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# Adsorption and separation of cations on chemically modified silica gel synthesised *via* the sol–gel process

**Alexandre G. S. Prado, Luiza N. H. Arakaki and Claudio Airoldi***

*Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154,
13083-970 Campinas, São Paulo, Brasil. E-mail: airoldi@iqm.unicamp.br*

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The reaction of ethylene sulfide [$(H_2C)_2S$] with 3-aminopropyltrimethoxysilane resulted in a new silylating agent, which was anchored onto a silica surface *via* the sol–gel procedure. The synthesised silica gel surface has been used to adsorb divalent cations from aqueous solutions at room temperature. The series of isotherms of adsorption were adjusted to a modified Langmuir equation from data obtained by suspending the solid in water with $MCl_2$ (M = Cu, Ni, Co, Pb and Hg) solutions, which gave the maximum number of moles adsorbed as 1.66, 1.44, 1.26, 1.90 and 8.51 mmol $g^{-1}$, respectively. The immobilised surface was also used for the separation of these five cations in a column. Column resolution, $R_{(s)}$, was determined for all cations as the ability of the surface to separate metal ions, determined as $R_{(s)Co\text{–}Ni} = 0.20$, $R_{(s)Co\text{–}Cu} = 0.73$, $R_{(s)Co\text{–}Pb} = 2.50$, $R_{(s)Co\text{–}Hg} = 1.73$, $R_{(s)Ni\text{–}Cu} = 0.55$, $R_{(s)Ni\text{–}Pb} = 2.25$, $R_{(s)Ni\text{–}Hg} = 1.69$, $R_{(s)Cu\text{–}Pb} = 1.33$, $R_{(s)Cu\text{–}Hg} = 1.52$ and $R_{(s)Pb\text{–}Hg} = 1.35$.

The toxic effects of heavy metals present many risks to humans, particularly in the case of water and food.[1,2] When heavy metal contents are monitored in natural water, of paramount importance is a reliable indication of the effect to the normal life of a given community.[2,3] Even low concentrations of heavy metals (ppb) in natural water supplies can have detrimental effects on wildlife and humans.[4] Nevertheless, to determine these low cation concentrations often requires preconcentration before analyses can be undertaken.[5]

One of the most well developed methods for determining heavy metals in aquatic environments is atomic spectroscopy, in spite of systematic interference from other simple water constituents. Preconcentration and/or separation steps are often necessary to quantify the desired analytes[3] and the development of solid adsorbents to remove contaminants from waste effluent streams is one of the major goals of green chemistry.[4] Thus, applications designed to improve analytical chemistry and environmental metallic depollution methods have emerged in order to eliminate and/or separate toxic trace metals from waste waters,[2–5] and to monitor rivers and a diversity of sources of natural water.[3]

The organofunctionalization of inorganic solid surfaces is normally used to introduce basic groups on anchored pendant chains.[4–6] The synthesised materials change the properties of the original matrix, with the preference for trace metals from solvents, by adsorbing these contaminants on the chemically modified surface.[7,8]

The great interest devoted to anchored silica gel studies has focused on high performance liquid chromatography for the separation of organic compounds,[9] inorganic anions,[10] cation mixtures,[11] preconcentration,[12] and ion-exchange,[13] as well as such uses as catalysts[4] and chemical sensors.[14]

The most effective applications of immobilised silica gel consist of exploring the ability of the basic atoms anchored on pendant chains to preconcentrate cations dispersed in solution. However, when cations are irreversibly bonded to the basic centres, the lack of selectivity is the main disadvantage of the attached ligand in cation complexation.[15,16] However, an active adsorbent has the purpose of attaining to the following characteristics: good sorption capacity, chemical stability under employed conditions, especially, high selectivity.[17–20] The advantages of the immobilisation of a desired organic compound onto the silica gel are the great versatility arising from the various functionalities of the bonded groups, which should be resistant to removal from the surface by organic solvents or water.[19–23] Mercapto groups covalently bonded to silica have shown high chemical selectivity for mercury ion removal from solvents.[23]

The aim of the present study is to report the ability of a silica gel obtained from the sol–gel process—based on the reaction of a new silylating agent formed by the condensation of 3-aminopropyltrimethoxysilane with ethylene sulfide—to extract and separate cations from aqueous solutions.

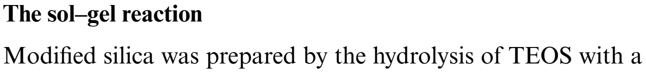
## Experimental

### Chemicals

The three membered ring ethylene sulfide (Aldrich) and 3-aminopropyltrimethoxysilane (APTS) (Fluka) were used without purification. Tetraethoxysilane (TEOS) was distilled under reduced pressure before use. Silica gel (Merck) with a particle size of 70–230 mesh and with a mean pore diameter of 60 Å was activated in a stream of dry nitrogen by heating at 423 K for 10 h and used immediately.

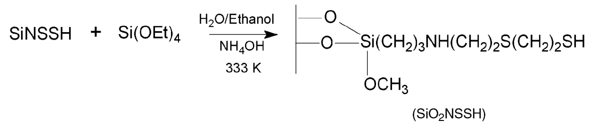
### Synthesis of the new silylating agent

The silylating agent APTS, 10.0 $cm^3$ (57.3 mmol), reacted with 7.0 $cm^3$ (114.6 mmol) of ethylene sulfide. The mixture was reacted inside a sealed tube under reflux at 373 K during 48 h. The resulting product was named SiNSSH,[19] the synthetic reaction for which is presented below:



### The sol–gel reaction

Modified silica was prepared by the hydrolysis of TEOS with a mineral base ($NH_4OH$) as catalyst, in the presence of the new silylating agent. First, 24.0 $cm^3$ of TEOS was added to 17.0 $cm^3$ of SiNSSH. This mixture was mechanically stirred as 4.0 $cm^3$ of water and 3.0 cm$^3$ of ethanol were added at 333 K, followed by the slow addition of 3.0 cm$^3$ of the catalyst $NH_4OH$ (0.080 mol dm$^{-3}$). The gel was formed after 30 min, aged for 48 h at 323 K and for a further period of 48 h at room temperature. At the end of the reaction the solid was filtered off, washed with water and ethanol, and dried *in vacuo* at room temperature.[24,25] The synthesis of the new anchored surface can be represented by the reaction:



### Isotherms of adsorption

The isotherms of adsorption were obtained using the batchwise method,[17–19,26,27] which involved suspending a series of samples (50.0 mg) of the modified silica with 20.0 cm$^3$ aqueous solutions of each cation at several concentrations, varying from 0 to 50.0 mmol dm$^{-3}$. The samples were mechanically stirred for 4 h at 298 K. After this time, the solid was separated by centrifugation and dried as before at 313 K.[28] The content of adsorbed metal was determined by sampling the supernatant, which was complexometrically titrated by EDTA, using convenient indicators for cobalt, nickel and copper.[29] Other cations, such as lead and mercury, were determined by ICP-AES (Perkin-Elmer 3000 DV).

### Separation of cations

The ability to separate the cations was followed by using a glass column with a 0.50 cm internal diameter packed with 1.00 g of the immobilised SiNSSH material. To this column 80.0 cm$^3$ of a solution containing a mixture of divalent metal chloride solutions of copper, nickel, zinc and cadmium (0.50 mmol dm$^{-3}$ each) was percolated through the solid bed with a flow rate of $8.33 \times 10^{-3}$ cm$^3$ s$^{-1}$.[5] The adsorbed cations were eluted by passing aliquots of 2.0 cm$^3$ of a Clark/Lubs buffer mixture of KCl–HCl solutions at four distinct pH values varying from 4.0, 3.0, 2.0 to 1.0, respectively.[12] The amount of cations recovered in each fraction was determined by ICP-AES with a Perkin-Elmer 3000 DV apparatus.

## Results and discussion

The reaction of the precursor silylating agent 3-aminopropyltrimethoxysilane with a double stoichiometric amount of ethylene sulfide under homogeneous conditions caused the opening of the three membered ring to yield the new silylating agent SiNSSH, as described previously.[19]

During the sol–gel process the SiNSSH molecule condenses at the active silanol groups formed in the inorganic structure on the silica surface. This reaction resulted in 2.50 mmol of SiNSSH per gram of support, as determined from nitrogen analysis by the Kjeldahl method.[21,28]

After incorporating the silylating agent into the inorganic framework, the pendant groups disposed on the structure enable this material to interact with a wide range of cations due to the presence of three basic centres; two characteristically soft basic centres and another one that behaves as a hard base. This fact improves the process of interaction with various metal ions, in particular, the presence of two sulfur donor atoms bonded in each pendant group makes the interaction with soft divalent mercury easy.[30] These characteristics enable this modified silica to be used in clean technology, in applications such as the selective separation of trace metals from natural water supplies.[4]

Based on the structural features presented by the pendant groups attached to the inorganic backbone, both kinds of donor atoms (hard and soft) can bond simultaneously to the same cation. However, the soft–hard characteristic of the material will govern the interaction.[31–33] Thus, metal ion adsorption should be *via* sulfur in the case of soft metal cations and *via* nitrogen in the case of hard metal cations, as proposed in Fig. 1.

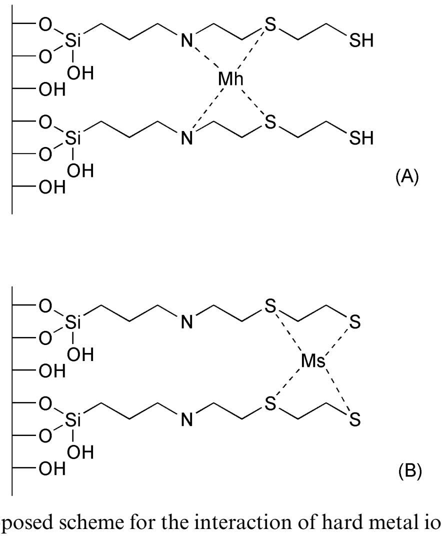


**Fig. 1** Proposed scheme for the interaction of hard metal ions (A) and soft metal ions (B) on the $SiO_2NSSH$ surface. Mh represents a hard and Ms a soft metal ion.

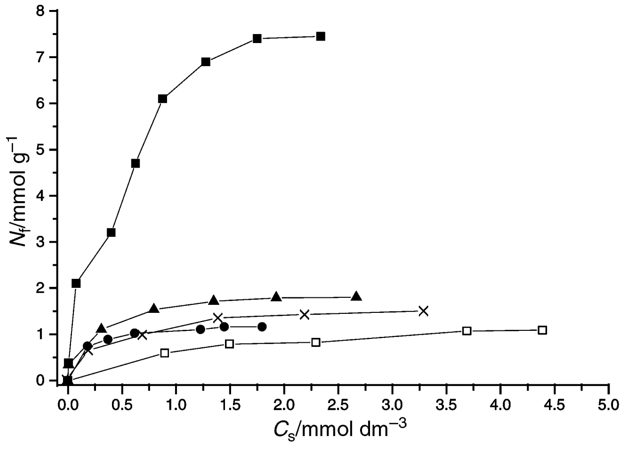


**Fig. 2** Isotherms of adsorption of divalent cations onto the modified silica gel surface for Cu (×), Ni (●), Co (□), Pb (▲) and Hg (■) at 298 ± 1 K.

The ability of this surface to extract cations from aqueous solution was evaluated by measuring the sorption isotherms for a series of divalent cations, such as copper, nickel, cobalt, lead and mercury. Under equilibrium conditions, the exchange processes at the solid–liquid interface can be characterised by the number of moles adsorbed ($N_f$) per gram of support. This value was calculated from the initial number of moles of cation added ($n_i$) and those at the equilibrium point ($n_s$) for a mass ($m$) of the support, in grams, by applying the expression:

$$N_f = \frac{n_i - n_s}{m} \qquad (1)$$

Profiles of the adsorption isotherms for all cations in water are represented in Fig. 2, representing the number of moles adsorbed *versus* the concentration of the supernatant under equilibrium conditions. A simple observation of these profiles, which define the maximum adsorption values, can lead to a perfect distinction of these cations, from the point of view of adsorption. For the series of isotherms, the data reveal that the adsorption process conforms to the Langmuir model, as

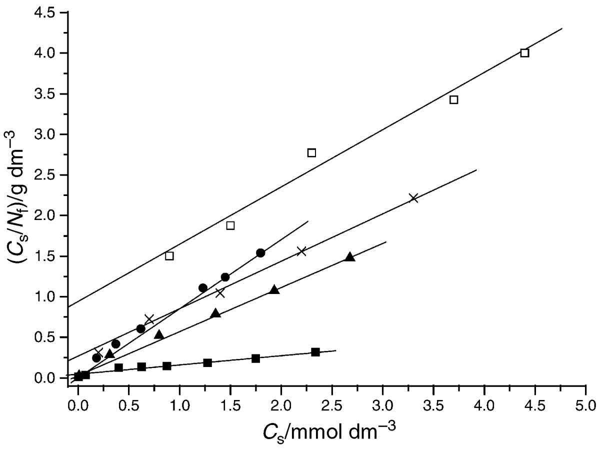


**Fig. 3** Linearization of isotherms of adsorption of divalent cations adsorbed on the modified silica gel surface for Cu (×), Ni (●), Co (□), Pb (▲) and Hg (■) at 298 ± 1 K.

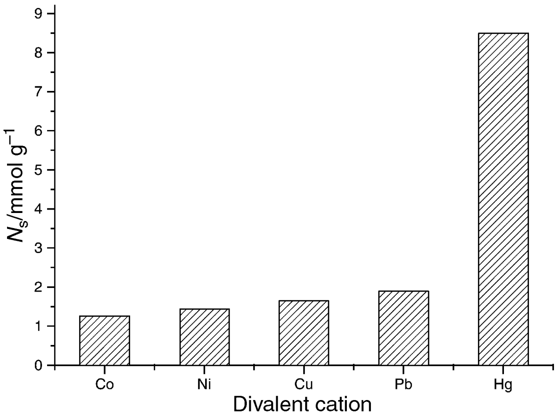


**Fig. 4** Maximum amount of divalent cations: Cu, Ni, Co, Pb and Hg adsorbed per gram of $SiO_2NSSH$.

proposed for a series of systems,[17–19] the general equation for which is presented as:

$$\frac{C_s}{N_f}=\frac{C_s}{N_s}+\frac{1}{N_s b} \quad (2)$$

From this expression, $C_s$ is the concentration of solution at equilibrium (mol dm$^{-3}$), $N_f$ as defined before (mol g$^{-1}$), $N_s$ is the maximum amount of solute adsorbed per gram of surface (mol g$^{-1}$), which depends on the number of adsorption sites, and $b$ is a constant. All these adsorption studies were based on the linearized form of the adsorption isotherm derived from $C_s/N_f$ as a function of the $C_s$ plot. From these data, represented in Fig. 3, the maximum retention capacity ($N_s$) was determined for each cation–matrix interaction through application of the modified Langmuir equation, whose values were obtained from the angular coefficient while $b$ is the linear coefficient of the same straight line.[17–19]

The isotherms presented in Fig. 3 showed that the adsorption followed the sequence Hg ≫ Pb > Cu > Ni > Co. $N_s$ values were obtained from linearization of the isotherms as represented in Fig. 3 and the behaviours are shown in Fig. 4. The maximum retention capacites ($N_s$) were 8.52, 1.90, 1.66, 1.44 and 1.26 mmol g$^{-1}$ for Hg, Pb, Cu, Ni and Co, respectively.

An inspection of the $N_s$ values plotted in Fig. 4 demonstrate that mercury is easily the most effective in binding to the pendant groups. This behaviour reflects the high affinity of the sulfur basic centres for mercury. This fact suggests that this surface is more favourable in reacting with soft cations, as a consequence of the larger population of the two soft base centres in each pendant group. In light of these observations, this material could be potentially applied as a selective electrode when the objective is to determine or identify soft acids.

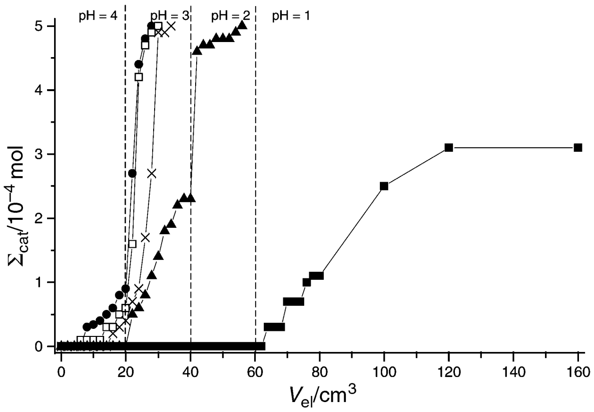


**Fig. 5** Extraction of the divalent cations: Cu (×), Ni (●), Co (□), Pb (▲) and Hg (■) from a column packed with $SiO_2NSSH$. The amount of catalyst ($\Sigma_{cat}$) was collected by elution with variable amounts ($V_{el}$) of aqueous buffer solutions by varying the pH.

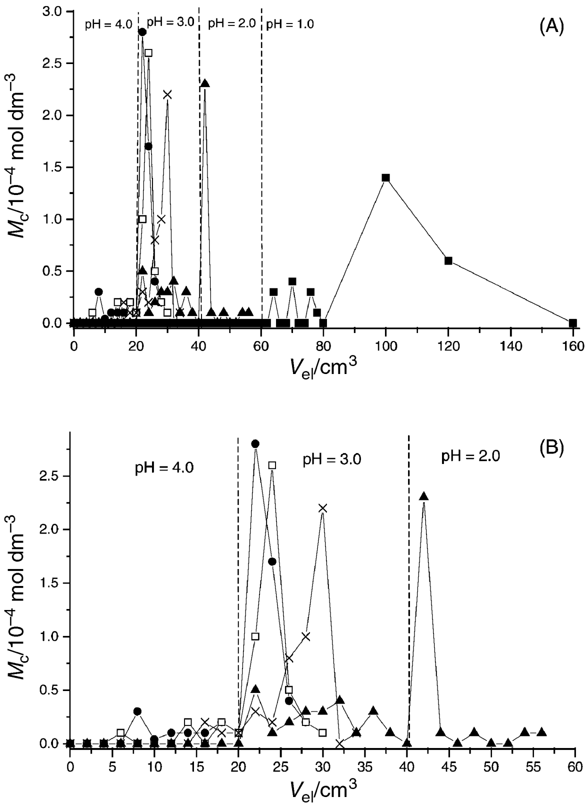


**Fig. 6** Separation of the divalent cations: Cu (×), Ni (●), Co (□), Pb (▲) and Hg (■) from a column packed with $SiO_2NSSH$. The uptake cation concentration ($M_c$) was collected by elution with variable amounts ($V_{el}$) of aqueous buffer solutions, with decreasing pH values (A) and using the same procedure, but without mercury (B).

The separation ability of this surface was determined through the percolation of a solution containing a mixture of these five cations. The pH is one of the most important factors for controlling the extraction of metal ions from solution.[34] Figs. 5 and 6 present the ability of the $SiO_2NSSH$ surface to separate these cations at different pH values. Elution of the loaded $SiO_2NSSH$ column with various buffer solutions fully removed nickel, cobalt and copper at pH 3 and lead at pH 2. However, mercury ions were not totally removed. A volume of 160 cm$^3$ of water was percolated through the column at pH 1 and even this was not sufficient to totally remove Hg(II). In this operation, only 62% of the mercury cation adsorbed onto the column was removed by acid solution percolation. This fact is more evidence that $SiO_2NSSH$ can be applied as a chemical sensor for mercury ions in solution.

Another feature connected to the use of this surface is its good ability to separate these cations from a water solution. The separations between the couples cobalt–nickel, and nickel–copper were not effective. However, the other cations were separated successfully. To confirm this ability of the $SiO_2NSSH$ surface for separating cations, the separation resolution ($R_{(s)}$) was calculated for this column by using eqn. (3), where $\Delta V$ is

$$R_s = 2\frac{\Delta V}{(w_A + w_B)} \quad (3)$$

the difference between two successive peaks, as eluent volumes of the analytes, and $w$ is the base width measured in terms of elutant volume.[35]

Application of this equation to the results obtained for this surface with divalent cation separations, the resolutions represented by the couples, were determined as: $R_{(s)Co-Ni} = 0.20$, $R_{(s)Co-Cu} = 0.73$, $R_{(s)Co-Pb} = 2.50$, $R_{(s)Co-Hg} = 1.73$, $R_{(s)Ni-Cu} = 0.55$, $R_{(s)Ni-Pb} = 2.25$, $R_{(s)Ni-Hg} = 1.69$, $R_{(s)Cu-Pb} = 1.33$, $R_{(s)Cu-Hg} = 1.52$ and $R_{(s)Pb-Hg} = 1.35$. These results confirm the effectiveness of the $SiO_2NSSH$ surface in separating divalent cations.

The presence of mercury, even at very low levels in natural water supplies, can cause considerable problems.[4] Thus, the separation and determination of mercury content is of vital importance.[22,36,37] The modified silica $SiO_2NSSH$ exhibits high selectivity for binding mercury ions from a mixture of cations dispersed in aqueous solution. Results in separating and removing cations from water by using such anchored silicas come into view with good potential for applications to aqueous solution. The use of this inorganic chemically modified matrix corroborates with the advanced principle postulated by clean technology with the procedure being applied to manipulate traces of toxic heavy metals dispersed in aqueous solution.

## Conclusion

A silica gel surface modified with a new silylating agent was successfully obtained. This surface presents a high affinity for Hg(II), due to the presence of two basic sulfur centres. This anchored surface, $SiO_2NSSH$, also presents a good adsorption capability for other divalent cations, which permits its use in the extraction of toxic metal ions from aqueous solutions. The separation of divalent cations with this surface suggests scope for exploitation in chromatographic applications. On the other hand, in exploring the selectivity in binding mercury, this behaviour suggests its possible use in the manufacture of a chemical sensor for this toxic metal.

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