Calorimetric aspects of adsorption of pesticides 2,4-D, diuron and atrazine on a magadiite surface

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Abstract H-magadiite was applied to remove the pesticides 2,4-D, diuron, and atrazine from water. The H-magadiite containing herbicides adsorbed were investigated by FTIR, DRX, N_2 adsorption and desorption isotherms, and surface area. Calorimetric studies were carried out to determine the heat of interaction between pesticides and magadiite. It was possible to ride the cycle of interaction of magadiite–pesticide for a better understanding of the process involved. From the results of the thermal effect of the interaction of magadiite–pesticide, the thermochemical parameters can be determined by using the relationship between the data obtained from adsorption and calorimetry results. The interaction of pesticide–magadiite follows the sequence of adsorption: diuron > atrazine > 2,4-D. The ΔH values for the interactions were determined to be -20.62 ± 1.08, -24.04 ± 0.86–26.34 ± 0.93 kJ mol^{-1} for 2,4-D, diuron and atrazine, respectively. All the interactions were spontaneous, enthalpically and entropically favored demonstrating the effectiveness and efficiency of the method.

Keywords Magadiite · Herbicides · Calorimetry

Introduction

The herbicides were applied to eliminate different unnecessary forms of life in agriculture and urban areas. The use of herbicides is associated with the pollution of the soil and the water [1].

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The indiscriminate application of pesticides in agriculture leads to increase the amounts of these compounds on the surface and underground waters. The application of the concentrations exceeding those required for control of the target organisms has caused the surface water contamination due to runoff and leaching. The toxic effect of the herbicides on the environment can disturb the natural ecological equilibrium, and presents risks to human and animal health [2–4].

The harmful effects of herbicides on the environment have stimulated researchers to develop efficient technologies for water treatment in order to remove and/or degrade organic contaminants from water. Among these methods, the adsorption can be highlighted [5, 6]. The adsorption enables the understanding of the adsorbate–adsorbent interaction, from which the thermodynamic data can be determined [7, 8].

Low-cost adsorbents such as sawdust, chitosans, clays, zeolites, soils, coals, natural oxides, humic substances, and layered materials have been used to remove contaminants from water in recent years [9–14].

The layered materials have attracted much interest because of their properties as sorption of polar organic molecules in aqueous solution and ion exchange. The hydrous, layered alkali silicate magadiite is a material that can be easily prepared by hydrothermal reaction with silica gel and aqueous sodium hydroxide. The magadiite structure presents silicate layers separated by hydrated sodium cations. Its chemical composition was determined to be as $Na_2Si_{14}O_{29}\cdot 9H_2O$ [15, 16].

In this study, magadiite was used as host to remove the following herbicides: 2,4-D (2,4-dichlorophenoxyacetic acid), and Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and atrazine Atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine), which are herbicides

commonly used in Brazilian sugarcane crops. The energetic effect caused by interaction of these herbicides on H-magadiite was determined from calorimetric titration procedures.

Experimental

Reagents

Bidistilled water was used throughout the experiments. All the chemicals used were reagent grade. Sodium hydroxide (Sinth), Silica gel (Merck), Diuron (Sigma), Atrazine (Sigma), and 2,4-D (Sigma) were used without further purification.

Synthesis

Na-magadiite was prepared by the hydrothermal reaction of 2.0 g of silica gel in 10.0 mL of NaOH 1.1 mol L^{-1} according to the previously described methods [16].

H-magadiite was obtained by suspending Na-magadiite into HCl 0.2 mol L^{-1} with stirring for 24 h at room temperature [17]. The solid was filtered, washed with water and air dried at 60 °C. The compound was named H-MAG.

H-magadiite containing herbicides 2,4-D, diuron and atrazine adsorbed were prepared by mixing 1.0 g of H-MAG, 0.1 g of herbicide and 33.0 mL of methanol. The mixture was allowed to digest without stirring at 75 °C in a Teflon-lined stainless steel autoclave for 24 h. The solids were air dried at room temperature and named MAG-2,4-D, and MAG-DIU e MAG-ATRA corresponding to 2,4-D, diuron and atrazine herbicides, respectively.

Characterization

Powder X-ray diffraction patterns were measured on a Rigaku model D/Max-2A/C diffractometer using Cu Kα radiation. All the samples were scanned in the 2θ range of 2–50° at a scan rate 2° min^{-1}.

Surface area was calculated by the Brunauer–Emmett–Teller (BET) method from Nitrogen adsorption–desorption data, which were measured on a Quantachrome Nova 2200 analyzer.

Infrared spectra were obtained on a JASCO 4100 spectrometer, with pressed KBr pellets with 32 scans in the 4,000–400 cm^{-1} region with resolution of 4 cm^{-1}.

Herbicide adsorption

The adsorption process was followed batchwise in an aqueous solution of 2,4-D, diuron and atrazine. For this process, a series of samples of about 50.0 mg of H-magadiite were suspended in 50.0 mL of aqueous herbicides solutions of different concentrations, varying from zero to 1.0×10^{-4} mol L^{-1}. The amount of adsorbed herbicide was determined by the difference between the initial concentration in aqueous solution and the one found in the supernatant, by using a Spectrophotometer Cary-50 at 221, 227 e 248 nm for atrazine, 2,4-D and e Diuron. In every case, all the samples were analyzed in triplicate.

Calorimetric analyses

Herbicide adsorption interactions were followed by calorimetric titration using an Adiabatic calorimeter PARR 6275.

In a typical process, 0.50 g of H-magadiite suspended in 50.0 cm^3 of water was incrementally titrated with a 2,4-D ethanolic solution 0.05 mol L^{-1}, diuron ethanolic solution 0.05 mol L^{-1} and atrazine methanolic solution 0.05 mol L^{-1}, under stirring, at 298.15 ± 0.02 K. Herbicide solution was added in increments of 0.50 mL up to saturation of the active surface sites of the modified material. After equilibration, the pesticide solution was incrementally added using a syringe coupled to the calorimetric vessel. For each increment, the heat flux (ΔQ_{tit}) was recorded, as indicated by a constant heat flux at the end of each operation. The same procedure was employed to monitor the heat flux due to pesticide dilution (ΔQ_{dil}) without the solid and also the heat flux of solvation on the suspended modified material (ΔQ_{sol}).

Results and discussion

Characterization and intercalation studies

The X-ray diffraction patterns of Mag and H-MAG are shown in Fig. 1. The XRD showed d_{001} reflection corresponding to a basal spacing of 1.54 and 1.24 nm, for MAG and H-MAG, respectively. This interlayer spacing is according to the literature. The decrease of basal spacing is due to the loss of solvated sodium ions in the exchange process [16, 18–20]. The intercalation of herbicides resulted in an increase in interlayer distances from 1.24 to 1.52; 1.68, and 1.98 nm, for MAG-DIU, MAG-2,4-D, and MAG-ATRA, respectively, as shown in Fig. 1.

The infrared spectra of H-magadiite and herbicides intercalated in magadiite are shown in Fig. 2. The main features of all materials are the similarity of bands, such as a large broad band between 3,400 to 3,200 cm^{-1}, which is attributed to the presence of the O–H stretching frequency of silanol groups and also to the adsorbed water remaining. The peak at 1,630 cm^{-1} is assigned to the angular vibration of the water molecule and the region between 1,400 and

Fig. 1 X-ray diffraction patterns of Na-magadiite (*a*) and H-magadiite (*a*) in **A** and X-ray diffraction patterns of H-MAG (*a*), MAG-DIU (*b*), MAG-2,4-D (*c*) and MAG-ATRA (*d*) in **B**
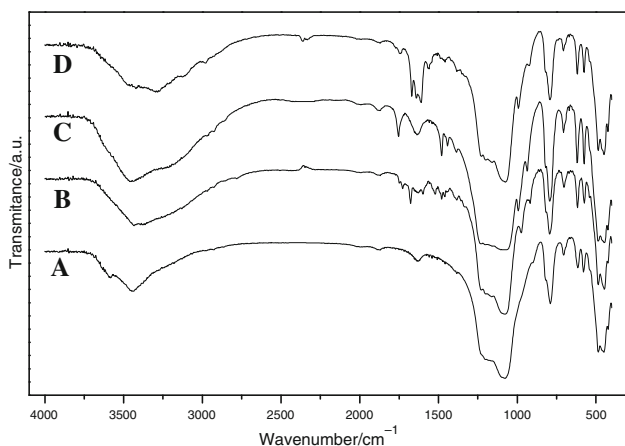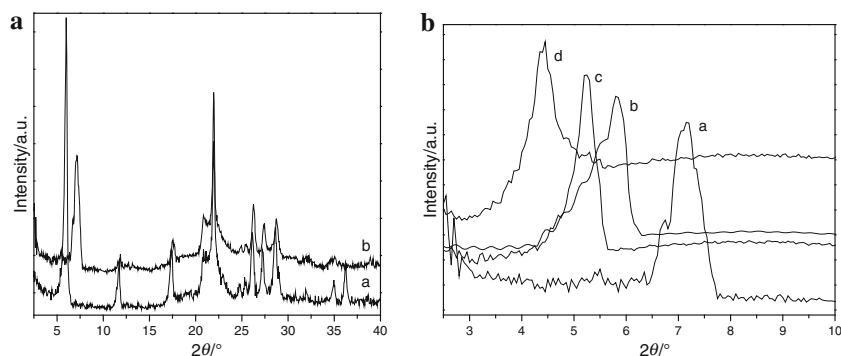

Fig. 2 Infrared spectra of H-MAG (*a*), MAG-DIU (*b*), MAG-2,4-D (*c*) and MAG-ATRA (*d*)

400 cm^{-1} presented the vibrations due to the silicate layer and charge-balancing cations; one peak at 704 cm^{-1} which is assigned to some coupling between adjacent silicate layers [21–23]. The spectrum of MAG-2,4-D (Fig. 2b) shows a peak at 1,750 cm^{-1} related to the stretching C=O of carboxylic acid. The peaks in the region between 1,500 and 1,450 cm^{-1} are related to the stretching of the C=C aromatic bonds. Besides, the band at 2,950 cm^{-1} is attributed to the C–H stretching of the sp^3 carbon.

The spectrum of MAG-DIU (Fig. 2c) shows a peak at 1,675 cm^{-1} related to the stretching of C=O of urea. The peaks in the region between 1,500 and 1,450 cm^{-1} are related to stretching of C=C bonds of aromatic. The band at 2,950 cm^{-1} is attributed to C–H bond of the sp^3 carbon. In the region 1,560 cm^{-1}, a small signal associated to the protonation of the nitrogens of atrazine can be observed. The appearance of this peak may be associated to the interaction between the acid site structure of magadiite and diuron.

The spectrum of MAG-ATRA (Fig. 2d) shows peaks in the region between 1,670 and 1,610 cm^{-1} assigned to stretching of C=N bonds and water molecules adsorbed, and the band at 2,950 cm^{-1} related to C–H bond of

aliphatic. One singular peak around 1,490 cm^{-1} can be observed in spectra of magadiite with herbicides. These peaks corroborate with the protonation of the nitrogen atoms of the herbicide, confirming the interaction between herbicides and magadiite.

The nitrogen adsorption/desorption isotherms for MAG and H-MAG are shown in Fig. 3. The surface areas of MAG and H-MAG were 35 and 28 m^2 g^{-1}, respectively. This decrease can be explained by the greater interaction between the layers of H-magadiite, as observed in X-ray patterns and FTIR. The surface areas of MAG-DIU, MAG-2,4-D and MAG-ATRA were 13; 16 and 15 m^2 g^{-1}, respectively. The values of surface area were smaller than H-MAG, showing that the herbicides occupy the interlamellar spacing, causing the decrease of the surface area due to the introduction of these herbicides between lamellas of magadiite. Thus, these intercalated herbicides block partially the adsorption of nitrogen molecules on the surface, resulting in the reduction of the surface area.

The intercalation of herbicides 2,4-D, diuron and atrazine in H-magadiite caused an increase on basal spacing and a surface area decrease, confirming the success of the reaction. These data indicate that magadiite can be used as an efficient host for the adsorption of herbicides from water. From these data, a scheme of interaction between herbicides and magadiite was represented based on hydrogen bond interactions, as shown in Fig. 4.

Herbicide removal

The H-MAG was applied to remove 2,4-D, diuron and atrazine from water. The adsorption capacity of H-MAG was evaluated by measuring the sorption isotherms.

The number of moles of the herbicides adsorbed per gram of adsorbent (N_f; mol g^{-1}) was obtained from Eq. 1:

$$N_f = \frac{n_i - n_s}{m} \tag{1}$$

where n_i is the initial number of moles of herbicides added to the system, n_s is the number of moles at equilibrium after adsorption, and m is the mass (g) of H-MAG [1, 9]. The
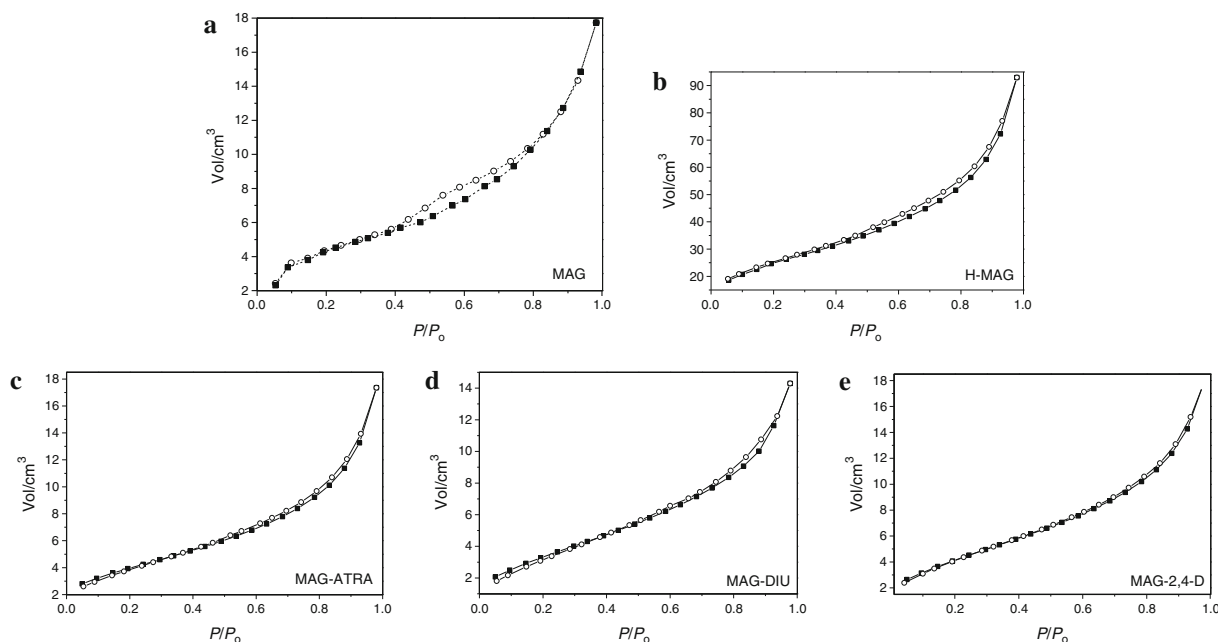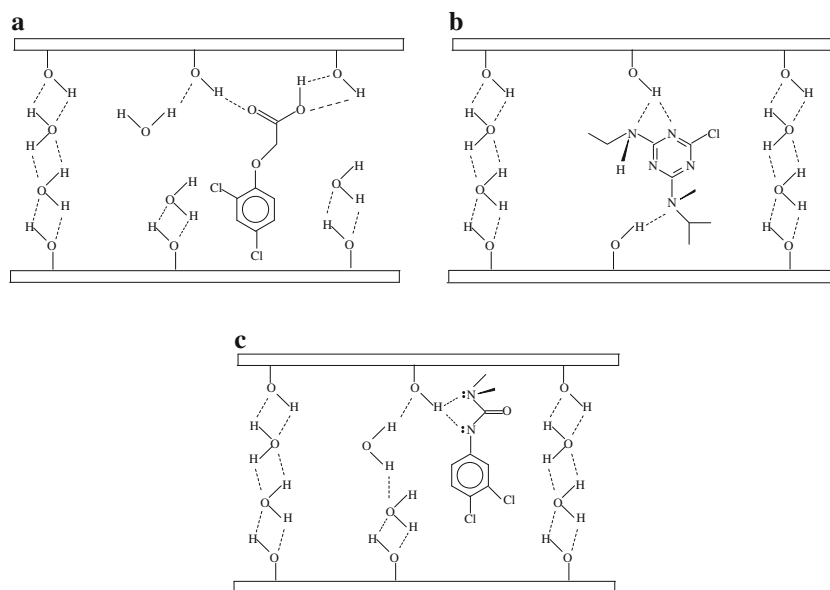
Fig. 3 Nitrogen adsorption (*filled squares*)–desorption (*open circles*) isotherms for the Na-MAG (**a**), H-MAG (**b**), MAG-ATRA (**c**), MAG-DIU (**d**) and MAG-2,4-D (**e**)

Fig. 4 Scheme for interaction between magadiite and herbicides: 2,4-D (**a**), atrazine (**b**) and diuron (**c**)

adsorptive behavior represented by the number of moles adsorbed (N_f), versus the number of moles at equilibrium per volume of solution (C_s) is presented in Fig. 5a.

The experimental data were applied into the general equation of the modified Langmuir model presented in Eq. 2.

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s \cdot K} \tag{2}$$

where C_s is the concentration (mol dm^{-3}) of the solution at equilibrium, N_s is the maximum amount of herbicide

adsorbed per gram of adsorbent (mol g^{-1}), which depends on the number of adsorption sites, and K is a equilibrium constant (mol L^{-1}) [24–27]. The linear form of the adsorption isotherm, i.e., from plots of C_s/N_f versus C_s, in which N_s and K are represented by the slope and intercept, respectively, as shown in Fig. 5b. The values of the maximum amount of herbicide adsorbed per gram of adsorbent were 4.27 ± 0.31, 4.24 ± 0.22, and $2.36 \pm 0.21 \times 10^{-5}$ mol for diuron, atrazine, and 2,4-D, respectively. The adsorbed amounts of pesticides diuron and atrazine by magadiite were very close, and the adsorbed amounts of

Fig. 5 Isotherms (**a**) of 2,4-D (*filled triangles*), atrazine (*filled squares*) and diuron (*open circles*) adsorbed on H-MAG and the linear form (**b**) of these isotherms. *Inset* Fig. 5b: the correlation coefficients of linear forms
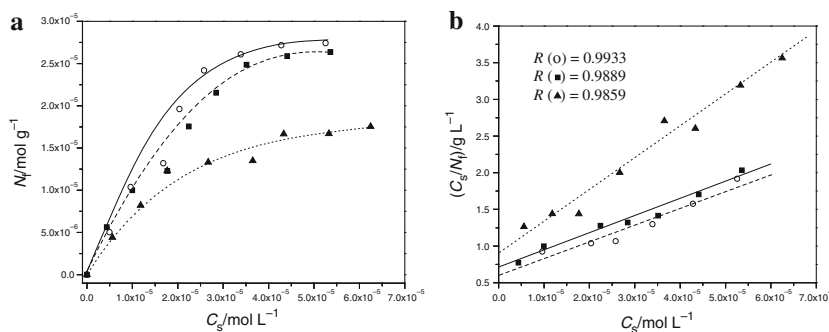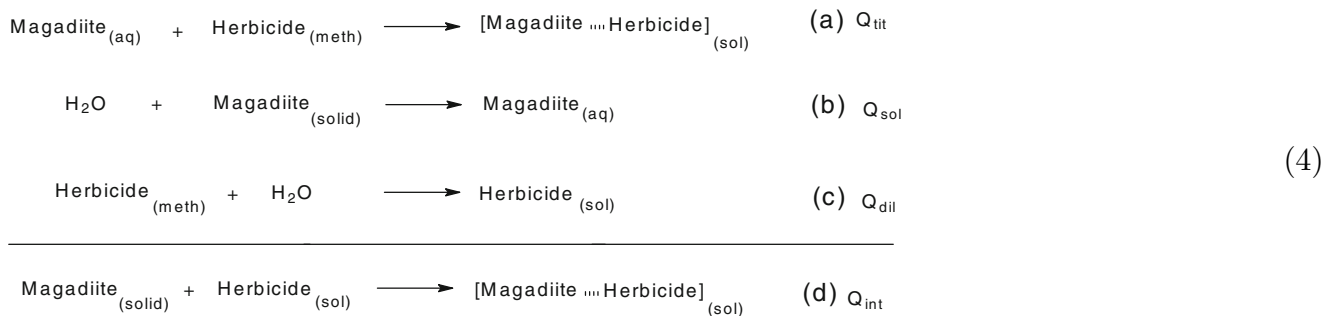

diuron and atrazine were almost the double of the adsorbed amount of pesticide 2,4-D. In order to understand this behavior, it is important to analyze the pesticides structures and the possible interaction with magadiite surface. Diuron presents two nitrogen atoms from urea group; atrazine showed two basic nitrogen outside the aromatic ring and 3 nitrogen atoms inside the aromatic ring. On the other hand, the pesticide 2,4-D presents oxygen groups from carboxylic acid function, whereas other pesticides must interact by basic nitrogen groups. Indeed, the obtained data suggest that the silanol groups of magadiite must have a preference for nitrogen groups, as proposed in Fig. 4.

The Gibbs free energy changes may be calculated from Eq. 3, which correspond to a ΔG value of -25.83 ± 1.86, -26.34 ± 1.36, -26.62 ± 2.36 kJ mol^{-1} for diuron, atrazine and 2,4-D, respectively.

$$\Delta G = -RT \ln K \tag{3}$$

The thermal effects of the interaction of herbicide with magadiite were determined from a series of calorimetric experiments. The complete thermodynamic cycle can be summarized in Eq. 4 as follows:

dilution of herbicide solution (Q_{dil}). The net interaction heat change Q_{int} (d) is given by Eq. 5 [1, 9].

$$\Sigma Q_{int} = \Sigma Q_{tit} + \Delta Q_{sol} - \Delta Q_{dil} \tag{5}$$

Since the heat of solvation of the aqueous, suspended modified material was zero, the expression was reduced to Eq. 6 [1, 9]. The heat evolved by the host/Herbicide interaction (Q_{tit}) and the heat of dilution of herbicide solution are presented in Fig. 6a, and the net resultant heat output for this interaction in the solid/liquid interface obtained is illustrated in Fig. 6b.

$$\Sigma Q_{int} = \Sigma Q_{tit} - \Delta Q_{dil} \tag{6}$$

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, $\Delta_{mono}H$ (Fig. 7), were calculated through Eq. 7 [24–27].

$$\frac{\Sigma X}{\Sigma \Delta_R H} = \frac{1}{(K_{ap} - 1)\Delta_{mono}H} + \frac{\Sigma X}{\Delta_{mono}H} \tag{7}$$

where $\sum X$ is the sum of the molar fractions of the herbicide remaining in solution after adsorption and X values are

Three separated titration experiments were carried out to determine the component parts, namely: (a) the heat evolved by the host/Herbicide interaction (Q_{tit}); (b) the heat of solvation of the solid H-mag (Q_{sol}); and (c) the heat of

obtained for each addition of titrant, using the modified Langmuir equation, K_{ap} is a proportionality constant that also includes the equilibrium constant, and $\sum \Delta_R H$ is the integral enthalpy of adsorption (J g^{-1}) obtained from the
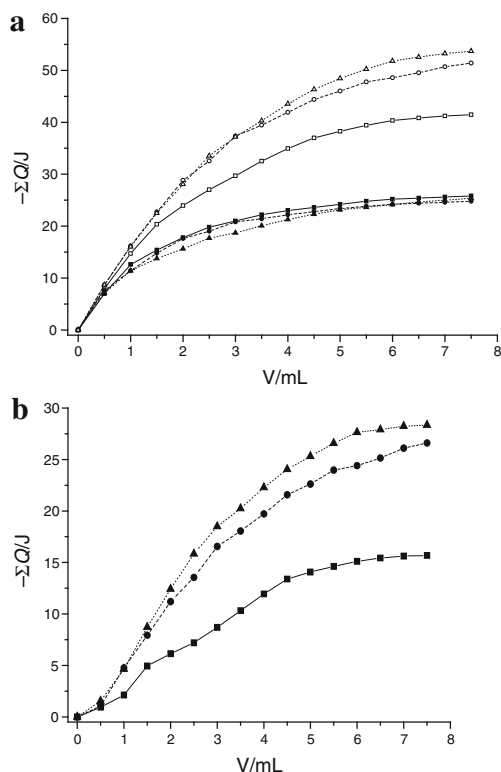
Fig. 6 The measured heat output (ΣQ_{tit}) for calorimetric titrations of diuron (*open triangles*), 2,4-D (*open squares*) and atrazine (*open circles*) onto H-MAG and the heat of dilution (ΣQ_{dil}) of diuron (*filled triangles*), 2,4-D (*filled squares*) and atrazine (*filled circles*) solution (**a**) and the net heat change during the interaction (ΣQ_{int}) for 2,4-D (*filled squares*), atrazina (*filled circles*) and diuron (*filled triangles*) (**b**)
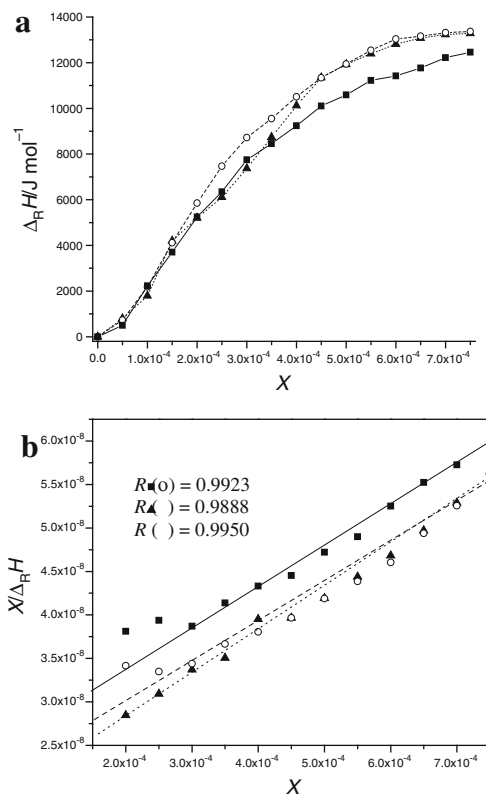

Fig. 7 Isotherm for the integral enthalpy (**a**) of the adsorption of 2,4-D (*filled triangles*), diuron (*filled squares*) and atrazine (*open circles*) adsorption onto the surface of solid onto H-MAG obtained from calorimetric titration and the linear form of this isotherm (**b**) at 298.1 K. *Inset* Fig. 7b: the correlation coefficients of linear forms

net thermal effect of adsorption and the number of moles of the adsorbate. Based on the Langmuir equation, it is possible to calculate the reaction enthalpy of the monolayer formed, $\Delta_{\text{mono}}H$, from plots of $\sum X/\sum \Delta_R H$ versus $\sum X$ [1, 9].

The molar enthalpy, ΔH, of the interaction process was calculated from $\Delta_{\text{mono}}H$ and the maximum number of moles inserted, Ns, using Eq. 8 [24–27].

$$\Delta H = \frac{\Delta_{\text{mono}}H}{N_s} \tag{8}$$

The entropy values, ΔS, were determined from Eq. 9. All thermodynamic data are listed in Table 1.

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

Consideration of the set of thermodynamic data obtained for the adsorption process indicated that the reaction between herbicides and magadiite is spontaneous, since it is enthalpically and entropically favored. These data show the high ability of magadiite in removing herbicides from water.

The interaction of H-MAG with herbicides must have occurred due to the hydrogen bond between the hydrogen of silanol groups of lamellar magadiite and the nitrogen of amine groups of diuron and atrazine or the oxygen groups of 2,4-D, which can be observed on the proposal scheme of

Table 1 Maximum adsorbed amount of herbicides (N_s) per gram of H-magadiite and thermodynamic data for interactions at 298.1 K

	Diuron	Atrazina	2,4-D
$N_s/10^{-5}$ mol g^{-1}	4.27 ± 0.31	4.24 ± 0.22	2.36 ± 0.21
N_s/mg g^{-1}	9.95 ± 0.72	9.11 ± 0.47	5.22 ± 0.46
$K/10^3$ mol L^{-1}	33.58	41.12	46.39
ΔG (kJ mol^{-1})	-26.62 ± 2.36	-25.83 ± 1.86	-26.34 ± 1.36
ΔH (kJ mol^{-1})	-20.62 ± 1.08	-24.04 ± 0.86	-26.34 ± 0.93
ΔS (J/mol K)	20 ± 2	6 ± 1	6 ± 1

the interaction (Fig. 4). This interaction can be confirmed with the FTIR data (Fig. 2) which showed regions associated with the interaction between the acid site structures of magadiite and herbicides.

Thermodynamic data showed that the interaction enthalpy involving diuron and atrazine were more exothermic than the interaction between 2,4-D and magadiite. Adsorption results showed that magadiite adsorbed more effectively diuron and atrazine than 2,4-D. These facts suggest that magadiite has preference for the amine basic groups atrazine and diuron being more effective than the basic oxygen groups of 2,4-D.

Conclusions

Magadiite was obtained with success, which presented a high interaction with herbicides diuron, atrazine, and 2,4-D. The interaction between magadiite and herbicides must have occurred because of the hydrogen bonds between hydrogen of silanol groups of magadiite and nitrogen (diuron and atrazine) or oxygen basic center of herbicides (2,4-D).

The herbicides–magadiite interaction processes gave the following sequence of adsorption: diuron > atrazine > 2,4-D. All interactions were spontaneous accompanied by an increase in entropy and with exothermic enthalpy values. All data prove that the obtained lamellar material can be used to remove these contaminants from water.

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