogen percentages (Table 1). Similar results were previously reported when the immobilized iminodiethylacetate(P-DIDA) was treated with ethylene diamine [2]. The relative structure of P-I and P-DIDA systems were already reported [5, 9], whereas the relative chemical structure of the P-IAPA immobilized ligand system was identified in some details using FTIR spectra, ¹³C CP/MAS NMR spectra, XPS and the thermal analysis.

3.2 FTIR spectra

The FTIR spectra of P-I, P-DIDA and P-IAPA are given in Fig. 1a–c respectively. The spectra show three regions



Scheme 3

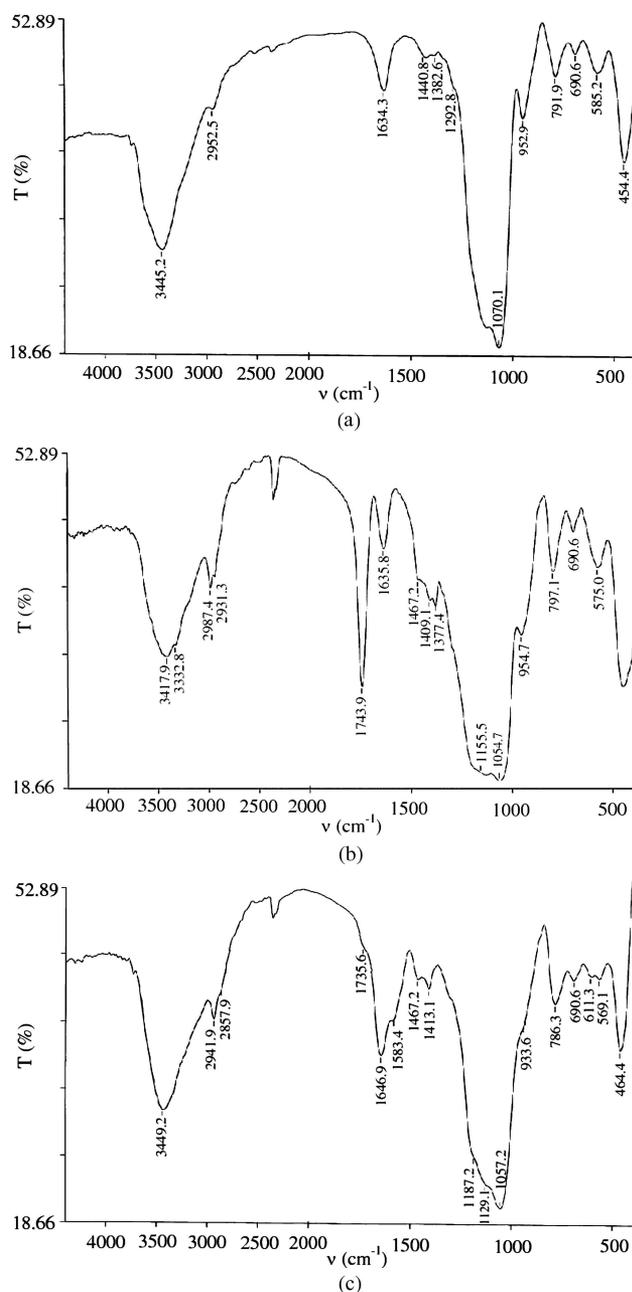
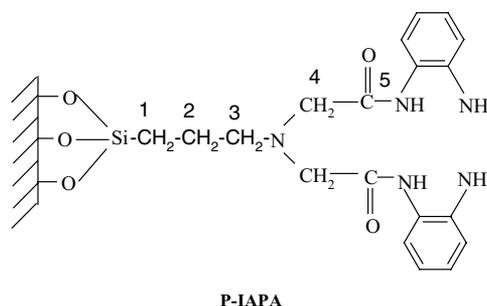


Fig. 1 FTIR spectra of: a) P-I, b) P-DIDA, c) P-IAPA

of absorption at $3500\text{--}3000\text{ cm}^{-1}$ due to $\nu(\text{OH})$ or $\nu(\text{NH})$, $1750\text{--}1500\text{ cm}^{-1}$ due to $\delta(\text{OH})$, $\delta(\text{NH})$, $\nu(\text{C}=\text{O})$ or $\nu(\text{CO}-\text{N})$ and $1200\text{--}900\text{ cm}^{-1}$ due to $\nu(\text{Si}=\text{O})$ [22, 23]. Figure 1a shows the spectrum of the polysiloxane P-I system where there is no peaks around 1740 cm^{-1} of the $\nu(\text{C}=\text{O})$ vibration.

The FTIR spectrum for the immobilized-polysiloxane P-DIDA (Fig. 1b) shows a strong absorption band at 1743.9 cm^{-1} due to $\nu(\text{C}=\text{O})$ vibration. The spectrum of P-IAPA ligand system (Fig. 1c) shows a strong absorption at 1646.9 cm^{-1} due to $\nu(\text{CO}-\text{N})$ vibration and a small shoulder at 1736.6 cm^{-1} for the $\nu(\text{C}=\text{O})$. The presence of small shoulder at 1736.6 cm^{-1}



Scheme 4

after treatment of the diethyliminodiacetate polysiloxane system (P-DIDA) with 1,2-diaminobenzene indicates that not all ethylacetate groups ($-\text{COOEt}$) were converted into the amide groups ($\text{N}-\text{CO}$). This is probably due to the steric hindrance of the 1,2-diaminobenzene.

3.3 ^{13}C CP-MAS NMR spectra

The ^{13}C CP-MAS NMR spectrum for P-IAPA (Scheme 4) is given in Fig. 2. The spectrum shows signals at 8.6, 25.5 and 46.4 ppm, corresponding to three methylene carbon atoms C1, C2 and C3 respectively. The spectrum shows the carbonyl carbon, C5 at 165.1 ppm and the methylene carbon C4 at 58.1(br) ppm. The carbon signals at 58.1(br) and 17.1 ppm are assigned for the un-reacted ethoxy groups ($-\text{OCH}_2\text{CH}_3$) [15–17]. This provides further evidence for incomplete reaction of P-DIDA with 1,2-diaminobenzene. This is in contrast with the reaction of P-DIDA with ethylene diamine where a complete reaction has confirmed [2]. The reason for this difference is probably that the 1,2-diaminobenzene has more steric hindrance than ethylene diamine molecule. The signals at the range 110–150 ppm, are assigned due to the aromatic carbons. The signal at 13.3 ppm was assigned for un-reacted iodopropyl groups. These assignments were based on spectral data of similar systems [2, 15–17].

3.4 XPS analysis

The XPS survey spectrum for the immobilized P-IAPA ligand system is given in Fig. 3. The spectrum of the P-IAPA shows signals at 102.5, 285, 400 and 532 eV corresponding to Si2p, C1s, N1s and O1s core levels, respectively. The spectrum also displays signal in the 618–630 eV range due to I3d doublet. This reflects the presence of un-reacted iodopropyl species, which has been confirmed earlier by the CP-MAS ^{13}C NMR and FT-IR results. Figure 4a and b display the C1s and N1s peak fitted spectra for P-IAEA ligand system. The tailed C1s peak is fitted with five components (Fig. 4a) assigned as follow: Peak A at 284.8 eV is due to $/\text{C}-\text{C}/\text{C}-\text{H}$; peak B at 285.7 eV is due to $\text{C}-\text{N}$; peak C at 286.8 eV is due to $\text{C}-\text{O}$; peak D at 287.9 eV is due to $\text{N}-\text{C}=\text{O}$; peak E

Fig. 2 ^{13}C CP-MAS NMR of P-IAPA

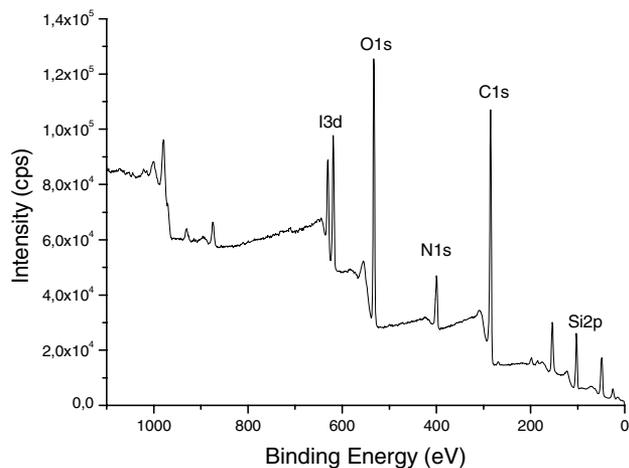
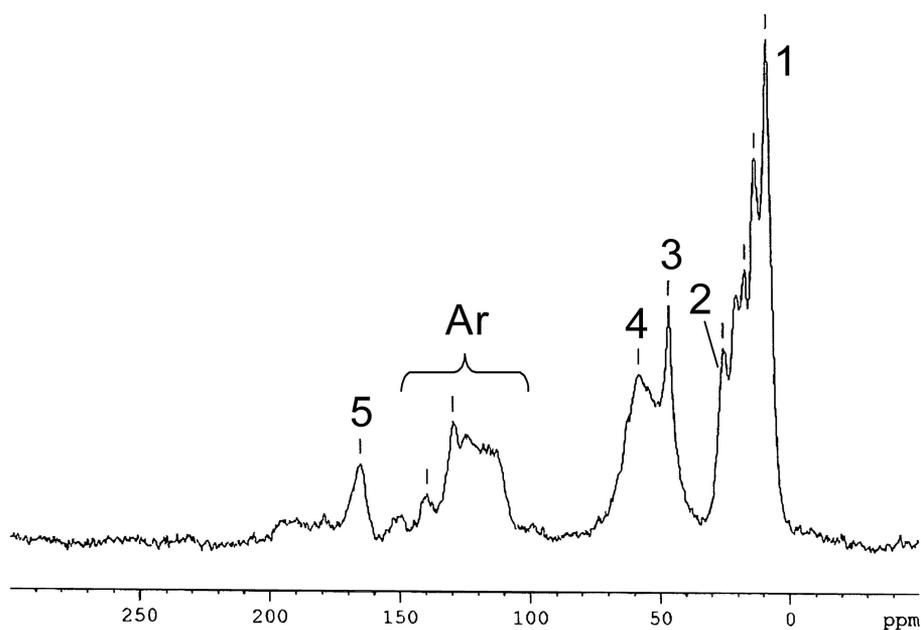


Fig. 3 XPS survey spectrum for P-IAPA

at 289.2 eV is due to surface unreacted $>\text{N}-\text{COOEt}$ groups [3]. The N1s region can be fitted with three main components centered at 399 eV (A), 400.6 eV (B) and 402 eV (C) (Fig. 4b) due to free and amine, conjugated and hydrogen bonding amine, and some protonated amine cations, respectively. The free amine proportion is around 60%.

Table 2 reports the surface composition of as-prepared and ground P-IAEA polysiloxane ligand systems. There is a significant difference in the surface composition before and after grinding the samples. The carbon and nitrogen percentages are decreased and the silicon and oxygen are increased (Table 2). Although there is no change of the composite of the P-IAEA system, but its surface chemistry has changed significantly after grinding. This was also confirmed with the fact that powder samples show less ligand density and therefore low metal uptake capacity for similar systems [2,

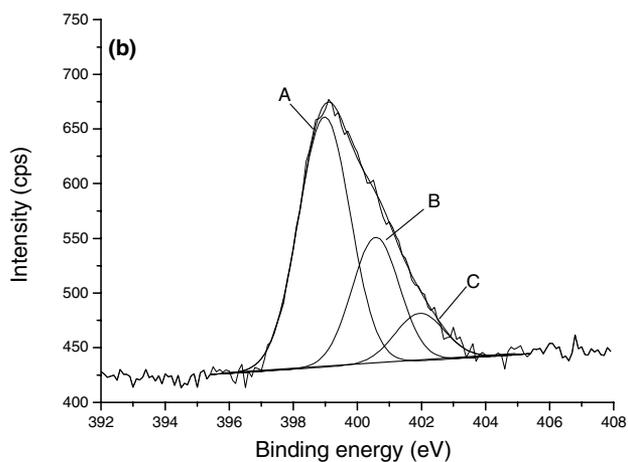
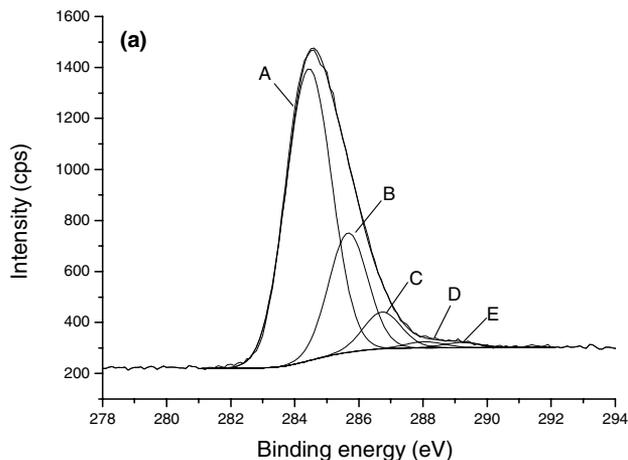


Fig. 4 High resolution XPS C1s (a) and N1s (b) spectra for P-IAPA

Table 2 XPS data and surface composition (in atomic%) of P-DIDA and P-IAPA

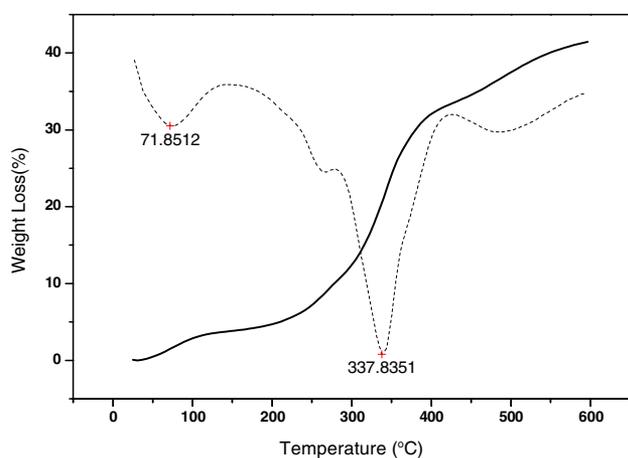
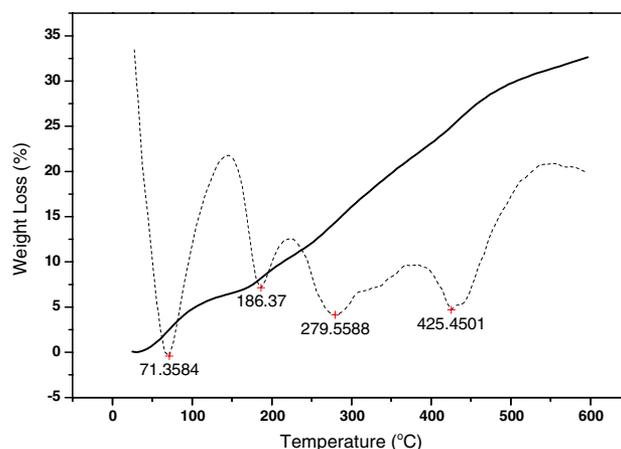
System	Element	C	Si	O	N
P-IAPA	Core-line	C1s	Si2p	O1s	N1s
		285	102	532	399.5
No-grinding	%Composition	54.1	13.9	22.6	7.4
Grinding	%Composition	43.5	20.3	30.3	3.5

5]. The reason for this change is probably that modification of polysiloxane precursor and introducing new ligand groups occurred mainly on the surface, so there are more ligand density on the polysiloxane surface than in the bulk. Grinding the material into fine powder results in less ligand containing groups density on the new surface.

3.5 Thermal analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) were examined for the P-IAPA immobilized ligand system and its copper complex P-IAPA-Cu(II). The TGA and DTA were performed under nitrogen atmosphere at temperature range 20°C–600°C.

Figure 5 shows the thermogram of the immobilized P-IAPA. Three peaks were observed. The first peak occurs at 75°C where the ligand system lost 3.8% of its initial weight. This is attributed to loss of physisorbed water and alcohol from the system pores [19, 20]. The second peak at 270–345°C is composed of two overlapped peaks which is due to further loss of 28.7%, this is probably due to degradation of the organofunctional groups bound to silicon atoms, dehydroxylation, and loss of water from the silica bulk [19, 20]. The third peak at temperature 400–600°C is due to further condensation of hydroxyl groups that left in the polymer forming siloxane bonds (dehydroxylation). The total loss of the immobilized ligand system was 41.5%.

**Fig. 5** Thermogravimetric analysis of P-IAPA**Fig. 6** Thermogravimetric analysis of P-IAPA-Cu(II) complex

The thermogram of the P-IAPA-Cu(II) complex (Fig. 6) shows three characteristic peaks at 70°C, 190°C and 280–440°C. The third broad peak is broad peak and composed of two peaks in which the complex lost 22.9% of its initial weight. This is probably due to complex decomposition and degradation of the ligand functional groups. The total loss of the complex was 32.7% which is smaller than its parent ligand precursor (P-IAPA) (41.5%). This provides evidence that this material becomes more stable upon complexation with metal ions.

3.6 Metal uptake

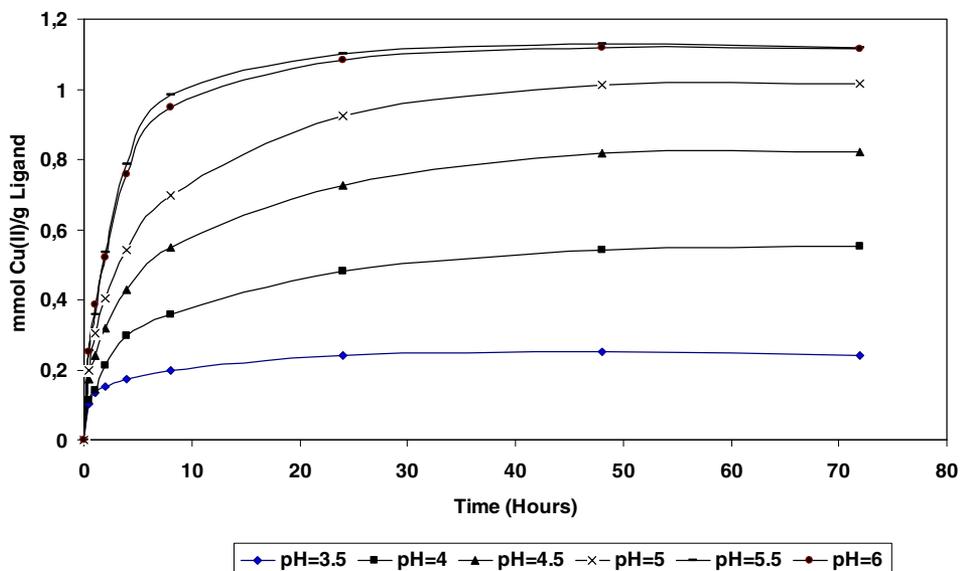
3.6.1 Effect of shaking time

The metal ion uptake capacity (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) was determined by shaking the functionalized ligand system (P-IAPA) with buffered solutions of the metal ions. Measurements were carried out at different time intervals. From the nitrogen analysis given in Table 1, as each functional group contains 5 nitrogen, it is possible to suggest that 0.95 mmol functional group was obtained per gram ligand system. Comparing this result with the metal uptake values given in Table 3 it is possible to suggest that the immobilized ligand P-IAPA form nearly 1:1 metal to ligand for all metal ions. The maximum metal uptake capacities for all metal ions (except Zn^{2+} ion) by the P-IAPA are slightly lower than that of the immobilized iminobis(N-2-aminoethylacetamide) ligand system (Table 3). This is probably that there were more functional ligand sites available

Table 3 Metal uptake of P-IAPA

Metal ion	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ref
Maximum uptake mmol M/g ligand	1.15	1.04	1.09	1.12	0.97	This work
	1.42	1.10	1.30	1.72	0.73	[2]

Fig. 7 Uptake of copper(II) ions by P-IAPA versus time



of iminobis(N-2-aminoethylacetamide) than in the case of P-IAPA.

The results of copper(II) ion uptake versus time are given in Fig 7. It is shown that the Cu²⁺ ion uptake is increased as a function of shaking time and reached equilibrium after about 24 h where maximum uptake is obtained. Similar results are obtained for the other Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ metal ions.

3.6.2 Effect of pH

The effect of the pH value on the uptake of Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ ions by P-IAPA is shown in Fig 8.

The results show an increase of metal ion uptake with increasing pH reaching its maximum at pH5.5. Low uptake capacity occurs at lower pH values (pH 1–3) due to protonation of amine species [24]. This reduces the ability of ligand groups to bind with metal ions. It is clear that metal uptake starts to decrease at higher pH values. This is probably due to the formation of hydrolyzed species of metal ions [24].

3.6.3 Recovery P-IAPA from its metal complexes

The complexes of the immobilized polysiloxane system P-IAPA were washed with HCl to remove the coordinated

Fig. 8 Uptake of metal ions by P-IAPA versus pH values, (72 h shaking time)

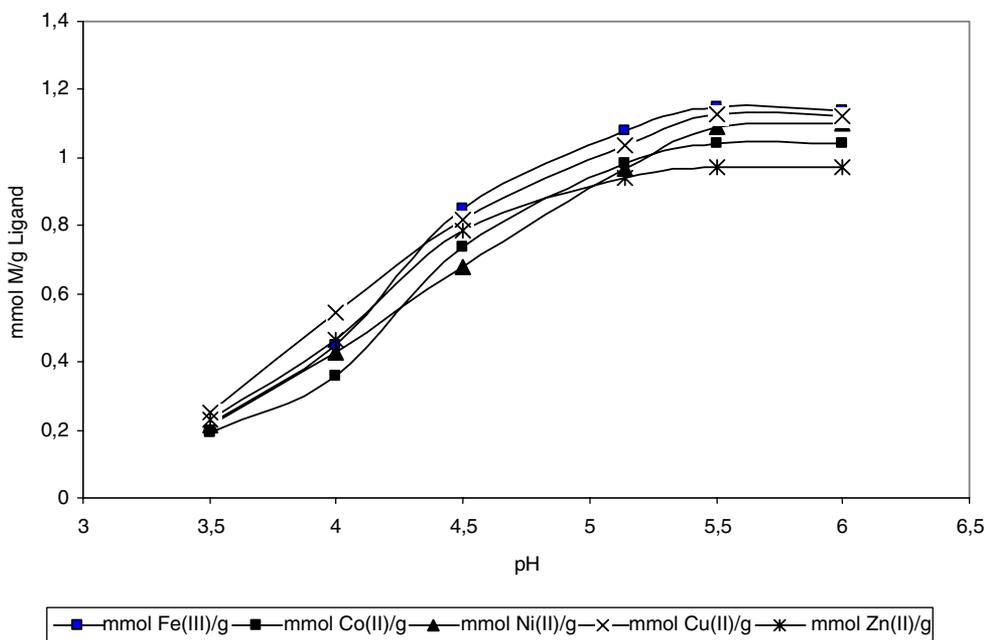


Table 4 Metal uptake capacity of original and the recovered P-IAPA

Metal ion	mmol of M/g Ligand System		
	Primary uptake	Re-uptake	Efficiency %
Cu(II)	1.11	1.15	96.5
Fe(III)	1.01	1.04	97.1
Ni(II)	1.04	1.09	95.4
Co(II)	1.06	1.12	94.6
Zn(II)	0.93	0.97	95.9

metal ions. The recovered P-IAPA was then reused to extract metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). The metal uptake capacity as mmol M^{n+} /g ligand, was determined and compared with the metal uptake capacity of the original P-IAPA. The results are presented in Table 4. The main reason for the slight decrease of the uptake capacities is that some ligand species were leached out during washing with acid solution, thus decreasing the number of ligand sites.

4 Conclusion

The immobilized ligand system P-IAPA was prepared by treatment of the immobilized diethyliminodiacetate ligand system with 1,2-diaminobenzene. FTIR spectra, NMR and XPS results suggest that not all the ester groups ($-\text{COOR}$) have disappeared upon treatment of the immobilized diethyliminodiacetate ligand system with 1,2-diaminobenzene, and the amide group ($-\text{CO}-\text{N}$) were mostly formed. The XPS results showed that the amine nitrogen atoms are exist in both forms: the free amine form and the protonated amine cation or hydrogen bonded with surface silanol groups. This immobilized ligand system exhibits high potential for extraction of metal ions from aqueous solutions. From the maximum metal uptake capacities it is possible to suggest that 1:1 metal to ligand ratio complexes are obtained. The recovery results indicate that the immobilized ligand system can be effectively reused.

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