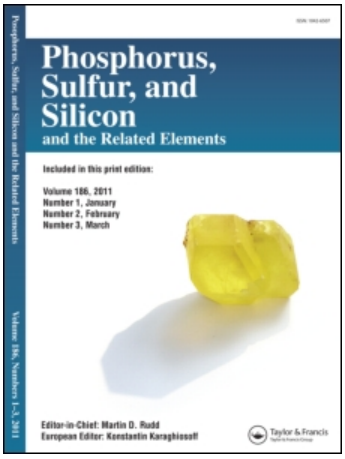

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Functionalized SiO_2 With *S*-Donor Thiophene: Synthesis, Characterization, and Its Heavy Metals Adsorption

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FUNCTIONALIZED SiO_2 WITH *S*-DONOR THIOPHENE: SYNTHESIS, CHARACTERIZATION, AND ITS HEAVY METALS ADSORPTION

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Porous silica has been chemically modified with thiophene using the heterogeneous route. This synthetic route involved the reaction of native silica, SiO_2, with a commercial silylating agent, 3-glycidoxypropyltrimethoxysilane, followed by the immobilization of the thiophene chelating groups on the support. The resulting material has been characterized by thermogravimetry, FTIR spectra, and elemental analysis. The solid was also studied and evaluated by determination of the surface area using the BET equation, and the adsorption and desorption capability using the isotherm of nitrogen and B.J.H. pore sizes. The new synthesized material was employed in a batch method as adsorbent from aqueous solutions of Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, K^{+}, Na^{+}, and Li^{+}.

Keywords Adsorption; chemical synthesis; metals; *S*-donor thiophene; silica

INTRODUCTION

It is well known that exposure to heavy metal ions through ingestion or uptake of drinking water and foods can lead to its accumulation in plants and animals. At high concentrations, some of these metals are very toxic to humans. Cadmium, copper, lead, mercury, and zinc are considered the most hazardous and are included on the U.S. Environmental Protection Agency's (EPA) list of priority pollutants.[1] Among the different techniques applied to the removal of heavy metal ions from solution, the metal adsorption onto solid supports such as activated carbon, zeolites, clays, and metal oxides has been used.[2]

Nevertheless, some of these materials suffer from inherent problems such as low removal capacity, low selectivity, long equilibrium time, and mechanical and thermal instability. In recent years, the preparation of silica-based adsorbents has generated considerable interest due to their unique, large specific surface area, regular pore structure, and well-modified surface properties.[3–5] Moreover, they can also be regenerated many times after adsorption saturation.[6] To enhance the adsorption capacity for heavy metals, organically modified porous silicas have drawn much attention as promising adsorbents.[7]

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The silica support is easily modified,[8] by reacting with organofuctionalized silanes through its surface silanol groups. These covalently bonded organic groups are highly stable and resistant to removal from the surface by organic solvents or water. Further treatment is also possible in order to immobilize new molecules with a variety of other organic functions even more active as chelating agents.

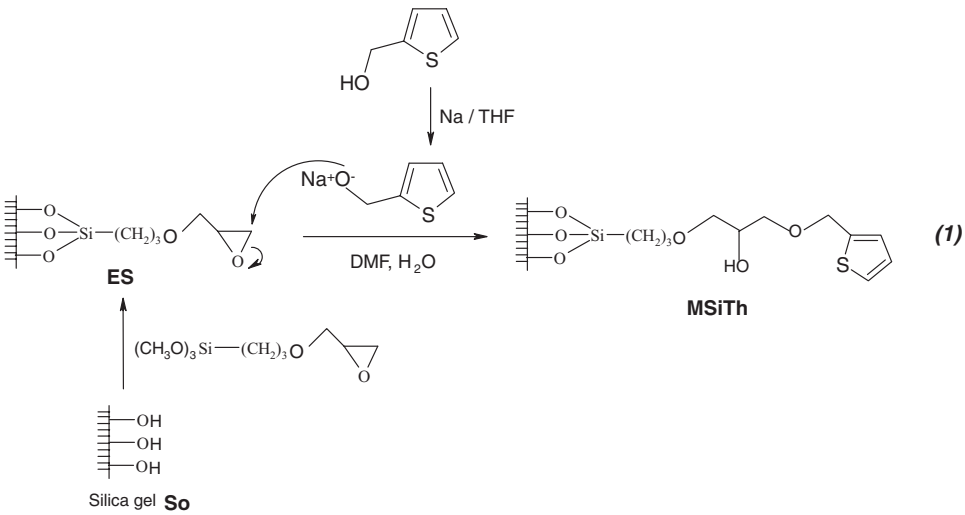
Indeed, the most commonly attached chelate ability for this purpose is devoted for donor atoms, such as *O*, *N*, and *S*, which have large capability in forming complexes with a series of metal ions, forcing, in some cases, a distinguishable selective extraction property.[9–13] In this context, several ligands containing *N*- or *O*-donor atoms have been successfully immobilized onto silica and applied to heavy metal extraction and preconcentration. In particular, materials whose surfaces are functionalized with groups containing sulfur as n active donor atom can present interesting intrinsic properties. For this purpose, we used thiophene to produce a sorbent with specific properties.

In this work, the chelating agent containing *S*-donor atom, based on thiophene group, was immobilized onto silica gel. The obtained material was characterized, and its capacities towards highly toxic heavy metals ions such as Hg(II), Pb(II), Cd(II), Zn(II), and Cu(II) and alkali metals such as K(I), Na(I), and Li(I) were investigated.

RESULTS AND DISCUSSION

Characterization of the Material

The synthetic procedure to describe the new material can be summarized in Scheme 1. The preparation consisted of reacting the activated silica gel with 3-glycidoxypropyltrimethoxysilane to form the epoxy-silica (ES)[14–19] that acts as a precursor for further immobilization of the molecule containing the donor atom. The immobilization of 2-thiophenmethanol salt on the surface of silica gel was achieved through a condensation between the epoxide group of ES and a nucleophilic salt in refluxing DMF.



Scheme 1 Synthetic modification of silica gel.

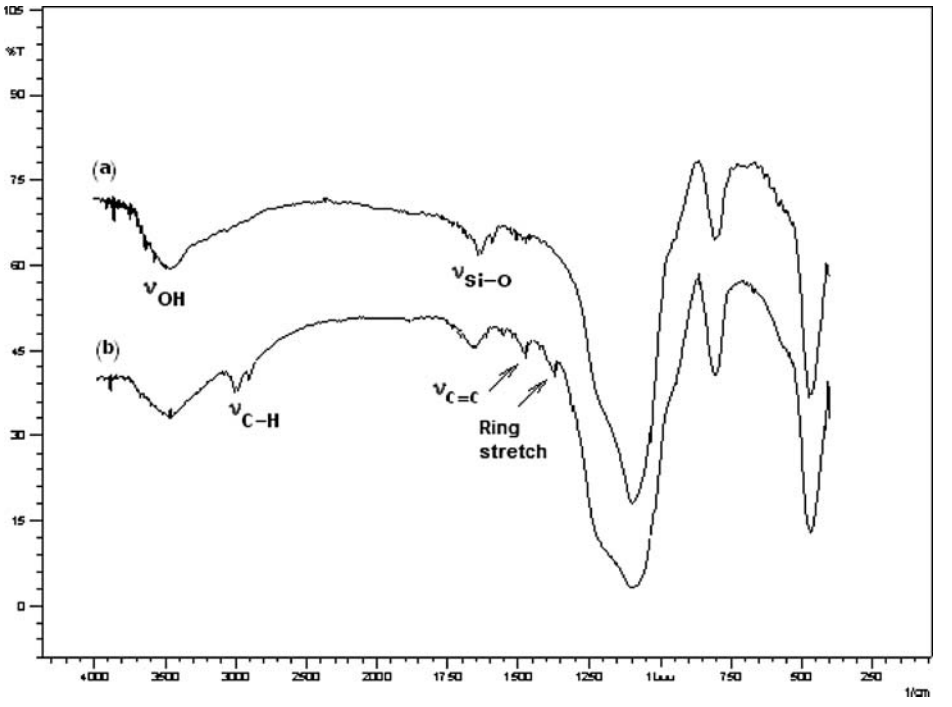


Figure 1 FT-IR spectra of (a) silica gel So and (b) thiophene-modified silica.

The results of the determination of the amount of thiophene groups determined by elemental analysis of sulfur (%S = 1%, %C = 4.12%) and thiosulfate method[20–22] gave concordant results at 312 μmol g^{-1} of thiophene groups per gram of silica. The FTIR spectra (Figure 1) present the strong decrease of the large ν(OH) adsorption around 3300 cm^{-1} and the appearance of a ν(C—H) weak band at around 3000–2800 cm^{-1}, corresponding to the carbon chain of the pendant group attached to the inorganic matrix. The spectrum also shows that the thiophene group was covalently grafted to the silica successfully (characteristic C=C stretching at 1475 cm^{-1} [23,24] and ring stretching at 1410 cm^{-1}) after the condensation process.

Thermogravimetric analysis (Figure 2) indicates a degradation process between 275–800°C that confirms the high thermal stability for the modified silica with thiophene (MSiTh). For the free silica (So), two stages of mass losses are to be distinguished: the first one corresponds to 3.30% (from 25°C to 150°C) assigned to physically adsorbed water; the second stage of mass loss of 2.84% in the 150–800°C range is allotted to the condensation of the free silanol groups to cause siloxane bond formation (Si—O—Si). In addition, the curve involving epoxy groups (ES) presented a mass loss, after the drainage of physically adsorbed water, of 12.84% in the 150–800°C range. The final material MSiTh showed an increase of mass loss of 3.52%, in the 150–800°C range, allotted to the decomposition of the organic thiophene group immobilized on the surface of silica gel. The mass loss observed is consistent with the amount of ligand covalently bound to the support (312 μmol g^{-1}), as calculated by elemental analysis and thiosulfate method. All these results provide evidence that the preparation of the functionalized material was successful.

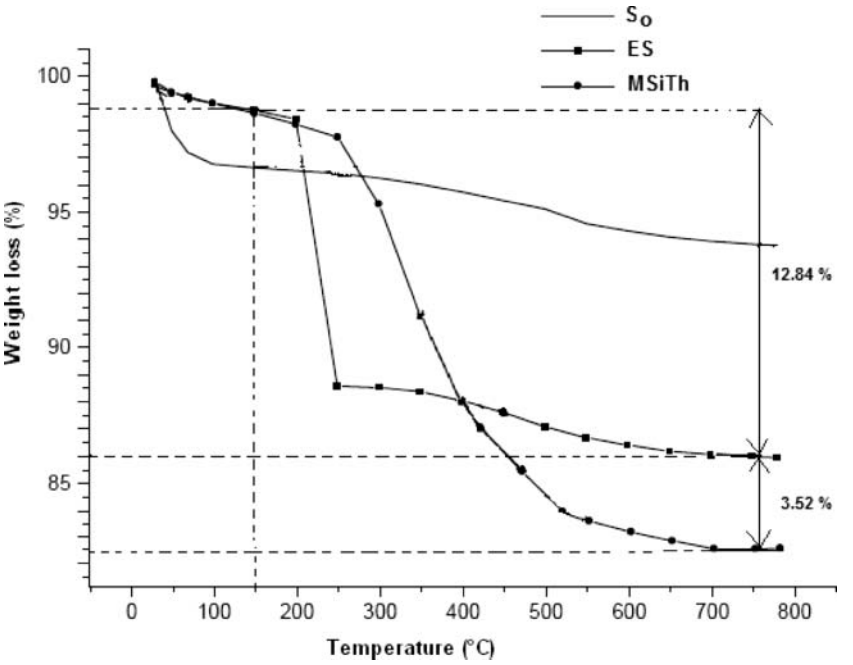


Figure 2 Thermogravimetric curves of free silica (So), epoxy-silica (ES), and silica immobilized thiophene (MSiTh).

The chemical stability of the newly chelating silica was examined in various acidic and buffer solutions (pH 1–7). Samples were mixed with different concentrations and stirred at room temperature for 24 h. The change in the degree of functionalization was calculated by elemental analysis of the samples both before and after the chemical treatment. After acid treatment, the percentages of sulfur and carbon in the functionalized silica were not modified (%S = 1%, %C = 4.12%). The high stability exhibited by the attached organofunctional group is presumably due to the pendant group, which binds the thiophene to the silica surface. It has been shown that when the length of the hydrocarbon bridge was more than two methylene groups, the rupture of Si—C bond did not occur in mineral acid medium, since longer chains no longer have a functional handle that can undergo beta-elimination of the Si cation.[25,26]

To show the porosity changes of the porous silica induced by the introduction of the thiophene ligand, we measured the surface area, pore volumes, and pore diameters of both porous free silica and MSiTh with nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters methods.[27,28] The porous silica possessed very high S_{BET} of 550 m^2/g, with a pore volume of 0.8 cm^3/g and a BJH pore diameter of 6 nm. After functionalization, a decrease in the S_{BET} (from 550 to 313 m^2/g), pore volume (Figure 3) (from 0.8 to 0.68 cm^3/g), and average BJH pore diameter (Figure 4) (from 6 to 2.866 nm) was observed. These changes were attributed to the presence of the thiophene groups on the surface, which partially blocks the adsorption of nitrogen molecules. The volume of nitrogen adsorbed and used to normalize the surface coverage decreased with functionalization, which is indicative of a reduction in pore size, leading thus to a

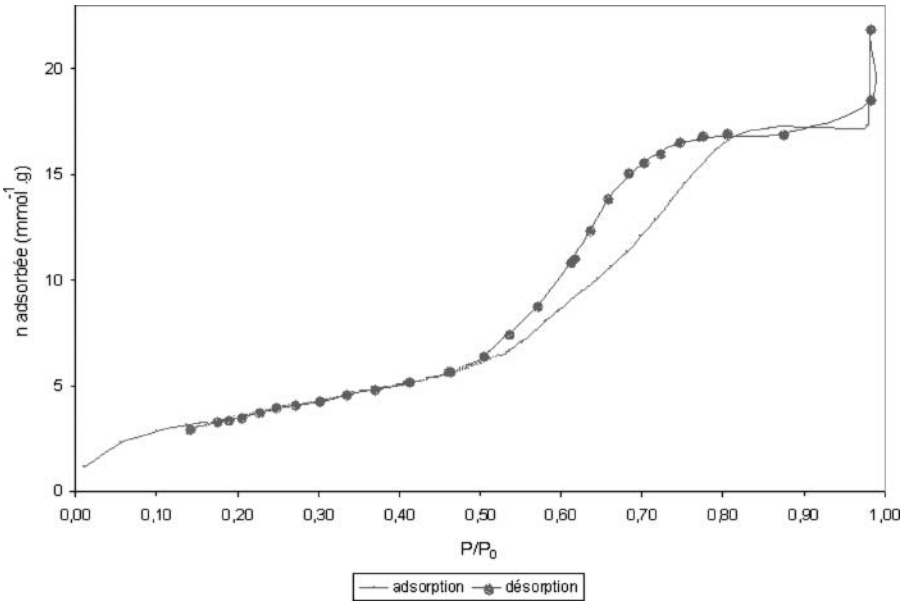


Figure 3 Nitrogen adsorption–desorption isotherm of MSiTh.

monolayer capacity of $N_m = 71.9676\ cm^3/g$, whereas native silica has a monolayer volume of $89.11\ cm^3/g$.

The nitrogen adsorption–desorption isotherm for MSiTh shown in Figure 3 is type *IV* according to the IUPAC classification[29,30] and displays a pronounced hysteresis for partial pressures $0.4 < P/P_0 < 1$, which is direct evidence of the presence of mesopores. The hysteresis loops are type H2, which indicates that there is a uniform pore diameter distribution.

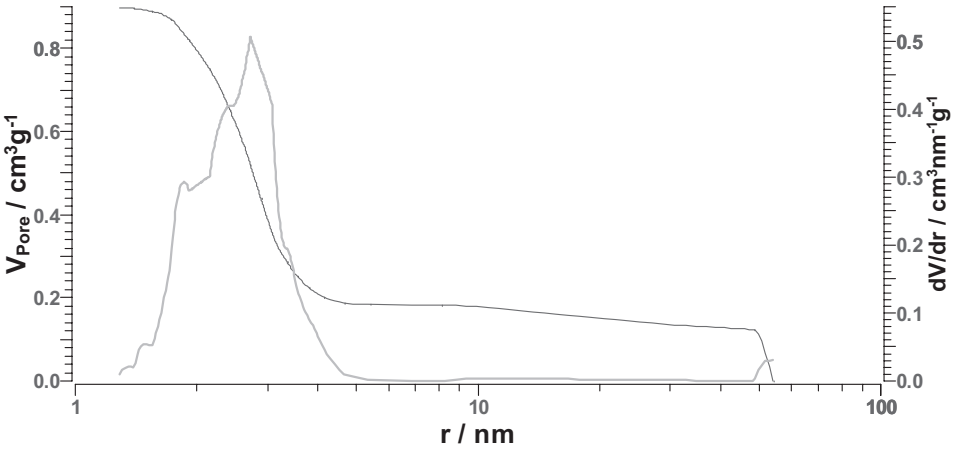


Figure 4 BJH pore size distribution.

The pore size distribution of 2.866 nm also provides evidence for the uniform framework porosity of the MSiTh.[31] The BET parameters are all within the range normally observed when the isotherm is adequately described by the BET equation.

Taking into account *Lo* and S_{BET} of the modified silica, the average surface density, *d*, of the attached molecule and the average intermolecular distance, *l*, can be calculated by applying the following equations[32,33]:

$$d = N.L_O/S_{BET} \quad (1)$$

$$l = (l/d)^{1/2} \quad (2)$$

where *N* is Avogadro's number and L_O is the proportion of functional groups attached on the surface. Results obtained ($d = 0.60$ molecule nm^{-2} and $l = 1.29$ nm) confirm an efficiency in the functionalization of the MSiTh. The considerable functionalization degree obtained can be explained as a consequence of its high surface area.

Adsorption of Metals from Aqueous Solution

The amount of metals adsorbed by the synthesized material from aqueous solution was determined using the following equations[34]:

$$Q_M = (C_0 - C_e) \times V/W \quad (3)$$

$$Q_W = Q_M \times M \quad (4)$$

$$K_d = 10^3 Q_M/C_e \quad (5)$$

where Q_M is the amount of the metal ion on the adsorbent (mmol/g), Q_W is the amount of the metal ion on the adsorbent (mg/g), K_d is the distribution ratio of the metal ion (mL/g), V is the volume of the aqueous solution (l), W is the weight of the adsorbent (g), C_0 the initial concentration of metal ion (mmol/l), C_e the equilibrium metal ion concentration in solution (mmol/L) and M the atomic weight for metals (g/mol). Analyses were performed in duplicate for each sample, and only the mean data were reported (Table I).

The complexing properties of the above thiophene-modified silica MSiTh towards various metal ions were evaluated by the batch method in individual and in competitive modes.

This acyclic ligand–modified material MSiTh does not present any complexation towards alkaline metal ions and Zn^{2+} ion. Indeed, it is known[14–19] that *N*-donor acyclic ligand–modified silicas extract only the divalent metal cations. We demonstrate here an affinity of this new acyclic *S*-donor-sorbent only with the divalent metal cations, with no complexation being observed toward alkali metal cations.

Native silica exhibits some weak complexing properties towards mercury (2 mg/g) and cadmium (1.1 mg/g) but not with lead and copper. This disappears when going to epoxy-substituted silica (ES) and thus can be attributed to the native hydroxyl groups.

The study of the individual complexation of each metal shows that the plateau was reached after about 5 min of contact. The maximum adsorption capacity of 25.07 mg/g was assigned to Hg^{2+}, whereas other metal ions are less well extracted (Pb^{2+}, Cd^{2+}, and Cu^{2+}) or not extracted (Zn^{2+}). This weak efficiencyin extracting these metal ions may be explained by the noninvolvement of the sulfur atom on the thiophene ring in metal coordination, as reported in the literature.[35–39] We can thus suggest an important selectivity for this sorbent toward mercury.

Table I Chelating properties of modified silica MSiTh towards various heavy metals in individual and in competitive mode

Sample	Specific area ($m^2\ g^{-1}$)	Amount grafted ($\mu mol\ g^{-1}$)	Capacity towards Hg		Capacity towards Cd		Capacity towards Pb		Capacity towards Cu	
			Q_M $mmol\ g^{-1}$	Q_W $mg\ g^{-1}$	Q_M $mmol\ g^{-1}$	Q_W $mg\ g^{-1}$	Q_M $mmol\ g^{-1}$	Q_W $mg\ g^{-1}$	Q_M $mmol\ g^{-1}$	Q_W $mg\ g^{-1}$
So[a]	550	0	0.01	2.0	0.01	1.1	0	0	0	0
MSiTh[b]	313	312	0.125	25.07	0.025	2.8	0.055	11.3	0.08	5.08
MSiTh[c]	313	312	0.145	29.08	0.01	1.1	0.045	9.3	0.08	5.08
K_d[d]			20.4		1.0		4.9		9.5	
Ki[e]			—		20.4		4.1		2.1	

[a]So: native silica.
[b]Solid–liquid extraction of individual cations using MSiTh.
[c]Solid–liquid extraction in competitive mode using MSiTh.
[d]K_d: The distribution ratio of the metal ion in competitive adsorption (mL/g).
[e]K_i: A selectivity coefficient for the binding of Hg^{2+} in competitive adsorption.

Table II Comparison of MSiTh with some recent sorbents used for Hg(II) separation and preconcentration

Sorbent	Metal uptake (mmol g^{-1})	Equilibrating time (min)	Reference
1,5-Diphenylcarbazide functionalized sol–gel material	0.028	30	41
Diphenylcarbazone-functionalized silica gel	0.028	40	42
Hg(II)-imprinted diazaminobenzene–vinylpyridine copolymers	0.205	60	43
TAN-functionalized AC	0.011	10	44
Xylenol orange-modified silica gel	0.018	3	45
Silica-modified thiophene	0.145	5	This work

In competitive solid–liquid extraction measurements, the obtained values are in perfect agreement with those measured by separate cation extraction. A selectivity coefficient (K_i) for the binding of Hg^{2+} in the presence of other metal ions was calculated according to the following equation[40]:

$$K_i = K_{d(Hg)}/K_{d(M)} \tag{6}$$

where K_i represents the ratio of the value of K_d of Hg^{2+} to K_d of M^{2+}: (Pb^{2+}, Cd^{2+}, and Cu^{2+}) in mixed solutions.

The values in Table I for the distribution constants (K_d) toward divalent metals and selectivity coefficients (K_i) of thiophene-modified silica MSiTh toward Hg^{2+} in the presence of other metal ions showed that all the K_i values were greater than 2, and the Hg(II) adsorption amount showed a weak increase in the presence of adsorptive competing ions compared with the individual adsorption. This suggested that the adsorptive competing ions in the aqueous solution had little effect on the adsorption of Hg(II) on MSiTh.

The prepared material was compared to a variety of recent sorbents reported in literature for the separation and preconcentration of Hg(II). The distinct features are summarized in Table II. We can thus note that the simplicity of implementation, the speed of extraction, and the high capacity in selective extraction of Hg(II) favored MSiTh compared to the other recent solid adsorbents.[41–46]

Regeneration of the Material

The sample was easily regenerated 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

Table III Complexation/regeneration using sample MSiTh and mercury

Cycle number	Capacity (mg g^{-1})
1	25.07
2	25.10
3	25.00
4	25.05

were measured again (Table III). No change was noticed when undergoing four cycles of complexation/regeneration.

CONCLUSION

A new material based on silica-bound thiophene with significant porosity (N_m = 71.9676 cm^3/g), pore volume (0.68 cm^3/g), pore size (2.866 nm), BET surface (313 m^2/g), and chemical (pH 1–7) and thermal (275–780°C) stability was synthesized. The density of the attached molecules (d = 0.6 molecule nm^{-2}) and the intermolecular distance (l = 1.29 nm) were also calculated. Elemental analysis, FT-IR spectroscopy, TGA, nitrogen adsorption–desorption isotherm, and BJH pore size distribution were used to characterize it. The complexing properties of this system towards various metal ions were evaluated by the batch method in individual and in competitive modes. This new material can be explored for extracting hazardous Hg(II) metals from water solutions if the high donor properties of nitrogen towards this metal are considered. The amount of the Hg(II) metal ion extracted (0.145 mmol g^{-1}, 29.08 mg g^{-1}) and the marked selectivity ($K_i > 2$) favored MSiTh compared to the other recent solid adsorbents. This system can be operated indefinitely without loss of the ligand.

EXPERIMENTAL

Chemicals

All solvents and others chemicals were purchased from commercial sources, were of analytical grade, and were used without further purification. Silica gel (E. Merck) with particle size in the range 70–230 mesh, median pore diameter 60 Å, was activated before use by heating at 160°C for 24 h. The silylating agent 3-glycidoxypropyltrimethoxysilane (Janssen Chimica) was used without purification.

Immobilization of Thiophene Compound on Silica Gel Surface

After converting the commercially available 2-thiophenmethanol to the alcoolate derivative using sodium metal in tetrahydrofuran, the resulting salt (0.8 mmol) was added to a suspension of epoxy-substituted silica (ES) (1.0 g) in dimethylformamide (30 mL). The mixture was stirred and refluxed under nitrogen for 24 h. The solid material was filtered, and the residue was washed with DMF, toluene, water (distilled and deionized), methanol, and dichloromethane (150 mL of each), and finally was dried.

Characterization

The sample was characterized by FT-IR spectra on a Perkin-Elmer 1310 and was analysed 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 nitrogen adsorption–desorption were obtained by means of a Thermoquest Sorpsomatic1990 analyzer, after the material had been purged in a stream of dry nitrogen (preparation of sample: 35–60°C, 5°C min^{-1}, 12 h), and the calculation used for BJH analysis was a desorption branch from p/p_o = 0.3 to 1 with standard isotherm. 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 a Spectra Varian A.A. 400 Spectrophotometer.

Determination of the Thiophene Groups

The amount of thiophene groups grafted on epoxy-silica was determined by four different methods: (i) elemental analysis of sulfur, (ii) from the determination of the unreacted epoxy groups by thiosulfate method, (iii) by thermogravimetry curves, and (iv) by simple weight measurement of the quantity of material before and after grafting on epoxy-silica.

Thiosulfate Method

3-Glycidoxypropyl-functionalized silica (MSiTh) (200×10^{-3} g) was vigorously shaken with sodium thiosulfate (10 mL, 6×10^{-3} M) to constant pH, and the released hydroxyl groups were titrated with hydrochloric acid (0.1 M).[20–22]

Batch Experiments

A 100 mg sample of modified silica (MSiTh) and an aqueous solution of a given metal ion (5 mL, 10^{-2} M) were shaken for 1 min to 24 h at 25°C. The mixture was then 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.

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