



## Rapid Communication

## Adsorption of arsenic(III) into modified lamellar Na-magadiite in aqueous medium—Thermodynamic of adsorption process

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## ABSTRACT

Synthetic Na-magadiite sample was used for organofunctionalization process with *N*-propyldiethylenetriethoxysilane and bis[3-(triethoxysilyl)propyl]tetrasulfide, after expanding the interlayer distance with polar organic solvents such as dimethylsulfoxide (DMSO). The resulted materials were submitted to process of adsorption with arsenic solution at pH 2.0 and  $298 \pm 1$  K. The adsorption isotherms were adjusted using a modified Langmuir equation with regression nonlinear; the net thermal effects obtained from calorimetric titration measurements were adjusted to a modified Langmuir equation. The adsorption process was exothermic ( $\Delta_{\text{int}}H = -4.15$ – $-5.98$  kJ mol<sup>-1</sup>) accompanied by increase in entropy ( $\Delta_{\text{int}}S = 41.32$ – $62.20$  J k<sup>-1</sup> mol<sup>-1</sup>) and Gibbs energy ( $\Delta_{\text{int}}G = -22.44$ – $-24.56$  kJ mol<sup>-1</sup>). The favorable values corroborate with the arsenic (III)/basic reactive centers interaction at the solid–liquid interface in the spontaneous process.

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## 1. Introduction

The surface organofunctionalization of synthetic and natural mineral matrix by grafting of silanol groups are expected to play important roles in the designing of novel organic–inorganic materials [1,2]. The available magadiite silanol groups on the multi-layered structure resemble those of silica surface, whose reactivity enables the attachment of organic molecules onto the inorganic polymeric structure, as previously observed for chrysotile fibers, synthetic phyllosilicate and mesoporous silica. The chemical modification of natural or synthetic material is an elaborate experimental task resulting in improvements in the original surface properties of the materials for use in academic and technological applications [3–6], are widely used in reaction catalysis, as adsorbents in aqueous medium [7,8], in production of nanocomposites [9], as antibacterial materials [10,11].

Among these techniques proposed in the literatures, techniques involving immobilization of arsenic by adsorption have received much attention on natural geomaterials, including natural zeolite, modified clays and volcanic stone [12]. Due to its high toxicity and the epidemiological evidence of arsenic carcinogenicity [13], various common and non-usual adsorbent materials have been tried for metal ion removal from aqueous solutions. Among these available materials [14], silica gel [15],

pillared clay of the smectite 2:1 group [2], exfoliated and intercalated kaolinite [16], blast furnace slag [17], etc., are examples of such applications.

The aim of the present investigation is to explore the performance of a synthetic Na-magadiite in unmodified and chemically modified form in adsorption process. This matrix was obtained through synthetic process with low temperature; the chemical modification process was developed with organofunctionalization with *N*-propyldiethylenetriethoxysilane and bis[3-(triethoxysilyl)propyl]tetrasulfide. The resulted matrices were characterized by XRD, <sup>29</sup>Si MAS/NMR, <sup>13</sup>C MAS/NMR, SEM and chemical analysis; the anchoring of alkylsilyl group in lamellar structure is proved with the spectra of modified matrices. The unmodified and chemically modified matrices were used for arsenic cation adsorption process investigated at pH 2.0 and temperature at  $298 \pm 1$  K. The energetic effect caused by arsenic–nitrogen and sulfur basic center on Na-magadiite interaction at the solid–liquid interface was determined through calorimetric titration procedure.

## 2. Experimental section

The layered silicate Na-magadiite was synthesized through the hydrothermal method in a Teflon reactor with autogenous pressure. Briefly, a suspension of amorphous silica gel was added to 0.15 mol dm<sup>-3</sup> sodium hydroxide solution and allowed to stand at  $453 \pm 1$  K for two weeks. The suspension containing alkali was

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obtained, stirred by 3 h at 77 K in nitrogen atmosphere was filtered and washed with sodium hydroxide solution. The resulted material was named  $M_{\text{synt}}$ .

The two portions of about 10 g of Na-magadiite ( $M_{\text{synt}}$ ) were suspended in 25.0 cm<sup>3</sup> of DMSO under a nitrogen purge at 298 ± 1 K for 1 h. In each case, 3.0 cm<sup>3</sup> of silylating agents, *N*-propyldiethylenetriethoxysilane and bis[3-(triethoxysilyl)propyl]tetrasulfide, were added under flowing nitrogen to the suspension and stirred for 1 h followed by another 72 h at 363 ± 1 K. The solids were filtered, washed with DMSO and again with acetone in a Soxhlet system to remove the inserting solvent from inside the layers, then dried in vacuum to yield the immobilized compounds denoted by  $M_{\text{NPTM}}$  and  $M_{\text{3TPT}}$ .

X-Ray powder diffraction (XRD) patterns were recorded with a Philips PW 1050 diffractometer using CuK $\alpha$  (0.154 nm) radiation in the region between 2° and 65° ( $2\theta$ ) at a speed of 2° per min and a step of 0.050°.

The nuclear magnetic resonance spectrum was recorded with a Bruker AC300/P solid state high-resolution spectrometer, by using cross-polarization and magic angle spinning (CP-MAS). The frequency was 75.5 MHz, with rotational frequency of 26 MHz and acquisition time of 0.8 s.

The samples for scanning electron microscopy (SEM) images were recorded on a model LEO-ZEISS, 430 Vp at LNLS/Brazil, in conditions of analysis using secondary images obtained to 20 kV, with a working distance of 11 mm.

The surface and porosity analyses were carried out with a volumetric adsorption analyzer, AZAP 2010, from Micrometrics, at 77 K. The samples were pre-treated at 373 K for 24 h. After that, the samples were submitted to 298 ± 1 K under vacuum, reaching the residual pressure of 10<sup>-4</sup> Pa. For area and pore calculations the DBET and BJH methods were evaluated. The carbon, nitrogen and hydrogen contents were determined on a Perkin-Elmer 2400 Series II microelemental analyzer, and at least two independent determinations were performed for each sample.

The thermal effects of the arsenic interaction on unmodified and modified Na-magadiite surfaces were followed in an isothermal LKB 2277 microcalorimetric system. Portions of approximately 10 mg of unmodified and modified Na-magadiite samples were suspending in 2.0 cm<sup>3</sup> of water in the calorimetric vessel, with vigorous stirring, at 298.15 ± 0.20 K. After calorimetric baseline stabilization, the titrand was incrementally added through a microsyringe coupled to the microcalorimeter, which was connected to a gold needle. For each increment the respective thermal effect was recorded during the progress of the reaction, up to its completion. Arsenic solution with a concentration of 0.050 mol dm<sup>-3</sup> was used as cation source, and it was added in increments of 10.0 mm<sup>3</sup>.

The amount of arsenic adsorbed was determined by the difference between the initial concentration in aqueous solution and that found in the supernatant by using an ICP-OES Perkin-Elmer 3000DV instrument. For each experimental pint, the reproducibility was checked by at least duplicate run.

### 3. Results and discussion

#### 3.1. Characterization of materials

The anchored silylating agents *N*-propyldiethylenetriethoxysilane caused a maximum interlayer distance of 3.1 nm, with a net increase in expansion of 1.8 nm (Fig. 1). This value is 1.2 nm for matrix organofunctionalized by bis[3-(triethoxysilyl)propyl]tetrasulfide. By considering these values it is reasonable to propose for these immobilized agents that the pendant organic chains could be inclined in relation to the inorganic layer, suggesting that the

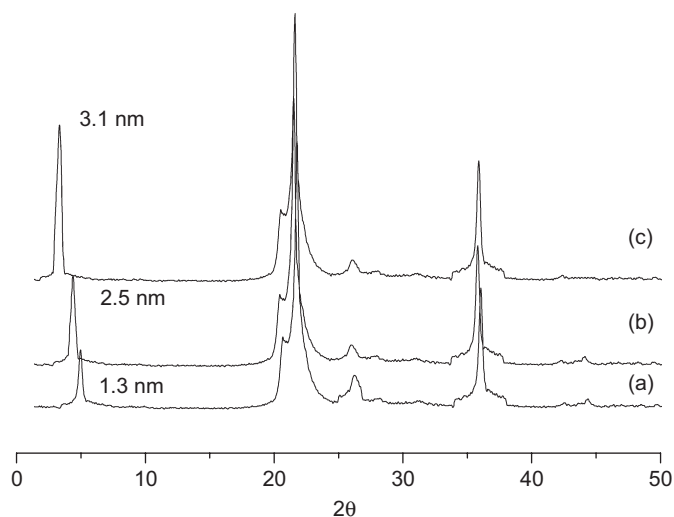


Fig. 1. X-Ray diffraction patterns of  $M_{\text{synt}}$  (a),  $M_{\text{3TPT}}$  (b) and  $M_{\text{NPTM}}$  (c).

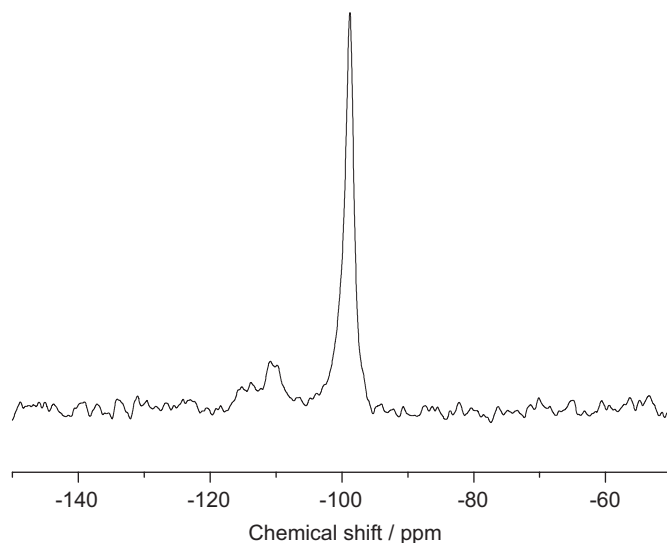


Fig. 2. <sup>29</sup>Si MAS NMR spectra for the synthesized lamellar Na-magadiite.

nitrogenated and sulfured chain of  $M_{\text{NPTM}}$  and  $M_{\text{3TPT}}$  respectively, could be distributed in a more vertical position. Based on the molecule size argument, the prior intercalation of longer dodecylamine molecules favors the immobilization of the silylating agent, to give an interlayer distance larger than 4000 pm, disposed in a bilayer arrangement inside the interlayer nano-space [14].

Solid state MAS/NMR spectroscopy is an important auxiliary tool to elucidate the structure of the silylating agents attached to the matrices of these silicates. Fig. 2 shows <sup>29</sup>Si-CP/NMR spectra of the unmodified Na-magadiite. The unmodified Na-magadiite  $M_{\text{synt}}$  presented resonance at -100.0 ppm; this peak is attributed to the silicon presented into structure matrix [15]. Clear evidence of alkylsilyl groups bonded in the interlayer surface of the polysilicate Na-magadiite was shown through <sup>13</sup>C-MAS/NMR, as shown in Fig. 3. The long chain pendant attached molecule modified  $M_{\text{NPTM}}$  presented a more complex spectrum, however, the C1 and C2 carbons atoms belonging to the spacer group appeared in nearly the same region, at 12 and 19 ppm. The sequence of carbon atoms 3–6 gave an intense peak at 30 ppm,

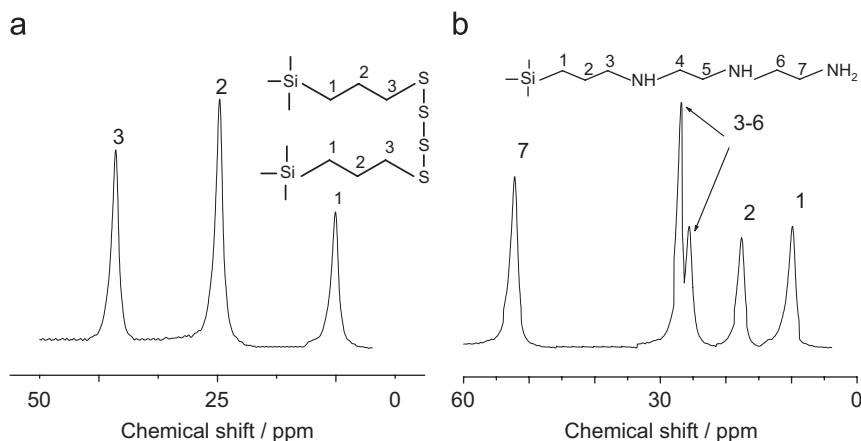


Fig. 3.  $^{13}\text{C}$  MAS NMR spectra for the synthesized lamellar Na-magadiite:  $M_{3\text{TPT}}$  (a) and  $M_{\text{NPTM}}$  (b).

**Table 1**  
Percentages of carbon (C), hydrogen (H) and nitrogen (N) obtained through elemental analysis of the inorganic–organic hybrid, density ( $d$ ) of the pendant molecules bonded on silicon layer, micropore area (MS), pore volume (PV) and surface area (S)

Matrix	C (%)	H (%)	N (%)	$d$ (mmol $\text{g}^{-1}$ )	MS ( $\text{m}^2 \text{g}^{-1}$ )	PV ( $\text{cm}^3 \text{g}^{-1}$ )	S ( $\text{m}^2 \text{g}^{-1}$ )
$M_{3\text{TPT}}$	$11.78 \pm 0.22$	$2.18 \pm 0.12$	—	$7.65 \pm 0.25$	$68 \pm 0.03$	$0.21 \pm 0.11$	$1726.63 \pm 0.11$
$M_{\text{NPTM}}$	$24.10 \pm 0.22$	$3.10 \pm 0.20$	$7.45 \pm 0.02$	$8.92 \pm 0.21$	$79 \pm 0.05$	$0.22 \pm 0.11$	$1865.81 \pm 0.17$

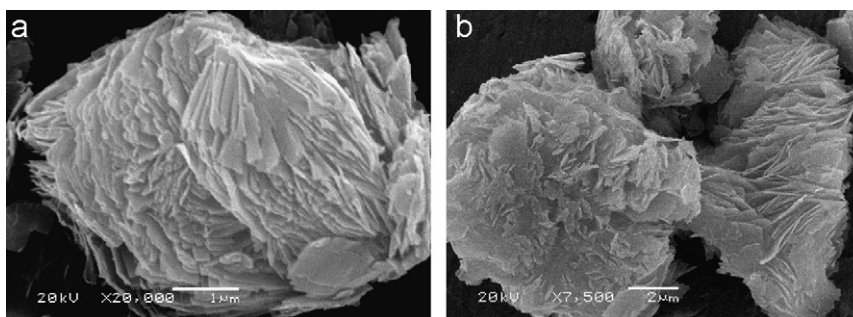


Fig. 4. SEM of unmodified and modified magadiite:  $M_{\text{synt}}$  (a) and  $M_{\text{NPTM}}$  (b).

followed by a shoulder at 26 ppm, while the seventh carbon atom gave a peak at 54 ppm [15].

The successful immobilization gave elemental analyses for the silylated surface as listed in Table 1. The amount incorporated was calculated based on the amount of sulfur, nitrogen and carbon exists in modified Na-magadiite samples. Based on the analytical data for both nanocompounds, the density of these pendant organic molecules immobilized on the Na-magadiite layer of the phyllosilicate can be calculated. Thus, the silylant agents grafted onto Na-magadiite structure gave an amount of  $7.65 \pm 0.25$  ( $M_{3\text{TPT}}$ ) and  $8.92 \pm 0.21$  mmol  $\text{g}^{-1}$  ( $M_{\text{NPTM}}$ ).

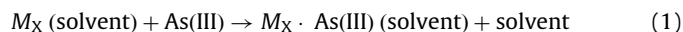
The gaseous nitrogen adsorption values for unmodified and modified Na-magadiite samples are also listed in Table 1. The specific surface areas were calculated by the BET method, in order to compare these three matrices, resulting in a higher surface area of the modified Na-magadiite samples, the unmodified Na-magadiite presented textural analysis values, specific area of  $105.8 \text{ m}^2 \text{ g}^{-1}$ , micropore area of  $15 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $0.12 \text{ cm}^3 \text{ g}^{-1}$ . The values obtained for organofunctionalized Na-magadiite samples presented increase of 1726.63 and 1865.81 relative to  $M_{3\text{TPT}}$  and  $M_{\text{NPTM}}$ , respectively.

The SEM images of unmodified ( $M_{\text{synt}}$ ) and modified ( $M_{\text{NPTM}}$ ) Na-magadiite samples are showed in Fig. 4, the morphology observed in two images are similar, with particles exhibiting parallel plates in agreement with the lamellar characteristics. However, the chemically immobilized surface with foliated form suggests a change in the structure, due to the attached silylating agent.

### 3.2. Adsorption and thermodynamic

Adsorption isotherms were obtained using the batchwise method [16–20] by suspending a series of samples of 20.0 mg of the each matrices ( $M_{\text{synt}}$ ,  $M_{3\text{TPT}}$  and  $M_{\text{NPTM}}$ ) ( $M_x$ ) with  $20.0 \text{ cm}^3$  aqueous solution of arsenic cation at concentration varying from 1.0 to  $2.5 \text{ mmol dm}^{-3}$ , mechanically stirred at  $298 \pm 1 \text{ K}$ . Based on the time required to reach equilibrium, which was previously established near 18 h, then 24 h was chosen to ensure maximum adsorption. After establishing equilibrium, the solid was separated by centrifugation and aliquots were removed from the supernatant for cation determination. The amount of the arsenic(III)

cation removed during adsorption was calculated by following the expression  $N_f = (N_i - N_s)/m$ , where  $N_f$  is the number of moles adsorbed on the pendant groups of the phyllosilicates,  $N_i$  and  $N_s$  are the number of moles on the initial solution and in supernatant after equilibrium, and  $m$  the mass of the solid phyllosilicate used in each adsorption process as represented reaction



For this adsorption the modified Langmuir equation. (2) can be applied [21,22]:

$$N_f = \frac{K_L b C_s}{1 + b C_s} \quad (2)$$

where  $C_s$  is the final number of moles in the supernatant in each point of the titration,  $N_f$  the number of moles of arsenic cation adsorbed per gram of the phyllosilicate in each adsorption obtained batch procedure. The plateau of the isotherm enables  $K_L$  determination that reflected the affinity of the adsorbate on the surface. The  $b$  value is the upper limit and represents the maximum adsorption, determined by the number of reactive surface reactive sites [21,22].

Non-linear regression was compared to obtain the optimum thermodynamic and isothermic adsorption parameters. A trial and error procedure was employed for non-linear methods using the solver add-in functions of Microsoft Excel software. In the trial and error procedure, adsorption isotherm and thermodynamic parameters were determined by maximizing the coefficient of determination values [23]. The least squares method was used to analyze the linear forms of the thermodynamic and isotherm models.

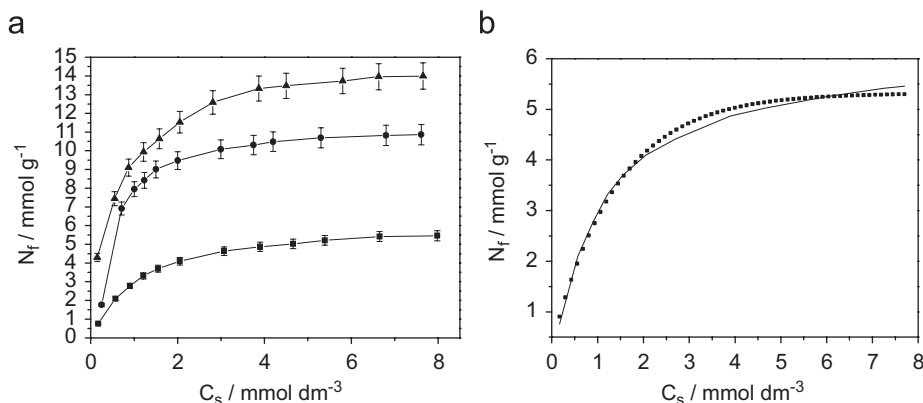
Coefficient of determination values ( $r^2$ ) were used in order to find the fitting degrees of isotherm adsorption and thermodynamic models by considering the experimental data [23], as defined by Eq. (3):

$$r^2 = \frac{\sum(N_{fCAL} - N_{fEXP})^2}{\sum(N_{fCAL} - N_{fEXP})^2 + (N_{fCAL} - N_{fEXP})^2} \quad (3)$$

**Table 2**  
Thermodynamic data for arsenic adsorption into unmodified and modified Na-magadiite

Adsorbent	$N_s$ (mmol g <sup>-1</sup> )	$N_{max}$ (mmol g <sup>-1</sup> )	$-\Delta_{int}h$ (Jg <sup>-1</sup> )	$-\Delta_{int}H^\circ$ (kJ mol <sup>-1</sup> )	$K_L \times 10^{-3}$	(kJ mol <sup>-1</sup> )	$\Delta_{int}S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )
$M_{synt}$	2.12 ± 0.11	5.50 ± 0.21	8.20 ± 0.05	4.15 ± 0.12	8.23 ± 0.11	22.44 ± 0.27	41.32 ± 0.13
$M_{3TPT}$	2.18 ± 0.12	11.06 ± 0.05	12.43 ± 0.05	5.78 ± 0.18	17.47 ± 0.11	24.28 ± 0.23	61.85 ± 0.11
$M_{NPTM}$	2.39 ± 0.15	14.05 ± 0.12	13.54 ± 0.14	5.98 ± 0.14	19.28 ± 0.11	24.56 ± 0.23	62.20 ± 0.13

Magadiite samples 3.0 g dm<sup>-3</sup>, initial As(III) 25.0 mg dm<sup>-3</sup>, pH 2.0, time 360 min and controlled temperature in 298 ± 1 K.



**Fig. 5.** Adsorption performance of unmodified and modified magadiite samples in aqueous medium of arsenic:  $M_{synt}$  (■),  $M_{3TPT}$  (●) and  $M_{NPTM}$  (▲) (a), experimentally adjusted data (—) with Langmuir nonlinear model (---) (Na-magadiite samples 3.0 g dm<sup>-3</sup>, initial As(III) 25.0 mg dm<sup>-3</sup>, pH 2.0, time 360 min and controlled temperature in 298 ± 1 K) (b).

where  $N_{fEXP}$  (mmol g<sup>-1</sup>) is the experimental amount of divalent cations exchanged by the unmodified and the modified Na-magadiite samples and  $N_{fCAL}$  is the amount of cations obtained by isotherm models.

The available nitrogen atoms from the *N*-propyldiethylenetri-methoxysilane and sulfur atoms from the bis[3-(triethoxysilyl)-propyl]tetrasulfide agent, the maximum adsorption values are listed in Table 2, 11.06 and 14.05 mmol g<sup>-1</sup> for matrices  $M_{3TPT}$  and  $M_{NPTM}$ , respectively (Fig. 5), suggested that only one cation can saturate these basic reactive centers introduced in Na-magadiite structure. For nitrogen and sulfur basic centers on these pendant groups the Gibbs free energies are favorable for interaction at solid-liquid interface process. The degree of adsorption depends on the combination of the reactive basic centers and the corresponding cation properties [24–26], the hard nitrogen and sulfur basic centers prefer hard cations and the chelating effect is clearly manifested double value from  $M_{NPTM}$  and  $M_{3TPT}$ , to illustrate the possible arsenic complexation on the sulfur and nitrogen groups anchored on the Na-magadiite surface, the structures are proposed as shown in Scheme 1.

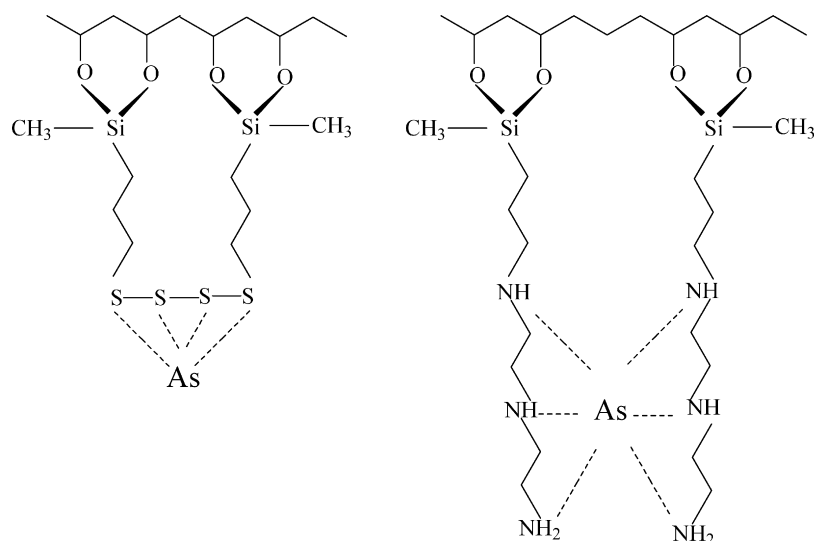
The equilibrium constants between the basic centers and arsenic cations at the solid-liquid interface, calculated from the batch process, are show in Table 2 and present values directly dependent on the degree of adsorption. These values reflected the nitrogen and sulfur donor atom-cation interactions according to Person's acid basic theory [27]. The Gibbs free energy values were calculated from these constant data, based on Eq. (4) [1].

$$\Delta_{int}G = -RT \ln K_L \quad (4)$$

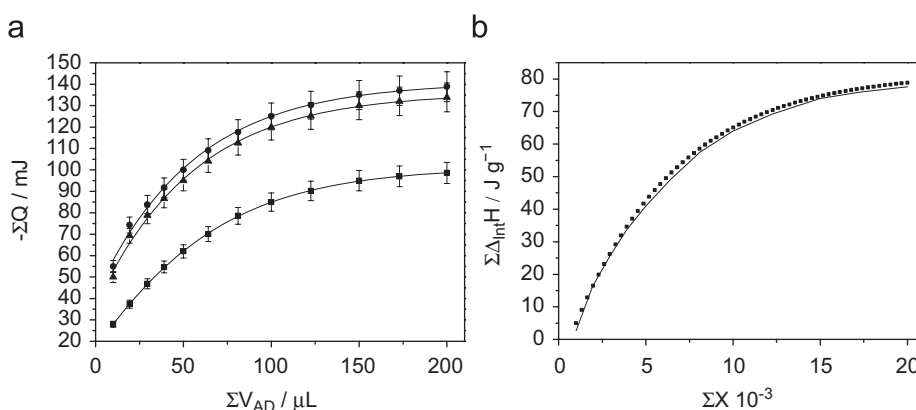
where  $K_L$  is the equilibrium constant obtained from Langmuir model,  $T$  the absolute temperature and the universal gas constant  $R = 8.314 \times 10^{-3}$  kJ K<sup>-1</sup> mol<sup>-1</sup>, and enthalpy values by considering (Eq. (5)) [25]:

$$\Delta G = \Delta_{int}H - T\Delta_{int}S \quad (5)$$

The resulting thermal effects due to the interaction of arsenic with unmodified and modified Na-magadiite matrices are



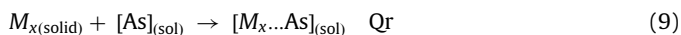
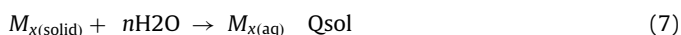
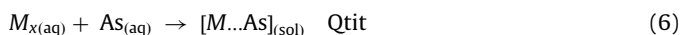
**Scheme 1.** Proposed modes of complexation of arsenic in layer structure of  $M_{\text{synt}}$  organofunctionalized with the silylating agents.



**Fig. 6.** The resulting thermal effects of the adsorption isotherms of the arsenic cation:  $M_{\text{synt}}$  (■),  $M_{3\text{TPT}}$  (●) and  $M_{\text{NPTM}}$  (▲) (a) and experimentally adjusted data with regression nonlinear:  $M_{\text{synt}}$  (–) and nonlinear adjust (—) (b).

obtained by considering the deduction of dilution of the dilution effect in water from the total thermal effect.

The effect thermodynamic cycles for this series of intercalations involving the unmodified and modified Na-magadiite matrices ( $M_x$ ) in solid state (solid) and in aqueous (aq) solution with arsenic cation (As) can be represented by the following calorimetric reaction:



The net thermal effect obtained for the calorimetric titration ( $\Sigma Q_{\text{r}} = \Sigma Q_{\text{tit}} - \Sigma Q_{\text{dil}} - \Sigma Q_{\text{sol}}$ ), as given by Eq. (9), was experimental represented as isotherms in Fig. 6. The charge in enthalpy associated with arsenic-matrix interaction can be determined by adjusting the adsorption data to a modified Langmuir equation to calculate the integral enthalpy involved in the formation of monolayer per unit mass of a monolayer per unit mass of adsorbent [27].

$$\frac{\Sigma X}{\Sigma \Delta_{\text{int}}H} = \frac{1}{(K_L - 1)\Delta_{\text{int}}h} + \frac{X}{\Delta_{\text{int}}h} \quad (10)$$

where  $\Sigma X$  is the sum of the mole fraction of the cation in the solution after adsorption, and  $X$  is obtained for each point of titrant addition by using the modified Langmuir equation.  $\Delta_{\text{int}}h$  is the enthalpy for monolayer formation and  $K_L$  a parameter associated with the equilibrium constant.  $\Delta_{\text{int}}h$  and  $K_L$  values can be determined from coefficients after regression nonlinear of the isotherm adsorption. The molar enthalpy of interaction process can be calculated through Eq. (11) [25–27].

$$\Delta_{\text{int}}H = \Delta_{\text{int}}h/N_s \quad (11)$$

The attached basic atoms can extract arsenic from aqueous solution, using nitrogen and sulfur atom to give a saturation plateau, as represented by number of moles adsorbed. Considering the numbers, the cations used more than one basic center with each grafter *N*-propyldiethylenetriammonium and bis[3-(triethoxysilyl)propyl]tetrasulfide agents; three basic centers can together embrace a arsenic in the coordination process to saturated amount.

#### 4. Conclusion

The isotherms for arsenic adsorption showed that this cation can be successfully extracted due to bond formation with the basic centers attached to the pendant molecules. The adsorption capacities of three matrices decreases in order

$M_{\text{NPTM}} > M_{\text{3TPT}} > M_{\text{synt}}$  with affinities of 14.05, 11.06 and  $5.50 \text{ mmol g}^{-1}$ , respectively. The results suggest that the adsorption capacities increased with an increase of reactive basic centers in the pendant organic chains of the intercalated silylating agent.

The maxima quantitative interaction between the arsenic and nitrogen and sulfur reactive basic centers of modified Na-magadiite–liquid interface were followed by calorimetry and gave favorable thermodynamic data, such as exothermic enthalpy, negative Gibbs free energy and positive entropy. These thermodynamic values suggest the application of this material, available worldwide, to improve the environment. The Langmuir isotherm with regression nonlinear yielded good fits with the adsorption data for metal–Na–magadiite interactions ( $r^2 > 0.99$ ).

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