



Sorption and thermodynamic of cation–basic center interactions of inorganic–organic hybrids synthesized from RUB-18

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ABSTRACT

Synthesized nanostructured hybrids from RUB-18 layered silicate, containing one (N) or three (3N) basic nitrogen atoms attached to pendant chains were applied for copper, nickel and cobalt sorptions. The isotherms obtained from batchwise processes were adjusted to the Freundlich and the Langmuir–Freundlich models for heterogeneous systems. The basic nitrogen centers/acidic cation interactions were followed by calorimetry under batchwise conditions and the results were analyzed by a modified Langmuir equation. The exothermic enthalpic values of -2.50 ± 0.30 , -1.62 ± 0.10 and -1.35 ± 0.20 and -15.61 ± 0.20 , -8.05 ± 0.14 and -20.48 ± 0.15 kJ mol^{-1} , obtained for Cu^{2+} , Ni^{2+} and Co^{2+} titrations with C-RUB- $x\text{N}$ ($x=1, 3$) materials, suggest a favorable process at the solid/liquid interface for inorganic/organic hybrid cation sorptions. These thermodynamic data, expressed also by reaction spontaneity, infer the use of such hybrids for cation removal from aqueous solution.

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1. Introduction

Sorption processes are of extreme importance for science and technology, when effectively applied to undesirable industrial residues removals, activities which are associated with mixture separation, catalysis, water purification and effluent treatment [1]. Industrial activities are normally responsible for generating large volumes of hazardous species that cause environment contamination, being an intense worldwide problem. Great amounts of dyes and metals are dispersed into the atmosphere, water and soil, and are harmful for the majority of the contaminated systems, directly affecting human life [2,3]. In this context, the development of new materials and methodologies for species concentration with the aim of their removal from aqueous solution to clean an ecosystem is continuously necessary, with the purpose to follow the established green chemistry principles [1–4].

Quantitative determinations from calorimetry of the acid/base interactions at the solid/liquid interface can elucidate the energetics involving any studied system [5]. Thus, this valuable practice quantifies the energies of interactions of, for example, metallic cations and properties associated with available basic centers on the material surface. From the experimental point of view, three

independent determinations enable obtaining the thermodynamic data of the system [6].

In attempting to investigate new materials, the hydrated crystalline layered RUB-18 silicate was chosen, taking into account that the acidic form has plenty of silanol groups on its surface [7,8]. These free groups are active sites for the effectiveness of anchoring reactions with silylating agents, to cause the chemical modification of the surface. The inorganic–organic nanostructured hybrids obtained through the organofunctionalization process enable the appearance of different active pendant chains on the layered surface. From this operation the synthesized new materials were designed to act as potential concentration systems for metallic ion sorption from aqueous solutions [7–10].

This present investigation studied the application for copper, nickel and cobalt sorptions from aqueous solution and the relevant microcalorimetric parameters to obtain the thermodynamic values of cation/basic center interactions for the synthesized hybrid.

2. Experimental

2.1. Materials

Amino functionalized materials were synthesized from the surfactant intercalated precursor CTA-RUB-18 as reported before [8], using silylating agents for the organofunctionalization involving 3-aminopropyltriethoxysilane (N) 97% (Aldrich) and N-3-trimethoxysilylpropylidietilenetriamine (3N) 97% (Aldrich), to give

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the inorganic–organic nanostructured hybrids named C-RUB-N and C-RUB-3N, respectively.

2.2. Sorption isotherm

Copper, nickel and cobalt sorption isotherms from aqueous solution were obtained by the batchwise method [4,7] from continuous orbital stirring of 20 mg of chemically modified compound, suspended in 25.0 cm³ of each cation solution, varying from 0.70 to 7.0 mmol dm⁻³ in concentration, at 298 ± 1 K for 24 h. Aliquots of the supernatant were pipetted and the metal quantities remaining in the supernatant were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES). The difference between the metal quantities added and that remaining in solution is sorbed on the hybrid surface. The isotherms obtained were adjusted to the sorption models described by the Freundlich and the Langmuir–Freundlich equations [9].

2.3. Calorimetry

The samples for calorimetric titrations were inserted in an LKB 2277 calorimeter at 298.15 ± 0.20 K. For each titration, 20 mg of the sample was suspended in 2.0 cm³ of deionized water in a stainless steel vessel under continuous stirring. After thermal equilibrium, aliquots of 20 μL of 0.10 mol dm⁻³ of metallic solution were added to the titration vessel through a gold cannula connected to a microsyringe. The thermal effect of titration ($\sum Q_{tit}$) for each increment of titrant solution was obtained until saturation, as indicated by a constant thermal effect. The same procedure was followed for monitoring the thermal effect of dilution of the metallic solution in water ($\sum Q_{dil}$), but without solid inside the calorimeter vessel. The last operation consisted in adding water to the suspended solid that corresponds to the hydration thermal effect ($\sum Q_{hyd}$) and results in a null value [10].

3. Results and discussion

3.1. Metal sorption

The number of moles of cation directly sorbed on the precursor layered Na-RUB-18 and the cetyltrimethylammonium exchanged form (CTA-RUB-18) gave negligible values, as already observed, demonstrating the necessity to first organofunctionalize the inorganic support prior to cation sorption [4,7].

Covalent incorporations of different silylating agents containing potentially coordinating nitrogen atoms attached to pendant inorganic chains onto RUB-18 silicate result in the incorporation of these Lewis basic centers on the inorganic structure. These centers are of great interest for interactive effects with acidic metallic cations such as copper, nickel and cobalt dissolved in aqueous solution. Thus, the sorption process is related to complex formation with divalent metals, which are progressively coordinated through the free available electrons on the nitrogen atom attached to the pendant chains [11].

The complexing effects of the chemically modified N and 3N hybrids were investigated through the sorption process. The samples were placed in contact with various metallic solutions with different concentrations. The amount of metallic ions present in solution after the sorption process was determined by ICP-OES and the sorbed amounts, N_f , were determined according to the equation $N_f = (n_i - n_s)/m$, where n_i and n_s were the moles of cations initially added and in equilibrium with the solid/liquid interface, respectively, and m is the mass used [7,12].

The values obtained for cation concentration in the supernatant (C_s) determined from the number of moles fixed by the modified surface (N_f) and the sorption isotherms for the C-RUB-3N

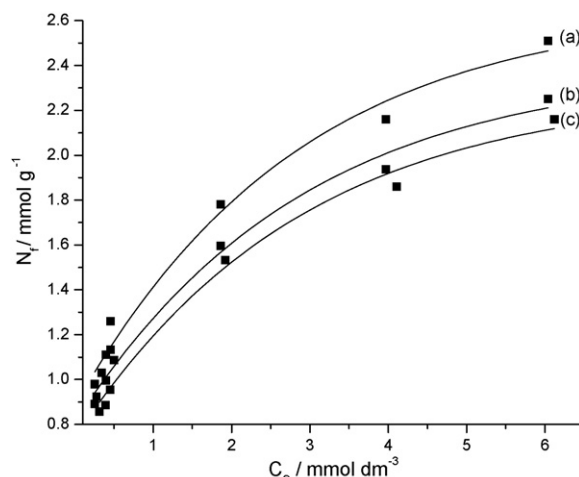


Fig. 1. Sorption isotherms of Cu²⁺ (a), Ni²⁺ (b) and Co²⁺ (c) with chemically functionalized C-RUB-3N.

hybrid [4,7,13] are shown in Fig. 1, while the linearized forms of the isotherms are represented in Fig. 2. Similar isotherms for the C-RUB-N hybrid were also obtained. All results from the sorption isotherms were fitted to the Freundlich and the Langmuir–Freundlich models and the adjustments for these models are listed in Table 1.

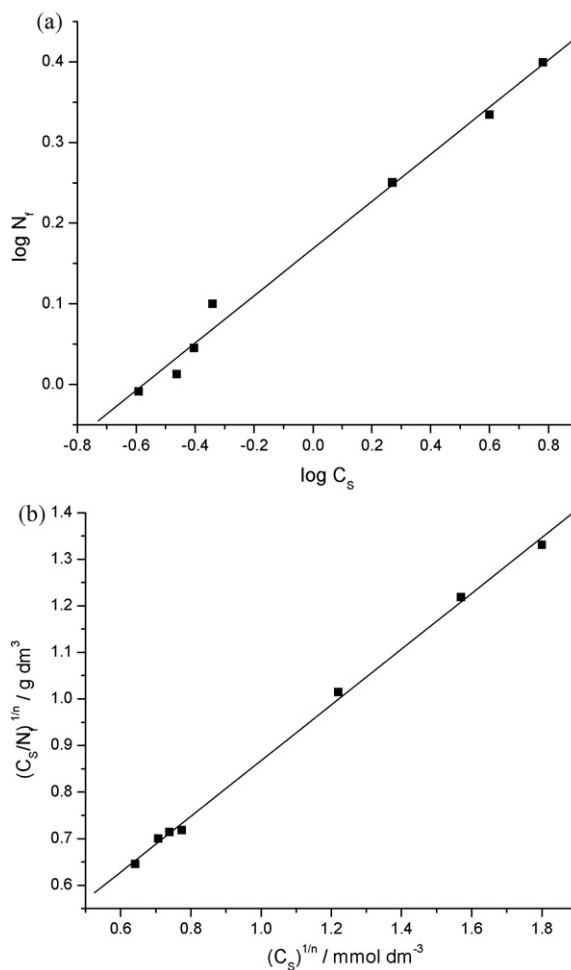


Fig. 2. The Freundlich (a) and the Langmuir–Freundlich isotherms (b) for Cu²⁺ sorption by C-Rub-3N hybrid.

Table 1
Results of sorption isotherms of M^{2+} (Cu, Ni and Co) with chemically modified RUB-18, following the Freundlich and the Langmuir–Freundlich models. N_f is the number of moles fixed; N_S the maximum sorption; K_F , n and b constants related to the sorption, sorption intensity and equilibrium constant, respectively, and R^2 the determination coefficient.

Material	Freundlich				Langmuir–Freundlich			
	M^{2+}	K_F	n	R^2	N_f (mmol g ⁻¹)	N_S (mmol g ⁻¹)	b	R^2
C-RUB-N	Cu	0.781	1.36	0.9819	3.83	3.86	0.28	0.9385
	Ni	2.58	2.74	0.8711	2.52	2.54	1.33	0.9664
	Co	0.786	1.42	0.9649	3.14	3.28	0.35	0.9129
C-RUB-3N	Cu	1.509	3.07	0.9844	1.83	1.83	1.74	0.9907
	Ni	1.363	3.22	0.9896	1.67	1.70	1.93	0.9941
	Co	1.242	3.19	0.9953	1.65	1.66	1.90	0.9986

The Freundlich equation [13] suggests a logarithmic decrease of the sorption energy as a function of metal surface completion, based on a theoretical model derived for heterogeneous surfaces, as expressed by Eq. (1). The linearized form is given by Eq. (2):

$$N_f = K_F C_S^{1/n} \quad (1)$$

$$\log N_f = \frac{1}{n} \log C_S + \log K_F \quad (2)$$

with N_f and C_S being defined as before, K_F is a constant related to the sorption capacity and n a constant associated with the sorption intensity. Those constants are empirical and dependable on several environmental factors [14], however, the capacity refers to the specific material and the intensity is related to the occurrence of this phenomenon, but, both are dependent on the experimental condition.

The Langmuir–Freundlich model [15] follows Eq. (3), and its linearized form is expressed by Eq. (4):

$$\frac{N_f}{N_S} = \frac{b C_S^{1/n}}{1 + b C_S^{1/n}} \quad (3)$$

$$\frac{(C_S)^{1/n}}{N_f} = \frac{1}{N_S b} + \frac{(C_S)^{1/n}}{N_S} \quad (4)$$

where N_f , C_S and n were defined before; N_S is the maximum number of moles for the monolayer formation and b is an equilibrium constant due to the surface/metal affinity.

The maximum sorption capacity, represented by N_S , was obtained through the Langmuir–Freundlich adjustment, consequently, in analyzing those values, the C-RUB-N material presented higher values for Cu^{2+} sorption, as expected, considering the values obtained through elemental analysis, since C-RUB-N hybrid contains a greater amount of attached groups on the surface that are completely available for cation/nitrogen interaction. The linearized values for N_S that are related to pendant chains on the surface, represented by n_N , obtained through elemental analysis and also the relation between them, N_S/n_N , are also listed in Table 2.

The N_S/n_N quotient represents a normalized value related to the amount of sorbent group for each material and an inversion sorption order is observed. Thus, it is expected that the C-RUB-

Table 2
Metal M^{2+} (M) removal by organofunctionalized RUB-18, the degree of functionalization (n_N), the maximum sorption (N_S) and the N_S/n_N relationship.

Material	n_N /mmol g ⁻¹	M	N_S /mmol g ⁻¹	N_S/n_N
C-RUB-N	2.60	Cu	3.86	1.48
		Ni	2.54	0.97
		Co	3.28	1.26
C-RUB-3N	0.81	Cu	1.83	2.26
		Ni	1.70	2.10
		Co	1.66	2.05

N hybrid with a higher amount of basic groups (2.60 mmol g⁻¹) attached would present greater ability to easily sorb a higher amount of metallic cations, resulting in a high quotient. However, a smaller value was obtained, as is clearly demonstrated by the normalized values calculated for this hybrid, which is near to unity (1.26 mmol g⁻¹) for cobalt sorption. These results suggest the existence of a simple interaction. In case of C-RUB-3N, with a quotient 2.05 for the same cation, the sorption from three nitrogen basic atoms attached to pendant chains is expected, reflecting a relatively higher sorption capacity, mainly when compared with the smaller amount of 0.81 mmol g⁻¹ of the atoms on the surface.

Based on n_N/N_S relationship the material with higher efficiency for cation sorption from aqueous solution was the inorganic–organic hybrid C-RUB-3N. This is expected due to the presence of three chelating groups on the chemically anchored organic structure. The order of cation sorption obtained for C-RUB-3N was $Cu > Ni > Co$, generally, following the Irving–Williams series [11], nevertheless some results are close to one another. In the case of C-RUB-N, the order was $Cu > Co > Ni$, again with very similar results.

Parameters referenced to the sorption process between chemically modified surfaces and metallic ions, such as the number of cations necessary for monolayer formation on the materials surface (N_S) and the respective equilibrium constants of the sorption process (b), obtained through linearization of the Langmuir–Freundlich model are very important to be considered for any sorption process [9]. From linearization the K_F and n parameters were obtained and are fundamental to describe these behaviors.

3.2. Microcalorimetry

Microcalorimetry is an important technique to obtain the thermodynamic values of the interactions between metallic cations and the basic centers attached to the pendant chains covalently bonded to the layered functionalized structures. Through such determinations the equilibrium constant and the sorption enthalpy are simultaneously obtained and, consequently, the Gibbs energy values. The enthalpy was calculated from the integral thermal effect values, resulting from the addition of divalent cation solutions to the suspended organofunctionalized RUB-18 sorbent inside the calorimeter vessel. These exothermic values contribute to the favorable thermodynamic data [9,16] as it is shown in Fig. 3, represented by the thermal effect against the sum of the titrant volume [17].

The set of calorimetric titration curves given by the sum of thermal effect as a function of the volume of the titrant added to the calorimetric vessel is shown in Fig. 3. From the total effect Q_{tit} , curve a, the content related to the dilution process Q_{dil} , curve b is subtracted. Considering also that the hydration process resulted in a null value, as also observed for other systems [9,16], the net thermal effect Q_R is given, curve c, calculated from Eq. (5), which represents

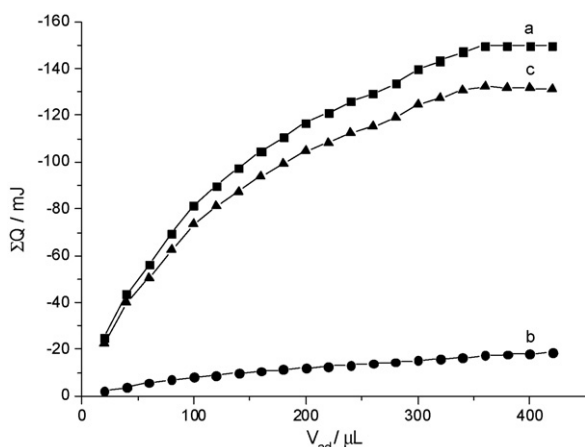
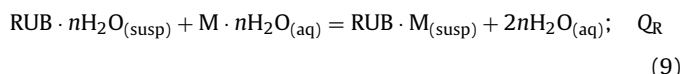
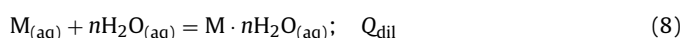
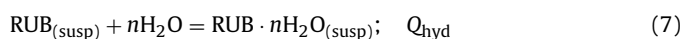
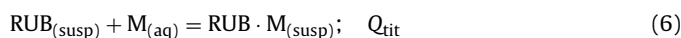


Fig. 3. Calorimetric titration curves representing the thermal effect of titration $\sum Q_{\text{tit}}$ (a), the thermal effect of dilution $\sum Q_{\text{dil}}$ (b) and the net thermal effect $\sum Q_{\text{R}}$ (c) for $0.104 \text{ mol dm}^{-3} \text{ Cu}^{2+}$ sorption by 20 mg of C-RUB-N, obtained through increments of $20.0 \mu\text{L}$ of metallic solution.

the values involved in pendant basic center–metal ions interaction.

$$\sum Q_{\text{R}} = \sum Q_{\text{tit}} - \sum Q_{\text{dil}} \quad (5)$$

The sequence of reactions in aqueous solution (aq) inside the calorimetric vessel takes place when the suspended (susp) layered crystalline organofunctionalized compound (RUB) is titrated with the divalent cations (M) solution, which gave the net thermal effect Q_{R} , as given by Eqs. (6)–(9).



The sum of enthalpic values obtained from calorimetry enable the determination of the thermodynamics of the equilibrium after adjusting the data to a modified Langmuir equation [18].

$$\frac{X}{\Delta_{\text{R}}h} = \frac{1}{(K-1)\Delta_{\text{int}}h} + \frac{X}{\Delta_{\text{int}}h} \quad (10)$$

with X being the molar fraction of metallic ion in solution at the equilibrium of the process, after addition of titrant, $\Delta_{\text{R}}h$ is the net enthalpy of reaction (J g^{-1}), K is a constant that includes the equilibrium constant and $\Delta_{\text{int}}h$ represents the specific enthalpy of the interactive process.

From the experimental point of view, the amount of cation sorbed by the free basic centers was previously determined through a batchwise isotherm that was adjusted to the Langmuir–Freundlich model, as given by Eq. (3). The graphical representation $C_{\text{S}}/N_{\text{f}}$ as a function of C_{S} enabled obtaining the

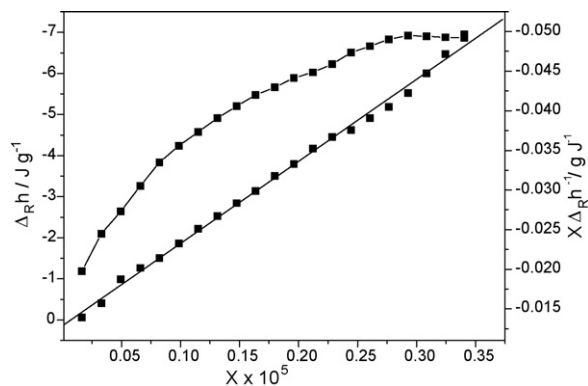


Fig. 4. Calorimetric isotherm for Cu^{2+} sorption by C-RUB-N, represented by $\Delta_{\text{R}}h$ as a function of X , with incremental additions of $20 \mu\text{L}$ of a $0.104 \text{ mol dm}^{-3}$ metallic cation solution. The linearized form of the isotherm presents a determination coefficient of 0.9999.

linearization of the isotherm, it being possible to determine the angular N_{S} and linear b coefficients [9,16–18].

By using the calorimetric data applied from the modified Langmuir equation, Eq. (10), represented by $X/\Delta_{\text{R}}h$ as a function of X , it is possible to determine $\Delta_{\text{int}}h$ and K values, through the angular and linear coefficients, respectively, as shown in Fig. 4.

From the enthalpy involving a monolayer interactive process and the respective number of moles, the molar enthalpy was calculated through Eq. (11).

$$\Delta H = \Delta_{\text{int}}h/N_{\text{S}} \quad (11)$$

As observed, the molar enthalpy characterizes the thermal effect involved in the system, due to the cation/basic center interactions and from the modified Langmuir equation it was possible to calculate simultaneously the enthalpy and the equilibrium constant of the process. From these values the Gibbs free energy can be calculated, Eq. (12), where $T=298.15 \text{ K}$ and R is the ideal gases constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

$$\Delta G = -RT \ln K \quad (12)$$

The entropic values that were calculated, Eq. (13), and the complete thermodynamic data are listed in Table 3. The observed enthalpic values are exothermic with favorable equilibrium constants, which are associated with negative Gibbs energies, indicating a spontaneous cation sorption for the organofunctionalized surfaces.

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

The chemically modified silicate containing three basic nitrogen centers attached to the pendant chains are more exothermic, a behavior that should be related to the minimizing hindrance effects, which can make cation interaction easier [17,18]. Thus, the variation in enthalpy reflects not only the degree of functionalization, but also the maximum sorption, as expressed by the quotient, as listed in Table 2.

Table 3

Thermodynamic data of interaction of the divalent cations copper, nickel and cobalt with basic nitrogen centers at $298.15 \pm 0.20 \text{ K}$.

Material	M^{2+}	$-\Delta_{\text{int}}h/\text{J g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$K \times 10^4$	$-\Delta G/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$
C-RUB-N	Cu	9.64	2.50 ± 0.30	8.1	28.0 ± 0.6	86 ± 1
	Ni	4.11	1.62 ± 0.10	38.1	31.9 ± 0.6	101 ± 1
	Co	4.44	1.35 ± 0.20	13.8	29.3 ± 0.2	94 ± 1
C-RUB-3N	Cu	28.56	15.61 ± 0.20	245.0	36.5 ± 0.6	70 ± 1
	Ni	13.68	8.05 ± 0.14	818.0	39.5 ± 0.5	105 ± 1
	Co	33.99	20.48 ± 0.15	515.0	38.3 ± 0.5	60 ± 1

The entropic data are all positive, indicating a change in solvent structure of the system as the sorption process progresses. During complex formation water molecules are displaced as a function of the dehydration of the metallic cations to which they were originally coordinated. In addition, the water molecules bonded to the basic centers through hydrogen bonds are also displaced as the cation interactions occur. Consequently, the sum of the solvent molecules entering the medium contributes to the disorder of the system, causing an increase in entropy. As observed for all cases, positive values were obtained, as listed in Table 3.

4. Conclusions

The synthesized inorganic–organic hybrids obtained from RUB-18 present interesting sorption properties, whose results demonstrate that the process of metal sorption was spontaneous in aqueous solution and at ambient conditions.

The experimental data obtained through sorption isotherms were adjusted to the Freundlich and the Langmuir–Freundlich models, explained by the heterogeneity of the studied systems, as the sorption processes occurs in two or more stages.

The calorimetry was of fundamental importance in obtaining the thermodynamic data of cation/basic nitrogen interactions at the solid/liquid interface. These interactions gave exothermic enthalpies and negative Gibbs energies, supporting spontaneous reactions as well as positive entropies. These values correspond to favorable conditions for cation removal using these systems.

Based on the calorimetric data, it is reasonable to propose that organofunctionalized RUB-18 layered compounds can be applied to clean an ecosystem by metal removal from aqueous solution in favorable conditions.

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