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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 $5.14 \pm 0.02\,\mathrm{mmol\,g^{-1}}$ for Pb(II), Cd(II), and Hg(II), respectively. The enthalpies of bending are: -1.16 ± 0.04, -3.60 ± 0.10, and $-8.94 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$ 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.

Keywords: Silica gel; Adsorption; Heavy metal; Calorimetric titration; Thermodynamic data

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 $20.0\,\mathrm{cm^3}$ (57.28 mmol) of the precursor 3-(trimethoxysily)propylamine (APTS) with $7.0\,\mathrm{cm^3}$ (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 $100\,\mathrm{cm^3}$ 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 $8.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ solution, as catalyst [7,8]. In a typical immobilization, $24.0\,\mathrm{cm^3}$ of TEOS and $17.0\,\mathrm{cm^3}$ of NSSH were mixed at room temperature (r.t.). To this solution, ethanol and water in a 2:1 molar ratio were added. Finally, $3.0\,\mathrm{cm^3}$ 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 Flowsorb 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 adsorption ($\sum Q_r$) was obtained from Eq. (1):

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

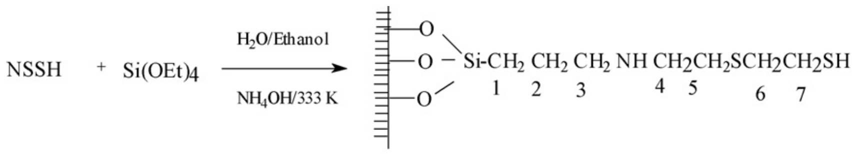
3. Results and discussion

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 ± 6.4 m^2 g^{-1} and for functionalized surface, Sil-NSSH, 82 ± 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].



SilNSSH

Scheme 1.