Synthesis and characterization of a new adsorbent for capture of metal from aqueous solutions

Luiza N. H. Arakaki · V. H. A. Pinto · V. L. S. Augusto Filha ·
M. G. Fonseca · J. G. P. Espínola · Tomaz Arakaki ·
Claudio Airoldi

Abstract A new material containing a potential ligand for transition metals was prepared through the reaction of 3-aminopropyltrimethoxysilane and thioglycolic acid. The new adsorbent was characterized by elemental analyses, infrared spectroscopy, solid-state ^{13}C nuclear magnetic resonance, thermogravimetric analysis, transmission electron microscopy, and specific surface area calculations. The formulated material was used in the removal of cobalt, copper, and nickel cations from aqueous solutions. Calorimetric titration was applied to study the interaction of these cations with the new adsorbent; the latter displayed a chelating moiety with basic centers containing nitrogen, oxygen, and several sulfur atoms, capable of capturing cations from aqueous solutions. This process of extraction was carried out by a batch method to yield the following order of maximum retention capacity: Ni > Co > Cu. The process of cation interactions showed exothermic enthalpies. The calculated ΔG values are in agreement with the spontaneity of the proposed reactions and conformed to the values found by applying the Langmuir model to these systems. The positive entropy and negative enthalpy values indicated that the reactions are favorable.

Introduction

The development of new materials that display an ability to coordinate metals provides an interesting approach in the fields of environmental metallic depollution, for instance, in the elimination of traces of toxic heavy metals from wastewaters [1, 2]. The interest in this type of materials is related to the diversity of applications found in many areas of science, such as in catalytic processes [3], in chromatography [4], for ion-exchange [5], as sequestration agents of metals [6, 7], as adsorbents for toxic organic compounds [8], and for many other such purposes. Many types of materials, such as silica gel, zeolites, lamellar inorganic phosphates, chrysotile, natural talc, chitosan, and agar agar, could be used for these purposes. The majority of these supports need to be modified by grafting organic molecules containing basic centers for improving their adsorption capacities. The modification of these materials, mainly using silica gel, is usually done using an appropriate molecule a silylating agent, and consequently, a stable covalent bond is formed [1]. Increasing the length of chain can be carried out by a further reaction with a variety of organic functions, for assisting the desired purposes. In a previous report [9], we have described the immobilization of thioglycolic acid (TG) on silica gel using 3-chloropropyltrimethoxysilane to yield silica 3-propythioacetic acid. The amount of TG immobilized was 0.90 mmol g^{-1} of silica. The adsorption capacities of this surface for divalent Cu, Ni, Zn, and Co were 0.73, 0.86, 0.79, and 0.57 mmol g^{-1}, respectively. TG molecules have also been immobilized on a silica surface using 3-aminopropyltrimethoxysilane, with 1.03 mmol of the

L. N. H. Arakaki (✉) · V. H. A. Pinto ·
V. L. S. Augusto Filha · M. G. Fonseca · J. G. P. Espínola
Departamento de Química, Centro de Ciências Exatas e da Natureza, Universidade Federal da Paraíba, 58051-900 João Pessoa, Paraíba, Brazil
e-mail: luiza_arakaki@yahoo.com.br

T. Arakaki
Departamento Engenharia de Alimentos, Centro de Tecnologia, Universidade Federal da Paraíba, 58051-900 João Pessoa, Paraíba, Brazil

C. Airoldi
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, São Paulo, Brazil

pendant groups being anchored per gram of support [10–12]. The adsorption capacities of this surface for the trivalent cations Fe, Cr, and Mo in ethanolic solutions were 0.67, 1.05, and 1.07 mmol g^{-1} of silica, respectively [10]. The adsorption capacities for the divalent cations Cu, Ni, and Co in aqueous solutions were 1.84, 1.18, and 1.02 mmol g^{-1} of modified silica, respectively [11]. In another study, the silylating agent, 3-[2(2-aminoethylamino)ethylamino]ptopyltrimethoxysilane, was immobilized onto the silica gel surface by condensation with the available silanol groups, and in the next step, the TG molecules were incorporated to enlarge the pendant chain; this modified surface was used for adsorbing the divalent Cu, Ni, and Co ions present in aqueous solutions. The adsorption capacities of this surface for these divalent cations were 0.33, 0.30, and 0.28 mmol g^{-1} of modified silica, respectively [13]. Soliman et al. [14] have described a method of immobilization of TG on a silica surface without using any silylating agent, which is an economical process, but it has the disadvantage of chemically anchoring fewer molecules of TG on the silica matrix, that is, 0.51 mmol g^{-1} of support. The disposal of TG groups on the silica surface after chemical immobilization yields attached molecules containing the basic atoms of nitrogen, sulfur, and oxygen. These anchored organic moieties on the surface usually act as chelating agents in processes dealing with cation extraction from solutions.

The main objectives of this study were (1) to prepare a new material containing basic centers, such as nitrogen, oxygen, and sulfur, and possessing a chelating property that complexes metallic cations; this was achieved using the silylating agent 3-aminopropyltrimethoxysilane and TG at room temperature without using any solvent; and (2) to study the processes of cation adsorption through construction of the adsorption isotherms using two procedures: the batch process and the calorimetric titration. The metals used in this study were the divalent cations nickel, cobalt, and copper dissolved in appropriate aqueous solutions.

The advantage of the new material is related to its adsorption capacity; the amounts of Cu, Ni, and Co it adsorbs from aqueous solutions are almost twice the adsorbed amounts reported earlier [9, 10, 12, 13]. Furthermore, this adsorbent also has immense thermal stability and its preparation requires only mild conditions, involving just the reagents.

Experimental

Materials

TG (Fluka) and 3-aminopropyltrimethoxysilane (Aldrich) were used without previous purification. Solutions of Cu(II), Ni(II), and Co(II) nitrates were prepared in bidistilled water from reagent-grade salts.
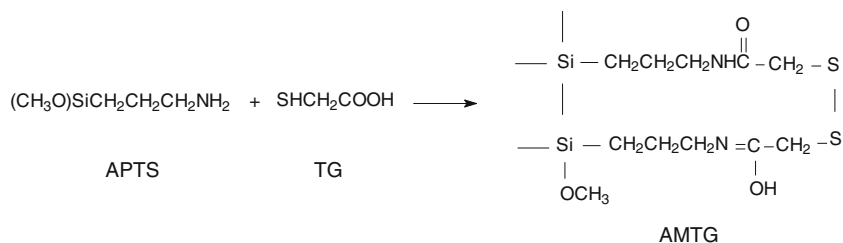
Synthesis of material

The new material was synthesized by mixing 10.0 cm^3 (8.07 mmol) of the precursor 3-(trimethoxysilyl)propylamine (APTS) with 7.0 cm^3 (96.13 mmol) of TG, maintained under a slight reflux in a sand bath at 313 K without any solvent to give the final product, designated as AMTG. The synthesis was carried out in a 250-cm^3 beaker for 24 h, as illustrated in Scheme 1, and then the solid was aged for 48 h at room temperature and dried in vacuum at room temperature for 8 h.

Physical measurements

The amount of carbon, nitrogen, and sulfur was analyzed with a Perkin-Elmer 2400 Series II elemental analyzer [1]. Thermogravimetric curves were obtained using a DuPont model 1090 B apparatus coupled with a thermobalance 951 by heating the samples from room temperature up to 1,300 K at a heating rate of 0.17 K s^{-1}, with the samples varying in mass from 5.0 to 15.0 mg [7, 9]. Infrared spectra for all compounds were obtained with a Fourier-transform infrared spectrophotometer (MB-Bomem) with KBr pellets in the 4,000–400 cm^{-1} region at a resolution of 4 cm^{-1}. Scanning electron microscopy was performed using a JEOL JSTM-300 microscope. Powder X-ray diffraction pattern was measured on a Shimadzu XRD-6000 diffractometer using Cu K$_\alpha$ radiation. ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra for the solid samples were obtained using an AC/300P Bruker spectrometer with cross polarization and magic angle spinning (CPMAS) at a frequency of 75.47 and 59.61 MHz for carbon and silicon, respectively. The ^{29}Si- and ^{13}C-CPMAS spectra were obtained with a contact time of 1 and 5 ms, respectively, and a pulse-repetition time of 4 s. The numbers of scans conducted were 16,470 and 532 scans for carbon and silicon, respectively.

Adsorption isotherms

The adsorption isotherm for each cation was obtained by the batch method, which consisted in suspending a series of flasks containing about 50 mg of the modified silica in 20.0 cm^3 of aqueous solutions of the cations at different concentrations (varying from 1×10^{-2} to 8×10^{-3} mol dm^{-3}); these flasks were mechanically stirred at 298 ± 1 K. The amounts of moles adsorbed were estimated by the difference between the initial concentration in the aqueous solutions and that found in the supernatant after adsorption, estimated using a GBC model 908 atomic

Scheme 1 Reaction scheme of the AMTG

$(CH_3O)SiCH_2CH_2CH_2NH_2$ + $SHCH_2COOH$ $\longrightarrow$

APTS   TG

$$\begin{array}{c} \text{—— Si — CH}_2\text{CH}_2\text{CH}_2\text{NHC} - \text{CH}_2 - \text{S} \\ | \qquad\qquad\qquad\qquad | \\ \text{—— Si — CH}_2\text{CH}_2\text{CH}_2\text{N} = \text{C} - \text{CH}_2 - \text{S} \\ | \qquad\qquad\qquad\qquad | \\ \text{OCH}_3 \qquad\qquad\qquad \text{OH} \end{array}$$

AMTG

absorption spectroscopy apparatus. The adsorption capacity (mmol g^{-1}) was calculated by applying the expression $n_f = (n_i - n_s)/m$, where n_f is the number of moles adsorbed on the modified silica, n_i and n_s are the numbers of moles present in the initial solution and the supernatant after equilibrium, and m is the mass of modified silica. For all samples, determinations were carried out in triplicate.

Calorimetry

The thermal effect obtained from the cation-basic center interaction on the anchored pendant groups at the solid/liquid interface was calorimetrically followed using an LKB 2277 microcalorimeter [15, 16]. For each operation, a sample of functionalized silica, varying from 15 to 50 mg, was suspended in 2.0 cm^3 of water under stirring at 298.15 ± 0.20 K. The thermostated solutions were added in increments of 0.50 mol dm^{-3} into the calorimetric vessel, and the thermal effect of the titration (Q_t) was determined [15, 16]. Under the same experimental conditions, the corresponding thermal effects of various dilutions of the cation solution (Q_d) were obtained in the absence of the anchored silica. The null thermal effect of the hydration of immobilized silica in water was determined as before [15, 16]. Under such experimental conditions, the net thermal effect of adsorption (ΣQ_r) was obtained using Eq. 1, as follows:

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

**Results and discussion**

Infrared spectroscopy is a useful tool to detect the progress and success of the reaction by comparing the precursors and the resultant material. Figure 1a is the infrared spectrum of the precursor APTS, which shows two well-defined bands at 3,363 and 3,286 cm^{-1}, which were attributed to the NH$_2$-stretching vibration modes of the primary amine. The small shoulder at 3,155 cm^{-1} is related to the intensification of the angular deformation of the N–H groups due to Fermi resonance [17]. The free TG molecule showed several bands: a large and strong band related to the O–H-stretching vibration mode, which is located in the region of 3,420 cm^{-1}; two well-defined bands located in the region of 2,920 and 2,842 cm^{-1}, which are attributed to the C–H-stretching vibrations; a weak band at 2,560 cm^{-1}, which is assigned to –SH stretching; a strong band found at 1,709 cm^{-1}, attributed to the –C=O stretching frequency; and a weak deformation band (in-plane C–S–H bending) located in the region of 893 cm^{-1}, as shown in Fig. 1b. However, some bands of the TG molecules disappeared after reaction with the APTS molecule. The weak band located at 2,930 cm^{-1} is related to the C–H-stretching vibration mode. The band at 1,553 cm^{-1} is related to the –C=N-stretching frequency region, and the band related to –SH-stretching frequency of free TG at 2,560 cm^{-1} was obscured, as shown in Fig. 1c, suggesting that the thiol group interacts with APTS in two modes or could be coalesced with other bands of the spectrum.
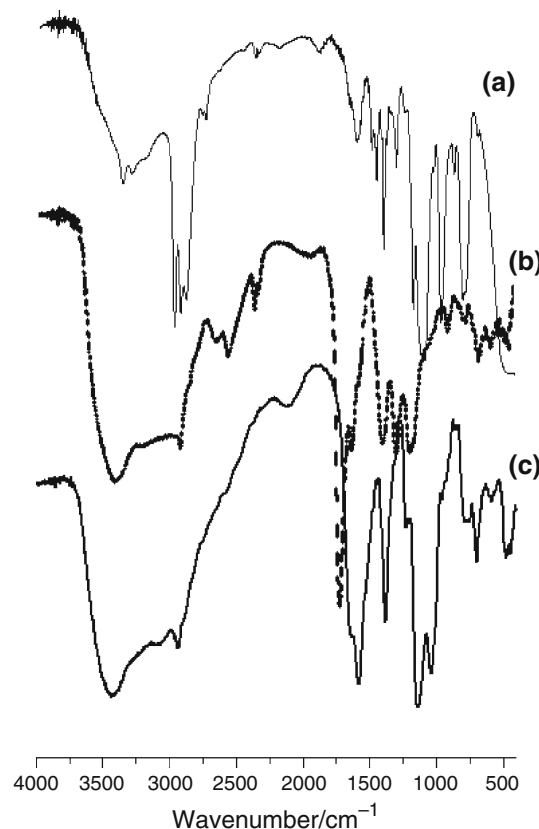
Fig. 1 Infrared spectra of **a** APTS, **b** TG, and **c** AMTG

Fig. 2 ^{13}C-NMR-CPMAS
spectrum of AMTG
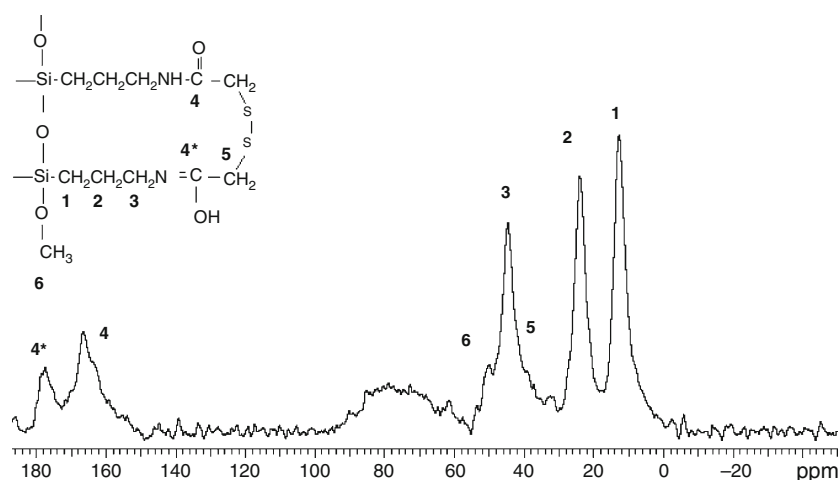

The solid-state ^{13}C-NMR-CPMAS spectra of AMTG are shown in Fig. 2. The weak signal observed at 52 ppm corresponded to the remaining methoxy carbon groups. The broad chemical shifts at 63–95 ppm could be due to different disposition of the organic chain, yielding some degree of polymerization, or due to impurities. The chemical shifts at 8, 21, 39, 43, and 168 ppm corresponded to the carbons 1, 2, 5, 3, and 4, respectively. The peak found at 179 ppm (carbon 4*) can be attributed to the different modes of linkages of molecules to each other, for instance, the –N=C linkage, as shown above the spectrum in Fig. 2.

The ^{29}Si-NMR-CPMAS spectrum of AMTG is shown in Fig. 3. The small peak observed at −58 ppm is an indication that some degree of polymerization has occurred. This peak can be assigned to the silicon atoms of the type R–Si*–$(OSi\Xi)_2$–(X), where X is an –OH group originating from alkoxide hydrolysis and the R groups are the aliphatic organic chains. The peak at −67 ppm can be attributed to the presence of silicon atoms bonded to both siloxane groups and an aliphatic chain, which might be represented as R–Si*–$(OSi\Xi)_3$.

The scanning electron micrograph of AMTG, depicting the morphology of the material, shows a porous network structure, with formation of particles as irregular plaques layered one above the other, as shown in Fig. 4, which is a characteristic of the sol–gel process.

The thermogravimetric curve of AMTG showed an initial weight loss of 6.42% in the range of 336–433 K, which is attributed to the release of water physically adsorbed on the surface. The next loss of mass, 12.62%, occurred in the range of 454–546 K, which is due to the decomposition of the thiol groups in the TG molecule, which react with APTS. The next stage of 11.48% loss of mass occurred in the 668–781 K range, which is attributed to the decomposition of organic groups; the last stage of loss of mass, 28.60%, which occurred in the range
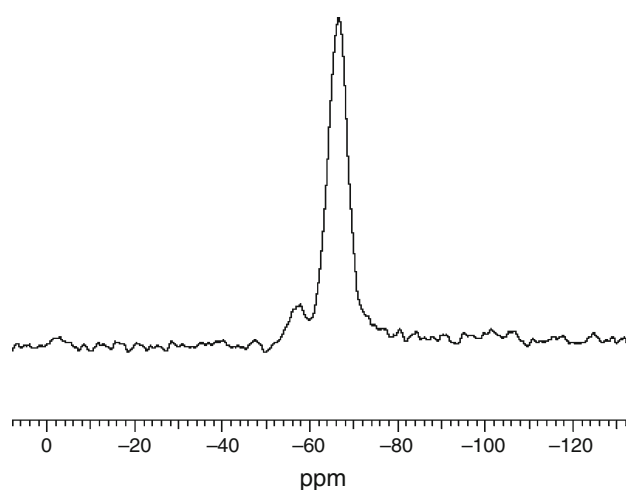
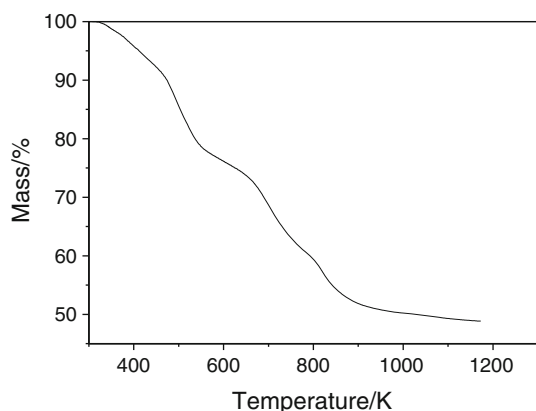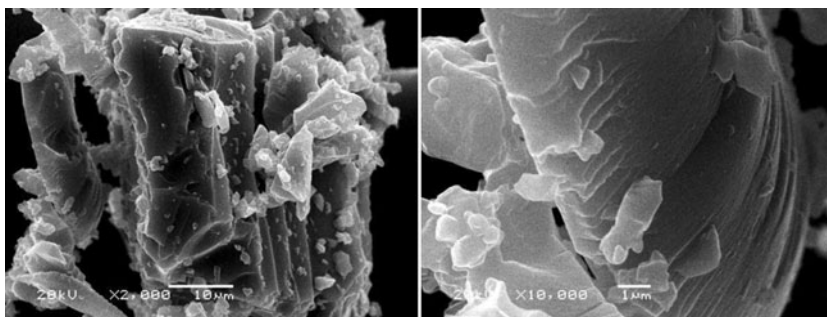
Fig. 3 ^{29}Si-NMR spectrum of AMTG

793–903 K, is related to the decomposition of the remaining organic groups and the condensation of silanol groups to yield siloxane residues, as shown in Fig. 5.

The determination of the specific surface area, S_{BET} [18], based on the adsorption of gaseous nitrogen at 77 K under several pressures, yielded the value 105 m^2 g^{-1} of the AMTG matrix, which is indicative of the presence of polymeric or lamellar type of material.

The elemental analysis of AMTG yielded values of 25.42, 7.27, 5.25, and 9.90% for carbon, nitrogen, hydrogen, and sulfur, respectively. The number of basic centers of nitrogen is 5.2 mmol g^{-1}. For each basic center containing nitrogen, we have two others, namely, oxygen and sulfur; thus, the total number of basic sites is 15.6 mmol per unit mass of AMTG.

The XRD patterns of the AMTG material presented a large single diffraction peak, characteristic of the amorphous material.

The AMTG matrix containing basic centers with sulfur, oxygen, and nitrogen permits the interaction of this

Fig. 4 Scanning electron micrograph of AMTG

Fig. 5 Thermogravimetric curves of AMTG

Table 1 Amount of adsorbed cations (n_f), maximum adsorption capacity (n^s), constant (b), and correlation coefficient (r^2) for the adsorption of divalent cations (MX$_2$) by AMTG at 298 ± 1 K

MX$_2$	n_f/mmol g^{-1}	n^s/mmol g^{-1}	b/dm^3 mol^{-1}	r^2
Cu(NO$_3$)$_2$	1.33	1.42 ± 0.02	702.66	0.9964
Ni(NO$_3$)$_2$	1.66	1.87 ± 0.03	536.15	0.9965
Co(NO$_3$)$_2$	1.34	1.51 ± 0.03	661.71	0.9993

material with a large variety of cations. The sulfur-containing basic centers have a more effective interaction as softer Lewis acids, whereas the nitrogen and oxygen atoms are characteristically harder Lewis acids, chelating with hard cations. The intensity of the colors acquired by the AMTG samples just after contact with the metal-salt solutions shows that the extraction of cations from aqueous solutions is due to metal-complex formation with the basic centers present on the material.

The AMTG stability in aqueous media was investigated measuring the conductibility and pH as a function of time. The results showed that the concentration of protons H$^+$ increases in solutions. The pH and the conductibility of deionized water were 6.8 and 3.0 μS, respectively. After adding the AMTG material, in water, the pH decreased to 5.20 and conductibility increased to 24.4 μS. 24 h later, the pH values were 4.34 and 61.5 μS the conductibility. After 48 h, the material presented the same values of pH and conductivity. The adsorption capacity of metal was not altered in these samples studied. Thus, according to this preliminary investigation, the data obtained showed that this material, is stable in aqueous solutions.

The results of the adsorption of the divalent cations copper, nickel, and cobalt dissolved in aqueous solutions are presented in Table 1 and shown in Fig. 6.

The experimental data were fit to the following modified Langmuir isotherm: $(C_s/n_f) = (C_s/n_f) + (1/n^s)(1/b)$ [15, 16, 19], where C_s is the concentration of the solution at equilibrium (mol dm^{-3}), and n_f and n^s (mol g^{-1}) are amount of adsorbed cations, and maximum adsorption capacity, respectively. 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 derived by the method of least squares. The (n_f) value is obtained from the last point of the isotherm of adsorption, being then an experimental value, whereas (n^s) is obtained from the linearized form of the isotherm and is a calculated value. From the angular coefficient, after linearization of the isotherms, the maximum adsorption capacity (n^s) was determined, the values being 1.42, 1.87, and 1.51 mmol g^{-1} for Cu(II), Ni(II), and Co(II), respectively. Adsorption for these three cations can be ordered as follows: Ni > Co > Cu. Comparing the number of adsorbed cations with the total number of basic centers in AMTG, the number of cations adsorbed is found to be very small in relation to the pendant groups on its surface, suggesting that not all the basic centers are available for cation coordination. Probably, each cation links to one or two pendant groups. The cations could be coordinated to the pendant groups in the mono- or bidentate configurations and never in the tridentate type, because the stereochemistry of the pendant groups do not permit this type of coordination.

The lower adsorption capacity for the Cu (II) may perhaps be explained if one considers the characteristics of the square-planar geometry of the complexes of this cation. This geometry, proceeding from the pronounced distortion
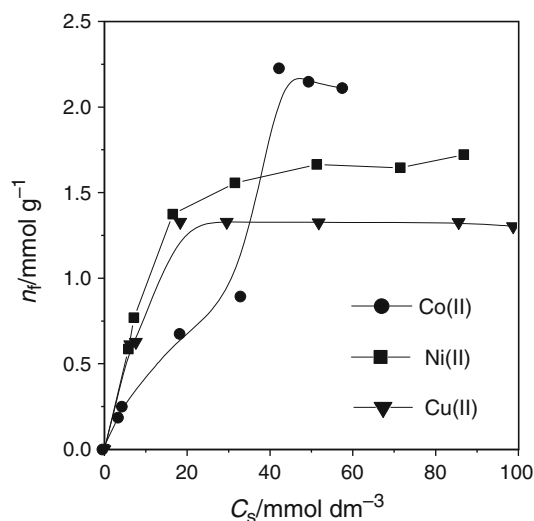
Fig. 6 Isotherms of adsorption of divalent cations on AMTG at room temperature

caused due to the Jahn–Teller effect, is more significant for cations having a d^9 configuration, such as [Cu (II)] [20].

In the present case, the thermodynamic data regarding the interactions of the divalent cations with the basic centers of the material were obtained by calorimetric titration through thermal effect measurements. Figure 7 illustrates an example of a calorimetric titration for one of these systems.

In this titration, the cation solutions were incrementally added to a suspension of the material until saturation of the surface was achieved. The saturation condition consisted in adding the maximum amount of the titrand that could be accommodated on the surface through the interactive effect of the cation/basic center. The system is expected to form a monolayer on the surface [21, 22]. Using the isotherm data obtained through a batch method, the molar fractions of the
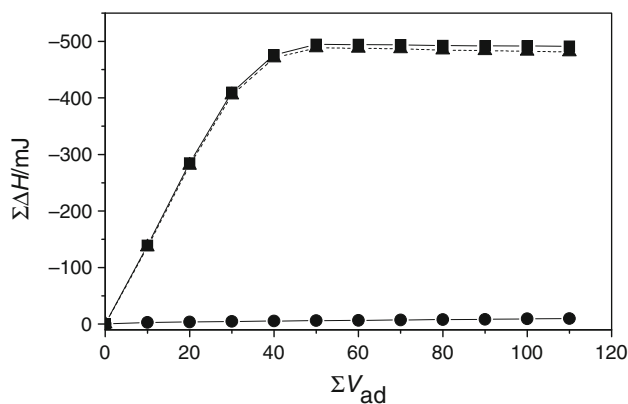
metal cations in equilibrium were obtained by using the slope and the intercept of the graph of $\sum X/\Delta_r H$ versus $\sum X$ to give $\Delta_{mon} H$ and k values, which are defined in the next paragraph. From these values, ΔG and ΔS values were calculated, and the values are listed in Table 2. The following Eq. 2 describes the process of reaction.

$$\frac{\sum X}{\sum \Delta_r H} = \frac{1}{(k-1)\Delta_{mon} H} + \frac{\sum X}{\Delta_{mon} H} \qquad (2)$$

where $\sum X$ is the sum of the mole fractions of the cation in solution after each volume of titrand injected, X being obtained for each point of the titration from the batch experiments; $\Delta_r H$ is the integral enthalpy of adsorption (J g^{-1}) obtained by dividing the thermal effect of adsorption (Q_r) by the number of moles of the adsorbate; k is a constant of proportionality that also includes the equilibrium constant; and $\Delta_{mon} H$ is the thermal effect of formation of the metal–ion complex in a monolayer on the surface. An example of the calorimetric isotherm and its linearized form is shown in Fig. 8. From the equilibrium constant, based on the expression $\Delta G^o = -RT\ln k$, the Gibbs free energy was calculated, whose negative values are in agreement with the spontaneity of the reaction. The enthalpies of adsorption (ΔH^o) for Ni(II), Co(II), and Cu(II) are all negative. The negative ΔH^o indicates that the adsorption of Ni(II), Co(II), and Cu(II) has an exothermic nature. The ΔH^o value also gives information regarding the type of adsorption, whether it is physical or chemical. If the ΔH^o value is in the range of 2.1–20.9 kJ/mol, physical adsorption takes place; whereas, if it is between 20.9 and 418.4 kJ/mol, chemical adsorption occurs [23].

The calculated ΔH^o values show that the removal of Cu(II) from aqueous solution onto the AMTG surface occurs through a chemisorption process, whereas for Ni(II) and Co(II), physical adsorption occurs. The entropy values were calculated using the expression $\Delta G^o = \Delta H^o - T\Delta S^o$, and a series of positive ΔS^o values were obtained. Such values are associated with the displacement of the water molecules bonded to the basic centers, in addition to those identically bonded to the cations, to enrich the free solvent molecules, as the reaction progresses at the solid/liquid interface [24, 25].

Fig. 7 Calorimetric titration of AMTG with cobalt nitrate at 298.15 ± 0.02 K. The points in the experimental curve are the sum of the thermal effects: ΣQ_{tit} (■), ΣQ_{dil} (●), and ΣQ_{res} (▲)

Table 2 Thermodynamic data for the interaction of divalent cations (MX_2) on AMTG at 298.15 ± 0.20 K and the corresponding coefficients of correlation (r)

MX_2	$-\Delta H/$ kJ mol^{-1}	$-\Delta G/$ kJ mol^{-1}	$\Delta S/$ J mol^{-1} K^{-1}	r
Cu(NO$_3$)$_2$	28.21 ± 0.33	31.59 ± 0.02	11 ± 1	0.9935
Ni(NO$_3$)$_2$	14.39 ± 0.38	41.47 ± 0.06	91 ± 1	0.9999
Co(NO$_3$)$_2$	11.91 ± 0.46	32.27 ± 0.33	68 ± 4	0.9806
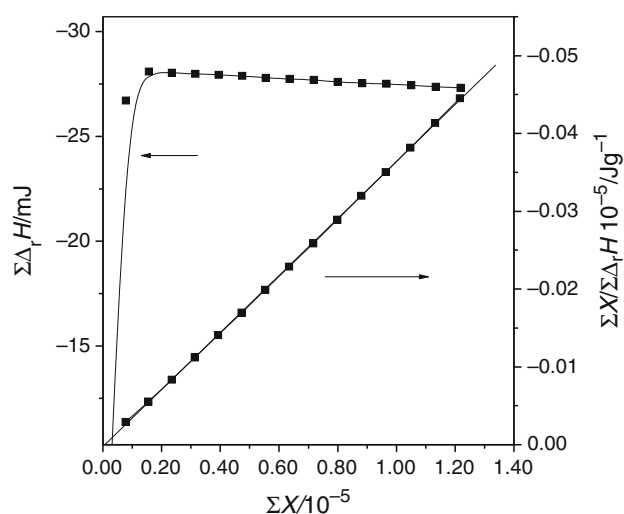
Fig. 8 Isotherm of the calorimetric titration of AMTG with nickel nitrate at 298.15 ± 0.02 K. The *straight line* is a linearized form of the isotherm

These thermodynamic values, represented by exothermic enthalpy, negative free Gibbs energy, and positive entropy, constitute a set of favorable data as the cations are progressively bonded to basic centers on the pendant chains.

Conclusions

This study indicated that the novel type of adsorbent developed for metal capture has affinities for divalent cations. Calorimetric titration of the new material with the cations Ni(II), Co(II), and Cu(II) resulted in the determination of the variations in enthalpy, Gibbs free energy, and entropy. The thermodynamics of adsorption on this material showed favorable interactions, in terms of variations in enthalpy, Gibbs free energy, and entropy values. This chelating material has a good adsorption capacity for removal of transition-metal cations and hence could be used for removing traces of heavy metals from wastewater.

References

1. Augusto Filha VLS, Silva OG, Costa JR, Wanderley AF, Fonseca MG, Arakaki LNH. Interaction of divalent cations Zn, Cd and Hg on surface of silica gel with aminoethanethiol as evaluated by calorimetric titration. J Therm Anal Calorim. 2007;87:621–5.

2. Unob F, Wongsiri B, Phaeon N, Puanngam M, Shiowatana J. Reuse of waste silica as adsorbent for metal removal by iron oxide. J Hazard Mater. 2007;142:455–62.

3. Matsumoto T, Ueno M, Wang N, Kobayashi S. Recent Advances in immobilized metal catalysts for environmentally benign oxidation of alcohols. Chem Asian J. 2008;3:196–214.

4. Zhong H, Zhu G, Wang P, Liu J, Uang J, Yang Q. Direct synthesis of hierarchical monolithic silica for high performance liquid chromatography. J Chromatogr A. 2008;1190:232–40.

5. Lei G, Xiong X, Wei Y, Zheng X, Zheing J. Novel tetrazole-functionalized ion exchanger for weak cation-exchange chromatography of proteins. J Chromatogr A. 2008;1187:197–204.

6. Airoldi C, Farias RF. O uso de silica gel organofuncionalizada como agente sequestrante para metais. Quim Nova. 2000;23(4):496–503.

7. Kocaoba S. Adsorption of Cd(II), Cr(III), and Mn(II) on natural sepiolite. Desalination. 2009;244:24–30.

8. Liu H, Sha W, Cooper AT, Fan M. The effect of stabilizer addition and sonication on nanoparticle agglomeration in a confined impinging jet reactor. Colloids Surf A Physicochem Eng Aspects. 2009;343:38–50.

9. Arakaki LNH, Espílola JGP, Oliveira SF. Calorimetric study of silica gel modified with thioglycolic acid with divalent cations from aqueous solution. Curr Top Colloid Interface Sci. 2002;4:210–25.

10. Arakaki LNH, Espínola JGP, Fonseca MG, Oliveira SF, Sousa AN, Arakaki T, Airoldi C. Thioglycolic acid grafted onto silica gel and its properties in relation to extracting cations from ethanolic solution determined by calorimetric technique. J Colloid Interface Sci. 2004;273:211–7.

11. Sousa KS, Augusto Filha VLS, Pinto VHA, Fonseca MG, Espínola JGP, Arakaki LNH. Quimissorção de cátions divalentes em sílica gel modificada com ácido tioglicólico—A influência do pH e força iônica. Quim Nova. 2007;30:528–34.

12. Machado RSA Jr, Fonseca MG, Arakaki LNH, Espínola JGP, Oliveira SF. Silica gel containing sulfur, nitrogen and oxygen as adsorbent centers onsurface for removing copper from aqueous/ethanolic solutions. Talanta. 2004;63:317–22.

13. Silva ALP, Sousa KS, Germano AFS, Oliveira VV, Espínola JGP, Fonseca MG, Airoldi C, Arakaki T, Arakaki LNH. A new organofunctionalized sílica containning thioglycolic acid incorporated for divalent cátions removal—A thermodynamic cátion/basic center interaction. Colloids Surf A Physicochem Eng Aspects. 2009;332:144–9.

14. Soliman EM, Mahmeud ME, Ahmed SA. Reactivity of thioglycolic acid physically and chemically bound to silica gel as new selective solid phase extractors for removal of heavy metal ions from natural water samples. Int J Environ Anal Chem. 2002;82(6):403–13.

15. Arakaki LNH, Alves APM, Silva Filho EC, Fonseca MG, Oliveira SF, Espínola JGP, Airoldi C. Sequestration of Cu(II), Ni(II), and Co(II) by ethyleneimine immobilized on silica. Thermochim Acta. 2007;453:72–4.

16. Sales JAA, Prado AGS, Airoldi C. Interaction of divalent copper with two diaminealkyl hexagonal mesoporous silicas evaluated by adsorption and thermochemical data. Surface Sci. 2005;590:51–62.

17. Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. The handbook of infrared and Raman characteristic frequencies of organic molecules. London: Academic Press; 1991. p. 160.

18. Brunauer S, Emett P, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc. 1938;60:309–19.

19. Silva CR, Airoldi C. Acid and base catalysts in the hybrid silica sol–gel process. J Colloid Interface Sci. 1997;195:381–7.

20. Arakaki LNH, Diniz JS, Silva ALP, Augusto Filha VLS, Fonseca MG, Espínola JGP, Arakaki T. Thermal study of chelates of

Co(II), Cu(II), Ni(II), Cr(III), Mo(III), and Fe(III) with bis(acetylacetone) ethylenediimine on activated silica gel surface. J Therm Anal Calorim. 2009;97:377–82.

21. Airoldi C, Arakaki LNH. Immobilization of ethylenesulfide on silica surface through sol–gel process and some thermodynamic data of divalent cation interactions. Polyhedron. 2001;20:929–36.

22. Airoldi C, Arakaki LNH. Two independent routes to synthesize identical sulicas by grafting ethylenimine or 2-aminoethanethiol, their cation adsorbing abilities, and thermodynamic data. J Colloid Interface Sci. 2002;249:1–7.

23. Smith JM. Chemical engineering kinetics. 3rd ed. New York: McGraw-Hill; 1981. p. 310–22.

24. Arakaki LNH, Fonseca MG, Espínola JGP, Wanderley AF, Martins EPS, Arakaki T, Airoldi C. Immobilization of ethylenesulfide on silica surface using acid and base catalysts: adsorption and thermodynamic data. J Therm Anal Calorim. 2009;97:383–9.

25. Fonseca MG, Almeida RKS, Wanderley AF, Ferreira UVS, Arakaki LNH, Simoni JA, Airoldi C. Vermiculite-aliphatic amine interactions at the solid/liquid interface: a thermodynamic approach. J Therm Anal Calorim. 2009;97:453–7.