

Synthesis, Characterization and Adsorption of Metal Ions on New Silica-Gel Organofunctionalized Compound

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Silica gel chemically modified with organic groups is widely used as an adsorbent for metal ions. In this investigation, silica gel was chemically modified with 3-chloropropyltrimethoxysilane and reacted with 2-aminothiophenol in order to yield an aromatic group immobilized on the silica gel surface and produced a compound for adsorbing Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Tl^+ and Tl^{3+} ions, which prepared in buffer solution at physiological pH. The characterization of new compound and its capability towards extraction of the above metal ions were studied and evaluated by a batch method. This compound showed high performance toward Fe^{3+} extraction, where its adsorption determined to be 98.1%. The order of increasing the metal ions uptake process satisfactorily coincides with increasing the hardness of these metal ions.

Key Words: Modified silica gel, Surface adsorbent, Metal ions.

INTRODUCTION

The pollution of heavy metal ions is an important physiological and environment concern due to their high toxicity. Heavy metal ions are toxic and harmful even at low concentrations. The efficient clean up technology emerges to be on the edge of necessity for bio and environmental chemists.

Adsorption is often used processes for removal of heavy metal ions. A special emphasis was given on designing the synthesis of adsorbents with desirable surface properties^{1,2}. The effort for synthesis was focused on the modification of silica in order to achieve highly selective materials for pre-concentration, adsorption and separation of heavy metal ions^{3,4}. Silica gel is an amorphous polymer compound of inert siloxane groups (Si-O-Si) with silanol groups (Si-OH) distributed on the surface^{5,6}. Chelating groups are bonded to silica gel after surface activation⁷⁻⁹. Thus, chemical bonding of functional groups offers a unique advantage. Since the detachment of the grafted molecule is prevented due to the strong covalent binding of the

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molecule to the substrate. Silica gel as a matrix for immobilizing organic molecule is highly developed¹⁰. It has been shown on the literature that, in most cases, the amine function is covalently grafted onto silica^{11,12}. In addition, silica gel is the most commonly used polar inorganic sorbent, due to its relative inertness, high mechanical and thermal stability, good adsorption capacity and ease of preparation of derivatives with different possible modifications of the surface with an impregnation medium or reagent¹³⁻¹⁵. Modification of the silica gel surface with donor atoms, such as N, P, O and S is recently aimed at improving the adsorption properties of silica gel as well as the incorporation of particular selectivity character in to the modified silica gel phases toward certain metal ions adsorption¹⁶. The immobilization of chelating compounds containing donor atoms on the silica gel surface can occur *via* chemical bond formation between the organic modifier and one or more amino-or chloro-modified silica gel phases¹⁷.

Several other newly modified silica gel phase were synthesized and applied as normal or selective solid phase extractors for many toxic and other metal ions. Some advantages of the modified solid phase extractors compared with the classical liquid extractors were reported¹⁸⁻²¹.

Solid phase extraction offers a number of advantages such as (i) higher enrichment factor, (ii) absence of emulsion formation, (iii) minimal costs due to low consumption of reagents, (iv) minimal waste generation, (v) flexibility of reagents, (vi) reusability and (vii) eco-friendliness^{22,23}. In addition, the use of inorganic supports have several advantages such as (a) good selectivity, (b) no swelling, (c) rapid adsorption of metal ions and (d) good mechanical stability²⁴.

In this research, a selective silica gel, chemically modified absorbent developed, in view of the growing interest in modification of silica gel. In present communication, a method for synthesizing modified silica gel compound, 3-2-aminothiophenolpropyltrimethoxysilane, as an inorganic solid support is reported. The characterization of such a new compound and its affinity were studied towards extraction and separation of Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Tl⁺ and Tl³⁺ ions from aqueous media at physiological pH.

EXPERIMENTAL

The used silica gel was of TLC grade (60 Å diameter), cobalt(II) nitrate 99%; thallium(III) acetate 95%; iron(III) chloride 99%; copper(II) nitrate 99%; zinc(II) nitrate (pure); iron(II) chloride 99%; cadmium(II) sulfate 99%; sodium chloride 99.5%; sodium hydrogen carbonate 99.5%; toluene 99%; nickel(II) nitrate 99%; 2-aminothiophenol; *tris*(hydroxymethyl)aminomethane (*tris*) 99.2%; 3-chloropropyltrimethoxy silane 98% and HCl were purchased from Merck, thallium(I) acetate 97% was

purchased from Fluka. FTIR, unicam, model Mattson 1000; pH meter, Metrohm 713; Centrifuge BHG and flame atomic absorption spectrophotometer, Varian 220, were used.

Preparation of silica-propylchloride matrix: This matrix was prepared as described²⁵. 31.9 g silica gel was initially dried at 120°C for 24 h. This dried silica gel was suspended in 100 mL toluene and then 32 mL (MeO)₃ Si CH₂CH₂CH₂Cl was added to it. The mixture was refluxed for 7 h. The solid was filtered and washed with toluene (soxhlet extraction for 24 h). Finally, the obtained silica propyl chloride was dried in air.

Preparation of SIL-CH₂CH₂CH₂ (C₆H₇NS) (I): A 1 g (0.0042 mol) silylated SIL-CH₂CH₂CH₂Cl was suspended in 100 mL toluene and then 0.6 mL (0.0042 mol) 2-aminothiophenol was added to it. The mixture brought to reflux with stirring for 24 h. The solid was filtered and washed with toluene (soxhlet extraction for 24 h). Finally, the obtained product SIL-CH₂CH₂CH₂ (C₆H₇NS) (I) was dried in air.

Preparation of tris buffer tris(hydroxymethyl)aminomethane: For preparation of 1 lit *tris* buffer, 12.21 g (0.10 mol) of *tris* compound; 2.35 g (0.04 mol) sodium chloride and 2.11 g (0.02) sodium hydrogen carbonate were dissolved in distilled water and the pH of solution was adjusted at 7.4 by conc. HCl and the buffer solution was stored at 3-5°C.

Adsorption of metal ions by SIL-CH₂CH₂CH₂ (C₆H₇NS) as adsorbent at physiological pH: The cations Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ as nitrates, Fe³⁺ as a chloride, Tl⁺ and Tl³⁺ as acetates and Cd²⁺ as sulfate were adsorbed on the surface of the compound I in *tris* buffer solution at 298 K and physiological pH.

The calibration curves were built at linear range at 0.5-3.0 ppm for Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ solutions and at 5.0-30.0 ppm for Fe³⁺, Tl⁺ and Tl³⁺ solutions. All these solutions were prepared in *tris* buffer from 100 ppm stock solutions of each metal ion and 100 mL of each was prepared. Their concentrations were determined by flame AAS.

In order to determine the amount of adsorbed metal ions on the modified silica gel surface of the compound I by batch method, 0.1 g of the compound I was suspended in 20 mL solution of 20 ppm metal ions for Fe³⁺, Tl⁺ and Tl³⁺ and 20 mL solution of 1.5 ppm metal ions for Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺. Each sample was stirred for 2 h and then filtered. When it was necessary, centrifuge technique was used and the amounts of cations in the moderates were measured by FAAS.

RESULTS AND DISCUSSION

Characterization of compound I: Fig. 1 shows schematically reaction for preparation of SIL-2-aminothiophenol from silica-chloropropyl

and 2-aminothiophenol. The infrared spectra were obtained after drying the samples and KBr at 120°C for 3 d. Preparation of tablets were accomplished by mixing 5 mg material mixed with 500 mg of KBr. The infrared spectra of pure silica gel and modified silica show small differences were observed in relation to the numbers and intensities of the bands. The same behaviour have been previously observed for the other anchored process²⁶. The infrared spectra confirm the presence of 2-aminothiophenol groups bond to the silica surface. The absorption band observed at 2361 cm^{-1} is due to the C-H stretching of aromatic olefins. The other two bands of interest are observed at 1617 and 1492 cm^{-1} , which could be assigned to the C-N stretching and C-H bending, respectively. The absorption band observed at 678 cm^{-1} is due to the C-S stretching. Between 2500 and 3800 cm^{-1} , the spectra exhibited a broad featureless band corresponding to the stretching vibrations of the surface silanols Si-OH perturbed by hydrogen bonding either intramolecularly or with adsorbed water, but two bands appeared around 3429 cm^{-1} is due to NH_2 stretching. Below 1500 cm^{-1} , the spectra exhibit a broad and intense band around 1100 cm^{-1} , characteristic of the asymmetric stretching vibration of Si-O-Si and a less intense band around 900 cm^{-1} due to Si-O-Si symmetric stretching vibrations.

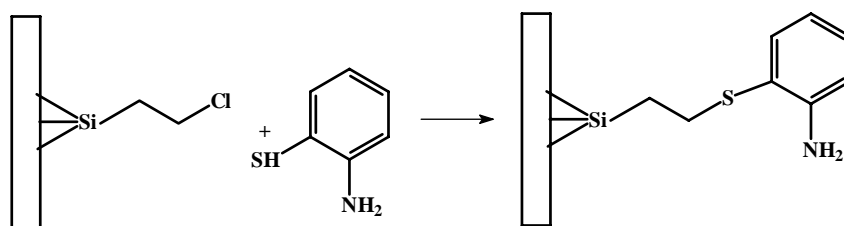


Fig. 1. Schematic reaction for preparation of SIL-2-aminothiophenol from silicachloropropyl and 2-aminothiophenol

The quantity of 2-aminothiophenol groups attached to the silica gel surface was determined by carbon and nitrogen analysis. The chemical analysis showed 11.063 % (0.922 mol) carbon and 1.776 % (0.127 mol) nitrogen. According to these obtained results, the mole ratio of carbon to nitrogen was found to be 7.25 which is less than the calculated mol ratio of carbon to nitrogen which is 9 (C/N, 9/1). This is probably due to the unreacted SIL- $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ which has not been converted to SIL- $\text{CH}_2\text{CH}_2\text{CH}_2\text{-(C}_6\text{H}_4\text{NS)}$. Therefore based on these results the amount of nitrogen compare to carbon is less and caused the mol ratio of C/N decreases.

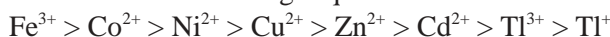
Metal uptake by compound I: In order to determine the amount of metal ions uptake by compound I, the calibration curves of absorption vs. concentrations were built. These curves were linear and the Bear-Lambert

law obeys for Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} in the range of 0.5-3.0 ppm and for Fe^{3+} , Tl^+ and Tl^{3+} in the range of 5.0-30.0 ppm. According to the measured values, adsorption percentages of these metal ions by compound **I** were calculated and the results were summarized in Table-1.

TABLE-1
PERCENTAGE OF METAL IONS ADSORPTION BY COMPOUND **I** AT pH 7.4

Metal ion	Absorption (%)	Metal ion	Absorption (%)
Fe^{3+}	98.1	Zn^{2+}	23.3
Co^{2+}	34.7	Cd^{2+}	13.3
Ni^{2+}	27.3	Tl^{3+}	9.0
Cu^{2+}	24.7	Tl^+	7.5

Evaluation of these results, reveals that the metal ions uptake by compound **I** varies in the following sequence:



Fe^{3+} is the best metal ion uptake by compound **I** due to its hardness. This is in consistent with hard-soft acids, bases (HSAB) principle of Pearson^{27,28}. Table-1 indicates that the best metal ion uptake is Fe^{3+} , because of its hardness. In the case of Co^{2+} , Ni^{2+} and Cu^{2+} the importance of both inherent acidity and hard-soft factor of the Irving Williams series is shown. The Irving-Williams series of increasing stability from Co^{2+} , Ni^{2+} and Cu^{2+} is a measure of increasing inherent acidity of the metal (largely due to decreasing size). Superimposed upon this, is a hardness-softness factor in which the softer species coming later in the series (greater number of *d*-electrons)²⁹. 2-Aminothiophenol grafted to the surface of $\text{SiO}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ by replacing Cl group with 2-aminothiophenol from sulfur atom, because the sulfur atom is a better nucleophile than nitrogen atom. The modified surface included a ligand with nitrogen donor atom which is hard and the sequence of metal ions uptake is confirm by (HSAB) principle of Pearson^{27,28}. Thus the complexes of softer acids such as Cd^{2+} is considerably weaker thus the amount of metal ion uptake is low. In the case of Tl^+ , due to its softness the complex is weak. In addition, due to the single charge of the cation, also result in a decrease of cation-ligand electrostatic interaction, the bond formation with the cation is weak, so the amount of the metal ion uptake is much lower, but for Tl^{3+} the metal ion uptake is slightly greater.

Conclusion

According to Table-1, it is well known that the best metal ion uptake is Fe^{3+} by compound **I** at physiological pH. Therefore, it can be used for adsorption of excess iron ion from human body as a drug for iron overload deceases.

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