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Column Extraction and Separation of Some Metal Ions by Diethylenetriamine Polysiloxane Immobilized Ligand System

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Abstract: An extraction chromatographic solid porous polysiloxane functionalized by chelating diethylenetriamine ligand of the general formula $P-(CH_2)_3-NH(CH_2)_2NH(CH_2)_2NH_2$, (Where P represents $[Si-O]_n$ siloxane network) has been evaluated for the separation of Co(II), Ni(II) and Cu(II) from aqueous solutions. The chromatographic parameters of the separation method have been optimized. The ligand system retained Co(II), Cu(II) and Zn(II) effectively when used as a metal ion extractant by controlling the pH value. The ligand system also shows a good separation of a mixture of metal ions Co(II), Ni(II) and Cu(II) when used as chromatographic stationary phase. The optimum separation pH values were 4.5, 4 for Co(II) and Ni(II) respectively, while a solution of 0.1 M HNO_3 was used to elute Cu(II). Metal ions were also preconcentrated at pH 5.5. The chemisorbed metal ions were regenerated from the solid extractant using 0.5 M HCl.

Keywords: Ion chromatography, Separation of metal ions, Polysiloxanes, Immobilized-polysiloxane ligand systems, Chelating ligands, Diethylenetriamine.

Introduction

Use of chelating agent-loaded organic and inorganic polymers for preconcentration and separation of trace metal ions are gaining a great interest. There is, consequently, interest in developing chelating insoluble matrices of good stability which have high capacity for metal ions and low analyte matrix effects that tolerate flexible working conditions¹⁻¹². The organofunctionalization of polysiloxanes is normally used to introduce many chelating ligand groups¹³⁻²³. The incorporation of chelating groups onto polysiloxanes is finding its way into an increasing number of applications in areas such as extraction of metal cations from organic and aqueous medium¹⁻¹², use as stationary phases in liquid chromatography^{11,20,24} and for the

catalysis of reactions^{17,25,26}. Such materials have many advantages over organic resins, due to their high thermal, hydrolytic and mechanical stability, in addition to lack of swelling in solvents²⁷⁻²⁸. Porous solid polysiloxanes have been synthesized by sol-gel process at ambient temperatures^{10-23,29,30}. Diethylenetriamine has been used as a chelating ligand for many decades. It could be introduced into the polysiloxane by substitution reaction of diethylenetriamine with halogen-functionalized polysiloxanes^{13,14,31}. In present work direct sol gel method was used to prepare this ligand system by hydrolytic polycondensation of diethylenetriaminopropytrimethoxysilane with TEOS. Interesting application was investigated by this ligand system for the separation and preconcentration of Co^{2+} , Ni^{2+} , Cu^{2+} metal ions from aqueous solutions.

Experimental

Reagents and Materials

Tetraethylorthosilicate, diethylenetriaminopropytrimethoxysilane, were purchased from MERCK and used as received. Diethyl ether and methanol (spectroscopic grade) were used as received. Solutions of metal ions of the appropriate concentrations were prepared by dissolving the metal chloride (analar grade) in deionized water. pH range of 3-6 was controlled by using acetic acid (0.1 M)/sodium acetate (0.1 M) buffer solutions.

General Techniques

Analysis for carbon, hydrogen and nitrogen was carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. The concentrations of metal ions in their aqueous buffer solutions were measured using a Perkin-Elmer A Analyst-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 cm^{-1} . All pH measurements were carried out using HM-40 V pH Meter.

Preparation of Polysiloxane-Immobilized Diethylenetriamine Ligand System (P-DTA).

Polysiloxane-Immobilized diethylenetriamine (P-DTA) was prepared by adding diethylenetriaminopropytrimethoxysilane (13.27, 50 mmol) to a stirred solution of tetraethylorthosilicate (20.83 g, 100 mmol) in 15 mL methanol and HCl (4.95 mL, 0.42 M). Gelation occurred within few seconds. The product was left to stand for 12 h 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 h.

Batch Experiments

A 100 mg of the functionalized polysiloxane-immobilized ligand system, P-DTA 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 AAS. 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-Preconcentration Experiment

A glass column (250 mm 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 (5.0 g, 60-80 mesh)

of the diethylenetriamine immobilized ligand system, P-DTA. The packed material was activated for each run by washing with 15 cm³ of aqueous solution of 0.5 M hydrochloric acid, followed by deionized water and finally with acetate buffer solution at pH 5.5. Solutions (50 cm³, 100 ppm) of each metal ion at different pH values were eluted with a flow rate at 1.0-1.5 cm³ min⁻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-DTA, 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 1.0-1.5 cm³ min⁻¹. The chemisorbed metal ion was eluted by passing 50 cm³ of an aqueous 0.5 M hydrochloric acid. The metal ions were quantified by atomic absorption spectroscopy.

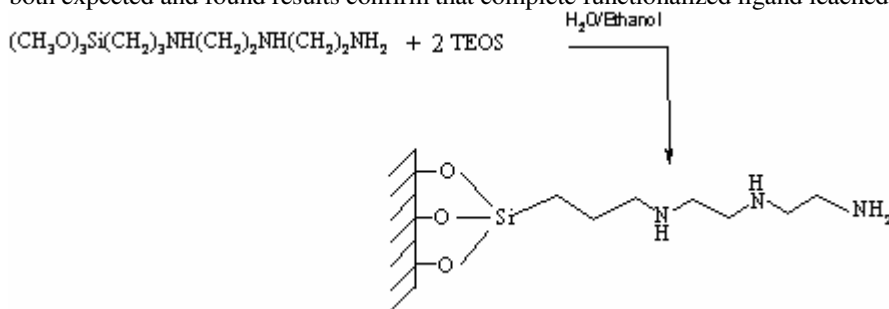
Column Separation Experiment

The column was packed with the functionalized diethylenetriaminopolysiloxane, P-DTA (5.0 g, 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. Before any sample injection, the column was 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 (Co²⁺, Ni²⁺ and Cu²⁺, 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 -1.5 cm³ min⁻¹ by gravity. The eluates were collected in fractions with a volume range 5-10 cm³. Each fraction was diluted to 50 cm³ and the amount of metal ion (mg) 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 50 cm³ and the metal concentrations in the solution were determined by using atomic absorption spectroscopy.

Results and Discussion

Synthesis of Polysiloxane-immobilized Triamine Ligand System (P-DTA)

The diethylenetriamine polysiloxane ligand system (P-DTA) was made by hydrolytic polycondensation between TEOS and diethylenetriaminopropyltrimethoxysilane (Scheme 1). The elemental analysis results of the prepared polysiloxane are given in Table 1. The functional group content of the ligand system is higher than previously reported results¹⁵. It is found that percentages of C and N are slightly lower than expected due to formation of small oligomers which leached during the washing process^{10, 29-31}. Formation of these small oligomers is enhanced by the presence of self base catalyzed amino groups which lead to rapid gelation, so small amounts of non-cross linked oligomers are formed^{10, 29-31}. The equal ratios of both expected and found results confirm that complete functionalized ligand leached.



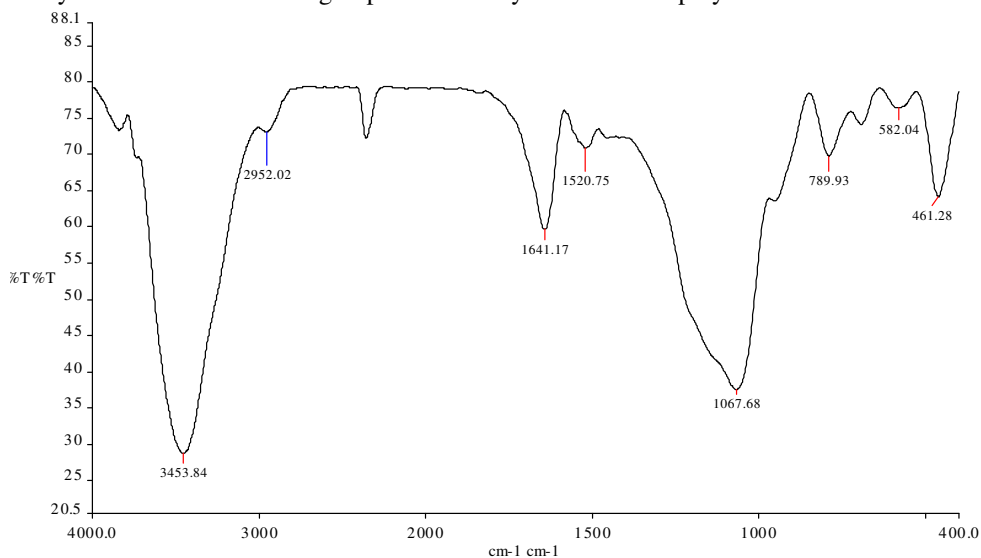
Scheme 1

Table 1. Elemental analysis for polysiloxane-immobilized triamine ligand system (P-DTA).

Element	C%	H%	N%	C/N	mmol N/g
Expected	26.56	5.73	13.28	2.33	9.5
Found	24.34	5.9	11.89	2.38	8.5

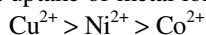
FTIR Spectrum

The FTIR spectrum of the immobilized diethylenetriaminepolysiloxane, P-DTA ligand system is given in Figure 1. The figure shows three characteristic absorption regions at 3500-3200 cm^{-1} due to $\nu(\text{OH})$, $\nu(\text{NH})$ or $\nu(\text{NH}_2)$, 1650-1560 cm^{-1} due to $\delta(\text{OH})$, $\delta(\text{NH}_2)$ or $\delta(\text{NH})$ and 1200-900 cm^{-1} due to $\nu(\text{Si-O})$ respectively. The strong bands at 3453 cm^{-1} and 1641 cm^{-1} are due to $\nu(\text{NH}_2/\text{NH}/\text{OH})$ and $\delta(\text{NH}_2/\text{NH}/\text{OH})$ vibrations respectively. This confirms that the diethylenetriamine functional group is chemically bonded to the polysiloxane surface.

**Figure 1.** FTIR spectrum of P-DTA

Metal Uptake Capacity of P-DTA

The metal ion uptake capacity of Co^{2+} , Ni^{2+} and Cu^{2+} , was determined by shaking the functionalized ligand system, P-DTA with buffered metal ions solutions for 48 h. The results in $\text{mg M}^{2+}/\text{g}$ ligand are given in Table 2. The elemental analysis of nitrogen of the immobilized ligand (P-DTA) as given in Table 1 was 11.89% *i.e.* 2.8 mmol 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 the ligand to metal complexation ratio is 1:1. It is clear that uptake of metal ions increases in the following order:

**Table 2.** Maximum metal uptake by P-DTA

Maximum Uptake	Co^{2+}	Ni^{2+}	Cu^{2+}
$\text{mg M}^{2+}/\text{g}$ Ligand	97.0	104.2	129
$\text{mmol M}^{2+}/\text{g}$ Ligand	1.64	1.77	2.03

Effect of pH on the metal ions chemisorption

The influence of pH of the aqueous solution on the retention of cobalt, nickel and copper was investigated in the pH range 3-6 by using acetate buffer solution. The results are depicted in Figure 2. The recovery values of the analyte ions were generally found to be very small at low pH values and increases by increasing pH. Maximum retention occurs at pH 5.5. In case of copper about 100% was retained while 93% and 88 % were retained in case of nickel and cobalt respectively.

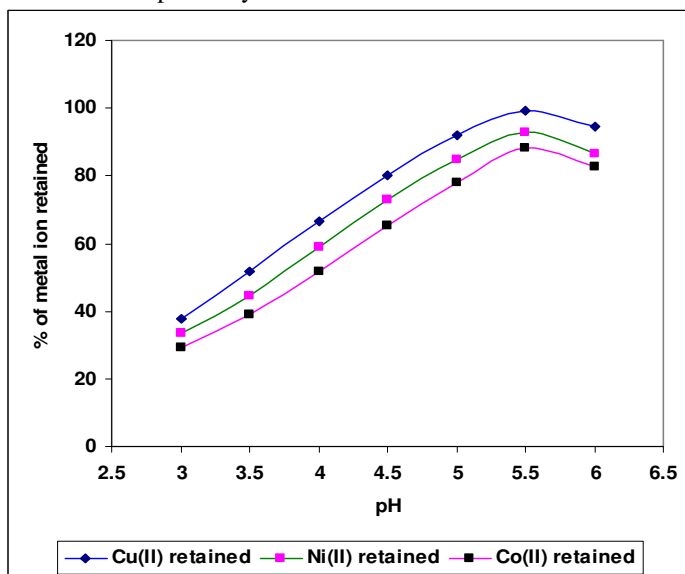


Figure 2. Chemisorption of metal ions by P- DTA versus pH values

Preconcentration of metal ions

The ability of P-DTA to extract cations from aqueous solution was evaluated using a series of concentrations of metal ions. The results are given in Figure 3. The amount of metal ion recovered by the ligand system increases with increasing concentration up to the maximum value. Based on elemental analysis of N (11.89 %) of the ligand system (each ligand contains 3 N atoms), there was 2.8 mmol ligand per gram of immobilized system. Assuming 1:1 complex formation of M:L mole ratio the maximum loading (theoretically) of metal ion would be 179 mg Cu, 164 mg Ni and 165 mg Co per gram ligand system. The maximum chemisorption values were obtained at concentration of 0.5 M of the eluted metal ions and found to be 128 mg Cu, 104 mg Ni and 97 mg Co per gram ligand system. These values represent preconcentration efficiency of the column in percentages of 73.5 %, 63.4 % and 58.8 % for copper, nickel and cobalt respectively. At low metal ion concentration, ~100 % extractions were achieved. This promises the column to be an excellent preconcentration system for these metal ions.

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 pH control. 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 metal ions were eluted cleanly from the mixture by pH control. Figure 4 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 4.5, 4 and 0.1 N HNO₃ respectively. This promises the ligand system to be efficient in a clean separation of these metal ions.

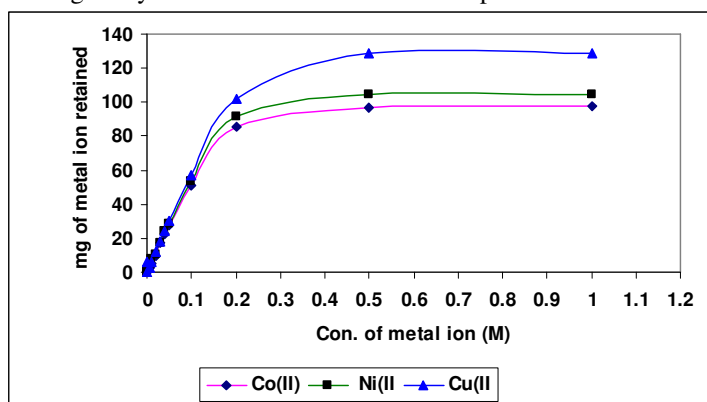


Figure 3. Preconcentration of Co(II), Ni(II) and Cu(II) as a function of concentration (5.0 g of ligand system, flow rate 1.0 -1.5 cm³ min⁻¹, pH = 5.5).

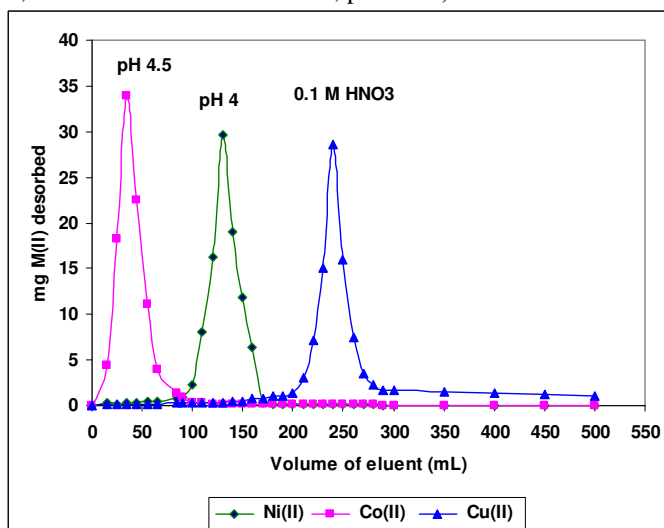


Figure 4. Separation of a mixture of Co(II), Ni(II) and Cu(II), (5.0 g of ligand system, flow rate 1.0 -1.5 cm³ min⁻¹, pH = 5.5, Total eluent volume = 500 cm³).

Conclusions

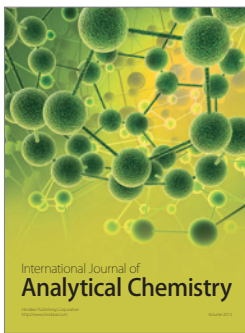
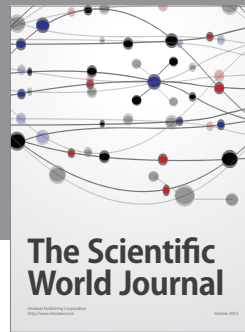
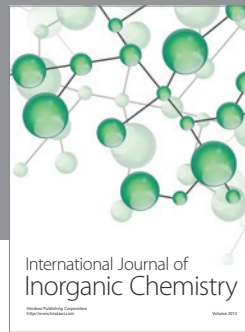
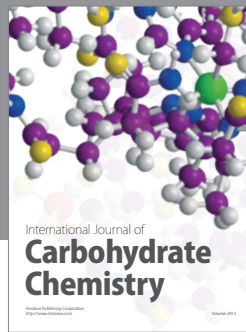
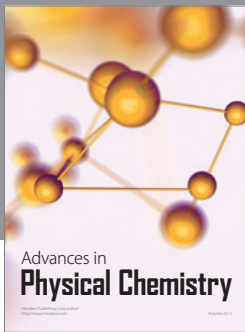
The immobilized diethylenetriamine ligand system was prepared by direct sol-gel hydrolytic polycondensation reaction of diethylenetriaminopropyltrimethoxysilane and tetraethyl-orthosilicate monomers at ambient temperature. This ligand system has been shown to be an effective solid-phase preconcentration agent for cobalt, nickel and copper at pH 5.5. The ligand system exhibits high potential for separation of a mixture of Co²⁺, Ni²⁺ and Cu²⁺ metal ions from aqueous solution by pH control.

Acknowledgements

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