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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article El-Ashgar, Nizam M. , El-Nahhal, Issa M. , Chehimi, Mohamed M. , Babonneau, Florence and Livage, Jacques(2009) 'Preparation of ethylenediaminetriacetic acid silica-gel immobilised ligand system and its application for trace metal analysis in aqueous samples', *International Journal of Environmental Analytical Chemistry*, 89: 14, 1057 – 1069

To link to this Article: DOI: 10.1080/03067310902717278

URL: <http://dx.doi.org/10.1080/03067310902717278>

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Preparation of ethylenediaminetriacetic acid silica-gel immobilised ligand system and its application for trace metal analysis in aqueous samples

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(Received 10 September 2008; final version received 29 December 2008)

This article reports on the preparation of porous solid ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA) of the general formula S-(CH₂)₃N(CH₂COOH)-(CH₂)₂-N(CH₂COOH)₂ (where S represents [Si-O]_n). This was prepared by modification of 3-(2-aminoethylaminopropyl)trimethoxysilane with ethyl chloroacetate followed by polycondensation with tetraethylorthosilicate via the sol-gel process. The immobilised ethylenediaminetriacetic acid ligand system (S-EDTA) was characterised by FTIR, ¹³C CS-MAS NMR and XPS spectroscopic techniques. The resulting functionalised ligand system showed high potential to extract and separate Co²⁺, Ni²⁺ and Cu²⁺ metal ions from aqueous samples. The saturation sorption capacities of Co²⁺, Ni²⁺ and Cu²⁺ metal ions were 77.6, 89.1 and 99.4 mg g⁻¹, respectively. The optimum separation pH values were 4.5 and 4 for Co(II) and Ni(II), respectively, while a solution of 0.1 mol L⁻¹ HNO₃ (pH = 1) was used to elute Cu(II).

Keywords: solid supports; functionalised silica gel; metal ions extraction; metal ions separation

1. Introduction

Pre-concentration and separation of trace metals using functionalised silica-gel materials have been developed in the last few decades either by the sol-gel method [1–5] or by modification of silica surfaces [6–8]. The use of modified silica in this field was initiated by Leyden and Luttrell [9–11], where they have used amine, thioether and dithiocarbamate derivatives modified silica for pre-concentration and/or separation of metal ions. Chelating functionalised groups, bonded to inorganic supports have several advantages over comparable functional polymers such as thermal, mechanical and chemical stability [12]. Reviews on polymeric supports as well as modified silica supports and their applications for extraction, separation and pre-concentration of trace metals have been reported [6,13,14]. Later, and in a parallel to this research, several publications dealing

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with functionalised silica-gel ligand systems and their applications were reported [6,15–22]. In addition to extraction and separation of metal cations from organic solvents and aqueous solutions, these functionalised systems have been used in many applications including chromatographic stationary phases [23,24] and heterogeneous catalysis [25–27].

Several spectroscopic techniques as well as other analytical methods have been used for structure determination of these ligand systems [28–34]. In this work, ethylenediaminetricetic acid immobilised ligand system was synthesised by pre-modification of the ethylenediamine silane agent with ethylchloroacetate followed by co-polymerisation with tetraethylorthosilicate. The resulting material was characterised using CP/MAS ^{13}C NMR spectra, FTIR spectra and XPS analysis. It is found that the ethylenediaminetricetic acid functionalised silica-gel (S-EDTA) showed high potential for the extraction and separation of Co^{2+} , Ni^{2+} and Cu^{2+} metal ions.

2. Experimental

2.1 Reagents and materials

Tetraethylorthosilicate, 3-(2-aminoethylaminopropyl)trimethoxysilane and ethylchloroacetate were purchased from Aldrich Chemical Company (USA) and used as received. Metal(II) solutions of the appropriate concentrations were prepared by dissolving the metal(II) chlorides (Analar grade) in deionised water. pH (3.5–5.5) was controlled by using acetic acid/sodium acetate buffer solutions.

2.2 General techniques

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo VG ESCALAB 250 instrument equipped with a monochromatic $\text{Al-K}\alpha$ 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 regions were recorded using pass energy of 10 eV. Charge compensation was achieved with an electron flood gun in the presence of argon at a partial pressure of 2×10^{-8} mBar. The energy and emission current of the electrons were 4 eV and 0.35 mA, respectively. Data acquisition and processing were achieved with the Avantage 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 peak areas and the corresponding Scofield sensitivity factors corrected for the analyser transmission function.

^{13}C CP-MAS solid state NMR experiments were carried out at room temperature on a Bruker MSL-400 MHz spectrometer at a frequency of 100.6 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 filled in a glove-box under dried argon atmosphere.

Analysis for carbon, hydrogen and nitrogen were carried out, using an Elemental Analyser 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 4000–400 cm^{-1} . The concentrations of metal ions in their aqueous solutions were measured using a Perkin-Elmer Analyst-100, spectrophotometer. 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-(ethylenediaminetriethylacetatepropyl)trimethoxysilane

Ethyl chloroacetate (18.37 g, 0.15 mol) was added dropwise to 3-(2-aminoethylaminopropyl)trimethoxysilane (11.12 g, 0.05 mol) in 25 cm³ ethanol with stirring. Stoichiometric amount of triethylamine was added to react with the liberated HCl. The mixture was refluxed with stirring at 100°C for 48 h and then cooled. A reddish yellow oily material was obtained after the ethanol had been removed. The functionalised silane coupling agent was identified by FTIR spectrum, where a strong absorption peak is observed at 1738 cm⁻¹ due to $\nu(\text{C}=\text{O})$ vibrations.

2.3.2 Preparation of ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA)

Tetraethylorthosilicate (20.8 g, 0.1 mole) in 25 cm³ absolute ethanol was stirred with 3-(ethylenediaminetriethylacetatepropyl)trimethoxysilane (0.05 mole) in the presence of 4.95 g 0.05 mol L⁻¹ HCl as catalyst. Gelation was occurred within 3 days. The gel material was dried in vacuum oven (0.1 torr) at 85°C, then crushed, sieved to 60–80 mesh. The material was washed with successive portions; 30 mL of 0.05 mol L⁻¹ NaOH, water, methanol and diethyl ether to remove the Et₃N–HCl. The product was dried for 12 h at 100°C in vacuum oven (0.1 torr). The immobilised ethylenediaminetriacetic acid ligand system, S-EDTA was obtained by hydrolysis of the immobilised ethylenediaminetriethylacetate system, S-EDTEA with 0.05 mol L⁻¹ HCl. The resulting material was washed and dried as described above.

2.4 Metal uptake experiments

A 100 mg sample of the functionalised silica-gel, S-EDTA was shaken with 25 cm³ of 0.02 mol L⁻¹ aqueous solution of the appropriate metal ions (Co²⁺, Ni²⁺ and Cu²⁺) using 100 cm³ polyethylene bottles. The metal ion concentration was determined 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 millimole or milligram of M²⁺/g ligand. Each study was performed at least in a triplicate. Metal uptake capacities were examined at different time intervals and pH values.

2.5 Column separation experiment

A glass column (250 mm long, 10 mm diameter) was washed sequentially with 0.1 mol L⁻¹ nitric acid, acetone and water, and then oven-dried. The functionalised ligand system (S-EDTA), (5.0 g, 60–80 mesh) was packed in the column. After each use, the column was flushed with 0.50 mol L⁻¹ HCl to remove any uneluted metal contaminant, followed by deionised water. Before any sample injection, the column was conditioned by passage of 50 cm³ of the appropriate eluent at a flow rate of 2.0 cm³ min⁻¹ to equilibrate the column. Solutions of metal ions (100 mg) were injected by means of micropipette. The pH of the

Table 1. Elemental analysis data for the silica-gel immobilised ester S-EDTEA and acid S-EDTA systems.

| Silica-gel | | % C | % H | % N | C/N |
|------------|----------|------|-----|-----|-----|
| S-EDTEA | Expected | 38.4 | 5.8 | 5.3 | 8.5 |
| | Found | 30.4 | 4.3 | 4.3 | 8.2 |
| S-EDTA | Expected | 23.2 | 3.4 | 4.9 | 5.5 |
| | Found | 21.8 | 3.5 | 4.4 | 5.8 |

Note: Analyses of expected results for the ester were based on complete reactions, while that of the acid form were based on the found results of the ester precursor.

eluent was controlled using the appropriate buffer. The eluent flow rate was in the range of 1.3–1.5 cm³ min⁻¹. The eluates were collected in fractions with a volume range 5–10 cm³. Each fraction was diluted to 25 cm³ and the amount of metal ion (mg) in each fraction was determined using atomic absorption spectroscopy.

3. Results and discussion

3.1 Preparation of the immobilised S-EDTA

The functionalised silica-gel ligand system, S-EDTA was prepared in two steps reaction based on direct sol-gel process:

- (i) The diamine silane coupling agent was functionalised using ethyl chloroacetate in 1:3 molar ratio, respectively. It can be assumed that the carboxymethylation of the amine groups was almost completed. This was evident from the FTIR and ¹³CNMR spectra discussed later.
- (ii) Hydrolytic polycondensation of the 3-(ethylenediaminetriethylacetatepropyl)trimethoxysilane with tetraethylorthosilicate, in 1:2 molar ratio, respectively. The functionalised ligand system S-EDTA was obtained by acidic hydrolysis of the immobilised ester material, S-EDTEA.

The elemental analysis for the S-EDTEA and S-EDTA are given in Table 1. The elemental results of the immobilised S-EDTA showed a lower carbon, hydrogen and nitrogen percentages than the expected values. This is probably due to the formation of low molecular weight oligomers, which perhaps was dissolved during the washing process [28,29]. The decrease of carbon percentage after treatment the S-EDTEA with diluted 0.05 mol L⁻¹ HCl solution is probably due to the conversion of ethyl acetate groups into acetic acid groups.

3.2 FTIR spectra

The FTIR spectra of the S-EDTEA ester and its acid form derivative, S-EDTA are given in Figure 1. The spectra showed three regions of absorption at 3500–3000, 1750–1600 and 1200–900 cm⁻¹ due to $\nu(\text{OH})$ or $\nu(\text{NH})$, $\delta(\text{OH})$ or $\nu(\text{C}=\text{O})$ and $\nu(\text{Si}-\text{O})$ vibrations, respectively [28–30]. The FTIR spectrum for the ester form functionalised silica-gel ligand system, S-EDTEA (Figure 1a) shows absorption bands at 3368 and 2940 cm⁻¹ due to

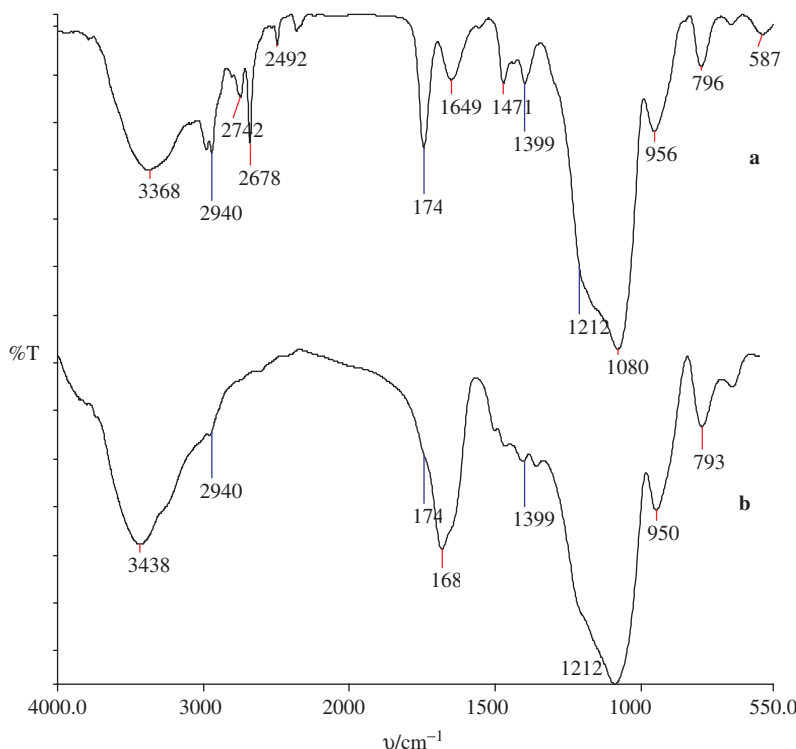


Figure 1. FTIR Spectra of (a) ethylenediaminetriethylacetate functionalised silica-gel (S-EDTEA); (b) ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA).

$\nu(\text{O-H})$ of the absorbed water and $\nu(\text{CH}_2)$ vibrations, respectively. The $\nu(\text{C=O})$ stretching vibration band that observed at 1743 cm^{-1} of the S-EDTEA ester was nearly disappeared and shifted to a lower frequency at 1682 cm^{-1} upon hydrolysis to the acid form, S-EDTA (Figure 1b). The presence of a shoulder at 1743 cm^{-1} provides that the hydrolysis reaction was not completely accomplished and that some ester groups were still unhydrolysed. The band at 1649 cm^{-1} is probably attributed to O-H bending vibration in which its intensity was enhanced in the acid form S-EDTA (Figure 1b). The absorption bands at 1080 and 795 cm^{-1} were attributed to Si-O-Si asymmetric and symmetric stretching vibrations, respectively [22].

3.3 ^{13}C CS-MAS NMR spectra

The CP/MAS ^{13}C NMR spectra for the immobilised S-EDTEA and S-EDTA ligand systems are shown in Figures 2(a) and (b), respectively. The spectrum of the immobilised ethylenediaminetriethylacetate silica-gel ligand system (S-EDTEA) (Figure 2a) shows three signals at 9.7, 20.0(sh) and 37.3 ppm were attributed to the three methylene carbons C1, C2 and C3, respectively. The broad signal at 164 ppm is assigned to the carbonyl C5. The two signals at 60.6 and 14.7 ppm are assigned due to C6 and C7, respectively of ethyl acetate group. The bulk broad signal centred at 57.4 ppm is associated with that of C4.

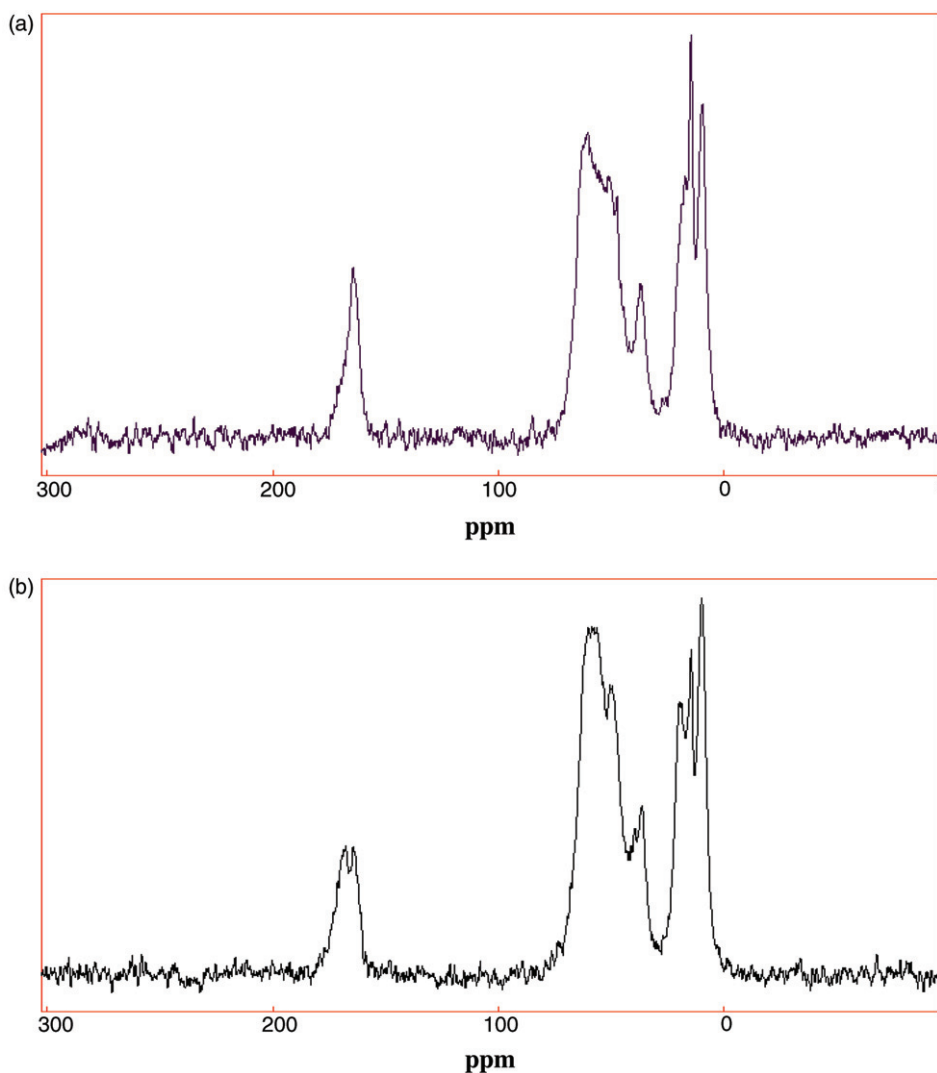


Figure 2. ^{13}C CS-MAS NMR of (a) ethylenediaminetriethylacetate functionalised silica-gel (S-EDTEA); (b) ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA).

The spectrum of S-EDTA immobilise ligand system shows a similar pattern as that of the S-EDTEA for which three methylene carbons signals at 10.1, 19.9, 36.7 ppm corresponds to carbons C1, C2 and C3, respectively (Figure 2b). The doublet signal at 164.5 and 168.7 ppm is assigned due to the presence of two different carbonyl groups of slightly different chemical shifts. The high shielding one at 168.7 ppm is probably associated with the carbonyl of the acid form, whereas the low shielding one at 164.5 ppm is associated to the carbonyl of the ester form. This provides evidence that not all the ester groups are hydrolysed due to deep incorporation in matrix pores. The signal at 57.4 ppm is assigned due to C4. The decreasing of signals intensities at 14.5 and 60 ppm, is probably due to a partial hydrolysis of ester groups upon treatment with HCl. The extra signals or

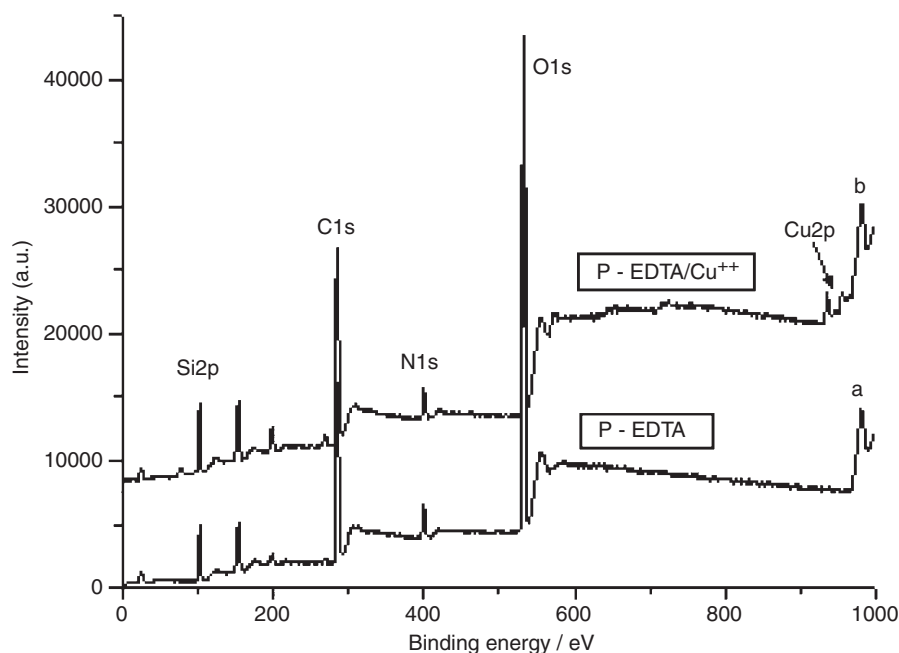


Figure 3. XPS survey scans of (a) ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA); (b) copper complex of ethylenediaminetriacetic functionalised silica-gel (S-EDTA/Cu²⁺).

shoulders at 15–18 and 47–51 ppm are probably due to residual alkoxyethyl groups (Si–O–CH₃ and Si–O–C₂H₅) from the silane agents, due to incomplete hydrolysis and condensation reactions [28–32].

3.4 XPS analysis

Figure 3 shows the survey spectra of S-EDTA as prepared and its Cu(II) complex. The main peaks Si2p, C1s, N1s and O1s are centred at *ca.* 103, 285, 400 and 532 eV, respectively (Figure 3a). In the case of S-EDTA after retention of copper ions (Figure 3b), an additional Cu2p doublet is observed at the 930–960 eV region.

The apparent surface compositions (atomic %) reported in Table 2 is in agreement with the elemental analysis. The XPS results showed a decrease in the carbon content as a result of treatment of the immobilised S-EDTEA with HCl. Indeed, either C/Si, C/N or C/(Si+N) ratios decrease by about 5% after ester hydrolysis. Considering the chemical structure of the ligand (two nitrogen atoms per ligand) and the atomic% of silicon and nitrogen, the ligand/Si ratio is about 0.17, that is one ligand per six silicon atoms. The presence of Cl (1.8%) in case of ester form S-EDTEA is probably due to the generated HCl during the course of the reaction between the amine silane agent and ethyl chloroacetate, which incorporated within the immobilised ligand matrix (Table 2).

The high resolution N1s region of S-EDTA is fitted with two components centred at 400.3 and 402.3 eV, which are assigned to the free neutral nitrogen atoms and their corresponding protonated form, respectively (Figure 4) [16,19]. The fraction of the N⁺ form levels off 22% and the neutral nitrogen form is about 78%.

Table 2. XPS data and surface composition (in atomic %) of S-EDTEA, S-EDTA and its Cu(II) complex.

| System | Element | C | Si | O | N | Cl | Na | Cu |
|-----------|---------------|------|------|------|-------|-------|--------|-------|
| S-EDTEA | | C1s | Si2p | O1s | N1s | Cl2p | Na1s | |
| | Core-line | 285 | 102 | 532 | 399.5 | 198.6 | 1073.8 | |
| | % Composition | 50.2 | 14.3 | 28.8 | 4.9 | 1.8 | 0.59 | |
| S-EDTA | | C1s | Si2p | O1s | N1s | | | |
| | Core-line | 285 | 102 | 532 | 399.5 | | | |
| | % Composition | 48.9 | 14.7 | 30.3 | 5.0 | 0.83 | 0.24 | |
| S-EDTA/Cu | | C1s | Si2p | O1s | N1s | | | Cu2p3 |
| | Core-line | 285 | 102 | 532 | 399.5 | | | 934.3 |
| | % Composition | 46.9 | 15.7 | 30.1 | 4.3 | 2.13 | | 0.92 |

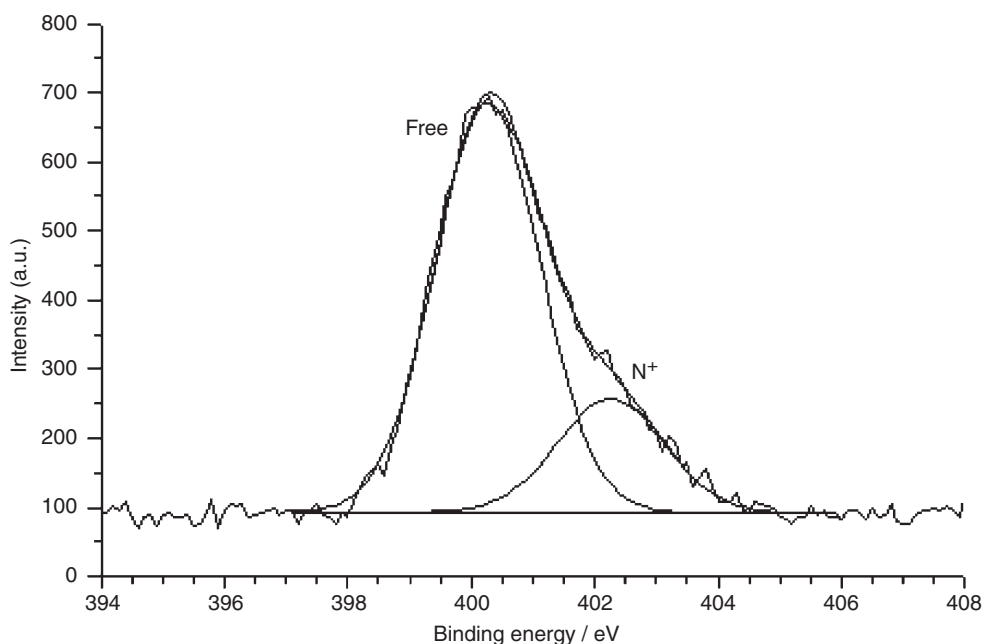


Figure 4. XPS peak fitted spectrum of N1s of ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA).

Figure 5 displays the fitted C1s region of the S-EDTA acid form system. The complex spectrum is fitted with five components centred at 284.3, 285, 286.2, 287.8 and 289.1 eV and assigned to Si-C (a), C-C/C-H (b), C-N/C-N⁺/C-O (c), C=O (d) and COOR (e), respectively. The latter component corresponds to COOR in S-EDTEA and which was remained unhydrolysed. Component (e), hereafter abbreviated by C₂₈₉, can be used as a chemical descriptor to account for the hydrolysis of the ester groups in S-EDTEA (C1s peak fitting not shown but similar to that of S-EDTA). The C₂₈₉/Si, C₂₈₉/N and C₂₈₉/(Si+N) ratios were

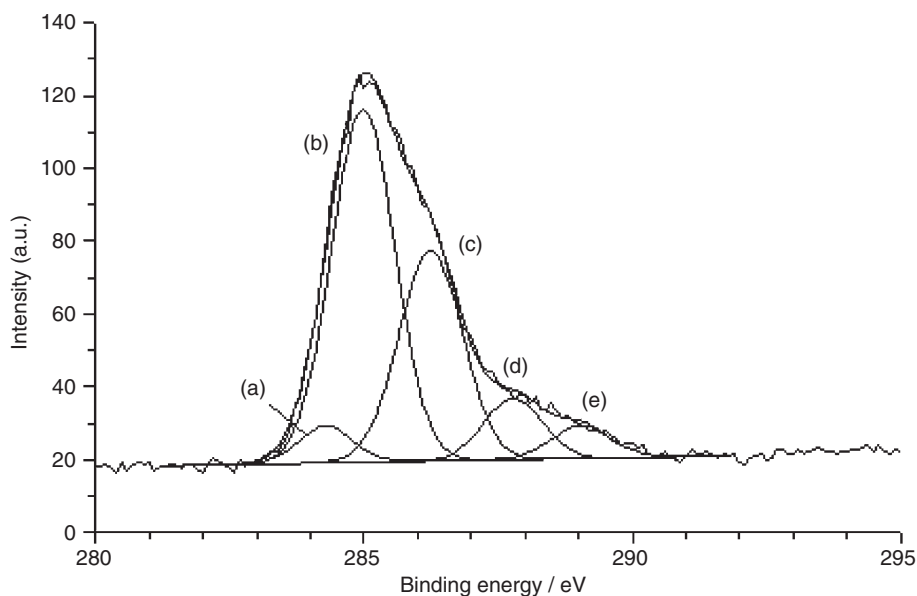


Figure 5. XPS peak fitted spectrum of C1s of ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA).

decreased by 21.7, 22.8 and 22.9%, respectively, after the hydrolysis of S-EDTEA to obtain the S-EDTA ligand. Such a hydrolysis results in removal of ethyl groups and therefore to a general relative increase of the Si and N atom percents (Table 2).

3.5 Batch method

3.5.1 Effect of shaking time on metal uptake

The metal ion uptake capacity (Co^{2+} , Ni^{2+} and Cu^{2+}) was determined by shaking the functionalised ligand system S-EDTA with buffered solutions of the metal ions. Measurements were carried out at different time intervals. Figure 6 illustrates the uptake capacity of copper ion as an example. The results show that, the metal uptake is reached the equilibrium after 48 h where maximum uptake is obtained. Similar results were found for Co^{2+} and Ni^{2+} metal ions.

3.5.2 Effect of pH

The effect of the pH on the uptake of Co^{2+} , Ni^{2+} and Cu^{2+} ions is shown in Figure 7. The results showed an increase of metal ion uptake with increasing pH reaching its maximum at pH 5.2. Low uptake capacity occurs at lower pH values due to protonation of amine species and undissociation of the acetate groups [35]. It is clear that the metal uptake starts to decrease at higher pH values. This is due to the formation of hydrolysed species of metal ions [35]. Maximum metal uptake capacities of the different metal ions are given in Table 3.

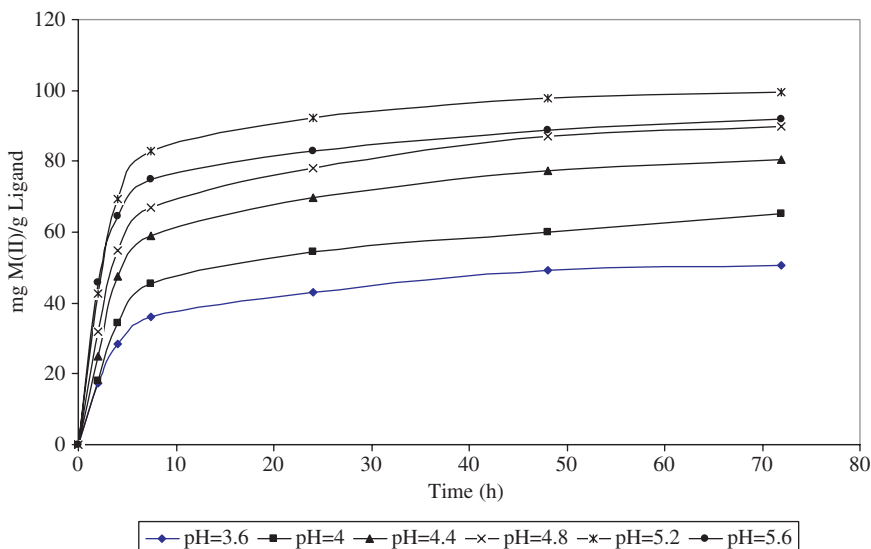


Figure 6. Uptake of Cu(II) ions by ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA) vs. time.

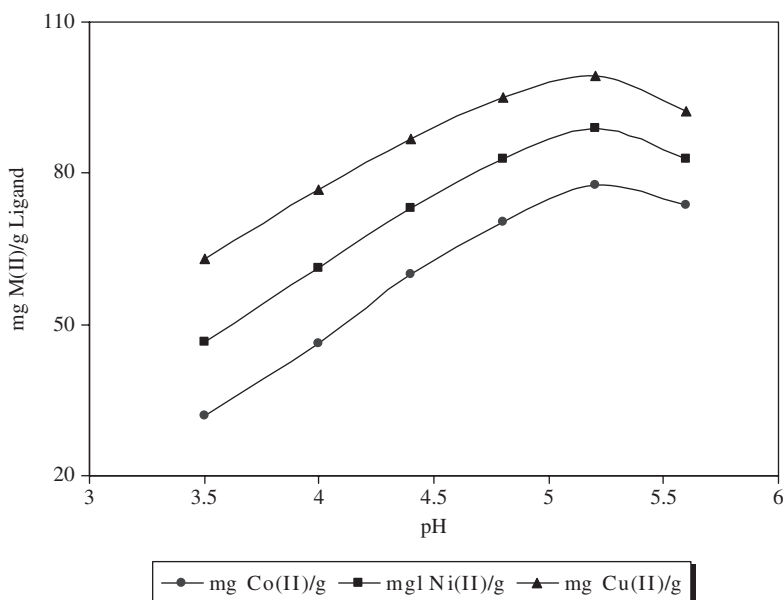
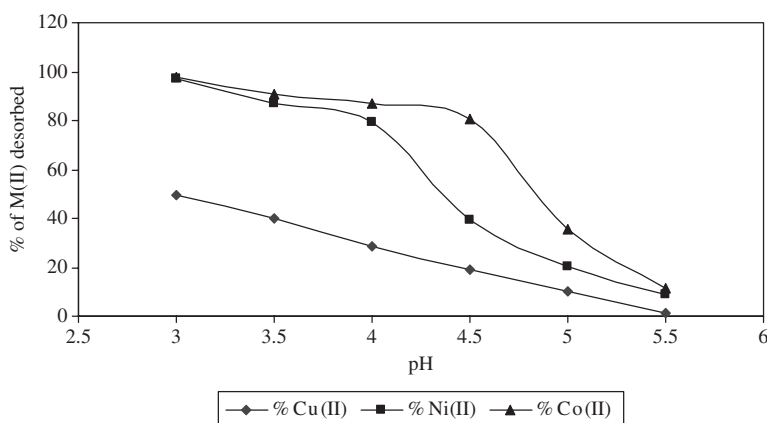


Figure 7. Uptake of metal ions by ethylenediaminetriacetic acid functionalised silica-gel (S-EDTA) vs. pH values, (72 h shaking time).

From the nitrogen analysis given in Table 1 (N% 4.4, 1.57 mmol L^{-1}) and considering the maximum metal ion uptake of the different metal ions it is possible to suggest that nearly 1:1 ligand to metal complexes was formed in case of Cu^{2+} and Ni^{2+} . Lower ratio was obtained for Co^{2+} because probably not all functional groups were accessible

Table 3. Maximum metal uptake capacities for the different metal ions.

| Maximum uptake | Co ²⁺ | Ni ²⁺ | Cu ²⁺ |
|---------------------|------------------|------------------|------------------|
| mg M(II)/g ligand | 77.6 | 89.1 | 99.4 |
| mmol M(II)/g ligand | 1.32 | 1.52 | 1.56 |

Figure 8. Percentage of metal ion desorbed vs. pH (5 g bed material, flow rate = 1.3–1.5 cm³ min⁻¹).

for binding with Co²⁺ ions. Based on similar systems, these ligand systems form an octahedral geometry with two bidentate ligands (N₂O₂) and two water molecules.

3.6 Column method

3.6.1 Effect of pH on metal ion desorption

A solution mixture (100 cm³) containing 250 mg of each of Co²⁺, Ni²⁺ and Cu²⁺ metal ions was eluted. Figure 8 shows that the percent of metal ions desorbed as a function of pH value. It is observed that the percent of metal ion desorbed increases by decreasing pH value. Low amounts of metal ions were desorbed by elution at pH 5.5. It was found that about 50% of Cu(II) ions was desorbed from the column at pH 3 while small percentages were desorbed at pH 4.5–5.5 range. In case of Ni(II) maximum amount desorbed was found at pH 3–4 range, where maximum amount of Co(II) ions desorbed reached at pH 3–4.5 range. The percent of metal ion desorbed *versus* pH appears in the following order:



This order is consistent with the Irving William series of the formation constant [36].

3.6.2 Metal ions separation

Separation of a mixture of metal ions Cu(II), Ni(II) and Co(II) was performed by elution with buffer solutions of different pH values. Three bands were observed by

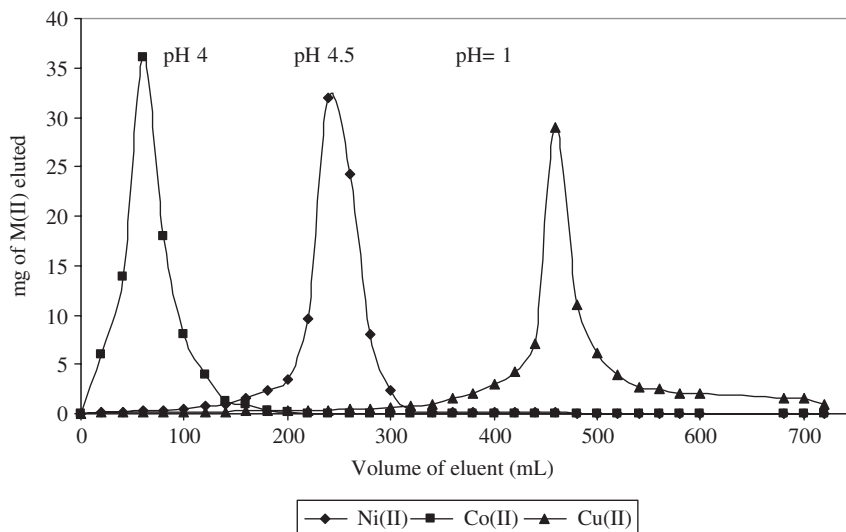


Figure 9. Separation of Co^{2+} , Ni^{2+} and Cu^{2+} as a function of eluent volume by pH control (5 g bed material, flow rate = $1.3\text{--}1.5\text{ cm}^3\text{ min}^{-1}$).

pH control. A dark blue colour band of Cu(II) was observed upstream followed by green and violet bands for Ni(II) and Co(II) , respectively. These metal ions were eluted approximately cleanly from the mixture by pH control. Figure 9 shows the separation of Cu(II) , Ni(II) and Co(II) metal ions as a function of elution volume at variable pH values. Separation of Co(II) , Ni(II) and Cu(II) metal ions was performed by decreasing the pH value, where similar results were observed [18]. The flow rate of eluent was $1.3\text{--}1.5\text{ cm}^3\text{ min}^{-1}$. The desorbed amounts of metal ions were calculated from the total fractions of 720 cm^3 . Three well resolved peaks of cobalt, nickel and copper ions were obtained with a very small portion of overlapping, at pH 4, 4.5 and 0.1 N HNO_3 (pH = 1), respectively. This promises the ligand system to be efficient in a clean separation of these metal ions.

4. Conclusions

New immobilised silica-gel ethylenediaminetriacetic acid ligand system, S-EDTA was prepared through treatment of 3-(ethylenediaminetriethylacetatepropyl)-trimethoxysilane agent with TEOS followed by acidic hydrolysis of the solid product. The immobilised S-EDTEA ester form and S-EDTA acid form ligand systems were well characterised using the CP/MAS ^{13}C NMR, FTIR and the XPS analysis. The immobilised S-EDTA silica-gel ligand system exhibits high potential for the extraction and separation of Co^{2+} , Ni^{2+} and Cu^{2+} metal ions from aqueous solutions.

Acknowledgement

The authors wish to thank Mrs Carole Connan for her assistance with XPS measurements.

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