



# Adsorption of methylene blue on raw and MTZ/imogolite hybrid surfaces: Effect of concentration and calorimetric investigation

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## ABSTRACT

The synthetic imogolite sample was used for organofunctionalization process with 2-mercaptothiazoline (MTZ). The compound 2-mercaptothiazoline was anchored onto imogolite surface by heterogeneous route. Due to the increment of basic centers attached to the pendant chains the dye adsorption capability of the final chelating material, was found to be higher than its precursor. The ability of these materials to remove methylene blue from aqueous solution was followed by a series of adsorption isotherms at room temperature and pH 4.0. The maximum number of moles adsorbed was determined to be  $40.32 \times 10^{-2}$  and  $65.13 \times 10^{-2} \text{ mmol g}^{-1}$  for IMO and IMO<sub>MTZ</sub>, respectively. The energetic effects caused by dye cations adsorption were determined through calorimetric titrations. Thermodynamics indicated the existence of favorable conditions for such methylene blue-nitrogen and sulfur interactions.

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## 1. Introduction

Imogolite and protoimogolite are hydrous silicate polymers, but paracrystalline aluminosilicates which consist of isolated silicon tetrahedral connected to a gibbsite octahedral framework [1–3]. Imogolite and allophane are most commonly associated with weathering of non-crystalline volcanic materials. They have been also identified in pumice deposits, coating of primary particles, stream sediments, and soils derived from igneous and sedimentary rock sandstone. The chemical composition is given by  $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ , which also reflects the arrangement of the atoms on passing from the exterior of the sheet [4–6].

Advances in the organofunctionalization field have been obtained by observing if any property of the nanocompound changes, by comparing these with those related to the host, as well as to the inserted guest molecules at the end of the process, the organofunctionalization behavior depends on several factors such as the compounds employed, their sizes and  $\text{pK}_a$  values of the guest molecules [7]. Among possible functional groups, the mercapto compounds have received considerable attention as dye ion trapping agents. High volumes of aqueous effluents contaminated with dyes such as methylene blue are generated by different industries, such as paper, textile and plastics [8]. Contamination of groundwater in many regions around the world is still a major concern

within global society. In addition, dyes have close relationship to human health because of their toxicity and carcinogenicity. Therefore, industrial effluents contained dyes need to be treated before being delivered to environment [9].

This investigation reports the use of original and modified imogolite aluminosilicates as alternative absorbents for extraction of toxic dye, which are commonly present in waters from a variety of sources and industrial effluents. For this purpose, the adsorption isotherms of methylene blue from aqueous medium at room temperature were explored. Synthetic imogolite aluminosilicate sample has been chemically modified with 2-mercaptothiazoline using the heterogeneous route. The spontaneity of these systems, reflected in the negative Gibbs free energies and the favorable positive entropic values, agrees with the displacement of coordinated solvent molecules as the intercalation takes place.

## 2. Materials and methods

### 2.1. Raw material

The method used for the synthesis of imogolite aluminosilicate is modified method of that described by Farmer et al. [1]. Approximately 100 mg of silicon dioxide was directly mixed with 500.0 mg of sodium bicarbonate and the mixture was melted in a platinum crucible at 1423 K and kept at 1073 K for about 90 h. The solid was cooling and dissolved into deionized water ( $100.0 \text{ cm}^3$ ). The resulted silicate solution was filtered. The clear filtrate was slowly added to a solution ( $20.0 \text{ cm}^3$ ) containing aluminum perchlorate

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and perchloric acid, giving a solution containing a hydroxylaluminum silicate complex. The resultant solution was centrifuged and the precipitant immediately was redispensed in  $60.0\text{ cm}^3$  of  $\text{HClO}_4$ . This solution was diluted and then heated at  $360 \pm 1\text{ K}$ . After 6 days the solution was flocculated with ammonia and the resulting material was separated by centrifugation. The material was purified by dialysis with deionized water for 4 days and collected via freeze drier. The imogolite sample was activated in a stream of dry nitrogen by heating at  $423\text{ K}$  for 10 h and used immediately.

## 2.2. Organofunctionalization of imogolite aluminosilicate

A sample of  $20.0\text{ g}$  of activated imogolite (IMO) was suspended in  $100\text{ cm}^3$  of dry toluene and  $20.0\text{ cm}^3$  ( $108.0\text{ mmol}$ ) of CPTS was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in an inert atmosphere for 72 h. The suspension was filtered and the solid was washed with toluene and dried under vacuum at  $230\text{ K}$  for several hours, to give the modified imogolite, named  $\text{IMO}_{\text{CL}}$  [10].

A sample of  $5.0\text{ g}$  of  $\text{IMO}_{\text{CL}}$  was heated for 5 h at  $383\text{ K}$  under vacuum, and then immersed in approximately  $60\text{ cm}^3$  of toluene and  $5.0\text{ g}$  ( $41.10\text{ mmol}$ ) of MTZ was added. The suspension was kept under reflux and mechanically stirred for 72 h at  $363\text{ K}$ . The final product,  $\text{IMO}_{\text{MTZ}}$ , was filtered, washed with toluene and ethanol, and dried under vacuum at  $230\text{ K}$  for 15 h.

The attachment of the 2-mercaptothiazoline onto original imogolite followed a sequence of two distinct steps. The first one consisted in grafting 3-chloropropyltriethoxysilane (CPTS) onto IMO to yield the new surface,  $\text{IMO}_{\text{CL}}$ . In the next stage, this precursor was reacted with 2-mercaptothiazoline (MTZ) to give the product  $\text{IMO}_{\text{MTZ}}$ , as represented in Scheme 1.

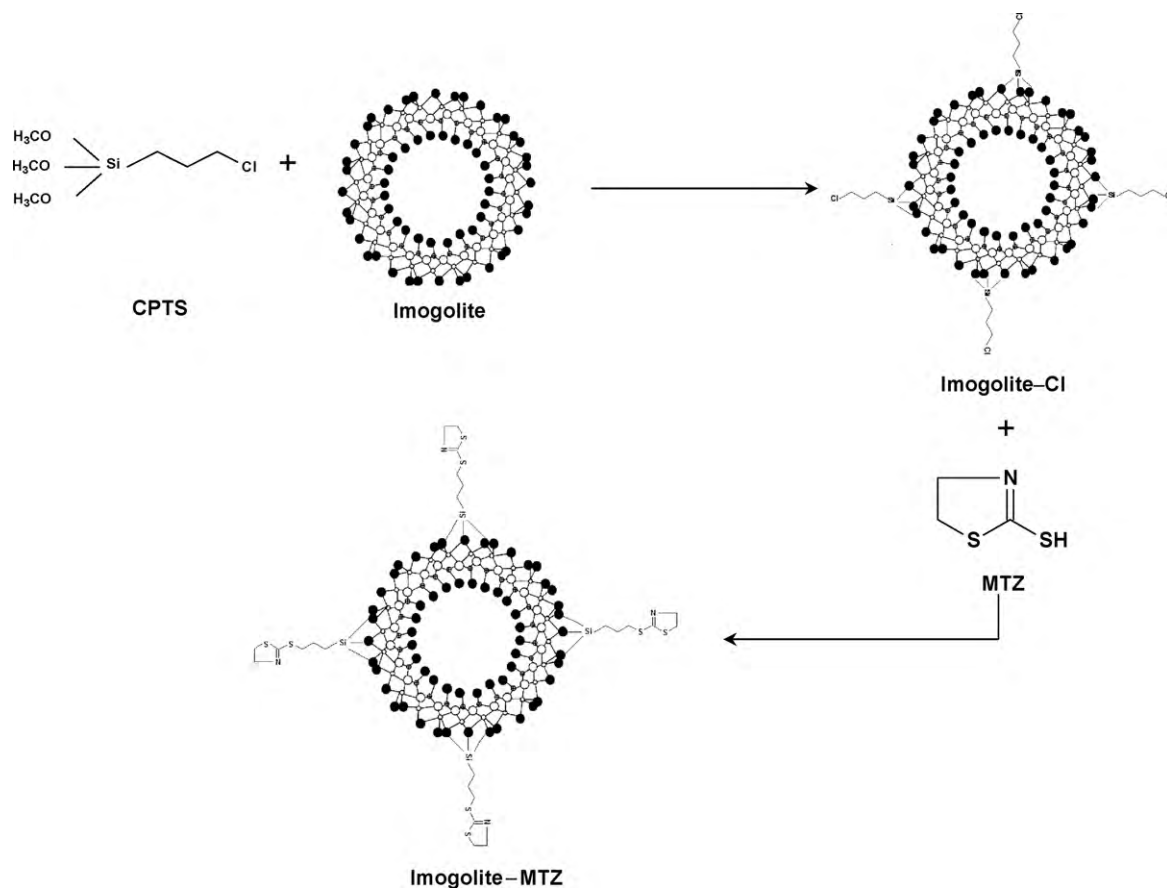
## 2.3. Characterization methods

Infrared spectra were recorded on a PerkinElmer Spectrum BX FT-IR system. Original and modified imogolite samples were mounted as KBr discs and was routinely recorded using a resolution of  $2.0\text{ cm}^{-1}$  and 64 scan between  $1400$  and  $400\text{ cm}^{-1}$ .

Nuclear magnetic resonance spectra of the samples were obtained on a Bruker AC 300/P spectrometer at room temperature. For each run, approximately  $1\text{ g}$  of each solid sample was compacted into a  $7\text{ mm}$  zirconium oxide rotor. The measurements were obtained at frequencies of  $59.63$ ,  $52.10$ , and  $75.47\text{ MHz}$ , for silicon, aluminum and carbon atoms, respectively, with a magic angle spinning of  $4\text{ kHz}$ . In order to increase the signal to noise ratio of the solid-state spectra, the CP/MAS technique was used.  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , and  $^{13}\text{C}$  CP/MAS spectra were obtained with pulse repetitions of  $3\text{ s}$  for both nuclei and contact times of  $1$ ,  $2$ , and  $3\text{ ms}$ , respectively.

## 2.4. Methylene blue batch adsorption procedure

Amounts of  $200.0\text{ mg}$  of IMO and  $\text{IMO}_{\text{MTZ}}$  were accurately weighed, with the precision of one tenth of a milligram, on  $200.0\text{ cm}^3$  glass Erlenmeyer flasks, containing  $100.0\text{ cm}^3$  of  $0.10\text{--}1.30\text{ mmol dm}^{-3}$  MB. The glass Erlenmeyer flasks were capped and agitated mechanically at  $60\text{ rpm}$  using a rotary orbital shaker at  $298\text{ K}$  for  $1\text{--}48\text{ h}$ . The sorbent was separated from the solution by centrifugation at  $3000\text{ rpm}$  for  $20\text{ min}$ . The solid phase was then separated by sedimentation/centrifugation, and then the amount of dye in the sample solution was determined by spectrophotometry using a PerkinElmer UV-vis spectrophotometer model 554 with silica cell of length  $1.00\text{ cm}$ . Absorbances were determined at wavelength of  $665\text{ nm}$ , which corresponds



**Scheme 1.** Incorporation of the 2-mercaptothiazoline (MTZ) onto imogolite surface by heterogeneous route.

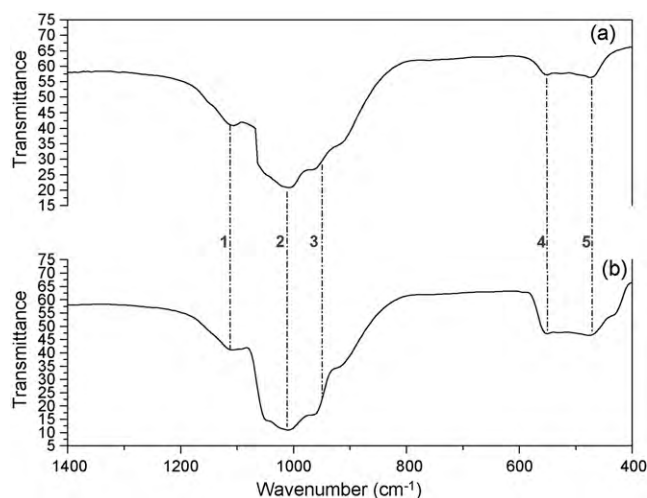


Fig. 1. Infrared spectra of original and modified imogolite samples, IMO (a) and IMO<sub>MTZ</sub> (b).

to the maximum absorption peak of MB [11,12]. Profiles of the obtained adsorption isotherms represented by the number of moles adsorbed ( $N_f$ ), versus the number of moles at equilibrium per volume of solution ( $C_S$ ), for series of isotherms. The isotherm of Langmuir–Freundlich type, named also Sips equation is valid for localized adsorption without adsorbate–adsorbate interactions [13] (Eq. (1)).

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

where  $C_S$  is the concentration of solution at equilibrium ( $\text{mol dm}^{-3}$ ),  $N_f$  is defined as before ( $\text{mmol g}^{-1}$ ) and  $N_S$  maximum number of moles of adsorbed per gram of the adsorbent ( $\text{mmol g}^{-1}$ ), which also depends upon the number of adsorption sites,  $K_S$  and  $n$  are equilibrium constants; number  $n$  being often lower than 1. This model has been derived by assuming the heterogeneity surface.

### 2.5. Calorimetry

The thermal effects from adsorption reaction were followed by calorimetric titrations using an isothermal calorimeter, Model LKB 2277, from thermometric. In this titration, the MB solution is added to a suspension of about 20 mg of the silicate sample in  $2.0 \text{ cm}^3$  of water, under stirring at  $298 \pm 1 \text{ K}$ . For each calorimetric titration about 20 mg of original and modified imogolite samples was suspended in a steel ampoule and stirred at room temperature. After equilibrium was established, as demonstrated by the base line, the cation solution was incrementally added in a previously programmed procedure at intervals of 2 h, using a microsyringe coupled to the calorimetric vessel. For each increment, the thermal effect ( $Q_t$ ) was recorded, and after a sequence, constant thermal effects were obtained as expected for the end of such operation. The same procedure was employed to monitor the thermal effect of cation dilution ( $Q_d$ ) in the calorimetric solvent. The effect of water on the anchored surface was noted as a null value. By combining these two output thermal effects, the net ( $\Sigma Q_r$ ) value was determined using the expression  $\Sigma Q_r = \Sigma(Q_t) - \Sigma(Q_d)$  [14].

## 3. Results and discussion

### 3.1. Characterization

The IR spectra of the original and modified imogolite, IMO and IMO<sub>MTZ</sub>, are shown in Fig. 1a and b, respectively. The both spectra

of five bands located at 1090, 995, 945, 576, and  $483 \text{ cm}^{-1}$ . These bands were numbered 1, 2, 3, 4, and 5, respectively. The first band (1090 No. 1) has been assigned to a  $\nu(\text{Si-O-Si})$  stretching vibration by a number of authors despite the fact that the structure is  $\text{Si}(\text{OAl})_3$  [15]. This is because an atom of silicon coordinates to an atom of oxygen which is shared by two atoms of aluminum octahedra. The spectrum of IMO indicated the characteristic absorption of stretching vibration band ( $\nu(\text{Si-O-Al})$ ) at 995 No. 2 and  $935 \text{ cm}^{-1}$  No. 3. One band has been assigned to a  $\nu(\text{O-Si-O})$  No. 4 stretching vibration at  $576 \text{ cm}^{-1}$  [4,7]. The other one band is attributed to pure surface signal described as  $\nu(\text{Al-OH})$  No. 5, at  $483 \text{ cm}^{-1}$ .

The  $^{29}\text{Si}$  NMR spectra in the solid state for both aluminosilicate samples confirm the covalent bond formed between the silylant agents and the silanol groups dispersed onto imogolite surface, as presented in Fig. 2a and b for IMO and IMO<sub>MTZ</sub>, respectively. The spectrum of IMO<sub>MTZ</sub> present three peaks located at  $-54.5$ ,  $-69.5$ , and  $-80.6 \text{ ppm}$ . The first one is assigned to the silicon atom of the silylant agent bonded to one OH group and forming two siloxane bonds with silicon of the aluminosilicate structure,  $\text{RSi}(\text{OSi})(\text{OH})_2$ , usually named as the  $T^2$  signal. The peak at  $-67.0 \text{ ppm}$  is assigned to  $\text{RSi}(\text{OSi})_3$ , the  $T^3$  signal. Both these signals confirm that organic groups were covalently bonded onto the imogolite surface. The other one peak is attributed to pure surface signal described as  $\text{Si}(\text{OSi})_3\text{OH}$ ,  $Q^3$  at  $-80.9 \text{ ppm}$  [16].

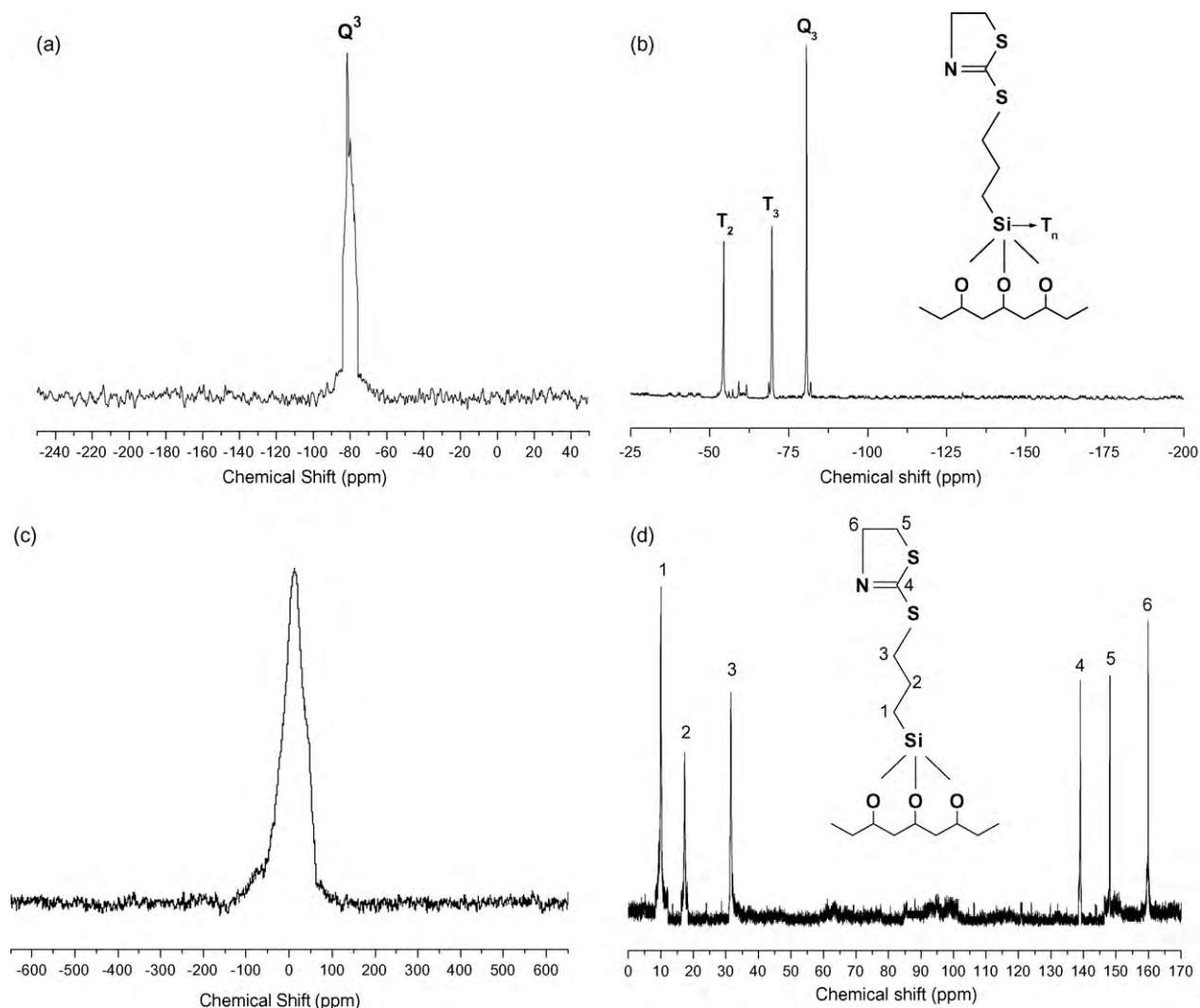
The  $^{27}\text{Al}$  NMR spectrum of the original imogolite aluminosilicate, presented in Fig. 2c. The peak at  $0.0 \text{ ppm}$  is assigned to the aluminum atom of the OH and O–Si groups. Thus while some Si may be bonded to octahedral aluminum, in some structures Al is replacing silicon structures in tetrahedral coordination. This should result in a negative on the macromolecule [5].

The  $^{13}\text{C}$  NMR spectrum of the modified imogolite aluminosilicate, presented in Fig. 2d, the proposed attachment of 2-mercaptothiazoline molecule to the precursor spacer modified agent is presented with carbon numbered. The three carbon atoms related to the spacer, numbered 1, 2, and 3 gave signals at 10.0, 26.0, and 39.0 ppm [17]. The aromatic carbons labeled 4–6 were assigned in the 130.0–160.0 ppm range, in good agreement with previous report [18].

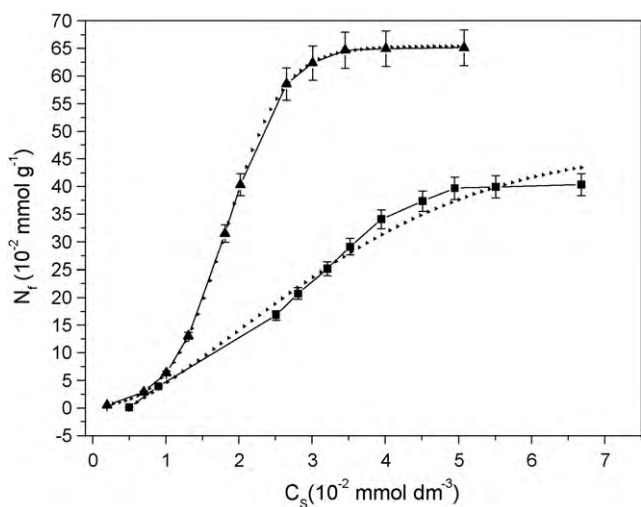
### 3.2. Effect of methylene blue concentration solution

The dye adsorptions on original and chemically immobilized imogolite samples are shown in Fig. 3. The influence of the silylant agents covalently bonded on the inorganic structure is clearly reflected in adsorption isotherms due to different basic centers attached to the pendant chains, as outlined by the saturation process [19,20]. The molecules anchored onto the oxides containing nitrogen and sulfur basic atoms on pendant chains favor a dye interaction, mainly of soft cations, due to the presence of the basic reactive centers [21]. Based on the structural features presented by basic groups on the original or modified aluminosilicate surfaces, the adsorption can be related directly to the available nitrogen and sulfur atoms. The Sips non-linear adsorption model was used to explain the significant capacity of these aluminosilicates to quantify MB interactions on these polymeric inorganic structures.

The non-linear Sips model presents a significant advantage when used with such experimental data, allowing the determination of the capacity of cations bonded to basic centers and to evaluate the constant related to the binding energy. The large capacity of modified imogolite sample was confirmed through constant values obtained with this model in the non-linear form, whose results gave the best approximation to the experimental data, as illustrated in Fig. 3. The values are listed in Table 1.



**Fig. 2.**  $^{29}\text{Si}$  MAS NMR spectra of unmodified and modified imogolite samples: IMO (a) and  $\text{IMO}_{\text{MITZ}}$  (b);  $^{27}\text{Al}$  spectrum of original imogolite sample, IMO (c);  $^{13}\text{C}$  MAS NMR spectrum of modified imogolite sample,  $\text{IMO}_{\text{MITZ}}$  (d).



**Fig. 3.** Effect of concentration on MB cations adsorption onto unmodified and modified imogolite samples from aqueous solution: IMO (■) and  $\text{IMO}_{\text{MITZ}}$  (▲) (aluminosilicate  $1.0\text{ g dm}^{-3}$ , time 8.0 h and controlled temperature in  $298 \pm 1\text{ K}$ ) – isotherms calculated with non-linear method (▶).

### 3.3. Thermodynamic of adsorption

The applicability of these kinds of porous materials depends on a series of physicochemical properties, on the degree of molecules immobilized, mainly when the adsorption is considered [22]. The adsorption process was also calorimetrically monitored by titration process. From this value, the thermal effect related to cation-basic center interactions on the modified surface is obtained. An illustration of all the steps of calorimetric titration of 20.0 mg of the anchored imogolite with  $0.050\text{ mol dm}^{-3}$  of MB solution is shown in Fig. 4a. This value was adjusted to the modified Langmuir model (Eq. (2)), a modified Langmuir model adjusted to describe several types of systems [22,23]:

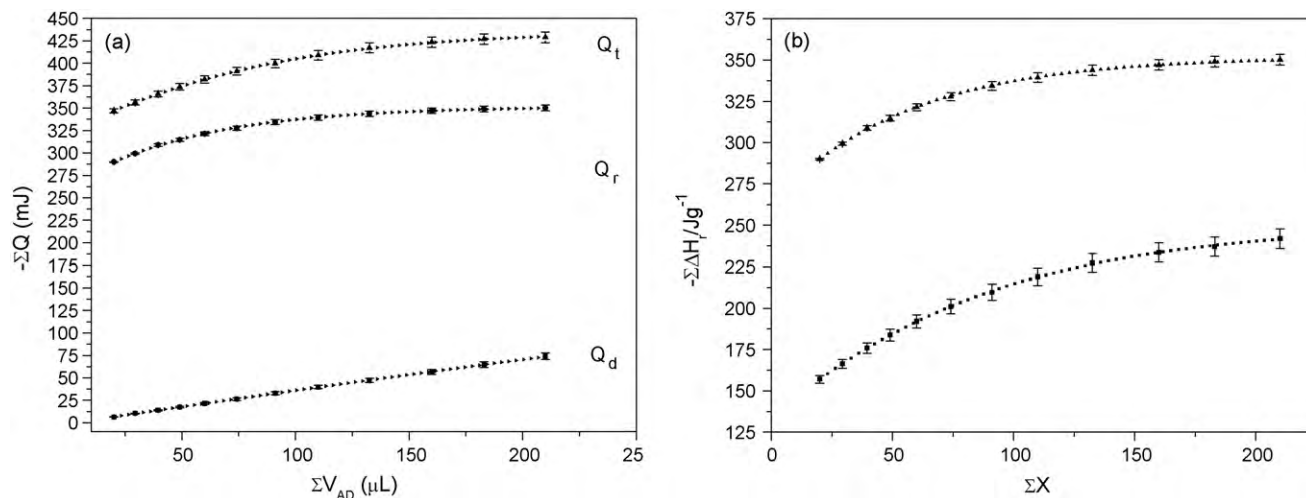
$$\frac{\Sigma X}{\Sigma \Delta_r H} = \frac{\Sigma X}{\Delta_{\text{mon}} H} + \frac{1}{\Delta_{\text{mon}} H (K_L - 1)} \quad (2)$$

where  $\Sigma X$  is the sum of the mole fraction of each MB cation in solution, after adsorption, obtained for each experimental point of titrand addition.  $\Delta_r H$  is the integral enthalpy of adsorption for each point of the calorimetric titration obtained by dividing the thermal effect related to adsorption by the number of moles of adsorbate,  $K_L$  is proportionality constant that also includes the equilibrium constant.  $\Delta_{\text{mon}} H$  is the thermal effect of formation of a monolayer on the surface. A plot of  $\Sigma X / \Sigma \Delta_r H$  versus  $\Sigma X$  gave

**Table 1**

Adsorption and thermodynamic data for MB interaction onto original and modified imogolite samples (aluminosilicate 1.0 g dm<sup>-3</sup>, pH 4.0, time 360 min and temperature of 298 ± 1 K).

Sample	$N_f^{\max}$ (10 <sup>-2</sup> mmol g <sup>-1</sup> )	$N_S$ (10 <sup>-2</sup> mmol g <sup>-1</sup> )	$K_S \times 10^{-3}$	$n$	$r^2$	$-\Delta_{\text{mon}}h$ (J g <sup>-1</sup> )	$-\Delta_{\text{ads}}H$ (kJ mol <sup>-1</sup> )	$-\Delta_{\text{mon}}G$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{mon}}S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$r^2$
IMO	40.32 ± 0.10	20.12 ± 0.12	8.78 ± 0.05	0.93	0.997	310.85 ± 0.11	7.71 ± 0.10	21.92 ± 0.03	51 ± 3	0.999
IMO <sub>MTZ</sub>	65.13 ± 0.15	31.04 ± 0.11	11.52 ± 0.04	0.99	0.994	483.27 ± 0.12	7.42 ± 0.12	22.98 ± 0.03	55 ± 3	0.998



**Fig. 4.** The resulting thermal effect of adsorption MB on modified imogolite at 298 ± 1 K. The experiment points represent the thermal effect of cation titration  $\sum Q_t$  (▲), cation dilution  $\sum Q_d$  (■) and the net thermal effect of interaction  $\sum Q_r$  (●).  $\sum Q_t$  and  $V_{\text{ad}}$  values are the sum of detected thermal effect and total injected volume of MB solution (a) and the net calorimetric data plotted in non-linear form for IMO (■) and IMO<sub>MTZ</sub> (▲) (b).

the values of  $\Delta_{\text{mon}}H$  and  $K_L$ , respectively, obtained from non-linear fitting method of the calorimetric isotherms, as shown in Fig. 4b. The enthalpy of adsorption  $\Delta_{\text{ads}}H$  is calculated using the expression (Eq. (3)) [23].

$$\Delta_{\text{ads}}H = \frac{\Delta_{\text{mon}}h}{N_S} \quad (3)$$

From  $K_S$  values, the Gibbs free energies were calculated by expression and the entropy value can be calculated through (Eqs. (4) and (5)).

$$\Delta G = -RT \ln K_S \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

A summary of the thermodynamic data is listed in Table 1. From the thermodynamic point of view, the obtained exothermic and positive entropic values establish the set of favorable results for the thermodynamic of MB-sulfur and nitrogen center interactions. Thus, the spontaneity of such reactions is expressed by the negative Gibbs free energy with a great contribution of the positive entropy due to the solvent displacement from the imogolite sample and those initially hydrogenated bonded to basic and reactive groups of the attached organic chains, as the imogolite/nitrogen-sulfur basic center interactions at the solid/liquid interface [22], which data also support the suitability of the present system in undertaking for a such a study. The adsorption results in connection with the thermodynamic data suggested that this kind of original and hybrid materials could be applied for the removal of dye contaminant cations from water.

#### 4. Summary

The immobilization of the 2-mercaptothiazoline molecule onto aluminosilicate surface was obtained with success though heterogeneous routes. The maximum adsorption capacity was

40.32 × 10<sup>-2</sup> and 65.13 × 10<sup>-2</sup> mmol g<sup>-1</sup> for IMO and IMO<sub>MTZ</sub>, respectively. The increment on the adsorption capacity of IMO<sub>MTZ</sub> in relation to IMO should be related to improvements on the physical-chemical properties of the hybrid material after the organofunctionalization process. Through calorimetric investigation information about all systems was obtained, resulting in exothermic enthalpy, negative Gibbs free energy and positive entropy. This series of thermodynamic data reflects the favorable cation/base center interaction at the solid/liquid interface. In addition to the present application related to contaminant removal from process and waste water systems, this material is expected to find other suitable applications such as in catalysis and chromatographic separation systems, due to its large area.

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