Extraction, preconcentration and separation of some metal ions by 2(propylamino)benzenethiol polysiloxane immobilized ligand system

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ABSTRACT

Porous solid polysiloxane functionalized by 2-(propylamino)benzenethiol ligand of the general formula $P\text{-}(CH_2)_3\text{-}NH(C_6H_4)SH$, (Where P represents $[Si\text{-}O]_n$ siloxane network) has been prepared by reaction of the immobilized 3-iodopropylpolysiloxane, $P\text{-}(CH_2)_3\text{-}I$ with an excess of 2-aminothiophenol. The ligand system was evaluated for extraction and preconcentartion of Co(II), Cu(II) and Ni(II) metal ions from aqueous solutions. The maximum retention capacity followed the sequence; Cu(II)>Ni(II) > Co(II). The ligand system was also applied as a stationary phase in a glass column and showed a clean separation of Co(II), Ni(II) and Cu(II) metal ions aqueous solution mixture. The optimum separation pH values were 5 and 4 for Co(II) and Ni(II) cations respectively, while a solution of 0.1 M HNO_3 was used to elute Cu(II) cation.

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INTRODUCTION

Preconcentration and separation of dissolved trace metal ions onto a chemically modified solid supports have been studied intensively in recent years[1-13]. Polysiloxane immobilized ligand systems are particularly attractive solid supports because of their high thermal, hydrolytic and mechanical stability in addition to lack of swelling in solvents[14,15]. Recently there is a growing interest in synthesis of inorganic polysiloxane supports bearing organofunctionalized groups[16-29]. Solid-phase extraction and separation of metal ions based on such solid supports modified with a suitable complexing agent is frequently used[16-29]. Preparation of these functionalized ligand systems could be achieved by two methods. The first method is the sol-gel process which involves hydrolysis and condensation of $Si(OEt)_4$ with the appropriate silane coupling agent $(RO)_3SiX$ where X represents an organofunctionalized

ligand[16-21]. The second approach is the chemical modification of the pre-prepared functionalized polysiloxane [22-29]. In addition to extraction and separation of metal cations from organic solvents and aqueous solutions these functionalized systems have been used in many important applications include chromatographic stationary phases[21,30] and heterogeneous catalysis[20,31,32]. The aim of the present work is to investigate the optimal analytical conditions, including pH, analyte concentration and sample volume, for the preconcentration and separation of Ni^{2+}, Co^{2+} and Cu^{2+} metal ions from aqueous solutions using a new prepared 2-propylamino) benzen ethiol polysiloxaneimmobilized ligand system.

EXPERIMENTAL

Reagents and materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxy

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silane, and 2-aminothiophenol were purchased from (Merk) and used as received. Diethyl ether and methanol (analytical 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 3.5-6.0, were controlled using acetic acid/sodium acetate buffer solutions.

General techniques

Analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer A Analyst-100 spectrometer. The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR, spectrophotometer using KBr disk in the range of 4000 to 400cm^{-1}. All pH measurements were obtained using HM-40V pH Meter.

Methods of preparation

1. Preparation of 3-iodopropyltrimethoxysilane (L-I)

The 3-iodopropyltrimethoxysilane was prepared as previously described[16], where 3-chloropropyl trime thoxysilane (19.87g, 0.10mole) was added dropwise to a solution of sodium iodide (15g, 0.10 mole) in 100 mL of dry acetone with stirring, at room temperature. The mixture was refluxed at 70°C for 48 hours. White solid of NaCl was filtered off and the solvent was removed under reduced pressure at 60°C. The residue was extracted four times using 100mL of diethyl ether using a separatory funnel. The diethyl ether was removed at 35°C under reduced pressure producing a light yellow oily product.

2. Preparation of 3-iodopropylpolysiloxane (P-I)

3-Iodopropylpolysiloxane was prepared as previously reported[16] by adding 3-iodopropyltrimethoxy silane(14.5g, 0.05mol) to stirred solution of tetraethyl orthosilicate (20.8g, 0.1mol) in 20 cm^3 methanol, followed by 4.95cm^3 of 0.42 M HCl as a catalyst. The mixture was stirred at room temperature for several hours. Gelation occurred after 24 hours, the gel was left for 12 hours then dried at 100°C overnight. The material was crushed, sieved, washed with successive

TABLE 1: Elemental analysis data for P-I and P-ABT

Polysiloxane	Element	C%	H%	I%	C/I
P-I	Expected*	10.5	1.8	37.2	2.98
	Found	9.7	2.2	34.3	2.99
Polysiloxane	Element	%C	%H	%N	C/N
P-ABT	Expected*	29.4	3.3	3.8	9.02
	Found	26.6	3.8	3.4	9.13

portions, of 50cm^3 of water, methanol and diethyl ether. Finally the product was dried for 12 hours at 10 °C. The elemental analysis for the iodopolysiloxane is given in TABLE 1.

3. Preparation of polysiloxane-immobilized 2-(propylamino)benzenethiol ligand system (P-ABT)

2-(propylamino)benzenethiol polysiloxane ligand was prepared by adding an excess of 2-aminothiophenol (6.25g, 0.05mol) to 10g of 3-iodopropylpolysiloxane (0.027 mol) in 50 ml of ethanol in presence of 1 ml triethylamine. The mixture was stirred and refluxed at 60°C for 48 hours. The product was filtered off, washed with successive portions (50 ml) of 0.025 M NaOH, water, methanol, and diethyl ether, then dried in vacuum oven (0.1 torr) at 60°C for 12 hours. The elemental analysis for the 2-(propylamino)benzenethiol poly siloxane is given in TABLE 1.

Batch experiments

A 100 mg of the 2-(propylamino)benzenethiol polysiloxane-immobilized ligand system, P-ABT was shaken with 25 cm^3 of 0.02 M aqueous solution of the appropriate metal ions (Co^{2+}, Ni^{2+} and Cu^{2+}) using 100-cm^3 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 using atomic absorption spectroscopy. The maximum metal ion uptake capacity was calculated as mg of M^{2+}/g ligand. Each study was performed at least in a triplicate.

Column experiments

1. Preconcentration experiment

A glass column (250mm long, 10 mm diameter) was washed sequentially with 0.1 M nitric acid, water and acetone. It was then oven-dried and packed with a bed (5.0g, 60-80 mesh) of the 2-(propylamino)benzenethiol immobilized ligand system, P-ABT. The

packed material was activated for each run by washing with 25cm³ of aqueous solution of 0.5 M hydrochloric acid, followed by deionized water. Finally, the column was preconditioned by passage of 25cm³ of the appropriate buffered aqueous solution to equilibrate the column as that of the working solution. Solutions (50cm³, 100 ppm) of each metal ion at different pH values were eluted with a flow rate at 1.0-1.5cm³min⁻¹ by gravity. When needed, vacuum pump was used to reach the desired flow rate. In another experiment, the column containing the bed (5.0 g, 60-80 mesh) of P-ABT, was activated as mentioned previously and solutions of different concentrations (0.0005-1.0 M) buffered at pH 5.5 were passed through the column with a flow rate at 1.0-1.5cm³ min⁻¹. The chemisorbed metal ion was eluted by passing 50 cm³ of an aqueous 0.5 M hydrochloric acid. The metal ions were determined by atomic absorption spectroscopy.

2. Column separation experiment

The column was packed with the functionalized 2-(propylamino)benzenethiol immobilized ligand system, P-ABT (5.0g, 60-80 mesh). After each use the column was flushed with 0.50 M hydrochloric acid, followed by deionized water, to remove any uneluted metal contaminant. The column was then preconditioned by passage of 25 cm³ of the appropriate buffered aqueous solution to equilibrate the column as that of the working solution. Solution of a mixture of metal ions (Co^{2+}, Ni^{2+}

and Cu^{2+}, each of 100 ppm) was injected in the column, then buffered solutions of controlled pH were passed through the column at a flow rate of 1.0-1.5cm³ min⁻¹ by gravity. The eluates were collected in fractions with a volume range 5-10cm³. Each fraction was diluted to 50cm³ and the amount of metal ion (mg/g ligand system) in each fraction was determined using atomic absorption spectroscopy. The retained metals on the ligand system were eluted with 10 cm³ of 0.50 M hydrochloric acid. The solution was then diluted to 50cm³ and the metal concentrations in the solution were determined by using atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Preparation of 2-(propylamino)benzenethiol polysiloxane ligand system (P-ABT)

The 2-(propylamino)benzenethiol ligand system (P-ABT) was prepared by two steps (SCHEME 1):

1. Preparation of 3-idopropylpolysiloxane was prepared as previously reported[16], by hydrolytic polycondensation of 3-idodopropyltrimethoxysilane and tetraethylorthosilicate (TEOS) in the ratio of 1:2 (SCHEME 1).
3. The new functionalized ligand system (P-ABT) was achieved by direct reaction of P-I ligand system with 2-aminothiophenol.

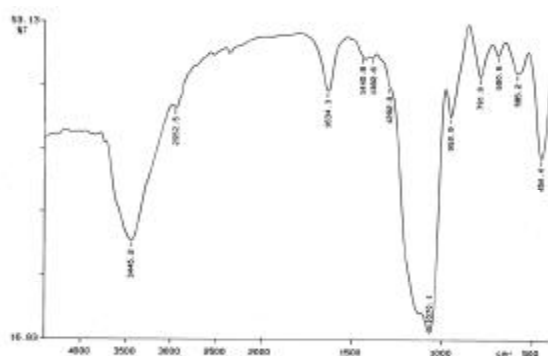The elemental analyses of both P-I and the modified form P-ABT are given in TABLE 1. The lower

SCHEME 1
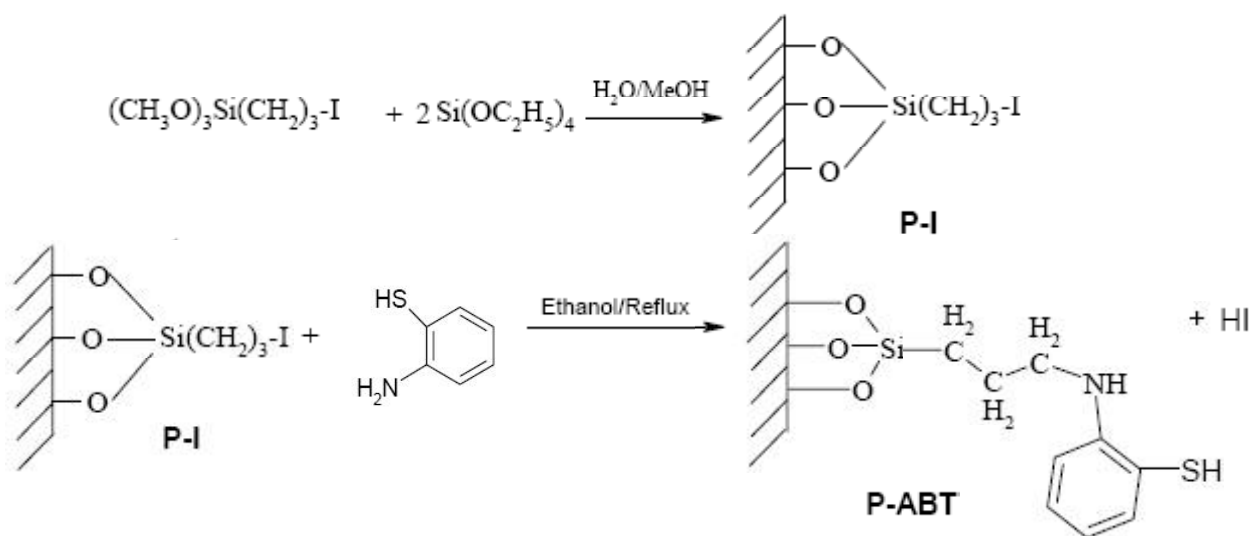
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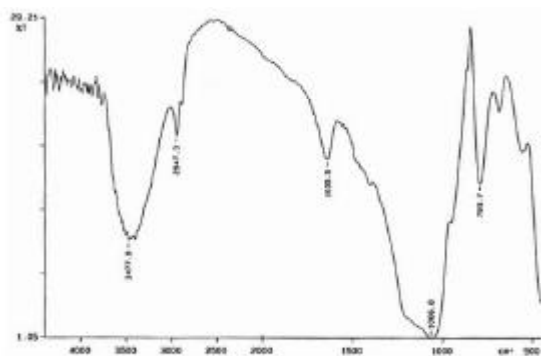

Figure 1: FTIR spectrum of P-I
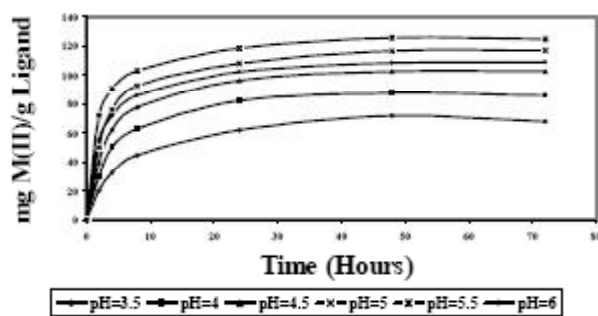

Figure 2: TIR spectrum of P-ABT

Figure 3 : Uptake of Cu(II) by P-ABT versus time

carbon and iodine percentages for the 3-iodopropyl polysiloxane, P-I than the expected values, is due to self condensation of 3-iodopropyltrimethoxy silane which result in the formation of low molecular weight products, which were washed away.

From the elemental analysis of P-ABT (TABLE 1), it is obvious that the reaction between 3-iodopropylpoly siloxane and 2-aminothiophenol occurred. The results show that the found percentages of C and N are slightly lower than expected ones, which is probably due to incomplete reaction of the iodo groups with 2-amino thiophenol.

FTIR spectra

The FTIR spectra of the immobilized 3-iodopropyl polysiloxane (P-I) and 2-(propylamino) benzenethiol polysiloxane (P-ABT) ligand systems are given in figures 1 and 2. The spectra show three characteristic absorption regions at 3500-3000 cm^{-1} due to ν(OH) and/or ν(NH$_2$), 1645-1560cm^{-1} due to δ(OH) and/or δ(NH$_2$) and 1200-900 cm^{-1} due to ν(Si-O). The un-smooth band around 3477 cm^{-1} of P-ABT spectrum (Figure 2) is due to the introduction of the amino group. The strong band at 3947cm^{-1} is due to ν(C-H) aromatic. This confirms that the 2-aminothiophenol functional group is chemically bonded to the polysiloxane matrix.

Metal uptake capacity of P-ABT

The uptake capacity of P-ABT for Co^{2+}, Ni^{2+} and Cu^{2+} metal ions, was determined by batch method. The functionalized ligand system, was shaken with buffered metal ions solutions for 48 hours. The results in mg M^{2+}/ g ligand are given in TABLE 2. The elemental analysis of nitrogen of the immobilized ligand (P-ABT) as given in TABLE 1 was 3.4 % i.e. 2.42mmol N/g ligand. Comparing this value with the maximum metal ion uptake, it is possible to suggest that not all functional groups are accessible to binding with the metal ions assuming that ligand to metal complexation ratio is 1:1. It is clear that uptake of metal ions increases in the order: Cu^{2+} > Ni^{2+} > Co^{2+}

TABLE 2: Maximum metal uptake by P-ABT

Maximum uptake	Co^{2+}	Ni^{2+}	Cu^{2+}
mg M^{2+}/g Ligand	103.7	106.8	125.5
mmol M^{2+}/g Ligand	1.76	1.82	1.98

Effect of shaking time

The metal ion uptake capacity of Co^{2+}, Ni^{2+} and Cu^{2+} was determined by shaking the functionalized ligand system, P-ABT with buffered solutions of the metal ions. Measurements were carried out at different time intervals. The uptake of copper ions versus time is given in figure 3. It is shown that the metal ion uptake is increased as a function of shaking time and reached equilibrium nearly after 48 hours where maximum uptake was obtained. Similar results were observed for the other metal ions.

Effect of pH

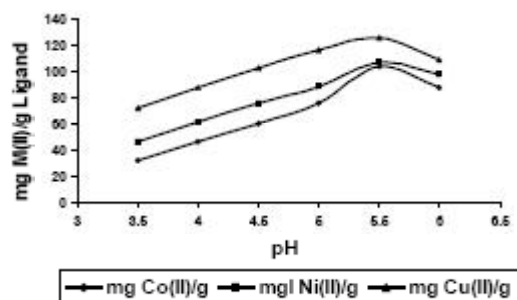The effect of the pH on uptake of metal ions (Co^{2+},

Figure 4: Utake of metal ions by P-ABT versus pH values, (48 hr shaking time)
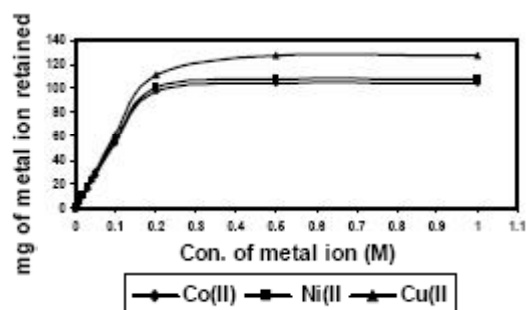

Figure 5: Preconcentration of Co(II), Ni(II) and Cu(II) as a function of metla ion concentration (5.0 g of ligand system; flow rate 1.0 -1.5 cm³ min⁻¹; pH = 5.5)
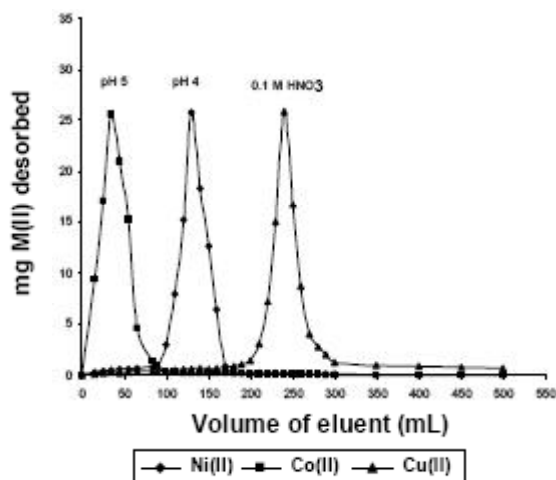

Figure 6: Separation of a mixture of Co(II), Ni(II) and Cu(II), (5.0 g of ligand system; flow rate = 1.0 -1.5 cm³ min⁻¹; total eluent volume = 500 cm³)

Ni^{2+} and Cu^{2+}) by P-ABT is shown in figure 4. The results show an increase of metal ion uptake with increasing pH value and reached its maximum at pH 5.5. Minor uptake capacity occurred at low pH values (pH =3.5) due to protonation of amine groups. This reduces the ability to form metal complexes. It is clear that the metal uptake starts to decrease after reaching the maxi-

mum value. This is probably due to the formation of hydrolyzed species of metal ions[33].

Preconcentration of metal ions

The ability of P-ABT to preconcentrate metal ions from aqueous solution was evaluated using aqueous solutions of metal ions at different concentrations. The results are given in figure 5. The amount of metal ion recovered by the ligand system increases with increasing concentration up to the maximum value. The maximum chemisorption values were obtained at concentration of 0.5 M of the eluted metal ions and found to be 127 mg Cu, 108 mg Ni and 105mg Co per gram ligand system. According to the elemental analysis of P-ABT, the N analysis was found to be 3.4% i.e. 2.43mmol N/ g ligand. These values give a preconcentration efficiency of the column in percentages of 82.3%, 75.7% and 73.4% for copper, nickel and cobalt respectively. At low metal ions concentration, ~100% extractions were achieved. This promises the column to preconcentrate these metal ions efficiently.

Separation of metal ions

Separation of a mixture of metal ions Cu(II), Ni(II) and Co(II) was performed by elution with buffer solutions at different pH values. Three bands were observed by controlling the pH. A blue color band of Cu(II) was observed upstream followed by a green and a pink bands of Ni(II) and Co(II) respectively. These bands were eluted cleanly from the mixture by pH control. Figure 6 shows the separation of Cu(II), Ni(II) and Co(II) metal ions as a function of elution volume at variable pH values. Complete separation of Co(II), Ni(II) and Cu(II) from solution mixture was performed and improved by stepwise pH control of the eluent . The desorbed amount of metal was calculated from the total fractions of 500 cm³. Three well resolved peaks of cobalt, nickel and copper ions were obtained, at pH 5, pH 4 and 0.1 N HNO_3 respectively. This promises the ligand system to be efficient in a clean separation of these metal ions.

CONCLUSION

The immobilized 2-(propylamino)benzenethiol ligand system was prepared by treatment of the 3-iodopropyl

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polysiloxane with 2-aminothiophenol. This immobilized ligand system exhibits high potential for extraction of Co^{2+}, Ni^{2+} and Cu^{2+} metal ions. This ligand system has been shown to be an effective solid-phase preconcentration agent for cobalt, nickel and copper at pH 5.5. The ligand system exhibits high potential for separation of a mixture of Co^{2+}, Ni^{2+} and Cu^{2+} metal ions from aqueous solution by pH control.

ACKNOWLEDGMENTS

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