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THERMODYNAMIC DATA FOR DIVALENT CATIONS ONTO NEW MODIFIED GLYCIDOXY SILICA SURFACE AT SOLID/LIQUID INTERFACE

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Abstract

Ethylenediamine molecule was chemically bonded on a silica gel surface previously anchored with 3-glycidoxypropyltrimethoxysilane. This new surface was employed to adsorb divalent cation from aqueous solutions at 298±1 K. The series of adsorption isotherms were adjusted to a modified Langmuir equation from data obtained by suspending the solid with MCl_2 (M=Cu, Ni, Zn and Co) solutions, which gave the maximum number of moles adsorbed as 1.54, 0.56, 0.45 and 0.36 mmol g^{-1} for Cu, Ni, Co and Zn, respectively. Suspended aliquots of the chemically modified surface were calorimetrically titrated and the thermodynamic data showed the system is favored enthalpically and by free Gibbs energy.

Keywords: adsorption, calorimetry, cations, silica

Introduction

The toxic effects of heavy metals can cause risks for humans in certain circumstances [1, 2]. Monitoring the heavy metal contents in natural water, is of paramount importance for the reliable indication of a normal life for a given community [2, 3]. However, even if it is found in low concentrations, in the order of ppb in natural waters, detrimental effects on wild and human lives might be observed [1–3]. Nevertheless, any effort to determine these low cation concentrations often require preconcentration processes, before analyses can be undertaken [3].

The acquisition of solid adsorbents, that can be potentially applied to remove these contaminants from waste effluent streams, is one of the major goals of green chemistry [4]. For instance, some of these are employed to eliminate and/or separate traces of toxic metals from waste waters [2, 3], and relevant aspects of interest appear for monitoring rivers and a diversity of sources of natural waters [3].

The organofunctionalization of inorganic solid surfaces is normally used to introduce basic groups on anchored pendant chains [4–6]. Thus, such new synthesized

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materials change the properties of the original matrix, which can now be explored for trace metal determinations from water and other solvents, through the adsorption of these contaminants on the chemically modified surface [7, 8].

One of the most effective applications is related to silica gel organofunctionalization by incorporating basic atoms on the anchored pendant chains, which have great applicability for operating adsorption and cation preconcentration from a variety of solutions. In the case of cations irreversibly bonded to the pendant basic centers, the lack of selectivity could be the principal disadvantage of some of the silica gels containing ligands available for cation complexation [9, 10].

Normally, such kinds of anchored materials have been prepared to obtain adsorbents with the purpose of attaining the following characteristics: good sorption capacity, chemical stability under conditions of use and, especially, high selectivity [11–14]. The advantages of the immobilization of a desired organic compound onto the silica gel surface are the great versatility of this surface in developing various functions, which is related to the covalently bonded groups, that are resistant to the removal from the surface by organic solvents or water [15, 16].

Many other applications in the field of chemical analyses have been found for materials with these characteristics [15, 16]. Thus, covalent mercapto molecules attached on a silica surface showed a particularly high chemical selectivity for mercury, with removal of this highly toxic ion from solvents [16].

A relevant goal for the modification of the silica surface is to establish appropriate experimental conditions to anchor molecules, which can then adsorb cations dispersed in solvent. Thus, this investigation is focused on the chelating property related to the ethylenediamine molecule after reacting with an epoxide moiety previously anchored on the surface. The adsorption ability of the new surface was calorimetrically followed with the purpose to understand the cation/surface interaction.

Experimental

Ethylenediamine and the silylant agent 3-glycidoxypropyltrimethoxysilane (GPTS) were used without purification. Silica gel was activated as before and the specific area of 420.8±3.4 $m^2\ g^{-1}$ was determined by BET method [17].

A sample of 20.0 g of activated silica gel suspended in 100.0 cm^3 of dry toluene was refluxed and mechanically stirred for 1 h under dry nitrogen. To this suspension 20.0 cm^3 (90.5 mmol) of GPTS was added dropwise and the mixture was refluxed for another 72 h. The resulting solid, named SiGPTS, was filtered, washed as before and dried in vacuum at 323 K for 24 h.

A sample of 5.0 of SiGPTS was suspended in 100.0 cm^3 of dry toluene and refluxed while being mechanically stirred with 8.0 cm^3 (119.8 mmol) of ethylenediamine for 72 h under dry nitrogen. The solid was filtered and the excess of ethylenediamine was eliminated by washing with methanol to give the anchored surface (SGEN), which was dried in vacuum at 323 K for 24 h.

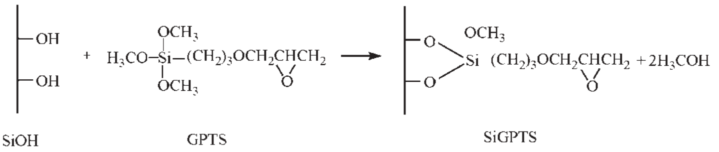
The degree of functionalization of each surface was based on the amount of carbon (SiGPTS) and nitrogen (SGEN) in the samples, which was determined through elemental analysis on a PE-2400 elemental analyzer. Infrared spectra of solid samples in the 4000 to 400 cm^{-1} ranges were performed in KBr pellets, with a resolution of 4 cm^{-1}, by accumulating 32 scans on a Bomem series spectrophotometer.

The isotherms of adsorption were obtained by using the batchwise method [18], where a series of samples of 50.0 mg of the modified silica were suspended in 20.0 cm^3 of aqueous solutions with cations at several concentrations, varying from 2.0 to 12.0 mmol dm^{-3}. The samples were mechanically stirred for 4 h at 298±1 K and the solid was separated by centrifugation. The concentrations adsorbed were determined by sampling the supernatant, using a Perkin Elmer 3000 DV ICP-AES.

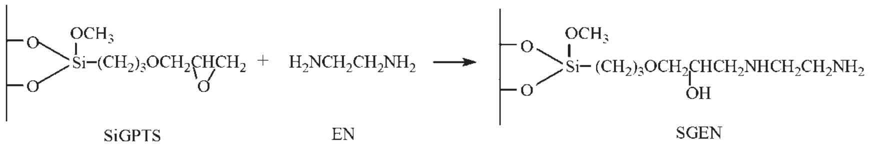
The calorimetric titrations were followed on a differential isothermic LKB 2277 microcalorimetric system [19, 20]. The titration consisted in suspending a sample of approximately 20.0 mg in a steel ampoule, which was vigorously stirred at 298.15± 0.02 K. After equilibrium, the cation solution was incrementally added through a microsyringe, coupled to the calorimetric vessel. For each increment, the thermal effect ($\Delta_{\text{tit}}Q$) was recorded, as indicated by a constant thermal effect at the end of operation. The same procedure was employed to monitor the thermal effect of cation dilution ($\Delta_{\text{dil}}Q$) without the solid and also the effect of water addition to the anchored surface, which gave a null value. By combining these two thermal effects, the net value ($\Sigma\Delta_{\text{r}}Q$) can be determined by the expression $\Sigma\Delta_{\text{r}}Q=\Sigma(\Delta_{\text{tit}}Q)-\Sigma(\Delta_{\text{dil}}Q)$.

Results and discussion

Reactions 1 and 2 summarize the complete process of immobilization. In the first stage, the activated silica gel (SiOH) had GPTS anchored to form the SiGPTS product (reaction 1). The next stage consisted in reacting this precursor with ethylenediamine molecule (EN), by opening the epoxide group to yield the final chelate moiety, as represented by the SGEN surface (reaction 2)



(1)



(2)

The amount of functional groups on this final new surface gave 0.84 mmol per gram of silica, as determined by nitrogen analysis [17], and the specific area decreased to 337.6±1.4 $\text{m}^2\ \text{g}^{-1}$, when compared to the original silica, as is also observed for other immobilizations [12].

The ability of this surface for extracting cations from water was evaluated by measuring the sorption isotherms for divalent cations such as copper, nickel, zinc and cobalt. Under equilibrium conditions, the exchange processes at the solid/liquid interface can be characterized by the numbers of moles adsorbed (n^σ) per gram of support. This value was calculated from the initial number of moles of cation $n(c°)$ and those at equilibrium $n(c)$ for a mass (m) of the support in grams, by applying the expression: $n^\sigma = n(c° - c)/m$.

Based on structural features presented by the pendant groups attached to the inorganic backbone, it is expected that both amine nitrogen groups and hydroxyl oxygen hard basic centers should do the adsorption.

Profiles of the adsorption isotherms for all cations in water are represented in Fig. 1. The number of moles adsorbed *vs.* the concentration at equilibrium (c) is illustrated for all cations. A simple observation is related to the maximum adsorption values, which are distinguishable for these aqueous cations.

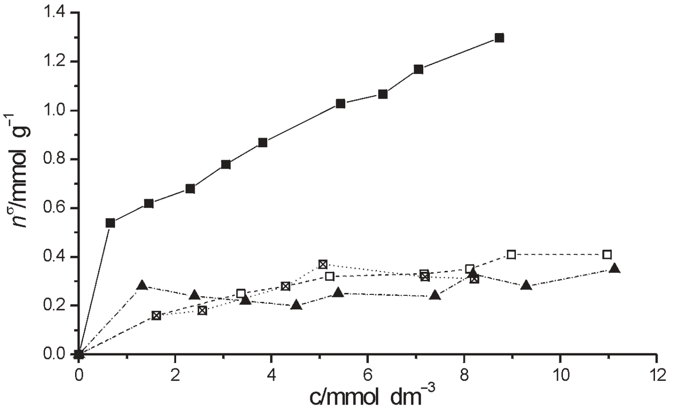


Fig. 1 Isotherms of adsorption of divalent cations onto the modified silica gel surface for ■ – Cu, ❑ – Ni, × – Co and ▲ – Zn at 298±1 K

For the series of isotherms, the data reveal that the adsorption process conforms to the Langmuir model, as proposed for a series of systems [18].

$$\frac{c}{n^\sigma} = \frac{c}{n^\sigma_\infty} + \frac{1}{n^\sigma_\infty b}$$

For this expression, c is the concentration of the solution in equilibrium (mol dm^{-3}), as previously defined (mol g^{-1}), n^σ_∞ 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 are based on the linearized form of the adsorption isotherm derived from plots of c/n^σ as a function of c. From these data, represented in Fig. 2, the maximum retention capacity (n^σ_∞) was determined for each cation-surface interaction through application of the modified Langmuir equation, where n^σ_∞ and b were obtained from the angular and linear coefficients of the linearized form. This behavior is presented in Fig. 2, showing that the adsorption followed the sequence Cu>Ni>Co>Zn, and n^σ_∞ values are listed in Table 1.

Table 1 Thermodynamic data ΔH, ΔG and ΔS for the adsorption of divalent cations MCl_2 (M=Cu, Ni, Co and Zn) onto anchored silica and the maximum number of moles adsorbed at 298.15±0.02 K

M^{2+}	$-\Delta H$/kJ mol^{-1}	$-\Delta G$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}	n^{σ}_{∞}/mmol g^{-1}
Cu	6.62±0.10	15.0±0.4	8±1	1.54±0.06
Ni	8.66±0.11	13.6±0.4	10±1	0.56±0.10
Co	28.42±0.06	14.6±0.4	14±1	0.45±0.4
Zn	4.22±0.01	15.6±0.3	11±1	0.36±0.4

The anchored silica was calorimetrically titrated with this series of cations, in order to obtain more information about their interactions with the basic centers of the pendant groups attached to the inorganic support. The net resultant thermal effects of the reaction, adjusted to a modified Langmuir equation [19, 20], were used to calculate the integral enthalpies involved in the formation of a monolayer per unit mass of adsorbate, $\Delta_{mono}H$, through the expression

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

where ΣX is the sum of the mole fraction of the cation in solution after adsorption, X values are obtained for each addition of titrand, by using the modified Langmuir equation, the behavior of which was shown to be a good adjustable model for such heterogeneous systems [19, 20], $\Delta_r H$ is the integral enthalpy of adsorption (J g^{-1}) obtained through the net thermal effect of adsorption and the number of moles of the adsorbate, K is a constant of proportionality that also includes the equilibrium constant. By using the angular and linear values from the $\Sigma X/\Delta_r H$ *vs.* ΣX plot, $\Delta_{mono}H$ and the enthalpy of adsorption, $\Delta_{ads}H$, can be calculated by means of the expression $\Delta_{ads}H=\Delta_{mono}H/n^{\sigma}_{\infty}$. From K values Gibbs free energies were calculated from the expres-

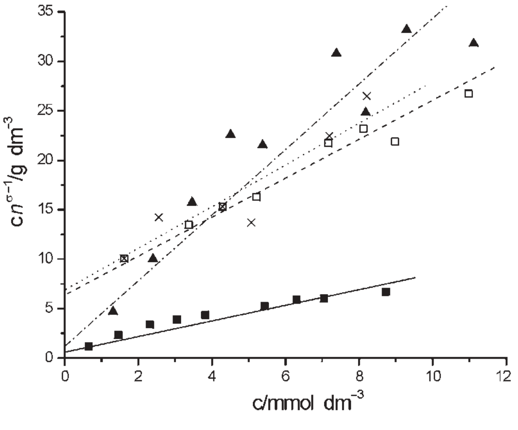


Fig. 2 Linearization of isotherms of adsorption of divalent cations adsorbed by the modified silica gel surface for ■ – Cu, □ – Ni, × – Co and ▲ – Zn at 298±1 K

sion: $\Delta G=-RT\ln K$, and the entropy value was calculated by $\Delta G=\Delta H-T\Delta S$. These data are listed in Table 1.

For all determinations the cation-basic center interactions on the surface demonstrated spontaneity of the proposed reactions, as shown by the negative ΔG values. All these interactive processes are enthalpically favored, but not entropically, results, which suggest an ordering arrangement of the solvent molecules in complex formation over the pendant moieties.

Conclusions

A silica gel surface, previously modified with a silylant agent, reacted successfully with ethylenediamine by opening the epoxide moiety. This surface presents high affinity for copper, due to presence of basic centers. This anchored surface also presents a good adsorption capability for other divalent cations, which permits its use in extracting toxic cations from aqueous solutions. All interactions were spontaneous, shown by Gibbs free energy data and are also enthalpically favored. The anchored pendant groups can act as chelating agents, behavior which suggests that this surface can be successfully explored for extracting toxic metal ions from water solutions.

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References

1 R. D. Wilken, Fresenius J. Anal. Chem., 342 (1992) 795.
2 P. M. Padilha, L. A. de Melo Gomes, C. C. F. Padilha, J. C. Moreira and N. L. Dias Filho, Anal. Lett., 32 (1999) 1807.
3 P. M. Padilha, J. C. Rocha, J. C. Moreira, J. T. S. Campos and C. C. Frederici, Talanta, 45 (1997) 317.
4 P. M. Price, J. H. Clark and D. J. Macquaire, J. Chem. Soc. Dalton Trans., (2000) 101.
5 L. N. H. Arakaki, L. M. Nunes and C. Airoldi, J. Coll. Int. Sci., 228 (2000) 46.
6 M. G. Voronkov, N. N. Vlasona and Y. N. Pozhidaev, Appl. Organometal. Chem., 14 (2000) 287.
7 M. R. M. C. Santos and C. Airoldi, J. Coll. Int. Sci., 183 (1996) 416.
8 J. G. P. Espinola, S. F. Oliveira, W. E. S. Lemus, A. G. Souza, C. Airoldi and J. C. A. Moreira, Colloids Surf. A., 166 (2000) 45.
9 D. E. Leyden and G. H. Luttrel, Anal. Chem., 47 (1975) 1612.
10 T. Seshadri and H. J. Haupt, Anal. Chem., 60 (1988) 47.
11 M. R. M. C. Santos and C. Airoldi, J. Coll. Int. Sci., 183 (1996) 416.
12 C. Airoldi and M. R. M. C. Santos, J. Mater. Chem., 4 (1994) 1479.
13 L. N. H. Arakaki and C. Airoldi, Polyhedron, 19 (2000) 367.
14 L. N. H. Arakaki and C. Airoldi, Quim. Nova, 22 (1999) 246.
15 A. G. S. Prado and C. Airoldi, Pest. Manag. Sci., 56 (2000) 419.

16 N. L. Dias Filho and Y. Gushikem, Sep. Sci. Technol., 32 (1997) 2535.
17 A. G. S. Prado and C. Airoldi, J. Coll. Int. Sci., 236 (2001) 161.
18 A. G. S. Prado and C. Airoldi, Anal. Chim. Acta., 432 (2001) 201.
19 M. G. Fonseca and C. Airoldi, J. Therm. Anal. Cal., 64 (2001) 273.
20 M. G. Fonseca, J. A. Simoni and C. Airoldi, Thermochim. Acta, 369 (2001) 17.