New Polysiloxane-Chemically Immobilized C,C-Bipyrazolic Receptor for Heavy Metals Adsorption

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ABSTRACT: A porous polysiloxane has been chemically modified with a functional C,C-bibyrazolic ligand using the heterogeneous route. This synthetic route involved the reaction of 3-glycidoxypropyltrimethoxysilane silylant agent, previously anchored on a silica surface, with C,C-bipyrazolic ligand. The new modified polysiloxane (SiL) has been characterized by elemental analysis and infrared spectra and was studied and evaluated by determination of the surface area using the BET equation, the adsorption and desorption capability using the isotherm of nitrogen and B.J.H. Pore sizes. The new inorganic-organic polymer exhibits good thermal stability determined by thermogravimetry curves and good chemical stability examined in various acidic and buffer solutions. The solid was utilized in batch method for separation and trace extraction of (Hg^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}) and compared with the results of classical liquid-liquid extraction with the unbound C,C-bipyrazole compound. The grafting at the surface of silica does not affect complexing properties of the ligand and the material exhibits a high selectivity toward Hg(II). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1393–1399, 2011

Key words: modified polysiloxane; chemical synthesis; characterization; adsorption; metals

INTRODUCTION

The chemistry underlying the use of chelating agents for metal ions separation and preconcentration of trace elements through solvent extraction is well known. However these chelating agents enhance the preconcentration factor to a greater extent when successfully adsorbed onto a solid adsorbent. Any efficient adsorbing material should consist of a stable and insoluble porous matrix having suitable active groups that interact with the analyte. The most common solid support for organic groups is polysiloxane (an inorganic material, nonswelling and stable under acidic conditions), not only due to their surface reactivity, but also to their ability in immobilizing organic molecules onto the surface.[1,2] On the other hand, the organofunctionalized silicas are resistant to removal the ligand from the surface by organic solvents or water, as well as having thermal resistance.[1,2]

In recent years, the preparation of silica-based adsorbents for heavy metal ions has generated considerable interest for analytical and environmental applications.[3] A recent review published by Jal et al.[1]

conclude that modification of silica gel by immobilization of chelation groups on a pendant organic chain provides scopes for trapping heavy metal ions, specifically and selectively, even at ultra trace level from aqueous and nonaqueous solutions. In fact, some authors have demonstrated that the use of chemically modified silica gel play very important role in preconcentration, as well as separation, of heavy metal ions before they are subjected to spectrometric instrumental methods of analysis.[4–13] This is an aspect of relevant interest, for example, to monitoring different natural water samples as sea water,[4] drinking tap water,[5,7,8] lake water,[10] river water,[11,12] etc.

In continuation of our work in this field,[14–19] this article describes the synthesis and the characterization of a new inorganic-organic polymer (SiL) (Fig. 1) obtained by grafting of functionalized compound on porous silica, based on a recent[20] synthesized C,C-bipyrazole which can acts as in N,N'-bidentate fashion[21,22] 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 an arm spacer rather long to facilitate the contact between the receiver and the metal ion, it is about the arm 3-glycidoxypropyl-trimethoxysilane which was used recently as silylating agent in the immobilization of many structures on silica gel.[23,24]
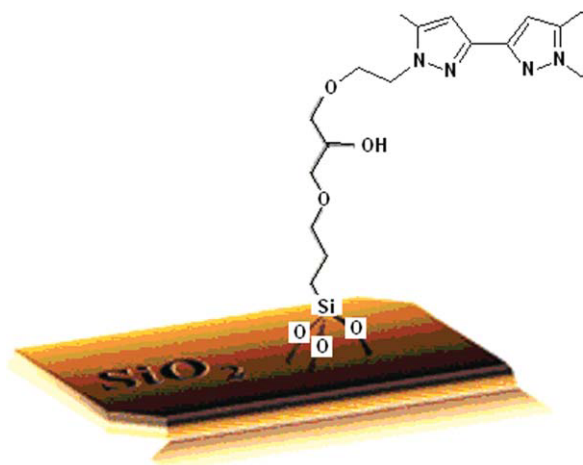
Figure 1 Modified SiO$_2$ with C,C-bipyrazolic receptor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The new material was used to separate and to extract bivalent and alkali metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, K$^+$, Na$^+$, and Li$^+$) from aqueous solutions. The results were compared with those obtained with the analog free organic monomer in liquid-liquid extraction with respect to capacity and selectivity. The percentages of adsorption were determined by atomic absorption measurements.

EXPERIMENTAL

Materials and methods

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification. Silica gel (E. Merck) with particle size in the range 70 to 230 mesh, median pore diameter 60 Å, was activated before use by heating it at 160°C during 24 h. The silylating agent 3-glycidoxypropyltrimethoxysilane (Janssen Chimica) was used without purification. Elemental analyses were performed by Microanalysis Central Service (CNRS: Centre National de la Recherche Scientifique). Infrared spectra (4000–500 cm^{-1}) were performed on Perkin–Elmer 1310; test conditions: potassium bromide pellets with 10 mg of material mixed with 500 mg of KBr and dried at 120°C for 2 h, diffuse reflectance, scanning 32 times, resolution are 4 cm^{-1}. The ^{13}C-NMR spectra of solid state were obtained with CP MAS CXP 300 MHz. Atomic absorption measurements were performed by Spectra Varian A.A. 400 Spectrophotometer. A specific area of modified silica was determined by using the BET equation. The nitrogen adsorption-desorption was obtained by means of a Thermoquest Sorpsomatic1990 analyzer, after the material had been purged in a stream of dry nitrogen. The mass loss determinations were

performed in 90 : 10 oxygen/nitrogen atmosphere on a TGA Q50 V6.7 Build 203 instrument, at a heating rate of 10°C/min.

Synthesis of epoxy-substituted silica (SiEp)

To porous polysiloxane (40 g), dried at 200°C for 24 h and then stirred in 300 mL of toluene previously dried over metal sodium, were added 960 µL of triethylamine (potassium hydroxide dried) and 53.2 mL of 3-glycidoxypropyltrimethoxysilane. The mixture was stirred and 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 (SiEp) as shown in Scheme 1. % yield = 780 µmol g^{-1} of epoxy groups per gram of silica. IR (KBr, cm^{-1}): ν(OH) = 3300, ν(C-H) = 3030. ^{13}C-NMR (solid state, ppm): 9 (Si-CH$_2$), 24 (-CH$_2$-), 51 (CH), 63 (CH$_2$-OH), 72 (CH$_2$-O-CH$_2$). S$_{BET}$ = 550 m^2/g. Pore volume = 0.8 cm^3/g. Pore diameters of 6 nm.

Synthesis of C,C-bipyrazole-substituted silica (SiL)

After converting the hydroxy-substituted ligand **1** to the alcholate derivative using sodium metal in tetrahydrofuran, the resulting salt (0.8 × 10^{-3}mol) was added to a suspension of 3-glycidoxypropyl-functionalized silica (SiEp) (1.00 g) in dimethylformamide (30 mL). The mixture was stirred and refluxed under nitrogen for 24 h. The solid material SiL was filtered and the residue was washed with DMF, toluene, water (distilled and deionized), methanol, dichloromethane (150 mL of each) and finally dried. % yield = 106 µmol g^{-1} of bipyrazole groups per gram of silica. Elem. Anal (%): N 0.60, C 1.53. TGA: mass loss = 2.33%, 23.3 mg g^{-1}. FT-IR (KBr, cm^{-1}): ν(C-H) = 3000-2800, ν(C = N) = 1600, ν(C = C) 1475, ν(Si-OH) = 965. S$_{BET}$ = 334.46 m^2/g. Pore volume = 0.665 cm^3/g. Pore diameters = 2.811 nm.

Determination of the epoxy groups: Thiosulfate method

The 3-Glycidoxypropyl-functionalized silica (SiL) (200 × 10^{-3} g) was vigorously shaken with 10 mL of sodium thiosulfate (6 × 10^{-3}M) to constant pH and the released hydroxyl groups were titrated with hydrochloric acid (0.1M).[25–27]

Liquid-liquid extraction experiments

A solution of 7 × 10^{-5}M of C,C-bipyrazolic ligand in 25 mL of CH$_2$Cl$_2$ was stirred for 2 h with an aqueous solution (25 mL) of metal nitrates 7 × 10^{-5}M; the complexation was followed by measuring the
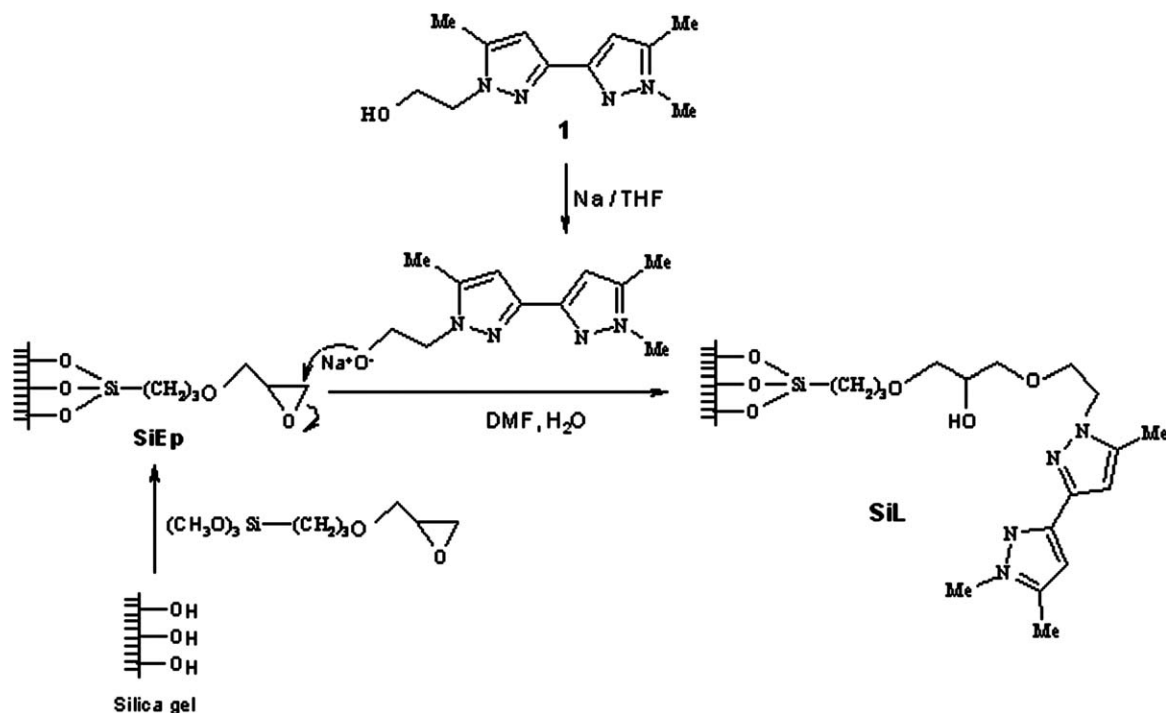
Scheme 1   Synthetic procedure of modified adsorbent SiL.

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.

Batch experiments

A 100 mg sample of modified silica (SiL) and 5 mL of an aqueous solution of a given metal ion ($10^{-2}M$) 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 (6N). Solutions of the metal ions were prepared by dissolution of the nitrate salt.

Chemical stability experiments

A 100 mg sample of modified silica (SiL) and 5 mL of buffer solution of a given pH 1 to 7 (Fluka) were stirred for 24 h at 25°C. The suspension was then filtered, washed with ultra pure water, and dried at 200°C for 24 h. The degree of functionalization was calculated by elemental analysis of the samples.

RESULTS AND DISCUSSION

Immobilization of bipyrazole group on polysiloxane

Generally, the modification of silica by chemical route with organic ligands is carried out in a conventional heterogeneous method which involves the reaction of surface hydroxyl groups with a commercial silylating agent, usually 3-glycidoxypropyltrimethoxysilane[28,29] that acts as precursor for further immobilization of the molecule containing the donor atom. Various procedures have been described in the literature for the coupling of an epoxysilane to silica[30,31] and a modification of one of these was used in this work.

The result of our investigation is given below (Scheme 1): The first stage of the preparation consisted in reacting the activated silica gel with 3-glycidoxy-propyltrimethoxy-silane to form the epoxy-silica (SiEp).[17] The presence of the spacer arm on the silica gel was asserted by FT-IR and ^{13}C solid state NMR spectroscopy.[17] Indeed, after hydrolysis of the epoxide groups to diols with diluted sulfuric acid (pH 2, 90°C, 1 h), five well-formed peaks, at 9, 24, 51, 63, and 72 ppm were observed on ^{13}C-NMR spectrum and were attributed to carbons of the pendant groups.[17]

Immobilization of bipyrazolic salt on the surface of silica gel was achieved through a one put reaction between the epoxide group of previous synthesized epoxy-silica SiEp[14–19] and a nucleophilic C,C-bipyrazole in refluxing DMF.

The results of the determination of the amount of bipyrazole groups determined by elemental analysis of nitrogen (% N = 0.6%) and thiosulfate method[25–27] gave concordant results at 106 µmol g^{-1} of bipyrazole groups per gram of silica.

An important aspect of the prepared material SiL is its thermal and chemical stability. Thermogravimetric analysis (Fig. 2) for the modified silica allows
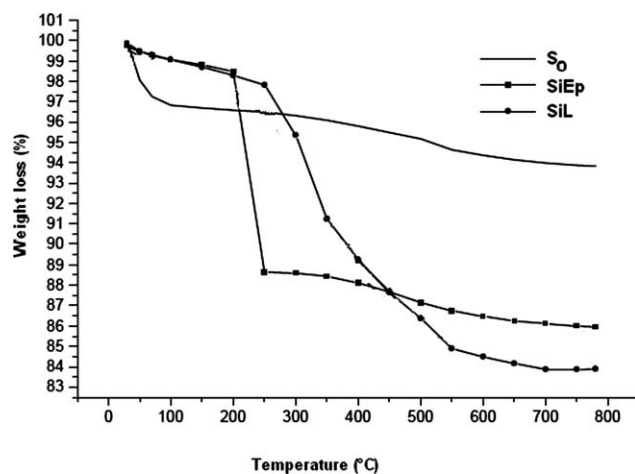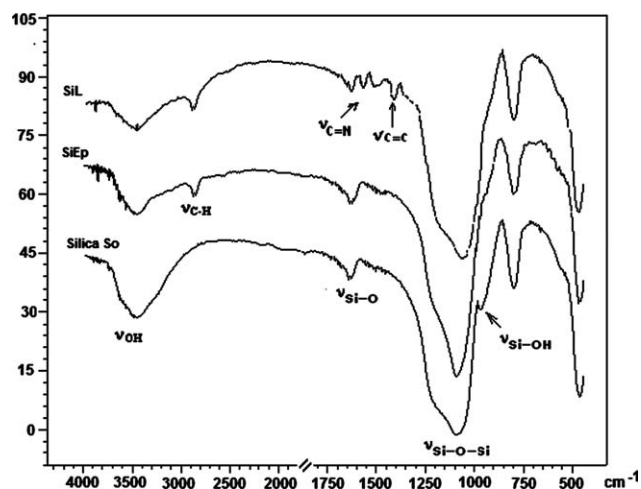
Figure 2 Termogravimetric curves of free silica (So), epoxy-silica (SiEp), and silica immobilized C,C-bipyrazole (SiL).

Figure 3 Infrared spectra of porous free silica (So), epoxy-silica (SiEp), and silica immobilized C,C-bipyrazole (SiL).

information concerning the thermal stability to be obtained and also confirm the amount of C,C-bipyrazolic compound immobilized on the silica surface. The profiles obtained indicate a degradation process between 275 and 780°C that confirms the high thermal stability of the prepared material. The mass loss observed is consistent with the amount of ligand covalently bound to the support, as calculated by elemental analysis and thiosulfate method (2.33%, 23.3 mg g^{-1}, 106 µmol g^{-1}).

The chemical stability of the newly chelating silica was also examined in various acidic and buffer solutions (pH 1–7). Samples were mixed with different concentrations and stirred at room temperature during 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 percentage of nitrogen in the functionalized silica was not modified (%N = 0.60 ± 0.02%) reflecting the persistence of a ~ 106 µmol g^{-1} of bipyrazole groups per gram of silica. This high stability of attached organofunctional group is presumably due to the pendant group, which binds the bipyrazole 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 β-elimination of the Si cation.[32,33]

Finally, functionalized silica was characterized by FT-IR spectroscopy (Fig. 3) between 4000 and 500 cm^{-1}. The main features of this spectrum were characteristic bands for aliphatic C-H stretching vibrations due to pendant alkyl chains at about 2900 cm^{-1}, the characteristic peak of C = N at 1600 cm^{-1} and C = C stretching vibrations at 1475 cm^{-1}.[34,35] Another characteristic band assigned to silanol groups (Si-OH) was observed near 965 cm^{-1} for the

activated silica. After immobilization of the organic groups, this band was considerably reduced as expected in such immobilization processes.[24] All these results provide evidence that the preparation of the functionalized material was successful.

To highlight the porosity changes of the porous silica induced by the introduction of bipyrazolic ligand, we measured the surface area, pore volumes, and pore diameters of both porous polysiloxane and SiL with nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore diameters methods[36,37] (Table I). The native porous silica has a BET (Brunauer-Emmett-Teller) surface area of 550 m^2/g and a pore volume of 0.8 cm^3/g. On the other hand, we observed that SiL has a decrease BET surface area as additional groups' immobilization takes place to give 334.46 m^2/g and a pore volume of 0.665 cm^3/g. Moreover, the SiL has a decrease BJH pore diameters of 2.811 nm. The decreased surface area and pore diameter in SiL are attributable to the presence of the grafted bipyrazole on the silica surface that partially blocks the adsorption of nitrogen molecules.

Moreover, the nitrogen adsorption-desorption isotherm for SiL shown in Figure 4 is type IV according to the I.U.P.A.C. classification and displays a pronounced hysteresis for partial pressures $P/P_0 \geq 0.4$ ($P_c/P_0 = 0.47$, where P_c is the capillary condensation pressure). The inflection position in the functionalized porous silica SiL shifted slightly toward lower

TABLE I
Physical Properties of Native Silica and Modified Silica

|	Specific surface (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Monolayer volume (cm^3/g)
Native silica	550.00	0.800	6.000	89.1100
Modified silica	334.46	0.665	2.811	76.8316
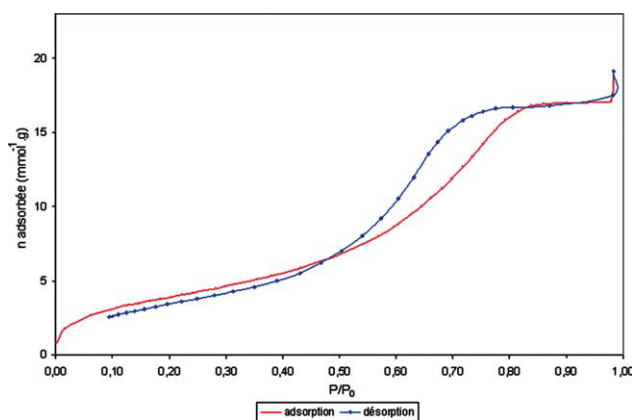
Figure 4 Nitrogen adsorption-desorption isotherm of SiL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

relative pressures (0.47) compared with the native silica ($P_c/P_0 = 0.53$)[38] and the volume of nitrogen adsorbed decreased with functionalization, which is indicative of a reduction in pore size. Thus, the isotherm indicates that the pore volume (Gurvich) at $P/P_0 = 0.984$ is 0.665 cm^3/g whereas native silica has 0.8 cm^3/g. The BET fit of the isotherm in the range $0.05 < P/P_0 < 0.31$ is shown in Figure 5 and leads to a decrease monolayer capacity of $N_m = 76.8316$ cm^3/g used to normalize the surface coverage, whereas native silica has a monolayer volume of 89.11 cm^3/g. The BET parameters are all within the range normally observed when the isotherm is adequately described by the BET equation. In addition, as can be calculated[39] from Figure 6, the pore size distribution of 2.811 nm is narrower in SiL that in native silica Si-60, providing evidence for the uniform framework porosity of the SiL.

Taking into account L_o and S_{BET} of the modified silica, the average surface density, d, of the attached molecule and the average intermolecular distance, l,
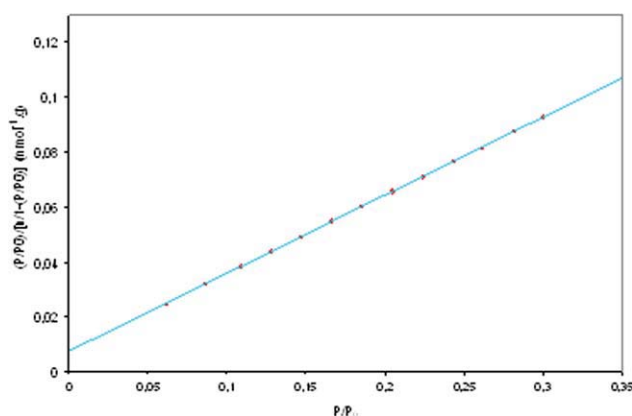
Figure 5 B.E.T. fit of SiL for partial pressures $0.05 < P/P_0 < 0.31$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
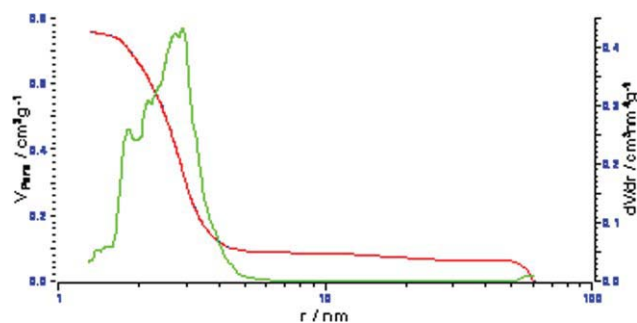
Figure 6 B.J.H. Pore sizes distribution of SiL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be calculated by applying the following equations[40,41]:

$$d = NL_0/S_{BET}$$
$$l = (l/d)^{1/2}$$

where N is Avogadro's number and L_o is the proportion of functional groups attached on the surface. Results obtained ($d = 0.19$ molecule nm^{-2} and $l = 2.294$ nm) confirm an efficiency in the functionalization of the SiL. The considerable functionalization degree obtained can be explained as a consequence of its high surface area.

Metal ions retention on synthesized material

The coordinating properties of the above C,C-bipyrazole-modified silica (SiL) toward various metal ions were evaluated by the batch method in individual and in competitive mode. The results are expressed in terms of μmol of metal ion bound per gram of sorbent, mg of metal ion per gram of sorbent and the yield of complexation is expressed as μmol of metal ion per μmol of bipyrazole ligand (Table II).

The study of the individual solid-liquid extraction shows that the obtained values are in perfect agreement with those measured by the free ligand and the plateau was reached after about 2 min of contact. This suggests that the N,N' active donor atoms on the modified silica gel surface are so oriented that their accessibility is not difficult and consequently fast interaction with the free metal ions present in solution is feasible. Indeed, bipyrazole groups act as convergent chelating bidentate donors. The term convergent refers to the nitrogen donor atoms coordinating to the same metal ion center leading thus to a five-membered ring which is part of several such rings when the whole ligand is considered. It is well known[42] that five-membered ring chelates are more stable than six-membered and four-membered ones.

The affinity of this host is especially high for mercury. This is not surprising if the high donor properties of nitrogen towards this metal are

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TABLE II
Chelating Properties of Free Ligand 1 and Modified Silica SiL toward Various Heavy Metals in Individual
and in Competitive Mode

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Sample	Specific area $(m^2\ g^{-1})$	Amount grafted $(\mu mol\ g^{-1})$	Capacity toward Hg			Capacity toward Cd			Capacity toward Pb			Capacity toward Cu		
			Yield[a] $\mu mol\ g^{-1}$ mg g^{-1} (%)			Yield[a] $\mu mol\ g^{-1}$ mg g^{-1} (%)			Yield[a] $\mu mol\ g^{-1}$ mg g^{-1} (%)			Yield[a] $\mu mol\ g^{-1}$ mg g^{-1} (%)		
LLE[b]	2													
SiL[c]	334.46	106	70.0	14.0	62	10.6	1.2	7	24.4	5.0	26	18.0	1.1	18
SiL[d]	334.46	106	73.1	14.7	69	6.3	0.7	6	18.0	3.7	17	11.7	0.7	11

[a] Yield of complexation calculated as: mol of metal per mol of free or grafted bipyrazole.
[b] Liquid-liquid extraction of individual cations using compound **1**.
[c] Solid-liquid extraction of individual cations using SiL.
[d] Solid-liquid extraction in competitive mode using SiL.

considered. The observed complexation towards Pb^{2+} and Cu^{2+} is also not surprising since the fragment N-(2-hydroxyethyl)-3,5-dimethylpyrazole may itself act as a bidentate N,O ligand in coordination compounds with some transition metal ions.[43] Moreover, no extraction was observed towards Zn^{2+} and alkali metal ions (K^+, Na^+, and Li^+). The order of adsorption is: $Hg^{2+} > Pb^{2+} > Cu^{2+} > Cd^{2+}$.

In competitive solid-liquid extraction measurements, the obtained values are in perfect agreement with those measured by separate cation extraction. Indeed, in this competitive extraction, we notice a high affinity only for mercury with zero extraction of alkali cations and a weak extraction of other bivalent metal ions. We can thus conclude that this sorbent is selective with the extraction of Hg(II).

Solid sorbent is clearly as efficient as the liquid-liquid extraction process, the amount adsorbed 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 adsorption sites.

The sample was easily regenerated by soaking the sample in 6N HCl for a few minutes (5–10 mL of 6N HCl per g of support). After washing, the adsorption properties were measured again. No change was noticed when undergoing five cycles of adsorption/regeneration. This new solid extractor has thus a good stability and can be reused without decreasing its extraction percentage.

CONCLUSION

Modified polysiloxane with significant porosity (N_m = 76.8316 cm^3/g), pore volume (0.665 cm^3/g), pore size (2.811 nm), BET surface (334.46 m^2/g), and chemical (pH 1-7) and thermal (275-780°C) stability was proved to change the chelating character of the silica matrix. The density of the attached molecules (d = 0.19 molecule nm^{-2}) and the intermolecular

distance (l = 2.294 nm) were also determined. Elemental analysis, IR and ^{13}C-NMR spectroscopy, TGA, and nitrogen adsorption-desorption isotherm were used to characterize it. The strong affinity of SiL to chelate toxic heavy metal ions especially Hg(II) compared with other tested metal ions can add another dimension to this work and direct more interest toward the potential application of this new chelating sorbent for extraction, removal, separation and preconcentration of this metal ion from their environments in a pure state and without interference of other metal ions.

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