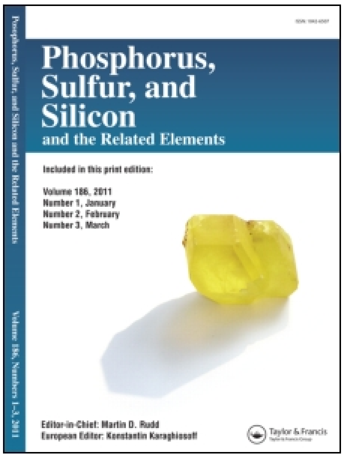

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Surface Modification of Porous Silica with Bi-thiophene Tripodal Ligand and Aplication to Adsorption of Toxic Metal Cations

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SURFACE MODIFICATION OF POROUS SILICA WITH BI-THIOPHENE TRIPODAL LIGAND AND APPLICATION TO ADSORPTION OF TOXIC METAL CATIONS

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The immobilization of a thiophene-based tripodal ligand, with a donor sulfur, on the surface of an epoxide group containing a silica gel phase for the synthesis of a newly functionalized material based on porous silica-bound bi-thiophene tripodal ligand (SGBT) is described. The modified silica surface was characterized by ^{13}C NMR of a solid sample, elemental analysis, and infrared spectra. This new material was also studied and evaluated by determination of the surface area using the BET equation, the adsorption and desorption capability using the isotherm of nitrogen and BJH pore sizes, respectively. The target material exhibits good thermal stability as determined by thermogravimetry curves. The synthesized material was utilized in column and batch methods for adsorption of Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, K^+, Na^+, and Li^+, and the material exhibits an affinity only towards toxic heavy metals.

Keywords Adsorption; chemical synthesis; metals; silica modification; thiophene

INTRODUCTION

Silica gel is an amorphous inorganic polymer with high concentrations of silanol groups (Si-OH) distributed on its surface.[1,2] The active hydrogen atom of the silanol groups has the ability to react with organosilyl groups in order to give some organic nature to the silica inorganic support.[2,3] These covalently bonded groups are resistant to removal from the surface by water or organic solvents.[2,3]

The principal success of such inorganic solid surfaces modified with organofunctional groups is the immobilization of the desired reactive atomic group, which causes a great versatility of this surface in developing various functions.[4,5] Thus, chemically modified silica gel can be used in various areas of chemistry, such as concentration and separation processes,[6–9] ion exchange,[10] chemical sensors,[11–13] heterogeneous catalysis,[14] biotechnology,[15] and electrochemistry.[12]

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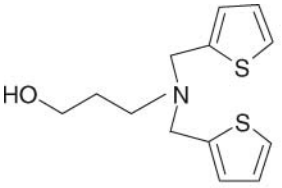
The development of methods to determine traces of metals belonging to the toxic elements that are dangerous for human health has been an aspect of interest in the research. Thus, due to environmental concerns, efficient separation, preconcentration, and recovery of metal ions from industrial wastes as well as from raw materials, are gaining more importance.[16]

In this context, a relevant goal for the modification of the silica surface is to establish appropriate experimental conditions to anchor molecules that can then extract traces of undesired cations dispersed into the water. Indeed, the most commonly attached chelate ability for this purpose is devoted to donor atoms, such as oxygen, nitrogen, and sulfur, that have a large capacity to form complexes with a series of metal ions, forcing, in some cases, a distinguishable selective extraction property.[17–21]

This article describes the synthesis and characterization of a new material obtained by grafting a functionalized 3-[bis(2-thienylmethyl)amino]propan-1-ol (Scheme 1) on porous silica. This ligand normally acts in a mono- or bidentate fashion, forming thus a five-membered chelating ring, which is part of several rings when the whole ligand is considered. The immobilization of this ligand on silica gel was carried out through a long arm spacer, 3-glycidoxypropyltrimethoxysilane, in order to facilitate the contact between the receiver and the metal ion. This intermediate arm was recently used as silylating agent in the immobilization of many structures on silica gel.[22,23]



(1)

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Scheme 1 Functionalized bi-thiophene tripod[24] immobilized on silica gel surface.

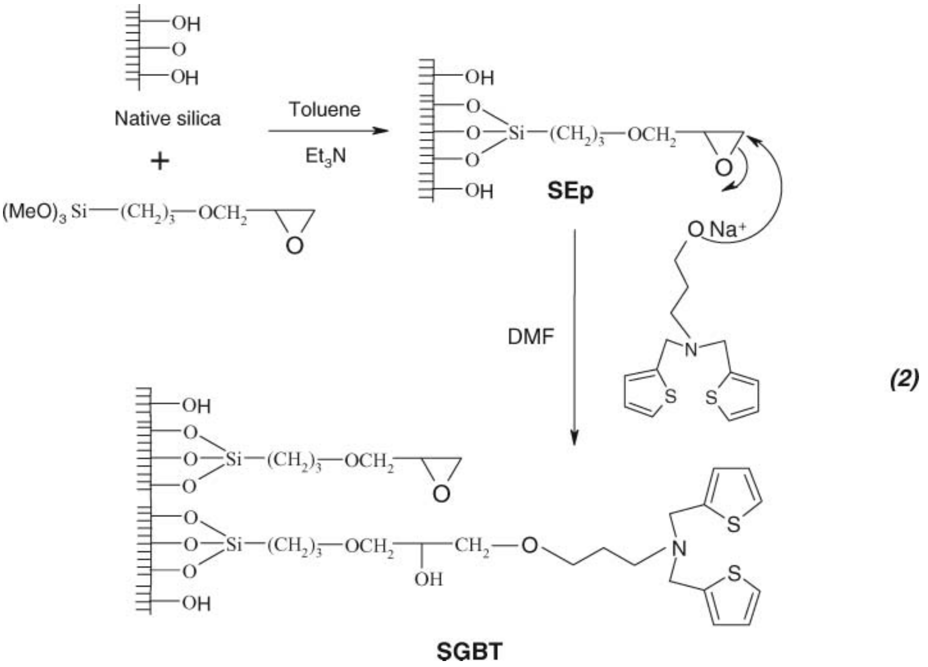
The purpose of this study is to develop a new material that can be operated indefinitely without loss of the expensive ligand by preserving its chelating properties.

The new material was applied for separating and extracting toxic heavy metals and alkaline metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, K^{+}, Na^{+}, and Li^{+}) from aqueous solutions. The results were compared to those obtained with the analogue free organic monomer **1** in liquid–liquid extraction with respect to capacity and selectivity. The percentages of complexation were determined by atomic absorption measurements.

RESULTS AND DISCUSSION

Characteristics of the Materials

The reaction that produces the modified silica gel is shown in Scheme 2. The first stage shows the reaction of the silylant precursor, 3-glycidoxypropyltrimethoxysilane, with activated silica gel to yield the epoxy-silica (SEp). In the second stage, the bi-thiophene tripodal salt is chemically incorporated onto the epoxy-silica, where the epoxide group is opened to form the SGBT product.



Scheme 2 Synthesis method of the modified silica gel.

The number of moles of the immobilized epoxy pendant chains covalently bonded on silica was determined both by elemental analysis of carbon (giving 787 μmol g^{-1}) and by titration with sodium thiosulfate (772 μmol g^{-1}) as described in the literature.[25] The two methods lead to the concordant results at 780 ± 10 μmol g^{-1} of epoxide groups per gram of silica. In IR spectroscopy, the strong decrease of the large ν_{OH} adsorption around 3200 cm^{-1}and the appearance of a $\nu_{\text{C-H}}$ sharp band at 3030 cm^{-1} attested to the grafting of the epoxide groups on the silica surface. Another characteristic band assigned to silanol groups ($\nu_{\text{Si-OH}}$) was observed near 965 cm^{-1} for the activated silica. This band was considerably reduced, after immobilization of the silane alkoxide groups, as expected in such immobilization processes. The ^{13}C solid-state NMR spectrum recorded after hydrolysis of the epoxide groups to diols with diluted sulfuric acid (pH 2, 90 °C, 1 h) also shows the formation of five peaks, at 9, 24, 51, 63, and 72 ppm which, were attributed to carbons of the pendant groups: $\mathrm{Si{-}\underline{CH_2}}$, $\mathrm{CH_2{-}\underline{CH_2}{-}CH_2}$, $\mathrm{\underline{CH}{-}OH}$, $\mathrm{\underline{CH_2}{-}OH}$, and $\mathrm{\underline{CH_2}{-}O{-}\underline{CH_2}}$, respectively.

In the target product, the amount of bi-thiophene tripod on the anchored silica gel surface, as determined both by elemental analysis and by thiosulfate method, gives ~210 μmol g^{-1} corresponding to 27% yield.

The thermogravimetric curves (Figure 1) reflect the thermal stability of these new materials. The quantity decomposed in each stage confirms the amount of the compounds grafted on silica gel. The curve involving epoxide groups presented a mass loss, after the drainage of physically adsorbed water, of 12.84% in the 150–780°C. The final material showed an increase of mass loss allotted to the decomposition of the organic fraction immobilized on the surface of silica gel, together with the condensation of the remaining

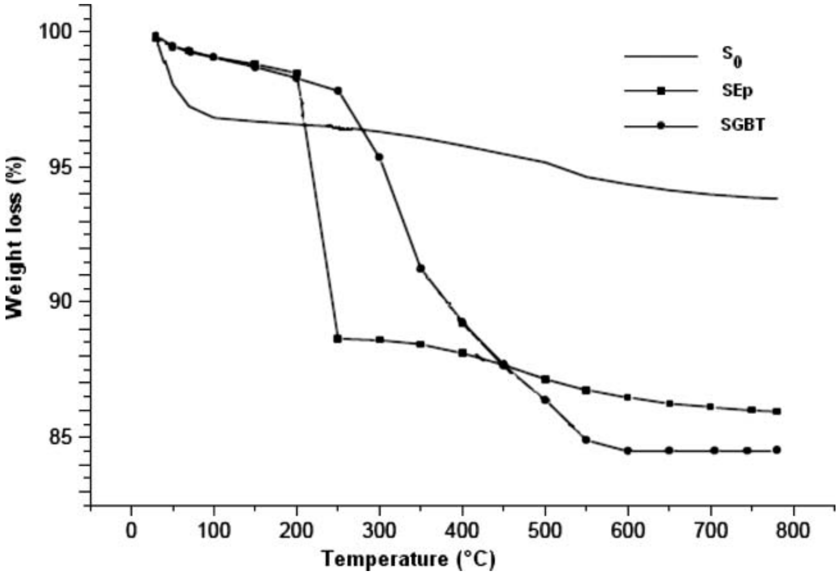


Figure 1 Thermogravimetric curves of native silica (So), epoxy-silica (SEp), and silica immobilized bi-thiophene tripod (SGBT).

silanol groups. The pronounced increase in mass loss for the SGBT matrix reflects the higher amount of the anchored organic groups.

The density of the organic groups covalently attached to the inorganic silica backbone modifies the original characteristics of the silica surface. Thus, the initial specific surface area of 550 m^2 g^{-1}decreases as the bi-thiophene tripod immobilization takes place to give 291.17 m^2 g^{-1} determined through the Brunauer–Emmett–Teller (BET) equation. The pore volume and the pore diameter of SGBT determined by nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters methods decrease also to give 0.722 cm^3 g^{-1} and 2.895 nm respectively.

The proportion of functional groups attached on the surface, N_0, was 0.21×10^{-3} mol g^{-1}. Assuming that the molecules uniformly cover the surface and knowing the specific surface area (S_{BET}), the average density, d, of the attached molecules, and the average intermolecular distance, l, can be calculated by applying the following equations:[26]

$$d = N.N_0/S_{\mathrm{BET}}$$
$$l = (1/d)^{1/2}$$

where N is the Avogadro's number. The calculated values are $d = 0.4$ molecule nm^{-2} and $l = 1.6$ nm.

Complexing Properties

The complexing properties of the new modified surface SGBT towards different metal ions were evaluated both by the batch method and the column method. It was checked that the precursor epoxide-substituted silica (SEp) was unable to bind the metal ions under

Table I Sorption capacities toward mercury, cadmium, lead, and copper

			Capacity towards Hg			Capacity towards Cd			Capacity towards Pb			Capacity towards Cu		
Sample	Specific area (m^2 g^{-1})	Amount grafted (μmol g^{-1})	μmol g^{-1}	mg g^{-1}	Yield[a] (%)	μmol g^{-1}	mg g^{-1}	Yield[a] (%)	μmol g^{-1}	mg g^{-1}	Yield[a] (%)	μmol g^{-1}	mg g^{-1}	Yield[a] (%)
So[b]	550	0	16.2	3.2	—	13	1.4	—	0	0	0	0	0	0
SEp[c]	311	780	0	0	0	0	0	0	0	0	0	0	0	0
SGBT[d]	291.17	210	69.3	13.9	33	29.4	3.3	14	35.7	7.4	17	31.5	2	15

[a] Yield of complexation calculated as μmol of metal per μmol of bi-thiophene tripod immobilized.

[b] So: native silica.

[c] SEp: epoxy modified silica.

[d] SGBT: silica grafted bi-thiophene tripod.

Table II Comparison of the % yields of extraction for liquid–liquid (LLE) and solid–liquid (SLE) extraction (calculated as μmol of metal per μmol of bi-thiophene tripod) in individual and in competitive mode

	Mercury	cadmium	Lead	Copper	Zinc	Potassium	Sodium	Lithium
LLE[a]	27	11	14	12	0	0	0	0
SLE[b]	33	14	17	15	0	0	0	0
SGBT[c]	34	11	13	10	0	0	0	0
S[d]	—	3.09	2.61	3.40	—	—	—	—

[a] Liquid–liquid extraction of individual metal ions.

[b] Solid–liquid extraction of individual metal ions.

[c] Solid–liquid extraction of competitive metal ions.

[d] Hg(II)/cation selectivity ratio in competitive conditions.

study, even by physical sorption. This result justifies the importance of the grafted tripodal ligand in the adsorption of metals.

On the other hand, no complexation was observed towards alkaline metal ions and Zn^{2+} ion. This result is in analogy with our previous work,[24,27–37] in which acyclic ligands, with nitrogen and sulfur donor atoms, extract only the transition metal cations, while the macrocyclic compounds are expected to form stable complexes both with transition and alkali metals because of their strong cohesion forces.

For mercury, cadmium, lead, and copper, the results are expressed in terms of μmol of metal bound per g of sorbent, mg of metal per g of sorbent, and the yield of complexation is expressed as μmol of metal per μmol of bi-thiophene tripodal ligand (Table I).

The study of the individual complexation of each metal in batch method shows that the solid sorbent SGBT is as efficient as the liquid–liquid extraction process (Table II). This result reflects that the formation of the bi-thiophene tripod-metal complex is not affected by the grafting on the silica surface. The length and the flexibility of the spacer arm are sufficient to allow a good accessibility to the complexation sites. We also notice that the plateau was reached after only about 2 min of contact (Figure 2). However, and with this pH 7 desired for our project, the complexing ability is rather far from the maximum theoretical

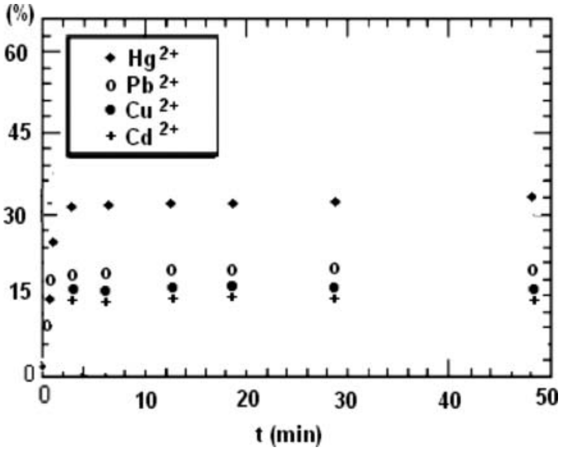


Figure 2 Kinetics of metal ion sorption on bi-thiophene tripod-loaded silica gel.

Table III Complexation/regeneration using sample SGBT and mercury

Cycle number	Capacity (μmol g^{-1})
1	33
2	32
3	34
4	33

value. The higher affinity of this sorbent towards mercury (II) ion is not surprising if the high donor properties of nitrogen and sulfur towards this metal are considered.

The result in competitive solid–liquid extraction measurements (Table II) are in perfect agreement with the obtained values by separate cation extraction. Indeed, in this competitive extraction, we notice a high affinity only for mercury with zero extraction of alkali cations and Zn^{2+} ion and a weak extraction of other bivalent metals. We can thus conclude that this sorbent is selective with the extraction of Hg(II). Moreover, the Hg(II)/cation selectivity ratio in these competitive conditions shows the good mercury selectivity.

The column method allows the retention only of toxic metals, and thereafter the separation of the mercury from the others (Cd^{2+}, Pb^{2+}, Cu^{2+}). Indeed, a set of solutions (volume: 50 mL) containing an equimolar quantity of the eight metal ions was taken. The optimum flow rate for loading these metal ions is 3 mL min^{-1}. In analogy to the batch method, no retention was observed towards zinc and alkali metals. The use of 4–5 mL of HCl 6 N allows the detachment of the less stable cadmium, copper, and leads complexes, whereas mercury is desorbed by elution of 18–20 mL of HCl 6 N at flow rate $\approx$1.5 ml min^{-1}. This is probably due to the strong stability of the complex formed by this cation and the ligand used.

Regeneration of the Material

The regeneration of complexed-sorbent SGBT was checked by soaking the sample in 6 N HCl for a few minutes (5–10 mL of 6 N HCl per g of support). After washing, the complexing properties were measured again. Table III shows the results obtained for SGBT with mercury when undergoing four cycles of complexation/regeneration.

CONCLUSION

A new silica surface functionalized with bi-thiophene tripodal ligand was developed and characterized through elemental analysis, infrared spectroscopy, ^{13}C NMR, surface area, pore volume, pore diameter, and thermogravimetry. The density of the attached molecules and the intermolecular distances were also calculated. The grafting at the surface of silica exhibits an affinity only towards toxic heavy metals. This system can be operated indefinitely without loss of the expensive ligand. The marked selectivity may also suggest that this surface can be successfully explored for extracting mercury from water solutions.

EXPERIMENTAL

Chemicals

Reagent solvents and others chemical products purchased from commercial sources were of analytical grade and used without further purification. Silica gel (E. Merck) with particle size in the range 70–230 mesh, average pore diameter 60 Å, pore volume 0.75 ml g^{-1}, and specific surface area 550 $m^2\ g^{-1}$, was treated and activated before use by heating at 160 °C for 24 h. The silylating agent 3-glycidoxypropyltrimethoxysilane (Janssen Chimica) was used without further purification. 3-[Bis(2-thienylmethyl)amino]propan-1-ol **1** was prepared as reported in our previous work.[24]

Organofunctionalization

To activated silica gel (40 g) suspended in dry toluene (300 mL), triethylamine (960 μL) (potassium hydroxide dried) and 3-glycidoxypropyltrimethoxy-silane (53.2 mL) were added. The mixture was refluxed under nitrogen overnight. Then the substituted silica was filtered off and washed on a glass filter funnel with toluene, acetone, and diethyl ether (150 mL of each) and finally dried to obtain the product named SEp as shown in Scheme 2.

Immobilization of Bi-thiophene Tripodal Ligand on Organofunctionalized Silica

The hydroxy-substituted ligand **1** (0.8 mmol) was first converted to the alcoolate derivative using sodium metal in tetrahydrofuran. The resulting salt (0.8 mmol) was suspended with the organofunctionalized silica (SEp) (1 g) in dry dimethylformamide (DMF) (30 mL). The mixture was stirred and refluxed under nitrogen for 24 h. The surface containing the immobilized bi-thiophene tripod, named SGBT, was filtered and the excess tripod was eliminated by washing with DMF, toluene, water (distilled and deionized), methanol, and dichloromethane (150 mL of each). This final functionalized surface was dried in vacuum at room temperature.

Characterization

The product was analyzed by elemental analysis on a Perkin-Elmer PE-2400 elemental analyzer. The specific area of modified silica was determined by using the BET equation. The isotherms for nitrogen adsorption–desorption were obtained by means of a Thermoquest Sorpsomatic1990 analyzer, after the material had been purged in a stream of dry nitrogen. Infrared spectra of solid samples were performed with KBr pellets on a Perkin-Elmer PE 1310 spectrometer. Nuclear magnetic resonance spectra of the solid samples were obtained on a CP MAS CXP 300 MHz spectrometer. The mass loss determinations were performed under (90% of oxygen and 10% of nitrogen) on a TGA Q50 V6.7 Build 203 instrument, at a heating rate of 10 °C min^{-1}. Atomic absorption measurements were performed by Spectra Varian A.A. 400 Spectrophotometer.

Procedure for the Liquid–Liquid Extraction Method

A solution of 7×10^{-5} M of organic monomer **1** in CH_2Cl_2 (25 mL) was stirred for 2 h with an aqueous solution of metal nitrates (25 mL, 7×10^{-5} M); the complexation was followed by measuring the concentration of cations in the aqueous phase by atomic absorption. The temperature was remained constant during all the experiments at 25°C and at pH = 7.

Procedure for the Batch Method

A sample solution (10 mL) containing 10^{-2} M of a given metal ion was placed in a glass stoppered tube. The bi-thiophene tripod-loaded silica gel SGBT (0.1 g) was added and the tube was stoppered and shaken for 1 min to 24 h at 25 °C. The modified silica gel was filtered off, and the unextracted metal ion in the filtrate was determined using an atomic absorption spectrometer. The samples can be regenerated by washing with a solution of hydrochloric acid (6 N). Solutions of the metal ions were prepared by dissolution of the nitrate salt.

Procedure for the Column Method

Bi-thiophene tripod anchored silica gel SGBT (1.0 g) was packed in a glass column (size: 10 cm × 10 mm). The column was treated with HCl (2 M) and washed with doubly distilled water until it was free from acid. A suitable aliquot of the sample solution containing Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, K^{+}, Na^{+}, and Li^{+} in 10^{-2} M was passed through the column at pH 7 and at a flow rate of 3 cm^3 min^{-1}. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the silica gel column with hydrochloric acid (6 N). The concentration of the metal ions in the eluate was determined using an atomic absorption spectrometer.

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