

# Adsorption and thermochemical data of divalent cations onto silica gel surface modified with humic acid at solid/liquid interface

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## Abstract

Humic acid immobilized onto silica gel surface was studied by the calorimetric titration of divalent cations in aqueous solution. The adsorption isotherms were obtained by the batchwise method and were fitted to a modified Langmuir equation. The maximum number of moles per gram of the material gave:  $10.42 \pm 0.75$ ,  $13.16 \pm 0.58$ ,  $7.87 \pm 0.58$  for copper, nickel and zinc, respectively. Gibbs free energies were negative for all systems and the adsorption interactions calorimetrically followed presented endothermic enthalpic values:  $6.24 \pm 0.47$ ,  $6.75 \pm 0.74$ ,  $6.97 \pm 0.58$  kJ mol<sup>-1</sup> for the same sequence of divalent cations. All liquid/solid interface adsorptions were entropically driven. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Humic acids; Adsorption isotherms; Silica gel; Metal ions

## 1. Introduction

One of the major environmental problems has been the presence of heavy metals in water due of their toxicity to aquatic life, human being and environment pollution. Moreover, metal ions do not degrade biologically like organic pollutants, their presence in industrial effluents or drinking water is a public health problem due to their ingestion and therefore possible accumulation in living organisms [1–4].

In order to avoid these problems, many processes have been used and developed over the years to remove metal ions dissolved in industrial wastewaters such as: chemical precipitation, ion exchange, membrane filtration or adsorption [4–10].

Among several adsorbents, development of organic–inorganic hybrids with ability to coordinate metal ions and other organic compounds, provides a special approach in the field of green chemistry as contaminants removal [11]. Composites based on inorganic silica matrix and chelant organic pendant groups are one of the most used to remove metal ions

from water and other solvents [12,13] due to the abundance, high thermal and chemical stabilities and specific bonding abilities of desired functional organic groups attached on silica surface [14–17].

Among many organic molecules, humic acid presents interesting properties, which makes feasible the attachment of humic acid onto silica gel due to the fact that it is a macromolecule formed by weak-acid polyelectrolytes with a large range of molar mass distribution, substructures and functionalities. This presents several advantages such as: abundance, easy obtaining, several chelant groups dispersed on its structure and high ability to adsorb organic and inorganic compounds [18–20]. However, humic acids present a good solubility in water, and this characteristic hinders the adsorption procedures. In order to overcome this disadvantage, humic acid can be attached onto silica gel surface to obtain a new material with complexation characteristics of the humic acids and with insolubility, thermal and chemical stability properties of silica gel [21,22].

The aim of the present study is to report the several divalent cations (Cu, Ni, Co and Zn) adsorption by silica gel modified with humic acid from aqueous solution and the thermochemical data of these interactions at solid/liquid interface.

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## 2. Experimental

### 2.1. Chemicals

Humic acid samples (HA) were obtained from Fluka, sodium hydroxide, hydrochloric acid, sodium chloride, 3-aminopropyltriethoxysilane (APTS) from Merck were used without any purification. Silica gel (Merck) was activated by heating for 24 h at 423 K [22].

### 2.2. Anchoring of humic acid on silica gel surface

First, a sample of 20.0 g of activated silica gel was suspended in 100.0 cm<sup>3</sup> of dry toluene and 20.0 cm<sup>3</sup> of 3-aminopropyltrimethoxysilane was added to this suspension. The mixture reacted during 72 h in a reflux system at 413.0 K in order to produce the precursor product named SiNH<sub>2</sub>.

After, 300.0 mg of HA sample were suspended in 30.0 cm<sup>3</sup> of a 0.10 mol dm<sup>-3</sup> NaOH aqueous solution. 1.00 g of SiNH<sub>2</sub> was added to this solution, the pH was adjusted to 7.5 pH, and the suspension was stirred for 20 h at room temperature to give the final material SiHA [22].

### 2.3. Adsorption studies

Adsorption isotherms were obtained by the batchwise method, in which a series of samples of 50.0 mg of SiHA were suspended in 20.0 cm<sup>3</sup> of aqueous solution with divalent metal ions concentration (Cu, Ni and Zn), varying from 0 to 15.0 mmol dm<sup>-3</sup>. Samples were mechanically stirred for 24 h at 298.1 K and the solid was separated by filtration. Adsorbed cation content was determined by difference by sampling the filtrated supernatant, using Varian 220 atomic absorption spectroscopy.

### 2.4. Calorimetry

Calorimetric titrations were done on an isoperibol calorimetric system CSC model ISC 4300. The titration consisted of suspending 100.0 mg of SiHA in 50.0 cm<sup>3</sup> of water in a Dewar ampoule, which was stirred at 298.15 ± 0.02 K. After thermal equilibration, the cation solution was incrementally added with a syringe. For each increment, the total heat ( $\Delta_{\text{tit}}Q$ ) was recorded. Same procedure was employed to monitor the heat of cation dilution ( $\Delta_{\text{dil}}Q$ ) with ampoule contents 50.0 cm<sup>3</sup> without solid sample. By combining these two heat outputs, the net value [ $\sum(\Delta_r Q)$ ] can be determined by the expression:  $\sum(\Delta_r Q) = \sum(\Delta_{\text{tit}}Q) - \sum(\Delta_{\text{dil}}Q)$  [23].

## 3. Results and discussion

The synthetic procedure to immobilize the humic acid on the inorganic support can be summarized by a simple attachment through hydrogen bond formation between carboxylate groups present on HA and the protonated amine pendant

groups of the modified silica SiNH<sub>2</sub> as detailed described before [22]. Amount of the humic acid attached on modified silica gel was determined by thermogravimetric analysis and gave 101.7 mg g<sup>-1</sup> [22]. Furthermore, the humic acid when immobilized on silica gel presented an increase of thermal stability and became insoluble in water, which are additional properties of this hybrid [22].

The ability of SiHA to adsorb metal ions from water was evaluated by measuring the sorption isotherms of divalent copper, nickel and zinc.

The number of moles adsorbed ( $N_f$ ), for 1 g of the solid, was obtained from the initial number of moles of cation ( $n_i$ ) added to the system and divalent metal ion at equilibrium ( $n_s$ ) for a mass ( $m$ ) of the hybrid, by applying the expression:  $N_f = (n_i - n_s)/m$ .

These experimental data are applied in the general equation for the modified Langmuir model:  $(C_s/N_f) = (C_s/N_s) + (1/N_s)(1/b)$  [23–25].

$C_s$  is the concentration of solution in equilibrium (mol dm<sup>-3</sup>),  $N_f$  as defined before (mol g<sup>-1</sup>),  $N_s$  the maximum amount of solute adsorbed per gram of adsorbent (mol g<sup>-1</sup>), which depends on the number of adsorption sites, and  $b$  is a constant (mol dm<sup>-3</sup>). All further data are derived from this linearized form of the adsorption isotherm, i.e. from plots of  $C_s/N_f$  as a function of  $C_s$ .  $N_s$  and  $b$  values were obtained from the slope and intercept of the linearized form.

Obtained adsorption results are presented in Fig. 1, which are isotherms data of cations adsorption by SiHA. Amount of moles of cations,  $N_s$ , obtained from application of modified Langmuir equation on linearized graphs of Fig. 1, and these values are listed in Table 1. Adsorption data followed the sequence: Ni > Cu > Zn. This sequence presented an interesting behavior related with number of electrons in d orbital. Number of moles adsorbed decreased with rise of electrons number in d orbital, as represented in Fig. 2 remembering that Ni(II) presents eight electrons, Cu(II) has nine and Zn(II) has 10. This observation can be explained by the decrease

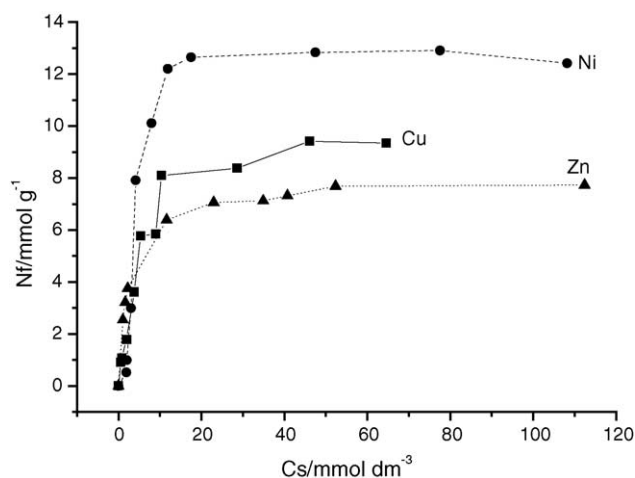


Fig. 1. Adsorption isotherms of aqueous solution for divalent copper, nickel and zinc on SiHA material at 298.1 K.

Table 1

Maximum adsorbed amounts ( $N_s$ ) and thermodynamic data for the interaction of divalent cations with SiHA material at 298.1 K

$M^{2+}$	$N_s$ (mmol g <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Cu	10.42 ± 0.75	-13.77 ± 0.89	6.24 ± 0.47	67 ± 8
Ni	13.16 ± 0.58	-14.29 ± 0.81	6.75 ± 0.54	71 ± 9
Zn	7.87 ± 0.58	-12.00 ± 1.11	6.97 ± 0.58	64 ± 9

of acidity with number of electrons in d orbital, as a consequence, the cation  $d^8$  tends to form octahedral complex,  $d^9$  tends to distorted Jahn Teller octahedral complex and  $d^{10}$  to tetrahedral complex [26].

Calorimetric titrations offer more information about the adsorption processes at solid/liquid interface. Heat outputs from the reactions between divalent metal ions and SiHA were obtained from the calorimetric results. The dilution heat of cations, the total heat and resulting adsorption heat effect values for all interactions are presented in Fig. 3.

Using the net resultant heat output from the reaction, adjusted to a modified Langmuir equation, the integral enthalpies involved in the formation of a monolayer per unit mass of adsorbate,  $\Delta_{\text{mono}}H$ , were calculated, through the expression:

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

In this equation,  $\sum X$  is the total mol fraction of metal ion in solution after adsorption,  $X$  values are obtained for each addition of titrant, by using the modified Langmuir equation, whose behavior was shown to be a good adjustable model for such heterogeneous systems.  $\Delta_r H$  is the integral enthalpy of adsorption (J g<sup>-1</sup>) obtained through the net thermal effect of adsorption and the number of moles of the adsorbate,  $K$  is a proportionality constant that also includes the equilibrium constant. By using the angular and linear values from the  $\sum X/\Delta_r H$  versus  $\sum X$  plot,  $\Delta_{\text{mono}}H$  and the enthalpy of adsorption  $\Delta_{\text{ads}}H$  values can be calculated by

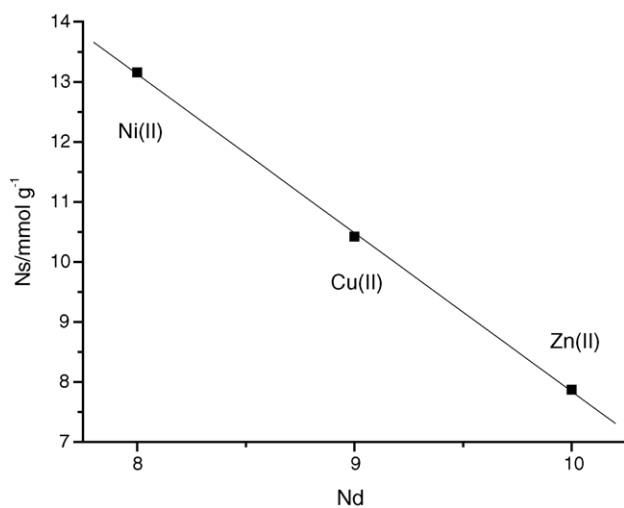


Fig. 2. Effect of the electrons number of d orbital of cations in maximum adsorbed moles on SiHA hybrid.

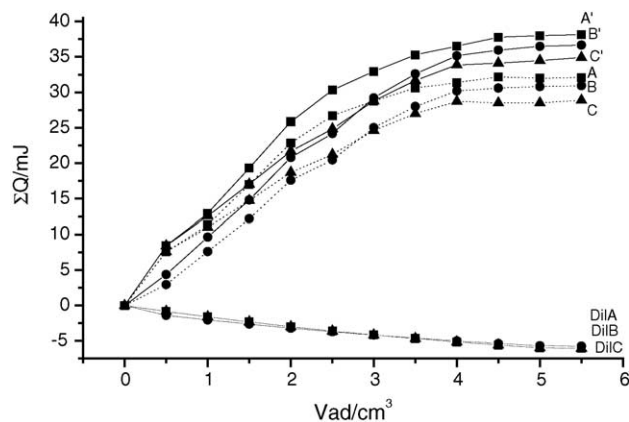


Fig. 3. Calorimetric titration of divalent cations onto SiHA sample. The curves (A), (B) and (C) represent the measured heat output,  $\sum Q_{\text{uit}}$ , for nickel, copper, and zinc, respectively; curves (dilA), (dilB) and (dilC) represent dilution heat output,  $\sum Q_{\text{dil}}$ , for copper, and zinc, respectively; (A'), (B') and (C') the resultant heat interaction,  $\sum Q_{\text{res}}$ , for nickel, copper, and zinc, respectively.

means of the expression  $\Delta_{\text{ads}}H = \Delta_{\text{mono}}H/N_s$  [23–25]. Resulting  $\Delta_{\text{ads}}H$  values were obtained from application of the Langmuir equation on linearized graphs of Figs. 4 and 5. From  $K_{\text{eq}}$  values, Gibbs free energies were calculated by the expression:  $\Delta G = -RT \ln K_{\text{eq}}$ , and the entropy value was calculated through  $\Delta G = \Delta H - T\Delta S$ . All thermodynamic data are listed in Table 1.

All adsorption processes were spontaneous in nature as observed by exoergic  $\Delta G$  values in Table 1. Although, the adsorptions showed endothermic enthalpy for interactions.

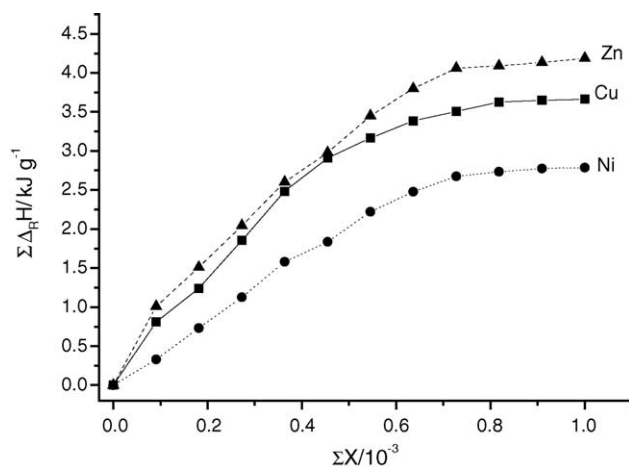


Fig. 4. Calorimetric titration isotherm of SiHA with divalent cations at 298.15 K.

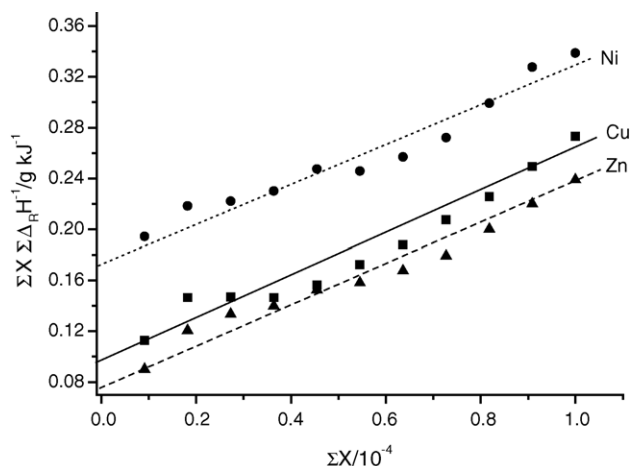


Fig. 5. Calorimetric titration isotherm of SiHA with divalent cations at 298.15 K.

Indeed, all interface solid/liquid interactions were entropically favored process. This phenomenon is caused by typical chelate effect, which is entropically favored, due to the fact that of releasing of more than one proton of the humic acid attached on surface for each adsorbed cation, and the replacement of solvent molecules that were previously bonded to the cation during ion exchange processes [25].

In sum, the development of low-cost adsorbents is one of methods to decrease the large volumes of waste and toxic effluents produced by a variety of chemical processes. Indeed, the immobilization of humic acid onto silica gel surface in order to remove inorganic contaminants with great advantage to avoid the solubilization of humic acids is very promissory to environmental issues.

#### 4. Conclusion

The immobilized humic acid onto modified silica gel surface showed ability to remove metal ions from water. This material presented spontaneous trapping of divalent cations in the sequence: Ni > Cu > Zn. Bonding metal ions ability of SiHA material suggests it may be useful for removal of these contaminants from wastewaters.

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