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Preparation and metal uptake capacity of pentaaza-macrocyclic polysiloxane immobilized ligand system

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ABSTRACT

Insoluble porous solid macrocyclic 1,4,7,10,13-pentaazapentadecane-3,14-dione-1-propyl-N-propyl polysiloxane ligand system of the general formula P-(CH$_2$)$_3$-NH-(CH$_2$)$_3$-C$_8$H$_{22}$O$_2$N$_3$, (where P represents [Si-O]$_n$ siloxane network) has been prepared by the reaction of macro-silane agent with tetraethyl orthosilicate. The macro-silane agent was prepared by the reaction of iminobis (N-2-aminoethylacetamide) ligand with 3-iodopropyltrimethoxysilane in 1:3 molar ratio respectively. The new prepared polysiloxane system exhibits high potential for the uptake of metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+}). Chemisorption of the metal ions by the ligand system at the optimum conditions was found in the order: Ag^{+} > Pb^{2+} > Hg^{2+} > Cu^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Cd^{2+} > Zn^{2+}

KEYWORDS

Metal uptake;
Macrocycle;
Inorganic polymers;
Chelating ligands;
Extraction of metal ions;
Immobilized-polysiloxane ligand systems.

1. INTRODUCTION

Preconcentration and separation of dissolved trace elements by a chemically modified solid supports have been studied intensively in recent years[1-15]. The polysiloxane immobilized ligand systems have become particularly attractive solid supports because of their mechanical, thermal and chemical stability. These organic/inorganic hybrid materials have also become of great importance in science and industry, because of their widespread applications. The polysiloxane immobilized ligand systems can be synthesized primarily by the sol-gel process[14-19]. The sol-gel method include hydrolysis and polycondensation of Si(OEt)$_4$ and an appropriate silane coupling agent[14-19]. Further chemical modification of functionalized polysiloxane immobilized ligand systems has been used to produce new polysiloxane derivatives[20-27]. 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 medium[14-22], use as stationary phases in liquid chromatography[23-26] and for the catalysis of reactions [17,27,28]. Such materials have many advantages over organic resins, due to their high thermal, hydrolytic and mechanical stability, in addition to lack of swelling in solvents[29,30]. Many techniques have recently been applied to characterize their chemical structures[31-36]. In this work, a new functionalized macrocyclic ligand system was made to investigate its metal uptake capacity toward some metal ions including (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+}) in aqueous solutions.

2. MATERIALS AND METHODS

2.1 Reagents and materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxy silane, ethylenediamine and iminodiacetic acid, were purchased from (MERCK) and used as received. Acetone, diethyl ether and methanol (spectroscopic grade) were used as received. Metal ion solutions of the appropriate concentrations were prepared by dissolving the metal chlorides (in case of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) and metal nitrates (in case of Ag^+, Hg^{2+} and Pb^{2+}) in deionized water, (all of them were an analar grade salts). Different pH ranges (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 lemental Analyzer EA 1110-CHNS CE Instrument. 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 obtained using HM-40 V pH meter.

2.3. Methods of preparation

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

The 3-iodopropyltrimethoxysilane was prepared as previously described[15], where 3-chloropropyl trime thoxysilane (19.87g, 0.10mole) was added dropwise to a solution of sodium iodide (15 g, 0.10 mole) in 100 mL of dry acetone with stirring, at room temperature. The mixture was refluxed at 70^0C for 48 hours. White solid of NaCl was filtered off and the solvent was removed under reduced pressure at 60^0C. The residue was extracted four times using 100 mL of diethyl ether using a separatory funnel. The diethyl ether was removed at 35^0C under reduced pressure producing a light yellow oily product.

2.3.2. Preparation of diethyliminodiacetae DEIDA

This compound was prepared as previously reported[20,25], by adding iminodiacetic acid (30.0 g, 0.4 mol) to 300 ml of absolute ethanol with stirring, to which thionyl chloride (93.86 g, 0.8 mol) was added dropwise. The reaction mixture was stirred and refluxed at 80°C until all the iminodiacetic acid was dissolved. The reaction was allowed to proceed under reflux for further 5 h. The mixture was cooled to room temperature and the excess of ethanol and SO_2 was removed by evaporation under vacuum. The residue was dissolved in 100 ml distilled water and 150 ml of chloroform was added. Then 33% of sodium hydroxide solution was added dropwise with shaking after each addition, so that the diethyliminidiacetate passed into the chloroform and the pH of the solution was adjusted to around 7. The aqueous layer was extracted repeatedly with chloroform (4×150 ml). The layer of chloroform was separated and then dried for 2 hours over anhydrous $MgSO_4$. The chloroform was removed at reduced pressure and the residue product was dried in vacuum (0.1 torr) for at least 1 hour.

2.3.3. Preparation of iminobis(N-2-aminoethyl acetamide) ligand (L-IBAEA)

Diethyliminodiacetate (18.9, 0.1 mol), was refluxed with (12.0 g, 0.2 mol) of ethylenediamine, in 100 ml of ethanol at 70^0C for 48 hours. Ethanol was removed at reduced pressure and the residue product was dried in vacuum (0.1 torr) for at least 1 hour.

2.3.4. Preparation of macro-silane agent L-macro

The iminobis(N-2-aminoethylacetamide) ligand 10.9 g 0.05 mol, was reacted with (43.5 g, 0.15 mol) of 3-idopropyltrimethoxysilane under reflux in presence of ethanol (50 ml) for 8 hours. Ethanol was removed at reduced pressure and the residue product was dried in vacuum (0.1 torr) for at least 1 hour.

2.3.5. Preparation of polysiloxane macrocyclic ligand system (P-macro)

The macrocyclic ligand system was prepared by adding (5.89g, 0.01 mol) of the macrocyclic silane agent to (6.24 g , 0.03 mol) of tetraethylorthosilicate in 20 ml ethanol while stirring, followed by 5.67g of H_2O. The mixture was left with stirring, gelation occurred within 1 minute the gel was left for 12 hours and dried at 100^0C. The material was crushed, sieved, washed with successive portions (50 ml) of water, methanol and diethyl ether. Finally the product was dried for 12 hours at 100^0C.

2.3.6. Metal uptake experiments

A 100 mg of functionalized polysiloxane-immobilized macrocyclic ligand system was shaken with 25 mL, 0.01 M of aqueous solution of the appropriate metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+}) using 100mL polyethylene bottles. Determination of the metal ion concentration was carried out by allowing the insoluble complex to settle down and appropriate volume of the supernatant was withdrawn using a micropipette then diluted to the linear range of the calibration curve for each metal. Each study was performed at least in a triplicate. The metal ion uptake was calculated as mg of M^{n+}/g ligand. Metal uptake was examined at different pH values and different time intervals.

2.3.7. Recovery of metal ions from their ligand complexes

Recovery of metal ions was carried out by two methods. The first was by treating the metal complexes of the immobilized ligand system with EDTA. A definite amount of the metal-ligand complex (100 mg) was mixed with 35 mL of EDTA (0.1 M) at pH 10 using ammonium buffer. The mixture was left with shaking for 72 hours. The metal ion concentration which detached from the solid ligand complex and bound to EDTA was diluted and determined by means of atomic absorption spectroscopy. The second method was achieved by washing the ligand complex with 50 mL of 1.0 M HCl for 30 minutes then diluted and determined using atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

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

The 3-iodopropyltrimethoxysilne was obtained from the reaction of 3-chloropropyltrimethoxysilane with an excess of sodium iodide using acetone as a solvent under reflux (SCHEME 1). The elemental analysis results of the product are given in TABLE 1.

From the elemental analysis given in TABLE 1 it is clear that most of chlorine atoms have been replaced by iodine. The slight decrease of the percentage of C, H and I from the expected values is obviously due to incomplete replacement of Cl with I.

$$(CH_3O)_3Si(CH_2)_3Cl + NaI \xrightarrow[\text{reflux 48 hr, } 70^0C]{\text{acetone}} (CH_3O)_3Si(CH_2)_3I + NaCl$$

SCHEME 1

3.2. Preparation of diethyliminodiacetate (DEIDA)

The diethyliminodiacetate was prepared by direct reaction of iminodiacetic acid with absolute ethanol in the presence of thionyl chloride as given in SCHEME 2. The elemental analysis is given in TABLE 2.

The FTIR spectrum of the diethyliminodiacetate is shown in figure 1. The spectrum shows two characteristic bands at 1738 cm^{-1} and 3352 cm^{-1} for ν(C=O) ester and ν(N-H) secondary amine stretching vibrations respectively. The spectrum shows also an absorption band at 1372 cm^{-1}, which belongs to CH_3 bending vibration of the aliphatic ethoxy groups.

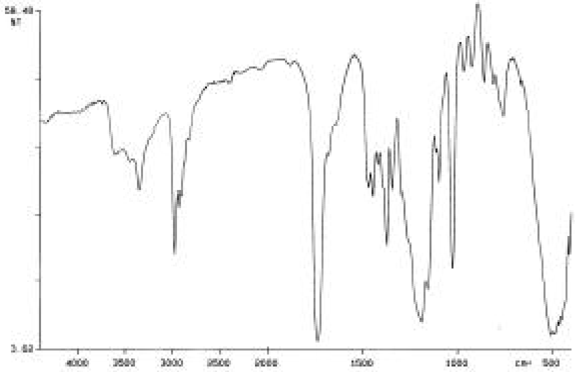


Figure 1: FTIR spectra of diethyliminodiacetate (DEDA)

TABLE 1: Elemental analysis data for 3-iodopropyltrimethoxy silane, L-I

Element	C %	H %	Cl %	I %	C/I
Expected	24.8	5.3	0.0	43.8	6.0
Found	23.2	4.6	1.5	40.5	6.0

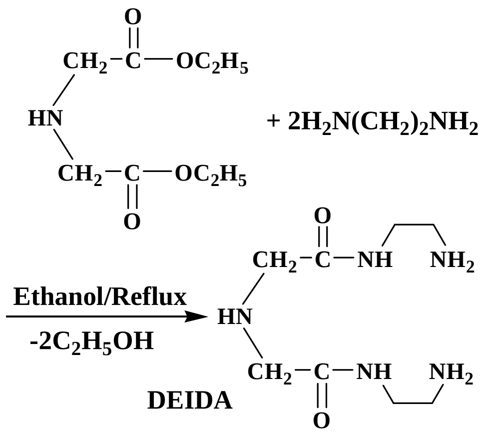
TABLE 2: Elemental analysis data for diethyliminodiacetate, DEIDA

Element	C %	H %	N %	C/N
Expected	50.8	8.20	7.30	8.00
Found	51.2	8.3	7.31	8.17

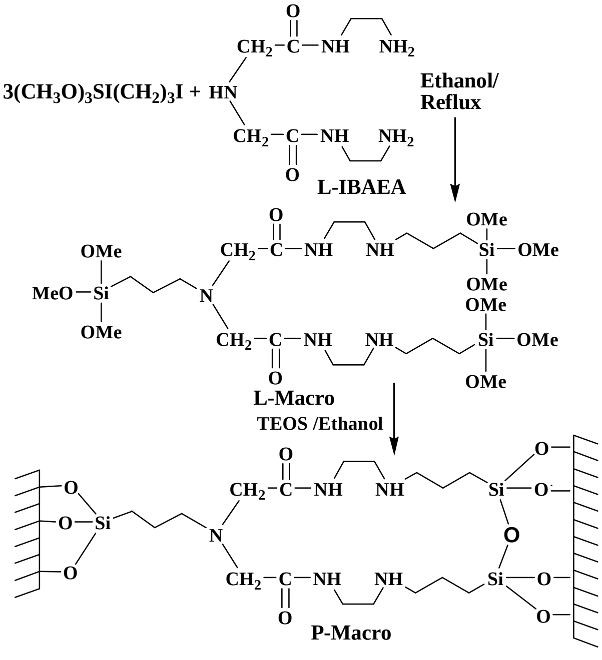
$$HN(CH_2CO_2H)_2 + EtOH \xrightarrow[70^oC,\ 32\ hrs]{SOCl_2}$$

$$NH(CH_2COCl)_2{}^{+}Cl^{-} + SO_2 \xrightarrow[]{\substack{NaOH \\ Chloroform}} HN(CH_2CO_2C_2H_5)_2$$

SCHEME 2



SCHEME 3



SCHEME 4

TABLE 3: Elemental analysis for macrocyclic polysiloxane ligand system, P-macro

Element	C%	H%	N%	C/N
Expected	31.7	5.3	10.9	40.1
Found	28.2	4.6	9.2	42.7

TABLE 4: Maximum metal uptake capacity by P-Macro polysiloxane ligand system

Metal ion	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ag^{+}	Hg^{2+}	Pb^{2+}
Maximum uptake (mg M^{n+}/g ligand)	31.3	24.7	32.9	59.1	7.2	21.4	211.5	172.4	176.0

3.3. Preparation of iminobis(N-2-aminoethyl acetamide) ligand (L-IBAEA)

This ligand was prepared by the reaction of diethyliminodiacetate (DEIDA), with ethylene diamine. (SCHEME 3).

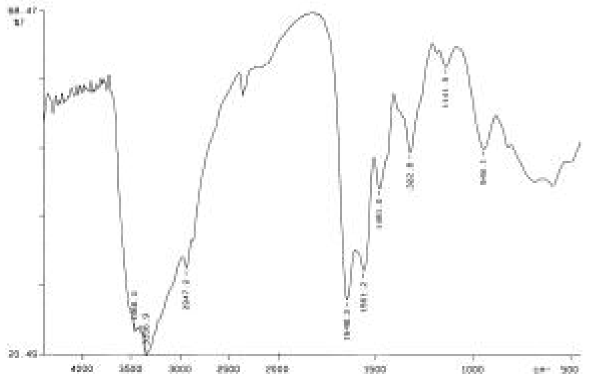


Figure 2: FTIR spectra of iminobis(N-2-aminoethyl acetamide) ligand (L-IBAEA)

The FTIR spectrum of the iminobis(N-2-aminoethyl acetamide) ligand; L-IBAEA is given in figure 2. The spectrum shows a characteristic absorption band at 1648 cm^{-1} for ν(N-C=O) amide, stretching vibration and no band for the ester carbonyl ν(C=O) vibration. This confirms that the reaction between diethyliminodiacetate and ethylenediamine is complete. The spectrum shows two peaks at 3357 and 3466cm^{-1} which assigned for the ν(N-H) and ν(N-H_2) stretching vibrations. The spectrum also shows a band at 1561 due to δ(N-H) bending vibration.

3.4. Preparation of polysiloxane immobilized macrocyclic, ligand system (P-Macro)

This ligand system was prepared in two steps

(I) Preparation of the macrocyclic silane agent precursor by the reaction of iminobis(N-2-aminoethyl acetamide) ligand (L-IBAEA) with 3-iodopropyl trimethoxy silane in 1:3 molar ratio respectively (SCHEME 4).

(II) Hydrolytic polycondensation of the previous precursor with tetraethylorthosilicate (TEOS) in 1:3 molar ratio respectively (SCHEME 4).

The elemental analysis result of P-Macro is given in TABLE 3. The lower C and N percentages than those expected is probably due to incomplete substitution reaction of the iodide with L-IBAEA amino groups. The nitrogen percentage indicates that each gram of P-Macro ligand system conatins 1.3 mmol of the macrocyclic organofunctionalized group.

The suggested structure of the P-Macro (SCHEME 4) is based on the stoichiometry of the reactants in step II. The found elemental analysis results of P-Macro

TABLE 5: Characteristic colors of the metal complexes of P-Macro polysiloxane ligand system

Metal ion	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ag^{+}	Hg^{2+}	Pb^{2+}
Color of M-pmacro complex	Brown	Violet	Green	Blue	White	White	Black	Red	Yellow

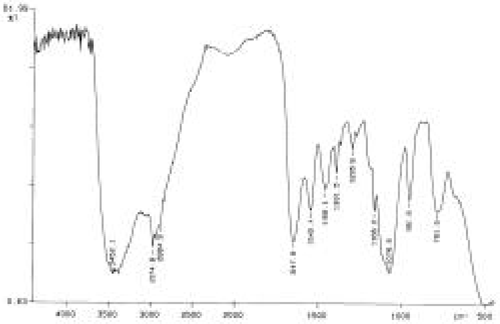


Figure 3: FTIR spectra of the macro-silane agent (L-macro)

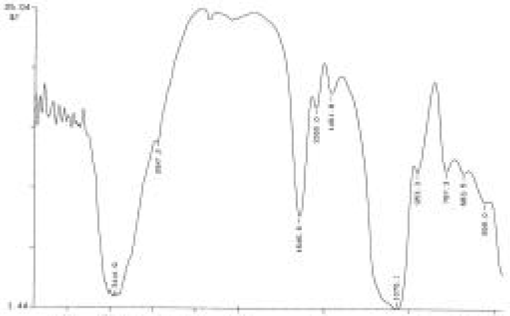


Figure 4: FTIR spectra of macrocyclic ligand system (P-macro)

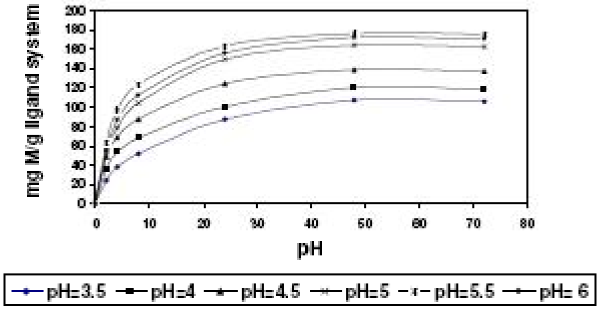


Figure 5: Metal uptake of Pb(II) by P-Macro versus time

compared with that expected (TABLE 3) may confirm the proposed structure.

The FTIR spectrum of the macro-silane agent (L-Macro) is shown in figure 3. The spectrum shows a charcteristic absorption bands at 1648 cm^{-1} for ν(N-C=O) amide, stretching vibration. Broad bands were observed at 3452 cm^{-1} and 1077 cm^{-1} which assigned for hydrolyzed and condensed silanol groups respectively.

The FTIR spectrum of the macrocyclic polysiloxane P-Macro is given in figure 4. The spectrum shows three characteristic absorptions at 3000-3500 cm^{-1} for overlapping ν(O-H) and ν(N-H), 1646.6 cm^{-1} for ν (N-C=O) amide and 950-1250 cm^{-1} for ν(Si-O-Si) stretching vibrations.

3.5. Metal uptake

The metal ion uptake capacity of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+} as mg M^{n+}/g ligand, was determined by shaking the functionalized ligand system (P-Macro) with buffered metal ions solutions.

Maximum metal uptake capacity by P-Macro ligand system is given in TABLE 4. The ligand system shows high extraction capacity for Ag^{+}, Pb^{2+} and Hg^{2+}. It is clear that uptake of metal ions increases in the order: $Ag^{+} > Pb^{2+} > Hg^{2+} > Cu^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Cd^{2+} > Zn^{2+}$

The colors of the metal ions complexes of the immobilized ligand systems are given in TABLE 5.

3.5.1. Effect of shaking time

The metal ion uptake capacity of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+}, was determined by shaking the functionalized ligand system (P-macro) with different pH buffered solutions of the metal ions. Measurements were carried out at different time intervals. The uptake of lead metal ions versus time is given in figure 5. It is shown that the metal ion uptake is increased as a function of shaking time and reached equilibrium nearly at 48 hours where maximum uptake is obtained. Similar results were observed for the other metal ions.

3.5.2. Effect of pH

The effect of pH on the metal ion uptake capacity of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+} by the functionalized ligand systems (P-macro) at 48 hours shaking time is given in figure 6.

The results show an increase of metal ion uptake with increasing pH value and reached its maximum nearly at pH 5.5. Lower uptake capacity occurs at lower pH values due to protonation of amine groups.

3.6. Recovery of the ligand system from its metal complexes

The recovery of metal ions after extraction by the immobilized ligand system, was examined to evaluate

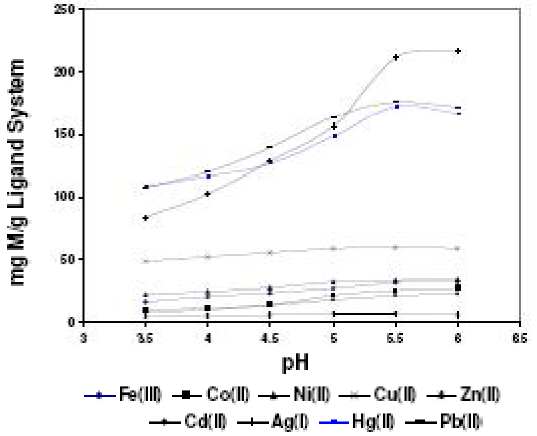


Figure 6: Metal uptake by P-Macro versus pH values, (48 hr shaking time)

TABLE 6: Maximum metal uptake versus amount recovered of metal ions by EDTA

	mg of Metal ion/g ligand system		
Metal	**Maximum uptake**	**Amount recovered**	**% Efficiency**
Fe^{3+}	31.3	15.3	49.1
Co^{2+}	24.7	20.5	82.9
Ni^{2+}	32.9	25.7	78.1
Cu^{2+}	59.06	36.0	61.0
Zn^{2+}	7.2	5.5	76.3
Cd^{2+}	21.4	12.3	57.5
Ag^{+}	211.5	3.05	1.4
Hg^{2+}	172.4	40.0	23.2
Pb^{2+}	176.0	96.7	55.0

the preconcentration and reuse efficiency of these functionalized polysiloxanes. The recovery of metal ions (Cu^{2+}, Hg^{2+}, Pb^{2+} and Ag^{+}) from their ligand complexes (at their optimum values) using an EDTA solution showed variable efficiencies. The results are given in TABLE 6.

It is observed that the efficiency of metal ion recovery is in the following order: $Co^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}Pb^{2+} > Fe^{3+} > Hg^{2+} > Ag^{+}$

On the other hand washing the ligand complex with HCl (1 M) removed nearly all the metal ions and produce a clean immobilized ligand system.

CONCLUSION

The immobilized ligand system P-Macro was prepared by sol gel method. The macro-silane agent was prepared firstly by the reaction of iminobis(N-2-amino ethylacetamide) ligand with 3-iodopropyl trimethoxy silane followed by hydrolytic polycondensation with tetraethylorthosilicate (TEOS). Elemental analysis and FTIR spectra suggest the incorporation of the macrocyclic ligand onto the polysiloxane matrix. This immobilized ligand system exhibits high potential for extraction of metal ions including Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+} and Pb^{2+} from aqueous solutions. Maximum metal uptake capacity occurred at pH 5.5.

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