Interaction of divalent cations with silica modified with histamine evaluated by adsorption and thermochemical data

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Abstract Silica gel was modified by silanization reaction followed by functionalization of histamine in a heterogeneous route. These materials were characterized by elementary nitrogen and chloride analyses, porosity, thermogravimetry, and infrared. The functionalized surface adsorbed Cu(II), Co(II), Ni(II), and Zn(II) ions in an aqueous solution at 25 °C. The isotherms of adsorption are in accordance with Langmuir model and the surface presented a great potential to form complexes metal-surface in the chemical reason of 1:1.

Keywords Silica · Histidine · Adsorption

Introduction

The disposal of metal ions by several industrial activities including chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear, and other industries have resulted in serious environmental problems [1–3]. Metal ions are not biodegradable and tend to accumulate in living organisms. The pollution caused by metals represents common and serious diseases for human beings and may be harmful to wild life due to the excessive release of metallic species into the aquatic and soil systems leading to the increasing contamination of urban and industrial wastewaters by toxic metal ions [4–6].

Many methods and processes have been extensively used to remove toxic metal ions from water such as: liquid–liquid extraction, ion exchange, electrochemical treatment, redox reaction, reverse osmosis, and others [4–6]. On the other hand, these methods have been usually presenting several disadvantages including low efficiency, high energy demand as well as time, and chemical consumption [3–6]. In order to solve these problems, metal ion extraction has been extensively applied to modified surfaces. In this way, solid modified silica with organofunctional groups is the immobilization of the desired reactive atomic group, which causes a great versatility of this surface in developing various functions [7, 8]. Thus, functional groups containing nitrogen, sulfur, oxygen, and phosphorus, disposed in the chains of cellulose, enable the surface to act in a number of academic or industrial applications.

This article reports the synthesis and characterization of silica gel modified with histamine aiming to find an efficient material for the removal of Cu, Cd, Ni, and Zn ions from water.

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Experimental

Chemicals

All reagents used such as *N,N*-dimethylformamide (DMF); ethanol and acetone (Dynamic); pyridine, triethylamine, 3-chloropropyltrimetoxysilane (Aldrich); histamine (Merck); $CuCl_2$, $CoCl_2$, $NiCl_2$, and $ZnCl_2$ (Vetec) were all regent grade.

Silica modification

A sample of 21 g of silica gel was suspended in 100 mL of dry xylene and 10.81 g of 3-chloropropyltrimethoxysilane was added to this suspension. The mixture reacted for 72 h in a reflux system at 140 °C. The suspension was filtered and washed, and the obtained product was named SiCl. A sample of 12 g of SiCl reacted with 4.0 g of histamine and 10 mL of deprotonating agent (triethylamine) in 50 mL of dimethylformamide. The suspension was kept in a reflux and mechanically stirred for 72 h at 150 °C. The final product was filtered off and washed with ethanol and water and named SiHa.

Characterization

The histamine amount attached to the silica surface was obtained from the nitrogen amount determined by the Kjeldahl method [9].

The surface area, pore diameter, and pore volume of materials were obtained by using the nitrogen adsorption technique in a Quantachrome NOVA 2200 porosimeter. Infrared spectra of solid samples were obtained using KBr pellets, with 60 scans accumulation in a JASCO 4100 FTIR spectrophotometer. ^{13}C and ^{29}Si nuclear magnetic resonance spectra of the solid samples were obtained from a Varian Mercury Plus 300 spectrometer at room temperature. The method and experimental details of NMR have been presented in detail elsewhere [10].

Adsorption of metal ions

The adsorption process was followed batchwise in an aqueous solution of $ZnCl_2$, $CoCl_2$, $CdCl_2$, and $CuCl_2$ at 298 ± 1 K. For this process, a series of samples of about 25.0 mg of SiHa were suspended in 50.0 mL of aqueous divalent metal ions solutions at different concentrations, varying from 0.50 to 15.00 mmol L^{-1}. The amount adsorbed was determined by the difference between the initial concentration in aqueous solution and the one found in the supernatant, using an atomic absorption spectrometer Buck model A-200. In every case, all samples were analyzed in triplicate.
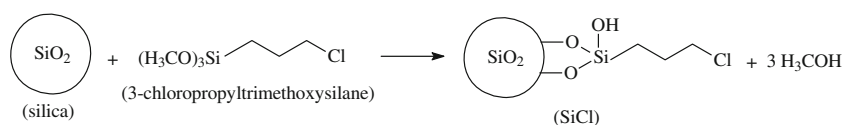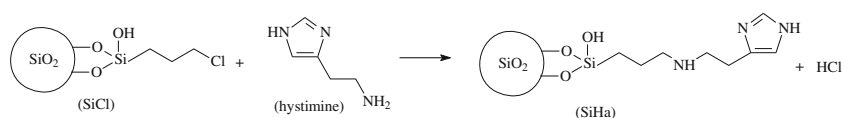
Calorimetry

The adsorption of divalent cations by SiHa was followed calorimetrically by titration using an adiabatic calorimeter PARR 6755. In a typical experiment, 0.50 g of the SiHa were suspended in 50.0 mL of water, equilibrated at 298.15 ± 0.02 K (thermostatically controlled), and titrated with an aqueous solution of divalent metal ions 0.50 mol L^{-1}. The metal solution was added in increments of 0.10 mL via a syringe coupled to the calorimetric vessel, up to saturation of the active surface sites of the material. Following each addition, the constant heat flux ($\Delta_{tit}Q$) was recorded at the end of the operation, and the mixture allowed to re-equilibrate. A similar procedure was employed to monitor the heat flux because of metal dilution ($\Delta_{dil}Q$) in the absence of modified silica.

Results and discussion

Reaction and characterization

An overview on the progress of the inorganic surface immobilization field is closely related to the advance of the synthetic chemistry involved. Relevant features associated with this subject are those that can cause expansion or insertion of the main organic chain precursor silylant agent, by exploring the presence of reactive centres on it. Silica gel reacts with 3-chloropropylktrimethoxysilane to produce the modified silica SiCl, as according to Fig. 1. This modified silica reacted with histamine in the presence of disprotonant agent tri-*n*-ethylamine in order to increase the yield of production of the desired material, named SiHa, as shown in Fig. 2.

The amount of histamine immobilized onto silica gel surface was determined by Kjeldahl analysis, which gave 3.40 mmol of histamine per gram of silica. The N_2 adsorption isotherms showed that the materials presented very high surface areas, which gave 466, 424, and 393 $m^2 \ g^{-1}$ for silica, SiCl, and SiHa, respectively. This decrease in surface area is caused by the incorporation of organic pendant groups on silica surface blocking the access to the porous of the material [11].
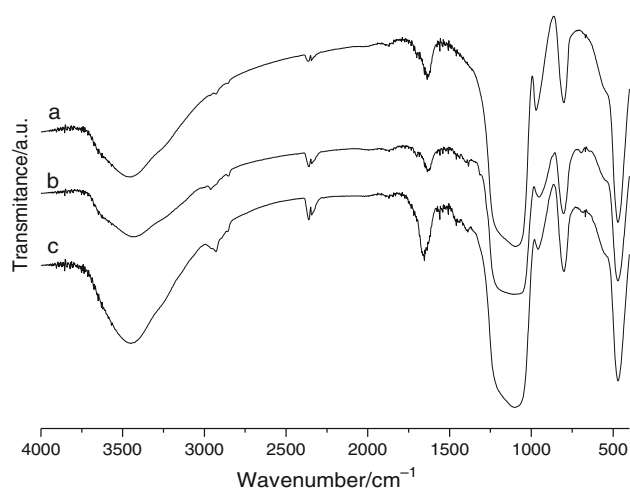

Fig. 1 Reaction between silica and 3-chloropropyltrimethoxysilane

Fig. 2 Reaction between SiCl and histamine to produce final material named SiHa

Fig. 3 Infrared spectra of silica (**a**), SiCl (**b**), and SiHa (**c**)

Fig. 4 ^{29}Si NMR solid state spectrum of SiHa

Infrared spectra for activated silica and both modified silicas are shown in Fig. 3. A small difference is observed in relation to the number and intensities of the bands in comparing activated silica and the other immobilized compounds. This same behavior was previously observed for other anchored processes. The main features of all silicas are connected to the similarity of bands associated with the inorganic backbone such as: the large broad band between 3500 and 3000 cm^{-1}, which is assigned to the presence of the O–H-stretching frequency of silanol groups and also to the adsorbed water remaining; the intense band related to siloxane stretching of these groups [12, 13]; one peak at 1100 cm^{-1}; which is attributed to Si–O–H stretching frequency for silanol groups at 900 cm^{-1}; and the band around 1650 cm^{-1} is also observed and is related to angular vibration of the water molecule. The anchored silicas presented two weak bands at 2950 and 2870 cm^{-1}; due to C–H stretching of the carbon sp^3 that confirmed the attachment of the organic molecule on the silica surface. For SiHa spectrum, the imidazole ring N–C, C=C, and C–N=C stretching frequencies were detected at 1559, 1507, and 1386 cm^{-1}. These are important bands because they also confirm the success of reaction between histamine and SiCl, which interaction should occur through a covalent bond between nitrogen of this precursor [12].

The solid state ^{29}Si NMR spectrum of SiHa confirms the presence of the covalent bond formed between the silylant agent and silanol groups dispersed on the silica gel surface, as shown in (Fig. 4). This spectrum shows four peaks at −51.3, −59.5, −95.5, and −104.9 ppm. The first one is assigned to the silicon atom of the silylant agent bonded to one OH group, thus forming the structure, $RSi(OSi)(OH)_2$, usually named as the T^2 signal. The peak at −59.5 is assigned to $RSi(OSi)_3$, the T^4 signal. Both signals confirm that the organic groups were covalently bonded onto the silica

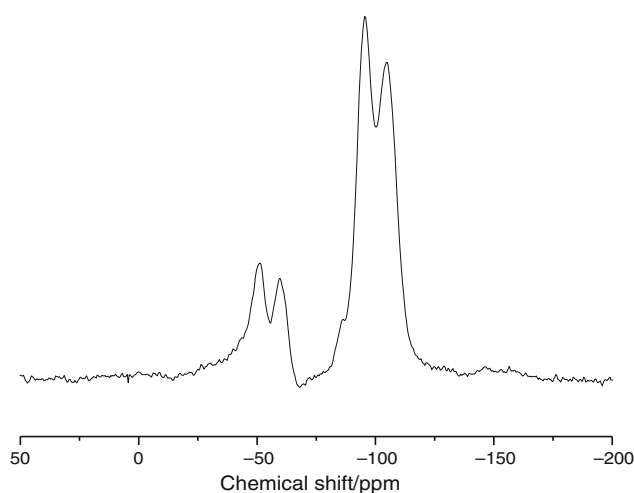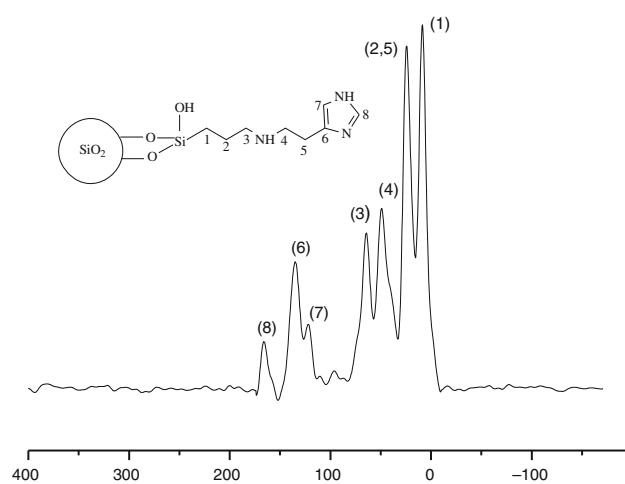**Fig. 5** ^{13}C NMR solid state spectrum of SiHa

surface. The other two peaks are attributed to pure surface signals described as: (i) $Si(OSi)_4$, Q^4 at −104.9 ppm; (ii) surface signal, $Si(OSi)_3OH$, Q^3 at −95.5 ppm [12].

Important information about anchorament of histamine groups on the inorganic structure can be observed in solid state ^{13}C NMR spectrum, as presented in Fig. 5. The SiHa spectrum presents the chemical modification of the silica surface with histamine group, which resulted in a series of signals with chemical shift in the range 8–170 ppm, presenting seven well-formed peaks at 8.72; 24.25; 49.17; 64.37; 121.96; 134.91; and 165.97 ppm, which are assigned to carbons labeled 1–8.

Adsorption

SiHa was used to remove divalent metal ions from water. Adsorptive and thermodynamic studies were followed in order to understand the capacity of this modified silica to

remove metal ions from water. Thus, the number of moles of the divalent metal ions adsorbed per gram of SiHa (N_f; mol g^{-1}) was obtained from Eq. 1 [14–17].

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

where n_i is the initial number of moles of metal ion added to the system, n_s is the number of moles at equilibrium after adsorption, and m is the mass (g) of SiHa. The experimental data were substituted into the general equation of the modified Langmuir model presented in Eq. 2.

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s \cdot K} \qquad (2)$$

where C_s is the concentration (mol L^{-1}) of the solution at equilibrium, N_s is the maximum amount of divalent cations adsorbed per gram of SiHa (mol g^{-1}), which depends on the number of adsorption sites, and K is an equilibrium constant (mol dm^{-3}) [14–17]. Adsorptive behavior is presented in Fig. 6. All further data from Fig. 6 were derived from the linear form of the adsorption isotherm, i.e., from plots of C_s/N_f versus C_s, in which N_s and K are represented by the slope and intercept, respectively, as shown in Fig. 7. The maximum amount of metal ions that could be adsorbed per gram of SiHa was described in Table 1.

The Gibbs free energy changes may be calculated from Eq. 3, and the obtained ΔG values were listed in Table 1.

$$\Delta G = -RT \ln K \qquad (3)$$

Thermal effects of the interaction of metal ions with SiHa were obtained from a series of calorimetric experiments. The complete thermodynamic cycle can be summarized as follows in Eq. 4 [15, 16].
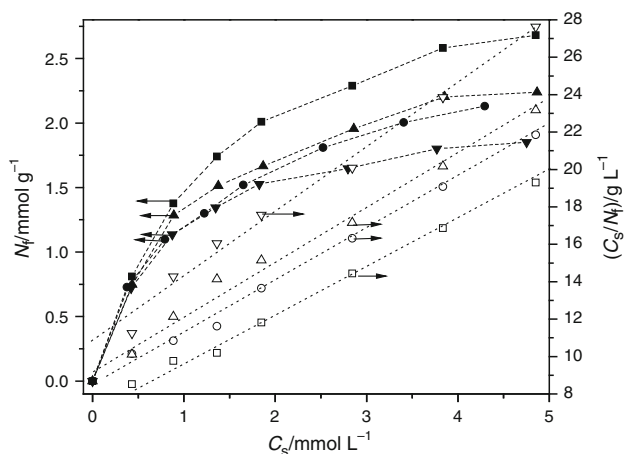

Fig. 6 Adsorption isotherms of divalent cation Cu (*filled square*), Co (*filled circle*), Ni (*filled triangle*), and Zn (*filled inverted triangle*) on the surface of $\equiv$Si–Ha in aqueous solution buffered at 25 °C and their respective linearizations Cu (*open square*), Co (*open circle*), Ni (*open triangle*), Zn (*filled inverted triangle*)
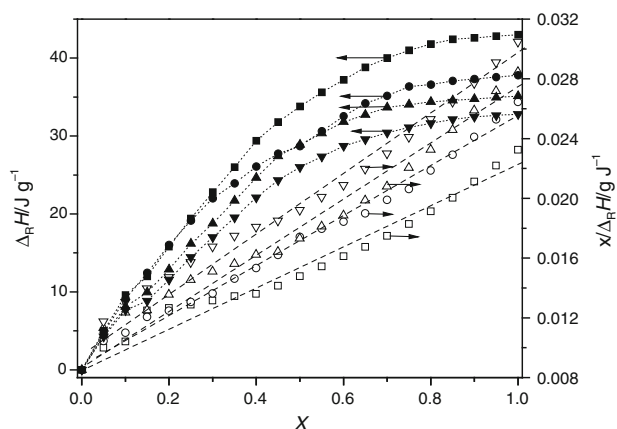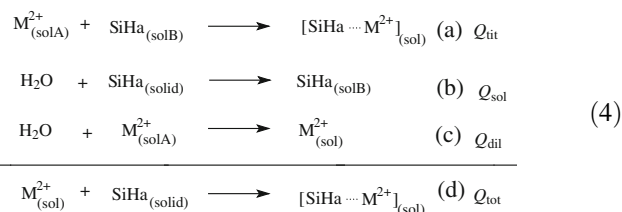

Fig. 7 Isothermal enthalpy integral adsorption of divalent cations Cu (*filled square*) Co (*filled circle*) Ni (*filled triangle*) and Zn (*filled inverted triangle*) on the surface of $\equiv$Si–Ha in aqueous solution buffered to 25 °C and their respective linearizations Cu (*open square*), Co (*open circle*), Ni (*open triangle*), Zn (*open inverted triangle*)

Table 1 Maximum number of moles adsorbed, N_s, equilibrium constant, K and thermodynamic data, ΔH, ΔG, and ΔS for interaction between divalent cations and SiHa

	N_s/mmol/g	K	ΔH/kJ/mol	ΔG/kJ/mol	ΔS/J/mol/K
Cu	3.45	1,356	−78.86	−17.87	204
Co	2.68	1,243	−62.50	−17.65	151
Ni	2.79	1,036	−58.21	−17.22	138
Zn	2.17	1,258	−54.31	−17.68	123

$$
\begin{array}{llll}
M^{2+}_{(solA)} + SiHa_{(solB)} & \longrightarrow & [SiHa \cdots M^{2+}]_{(sol)} & \text{(a) } Q_{tit} \\
H_2O + SiHa_{(solid)} & \longrightarrow & SiHa_{(solB)} & \text{(b) } Q_{sol} \\
H_2O + M^{2+}_{(solA)} & \longrightarrow & M^{2+}_{(sol)} & \text{(c) } Q_{dil} \\
\hline
M^{2+}_{(sol)} + SiHa_{(solid)} & \longrightarrow & [SiHa \cdots M^{2+}]_{(sol)} & \text{(d) } Q_{tot}
\end{array} \qquad (4)
$$

Three separated titration experiments were carried out in order to determine the component parts, named: (a) the heat evolved by the SiHa/M^{2+} interaction (Q_{tit}) (b) the heat of solvation of the solid SiHa (Q_{sol}), and (c) the heat of dilution of M^{2+} solution (Q_{dil}). The net heat change Q_{tot} (d) is given by Eq. 5.

$$\Sigma Q_{tot} = \Sigma Q_{tit} + \Delta Q_{sol} - \Delta Q_{dil} \qquad (5)$$

Since the heat of solvation of the aqueous suspended modified material was null, the expression was reduced to Eq. 6 [14–17].

$$\Sigma Q_{tot} = \Sigma Q_{tit} - \Delta Q_{dil} \qquad (6)$$

Calorimetric results are shown in Fig. 6. The enthalpy of interaction (Fig. 7), $\Delta_R H$, was obtained from an expression
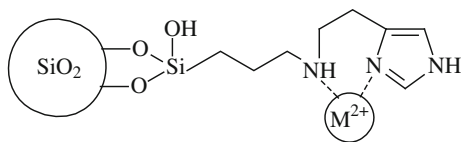
Fig. 8 Proposal scheme of the interaction between SiHa and divalent metal ions

fitted to the modified Langmuir equation represented in Eq. 7 [14–17].

$$\frac{\Sigma X}{\Sigma \Delta_R H} = \frac{1}{(K-1)\Delta_{mono}H} + \frac{\Sigma X}{\Delta_{mono}H} \qquad (7)$$

where ΣX is the sum of the molar fractions of the divalent metal ions remaining in solution after adsorption and $\Sigma \Delta_R H$ is the enthalpy of interaction per gram of SiHa. Based on the Langmuir equation, it was calculated the reaction enthalpy of the monolayer formed, $\Delta_{mono}H$, from plots of $\Sigma X/\Sigma \Delta_R H$ versus ΣX. The molar enthalpy, ΔH, of the interaction process was calculated from $\Delta_{mono}H$ and the maximum number of moles inserted, N_s, using Eq. 8.

$$\cdot \Delta H = \frac{\Delta_{mono}H}{N_s} \qquad (8)$$

The entropy, ΔS, was determined from Eq. 9.

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

All thermodynamic data about adsorption of metal ions onto SiHa surface were listed in Table 1. The obtained set of thermodynamic data for the adsorption process indicated that the reaction presented the following sequence Zn < Co < Ni < Cu. All interactions between metal ions and SiHa were spontaneous since they were enthalpically and entropically favored. The adsorbed Cu(II) ions occupied the active SiHa surface sites in the relationship 1:1, and other cations presented occupation relationship of less than 1 mol of cation per mol of active surface sites. Moreover, from the derived thermodynamic data and the proven presence of active amine basic groups on SiHa, which present an excellent interaction with these metal ions. Indeed, thermodynamic data, increasing in entropy, the structure of silica, and the occupation relationship suggest that this interaction presents a chelate effect, as the proposal scheme of the interaction (Fig. 8).

Conclusions

The silica modified with histamine can be used as a good adsorbent for the removal of ions in contaminated environments, adsorbing following sequence Zn < Co < Ni < Cu. Besides, all interactions spontaneous $\Delta G < 0$, being exothermic $\Delta H < 0$ (favored enthalpically) and endergonic $\Delta S > 0$ (favored entropically).

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