Extraction of Pb(II), Cd(II), and Hg(II) from aqueous solution by nitrogen and thiol functionality grafted to silica gel measured by calorimetry

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Abstract

The reaction of ethylene sulfide with 3-aminopropyltrimethoxysilane gave a new silylating agent, which was anchored onto a silica surface *via* the sol–gel procedure. This surface displayed a chelating moiety containing nitrogen and two sulfur basic centers potentially capable of extracting cations from aqueous solutions. The process of metal extraction was followed by a batch method, and fitted to a modified Langmuir equation. The maximum adsorption capacities found were: 2.06 ± 0.01, 3.72 ± 0.02, and 5.14 ± 0.02 mmol g^{-1} for Pb(II), Cd(II), and Hg(II), respectively. The enthalpies of bending are: -1.16 ± 0.04, -3.60 ± 0.10, and -8.94 ± 0.03 kJ mol^{-1} for Cd(II), Pb(II), and Hg(II), respectively. The Gibbs free energies of binding agree with the spontaneity of the proposed reactions between cations and basic centers.
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1. Introduction

Hybrid organic–inorganic materials can have relatively high metal ion loading capacities and strong affinities for selected metal ions. Functionalized oxides and polymers, mainly silica gel, are widely used in high performance liquid chromatography for separation of organic compounds [1], inorganic anions [2], and cation mixtures, for preconcentration [3] and ion-exchange [4], and as catalysts [5] and chemical sensors [6].

This article describes adsorption by modified silica of Pb(II), Cd(II), and Hg(II) from aqueous solutions, and gives thermochemical data on these interactions. Preparation of a silica gel obtained from the sol–gel process based on the reaction of a new silylating agent 2-{2-{3-(trimethoxysilyl)propylamino}-ethylthio}ethanethiol is characterized [7].

2. Experimental

2.1. Materials

Ethylene sulfide (ets) (Aldrich) was distilled before use. Tetraethoxysilane, TEOS (Aldrich) and 3-(trimethoxysily)-propylamine, APTS (Aldrich) were used without further purification. Solutions of Pb(II), Cd(II), and Hg(II) chlorides were prepared in bidistilled water from reagent grade (Merck) materials.

2.2. Synthesis of 2-{2-{3-(trimethoxysilyl)propylamino}-ethylthio}ethanethiol (NSSH)

The silylating agent was synthesized in anhydrous condition by mixing 20.0 cm^3 (57.28 mmol) of the precursor 3-(trimethoxysily)propylamine (APTS) with 7.0 cm^3 (114.56 mmol) of ethylene sulfide, maintained in a slight reflux in sand bath at 373 K in a sealed tube for 24 h to give the final product. The synthesis was carried out in a 100 cm^3 oval glass tube under slight vacuum.

2.3. Immobilization of silylating agent NSSH onto silica gel

The NSSH was anchored on silica surface by hydrolysis of alkoxydes by ammonium hydroxide 8.0×10^{-2} mol dm^{-3} solution, as catalyst [7,8]. In a typical immobilization, 24.0 cm^3 of TEOS and 17.0 cm^3 of NSSH were mixed at room temperature (r.t.). To this solution, ethanol and water in a 2:1 molar ratio were added. Finally, 3.0 cm^3 of basic catalyst was added dropwise under stirring at 333 K. After 0.5 h the gel was formed,

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which was aged for 48 h at r.t. The white solid was filtered, washed with water and ethanol and dried in *vacuum* at r.t. for another 8 h.

2.4. Physical measurements

The functionalized silica gel was analyzed with a Perkin-Elmer 2400 Series II microelemental analyzer [7]. Activated silica gel and functionalized silica gel were characterized by measuring the surface area with the BET [9] method in a Flow-sorb II 2300 Micrometrics apparatus. Thermogravimetric curves were obtained with a DuPont model 1090 B apparatus coupled with a thermobalance 951, by heating the samples from room temperature to 1273 K at a heating rate of $0.17\,K\,s^{-1}$, with samples varying in weight from 5.0 to 15.0 mg [7]. IR spectra for all compounds were obtained with a Fourier transform IR spectrophotometer MB-Bomem with KBr pellets in $4000–400\,cm^{-1}$ region, with a resolution of $4\,cm^{-1}$.

2.5. Adsorption isotherms

The isotherms of adsorption were obtained by the batch method, which consisted in suspending 50.0 mg of the modified silica in $20.0\,cm^3$ of aqueous solutions of cations at different concentrations, varying from 0.001 to $0.019\,mol\,dm^{-3}$ and was mechanically stirred at 298 ± 1 K. The amount adsorbed was estimated as the difference between the initial concentration in aqueous solution and that found in the supernatant by a GBC model 908 AA atomic absorption spectroscopy apparatus for Pb(II) and Cd(II), Hg(II) was estimated by EDTA complexometric titration. All samples were analyzed in triplicate.

2.6. Calorimetry

The thermal effect from cation–basic center interaction was measured in an isoperibol Hart Scientific calorimeter, model 4285 [10–12]. A sample of functionalized silica, varying in mass from 15.0 to 50.0 mg was suspended in $2.0\,cm^3$ of water under stirring at 298.15 ± 0.02 K. Thermostated solutions of the cations, in the $1.0–1.2\,mmol\,dm^{-3}$ range, were incrementally added into the calorimetric vessel and the thermal effect (Q_t) was then evaluated [10–12]. Under the same experimental conditions, the corresponding thermal effect of dilution of the titrant was obtained in the absence of the support (Q_d). The thermal effect of the hydration of the immobilized silica in water was estimated as before [10–13]. The net thermal effect of adsorp-

tion ($\sum Q_r$) was obtained from Eq. (1):

$$\sum Q_r = \sum Q_t - \sum Q_d. \tag{1}$$

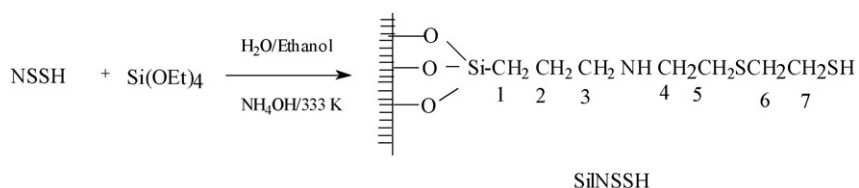## 3. Results and discussion

The reaction of the precursor silylating agent 3-(trimethoxysily)propylamine 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 2-{2-{3-(trimethoxysilyl)propylamino}-ethylthio}ethanethiol, as described previously [7]. This molecule, NSSH, reacted with TEOS and the copolymerization occurred due to the silica backbone formation, caused by the basic catalyst, as shown in Scheme 1. The elemental analysis of this matrix, Sil-NSSH, showed for carbon, nitrogen and sulfur: 24.32% (20.47 mmol), 3.50% (2.50 mmol) and 19.11% (5.97 mmol), respectively, in agreement with the expected composition from the reaction.

The measurement of the specific area, S_{BET}, based on the adsorption of gaseous nitrogen at several pressures at 77 K, generated for activated silica gel $484.2 \pm 6.4\,m^2\,g^{-1}$ and for functionalized surface, Sil-NSSH, $82 \pm 6\,m^2\,g^{-1}$. This lower surface area is due to the presence of pendant groups which block the access of molecules of gaseous nitrogen into the structure of the anchored silica [7,8].

The thermogravimetric curve of the activated silica gel is shown in Fig. 1(A). An initial 1.0% weight loss in the range 298–473 K is attributed to the release of water physically adsorbed on the surface. The following loss of mass of 2.60% with maximum at 1170 K, is related to the condensation of free silanol groups on the surface to form siloxane groups [10]. The immobilized Sil-NSSH compound showed a total mass loss of 51%, without any definition of steps, which could correspond to the decomposition of the organic groups [7,8]. However, the continuous decomposition occurred together with the condensation of remaining silanol groups to yield the final residue of siloxane.

The infrared spectrum (Fig. 2) showed a large and broad band near $3600\,cm^{-1}$ for the activated silica Fig. 2(A), which corresponds to O–H stretching vibration. Some additional bands appear after anchoring the NSSH silylating agent on the surface of silica by sol–gel process, as illustrated in Fig. 2(B). The material presented two well defined bands at 2947 and $2816\,cm^{-1}$ assigned to CH stretching vibrations [3,7,8,14,15], and a weak band at $2544\,cm^{-1}$ that is assigned to SH stretching frequency [16].

NSSH + Si(OEt)$_4$ $\xrightarrow[\text{NH}_4\text{OH/333 K}]{\text{H}_2\text{O/Ethanol}}$ O—Si-CH$_2$ CH$_2$ CH$_2$ NH CH$_2$CH$_2$SCH$_2$CH$_2$SH
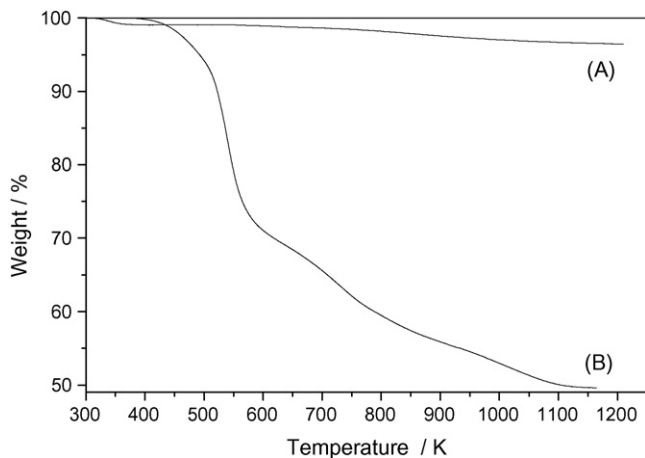
SilNSSH

Scheme 1.

Fig. 1. Thermogravimetric curve for silica gel (A), and for matrix Sil-NSSH (B).

The results of the adsorption of cadmium, lead, and mercury are presented in Table 1. Adsorption of Cu(II), Ni(II), and Co(II), and their (n^s) values, previously reported [7] were 1.66 ± 0.01, 1.42 ± 0.10, and 1.26 ± 0.02 mmol g^{-1}, respectively. The results obtained here demonstrate that mercury ion interacts more effectively in binding to the pendant groups than the other cations. This feature was also observed in other modified surfaces containing thiol groups [3,16,17]. This behavior reflects the high affinity of the sulfur basic centers for mercury [18].

The experimental data (Fig. 3) were fit to the modified Langmuir isotherm: $(C_s/n_f) = (C_s/n_f) + (1/n^s)(1/b)$ [3,14–16], where
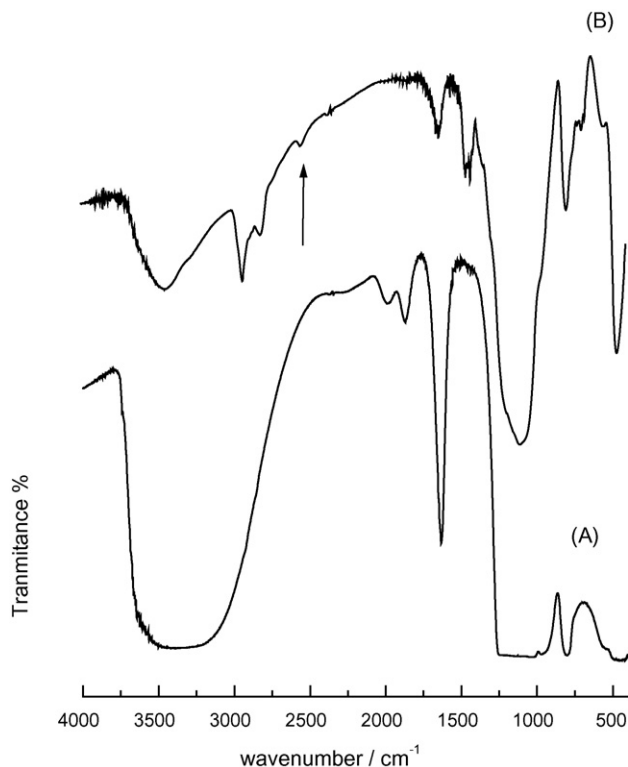

Fig. 2. IR spectra of silica gel (A), and modified silica, Sil-NSSH (B).

Table 1
Number of moles adsorbed (n_f), maximum adsorption capacity (n^s), correlation coefficient (r), and constant (b) for the interaction of divalent cations (M) with anchored Sil-NSSH at 298 K

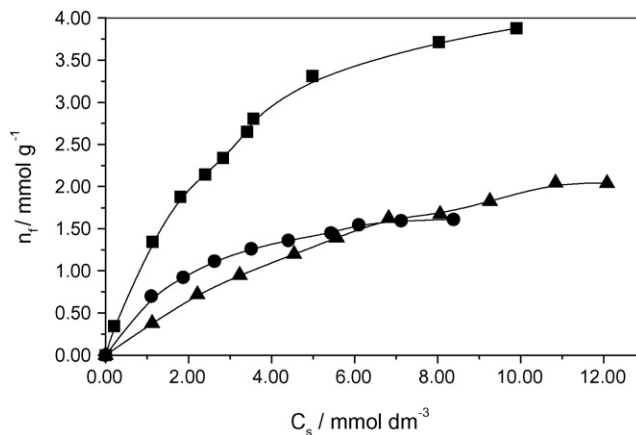| MCl$_2$	n_f (mmol g^{-1})	n^s (mmol g^{-1})	r	b
Pb	1.61	2.06 ± 0.01	0.9990	451
Cd	2.04	3.72 ± 0.02	0.9941	106
Hg	3.88	5.14 ± 0.02	0.9979	319

Fig. 3. Isotherms of adsorption of divalent cations onto the modified silica gel surface for Hg (■), Cd (▲), and Pb (●) at 298 ± 1 K.

C_s is the concentration of solution at equilibrium (mol dm^{-3}), and n_f and n^s (mol g^{-1}) are defined in Table 1. The n^s and b values for each adsorption process were obtained from the slope and intercept, respectively, of the linearized form of the adsorption isotherm, from plots of C_s/n_f versus C_s (Fig. 4), by the method of least squares. The (n_f) is obtained from the last point of isotherm of adsorption, being then an experimental value, whereas (n^s) is obtained from the linearized form and is a calculated value. Thermodynamic data were obtained from calorimetric titration. The collected thermal effect values for chelate–basic center interactions, due to the presence of the available groups disposed
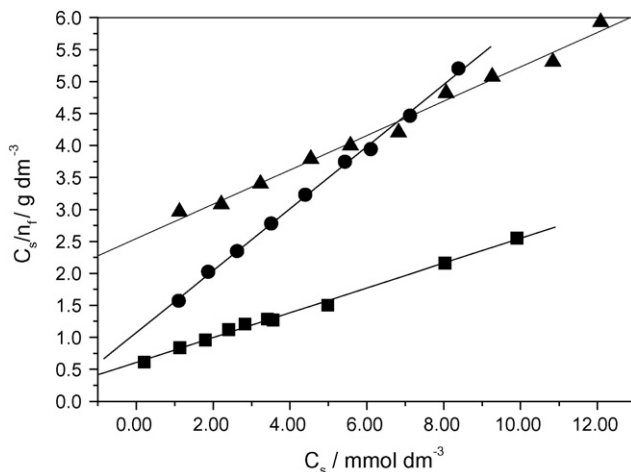

Fig. 4. Linearization of isotherms of adsorption of divalent cations adsorbed onto the modified silica gel surface for Hg (■), Cd (▲), and Pb (●) at 298 ± 1 K.

Table 2
Thermodynamic values for the interaction of metal (M) chlorides on anchored Sil-NSSH surface at 298.15 K

MCl_2	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cd	1.16 ± 0.04	25.11 ± 0.04	80 ± 2
Pb	3.60 ± 0.10	23.42 ± 0.02	66 ± 2
Hg	8.94 ± 0.03	22.55 ± 0.03	46 ± 1

on modified surface, were adjusted to the Langmuir modified equations, as represented by:

$$\frac{\sum X}{\sum \Delta_r H} = \frac{1}{(k-1)\Delta_{mono}H} + \frac{\sum X}{\Delta_{mono}H}$$

where $\sum X$ is the mole fraction of each cation in solution, $\Delta_r H$ the integral enthalpy of adsorption, k a proportionality factor which includes the equilibrium constant, and $\Delta_{mono}H$ is the integral heat of adsorption for formation of a monolayer of the unitary mass of immobilized material. The results are listed in Table 2. The molar fraction $\sum X$ of the acidic metal center in each chelate in equilibrium was calculated with the aid of the n_s values of the calorimetric titration process, which also included n_s values for the solvent used. These values associated with the calorimetric titration data permit one to obtain the enthalpy $\Delta_{mono}H$ of a monolayer formed on the surface and simultaneously k values, as explained above. The $\Delta_r H$ values representing the enthalpy of adsorption, were calculated by considering the number of the cations adsorbed, using the expression: $\Delta_r H = \Delta_{mono}H/n^s$. From these values other thermodynamic data, such as ΔG and ΔS were also calculated based on the expressions $\Delta G = -RT \ln K$ and $\Delta S = (\Delta_r H - \Delta G)T^{-1}$, and the results are listed in Table 2.

4. Conclusions

This study indicated that the surface modified with a new silylating agent presents a high affinity for mercury, due to the presence of two basic sulfur centers, and also presents a good adsorption capacity for other divalent cations.

The bonding of metal ions by the Sil-NSSH material suggests it may be useful for removing metal contaminants from wastewater and also for the manufacture of a chemical sensor for mercury.

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