THE TRAPPING OF B FROM WATER BY EXFOLIATED AND FUNCTIONALIZED VERMICULITE

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Abstract—Micron-grade natural vermiculite was modified by several physical and chemical treatments in order to increase the adsorption capacity of this material for B. A thermal exfoliation ($T = 600ºC$) of pristine material, a chemical exfoliation through reaction with hydrogen peroxide (H_2O_2 35%), or grafting of a specific B complexant (*i.e.* N-methyl-D-glucamine: NMDG) led to an increase in the uptake of B at low initial concentrations of the aqueous solutions ($[B] \approx 5$ mg L^{-1}). The more efficient material is the NMDG-grafted clay, for which the adsorption uptake is four times greater than that of raw vermiculite, and reaches 0.04 mmol g^{-1}. For all modified materials, the effect of the pH on B adsorption and the adsorption kinetics were studied and compared to raw vermiculite. Adsorption isotherms were also plotted and fitted well with the Freundlich equation.

Key Words—Adsorption, Grafting, N-methyl-D-glucamine.

INTRODUCTION

Boron is a micronutrient element for plants, animals, and human beings, but it is toxic at high concentrations (Sah and Brown, 1997). The acceptable daily intake is 0.3 mg B kg^{-1} day^{-1}, which is well above normal exposure levels (Murray, 1996). In the past decade, the increase in the use of B derivatives in various industrial processes has led to the release of large amounts of B into the environment. The B in water, from anthropogenic or natural sources, is found as undissociated H_3BO_3 boric acid in the dominant form and also borate anion ($B(OH)_4^-$), ($pKa(H_3BO_3/(B(OH)_4^-) = 9.24$ at 25ºC) (Weast, 1989−1990; Zeebe, 2005). The European Union standard concentration of B in drinkable water is 1 mg L^{-1}, but the value recommended by the World Health Organization is 0.3 mg L^{-1} (WHO, 1993). Methods such as precipitation (Remy *et al*., 2004), adsorption (Choi and Chen, 1979; Karahan *et al.*, 2006; Su and Suarez, 1997), selective complexation with functionalized resins (Simonnot *et al.*, 2000; Inukai *et al.*, 2005; Boncukcoğlu *et al.*, 2004), and ion exchange with basic exchangers (Popat *et al.*, 1988) or membranes (Smith *et al.*, 1995) proved to be effective in the removal of B from water.

Boron can also be adsorbed to the surface of inorganic materials: oxides (Choi and Chen, 1979; Su and Suarez, 1995; Peak *et al.*, 2003; del Mar de la Fuente García-Soto, 2006; Seki *et al.* 2006; Lemarchand *et al.*, 2007) and clay minerals (Sing, 1971; Keren *et al.*, 1981; Keren *et al.*, 1984; Hingston, 1964; Goldberg *et al.*, 1986; Palmer *et al.*, 1987; Karahan *et al.*, 2006, Pastor Ferreira *et al.*, 2006; Seyhan *et al.*, 2007). The adsorption sites for clay materials are mainly the -OH groups present at the edges of the layers (Keren and Talpaz, 1984). These groups react with B to form inner-sphere complexes (Goldberg and Glaubig, 1986). Karahan *et al.* (2006) tested modified clays (bentonite, sepiolite, and illite) for the removal of B. To date, apparently no other works have been published on the adsorption of B on vermiculite.

Boron is known to form borate−diol complexes with hydroxyl groups in the 1−2 or 1−3 positions of alkyl chains as in N-methyl-D-glucamine (CH$_3$NHCH$_2$ (CHOH)$_4$CH$_2$OH: NMDG) (Geffen *et al.*, 2006; Kunin and Preuss, 1964). At present, the materials used most commonly in the removal of B from water are chelating resins, such as polymers (polystyrene 'Amberlite' or crossed-linked polymethacrylate polymer) or cellulose resins. These materials are highly selective because the resins are grafted with NMDG functional groups (Simonnot *et al.*, 2000; Inukai *et al.*, 2005; Boncukcoğlu *et al.*, 2004) which can selectively form complexes between their polyol groups and the borate ions. Moreover, the complexation is accompanied by the

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protonation of the ternary amines of the grafted molecules (Simonnot *et al.*, 2000).

More recently, inorganic materials have been functionalized. The surface grafting of NMDG was achieved on the silanol groups (Si-OH) of silicate materials (Kaftan *et al.*, 2005; Wang *et al.*, 2006), *e.g.* the mesoporous silica MCM41 was successfully functionalized with NMDG, in order to prepare a new selective sorbent for the removal of B from water.

Among the clays, vermiculite has very highly charged layers and thus is a good candidate for donor-acceptor reactions with Lewis acids such as $B(OH)_3$. The B adsorption mechanism by vermiculite was not studied extensively even though B is believed to be complexed by the -OH groups of the layers.

The aims of this work were to obtain vermiculite-based materials that can be used for the removal of B from slightly polluted water and also to study their adsorption properties in conditions of small B concentrations ([B] ~5 mg L^{-1}). Vermiculite was modified by exfoliation and functionalization in order to obtain more efficient B-trapping materials. The effect of the surface enhancement of vermiculite by exfoliation on the B-sorption uptake was studied first. N-methyl-D-glucamine (Figure 1) was then grafted on the edges of the layers of vermiculite in order to prepare more selective B complexing materials.

EXPERIMENTAL

Exfoliation of vermiculite

Vermiculite is a phyllosilicate formed of mica-type layers separated by exchangeable cations solvated by water molecules (Walker, 1961). On the edges of the layers, the silanol Si−OH or aluminol Al−OH functional groups are able to form inner-sphere complexes with aqueous B (Su and Suarez, 1995; Goldberg, 2005). Under appropriate conditions (thermal shock or chemical treatment with hydrogen peroxide) the natural vermiculite can exfoliate (Üçgül and Gírgín, 2002; Muromtsev *et al.*, 1990) leading to a dramatic increase in the apparent material volume and basal surface area. The chemical exfoliation by reaction with hydrogen peroxide yields greater expansion rates due to the disproportionation of H_2O_2 into gaseous oxygen and
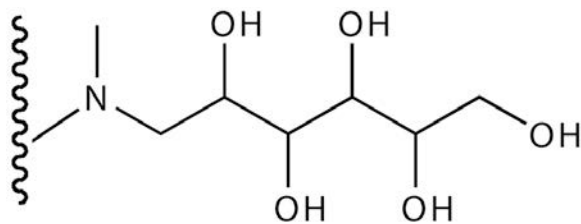

Figure 1. Chemical formula of the grafted N-methyl-D-glucamine (NMDG).

water between the layers, increasing the layer separation (Üçgül and Gírgín, 2002).

The 'Micron-grade' vermiculite from Palabora (South Africa) was used as the raw material. The material has the following characteristics: average chemical formula: $[Si_{3.02}Al_{0.79}Ti_{0.05}Fe_{0.14}^{III}][Mg_{2.50},Fe_{0.38}^{II}Fe_{0.09}^{III}(X^{3+})_{0.03}]$ $O_{10}(OH,F)_2Ba_{0.29}K_{0.14}Ca_{0.07}$ where X is a trivalent cation not defined by the authors (Del Rey-Perez-Caballero and Poncelet, 2000); density ~2.5; particle size ranging between 250 and 700 μm with an average size of 400 μm. The 'Micron-grade' vermiculite was first washed with UHQ water (18.2 MΩ cm) and then exfoliated by thermal shock in an oven at 600ºC for 5 min. The chemical exfoliation was typically operated by reaction of 1 g of raw washed vermiculite with 85 mL of hydrogen peroxide solution (35%, from Acros Organics) in a reflux at 100ºC for 5 min. After reaction, particles were filtrated, washed by immersion in 1 L of UHQ water, refiltrated, and dried at 150ºC for 12 h.

Reaction with NMDG

In a first step, the washed and dried, thermally exfoliated vermiculite (1 g) was reacted in a reflux with 50 mL of $SOCl_2$ (99.7%, from Acros Organics) and 2 mL of dimethylformamide (99.8%, from Aldrich) for 24 h at 70ºC under argon. After filtration, the chlorinated clay was washed by controlled agitation in tetrahydrofuran (99.9%, from Fluka) under an argon atmosphere for 12 h and then filtered and vacuum dried at room temperature.

The second step of the NMDG-grafting reaction by nucleophilic substitution on the chlorinated clay was carried out by two different ways: (1) the vermiculite separated by filtration (0.4 g), was reacted in a reflux with 50 mL of an aqueous solution of NMDG (80 g L^{-1}) for 24 h at 70ºC, according to the procedure described by Kaftan *et al.* (2005); and (2) ~0.2 g of chlorinated clay mixed with 1 g of NMDG (99%, from Acros Organics) were heated in a micro-wave furnace (SyntheWave 402, 60 Watt electric power) for 45 min at 135ºC (NMDG Melting Point ≈ 130ºC).

At the end, the filtrated materials (0.4 g) were washed by agitation in UHQ water (1 L) followed by filtration. The washing procedure was repeated at least three times to remove free NMDG from grafted vermiculite. The absence of NMDG in water was confirmed by the disappearance of its characteristic peak, normally observed by UV-visible spectrophotometry at 223 nm.

Characterization of the clay materials

Mid-infrared (IR) transmittance measurements (400−4000 cm^{-1}) were carried out using a Bruker IFS 113V spectrometer equipped with an N_2-cooled MCT detector, a glow bar source, and a KBr beam splitter. The spectral resolution was 2 cm^{-1} and 64 scans were co-added for each spectrum. Spectra were obtained at room temperature of 300 K (±1 K). Pellets (pressed under

370 MPa) were made of a mixture of 1.5 mg of modified (or pristine) vermiculite and 300 mg of dried KBr. The spectra were not smoothed and no baseline correction was performed. The given frequency corresponds to peak maxima. Due to the complex shape of the peaks, no fits were made to draw out a frequency which would have been very dependent on the model.

The samples were characterized by adsorption measurements of nitrogen gas at low pressure (P <0.35 bar) and T = 77 K. The specific surface areas were estimated by the BET model. The pH was measured in a water suspension of clay minerals in the volumetric ratio 1:5 (French standard NF ISO 10390: Soil quality, Determination of pH, 2005).

Typical procedure for B-sorption studies

The B stock standard solutions were prepared by dissolving 0.229 g of boric acid (99%, Selectra) in 1 L of UHQ water in order to obtain an initial solution of 40 mg L^{-1} of B, from which the batch aliquot solutions were prepared. The B aqueous solutions were stored in polyethylene containers.

Boron adsorption on the various substrates was carried out by shaking 6 g of vermiculite for 24 h at room temperature with 200 mL of various B concentration solutions (2, 5, 10, 20, 30, 40, and 80 ppm), prepared by dissolution of weighed amounts of boric acid in UHQ water. For pH-dependent B-adsorption studies, pH values of the vermiculite suspensions were adjusted by dropwise addition of 0.1 mol L^{-1} HCl (or 0.1 mol L^{-1} NaOH). After adsorption, the suspensions were filtrated and aliquots of the clear supernatant were taken for B analysis.

Among the methods for sensitive B titration in water, UV-visible spectrophotometry of complexed B species (Karahan *et al.*, 2006; Rodier, 1978; Yurdakoç *et al.*, 1999) is suitable for the accurate measurement of the small concentrations of B which are usually observed in natural surface or underground water. In a typical analysis (Yurdakoç *et al.*, 1999; Rodier, 1978), the titrated aliquot sample (0.2 mL) was agitated with 3 mL of a curcumin solution (0.125 g of curcumin in 100 mL of 99.5% acetic acid and 3 mL of an acid solution made of a 1:1 mixture of 99.5% glacial acetic acid and 95% 18 mol L^{-1} sulfuric acid), then left to settle for 45 min before the addition of the acetate buffer solution (15 mL). After standing for 30 min, the complex formed

(rosocyanin) in the sample solution was titrated, with absorbance measurements detected by a UV-visible spectrophotometer (HP 8453, Vectra XM) at 550 nm, with a detection limit of 0.05 mg L^{-1} (Rodier, 1978).

The B desorption was studied for the raw and grafted exfoliated vermiculite by shaking a suspension made of 6 g of the B-loaded materials in 200 mL of UHQ water for 24 h. The suspension pH was adjusted by addition of droplets of concentrated nitric or hydrochloric acid. After filtration, the B concentration of the suspension was obtained by the curcumin colorimetric titration method described previously.

RESULTS AND DISCUSSION

Characterization of the modified vermiculites

The exfoliation of vermiculite led to a dramatic expansion of its apparent volume and the BET specific surface area due to the separation of the layers (Table 1). Indeed, the apparent specific volume observed for vermiculite exfoliated in hydrogen peroxide is more than four times that of the pristine material. After H_2O_2 exfoliation treatment, the basal surfaces of the separated layers are exposed, so that the observed BET specific surface area is fourteen times that of the original pristine material.

The separation of two neighboring sheets of the vermiculite, due to exfoliation, is accompanied by the loss of the interfoliar cations (Mg^{2+} or Ca^{2+}) to solution (Walker, 1961; Su and Suarez, 1995; Üçgül and Gírgín, 2002; Muromtsev *et al.*, 1990), leading to a global negative charge of the clay. In order to maintain electrical neutrality, Üçgül and Gírgín (2002) proposed that this excess negative charge is counterbalanced by the desorption of OH^- anions from the solid surface, thus increasing the pH of the aqueous solution after exfoliation. In the present experiments, the pH of clays after exfoliation became more acidic (Table 1), confirming that some hydroxyl groups were desorbed from the surface of exfoliated materials. These observations agree with the work of Muromtsev *et al.* (1990). The acidity increase of the exfoliated clay can also be interpreted in terms of a reduction of the exchange of interfoliar cations with H^+ cations of the solution.

The IR spectra of raw, exfoliated, and chlorinated vermiculites were quite similar, showing the stretching bands of the free octahedral OH at 3720, 3663, and

Table 1. Characterization of the pristine and exfoliated vermiculite.

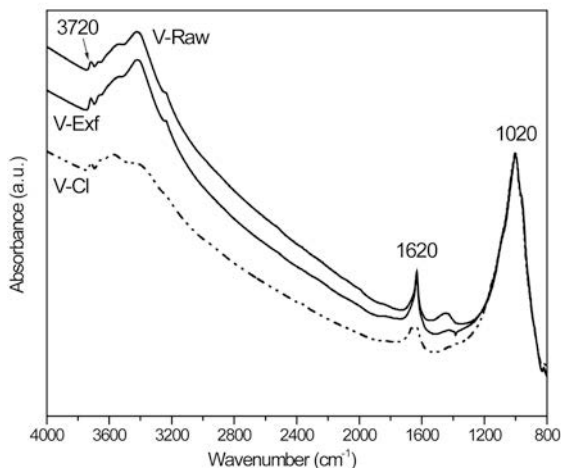|	Raw vermiculite	Thermally exfoliated vermiculite (600ºC)	Chemically exfoliated vermiculite
pH	9.46	6.95	6.80
BET surface area (m^2g^{-1})	14	80	200
Apparent specific volume ($cm^3\ g^{-1}$)	0.975	1.21	4.40

Figure 2. IR spectra of the raw (V-Raw), thermally exfoliated (V-Exf), and chlorinated (V-Cl) vermiculite.

3556 cm^{-1} (Farmer, 1974). The two lower-frequency components are characteristic of hydrogen-bonded surface hydroxyls (Babievskaya *et al.*, 2007). At lower frequency, the wide contribution between 3600 and 3000 cm^{-1} is mainly due to the stretching vibrations of H$_2$O (Bantignies *et al*, 1997). In the region of the ν(OH), a decrease in the amount of adsorbed H$_2$O was observed after chlorination. The bending band of OH from H$_2$O occurred at 1620 cm^{-1}, and a large absorption band at 1020 cm^{-1} (Figure 2), due to the stretching of the Si−O from the vermiculite layer, was observed (Farmer, 1974).

The IR spectra of NMDG-functionalized vermiculites were similar regardless of the synthesis process (conventional reflux or microwave activated reaction). The

ν(CO) stretching bands (five peaks) of the pure NMDG molecule (Figure 3a) were observed between 1010 and 1119 cm^{-1} (Socrates, 2001). A shoulder was observed at the same frequency close to 1080 cm^{-1} on the spectrum of the NMDG-grafted vermiculite. This broadening of the Si-O band (at 1020 cm^{-1}), still visible after washing, is expected to be the fingerprint of the presence of the NMDG molecule. As expected, the intra-molecular region, between 1400 and 1500 cm^{-1}, was the most sensitive to the interaction between the vermiculite and the NMDG (Figure 3a). Indeed, in this domain, the bands are assigned to the asymmetric out-of-phase CH$_3$ deformation band of NMDG. After the grafting reaction, both a shift and broadening of these bands were observed; the maxima being at 1465 and 1416 cm^{-1} (Colthup *et al.*, 1990). In the same domain, the spectrum of the extensively washed vermiculite (Figure 3b) displayed two characteristic peaks at 1458 and 1425 cm^{-1} (Figure 3b), attributed to the NMDG (Dambies *et al.*, 2004). Significant changes in the shape and position of the maximum of both bands were observed before and after washing, suggesting an enhanced interaction between the clay and the NMDG as expected from its attachment on the clay surface (Figure 3b). This assumption is supported by the results obtained by Dambies *et al.* (2004) showing similar δ(CH) bands at 1456 cm^{-1} and 1423 cm^{-1}, and ν(CO) bands at 1078 cm^{-1} and 1031 cm^{-1} for a NMDG-grafted resin (Dambies *et al.*, 2004).

B adsorption

Boron is known to adsorb onto clay minerals such as montmorillonite or kaolinite or clay mineral-based soils (Choi and Chen, 1979; Karahan *et al.*, 2006; Su and Suarez, 1997; Goldberg, 2005). Triple layer models were
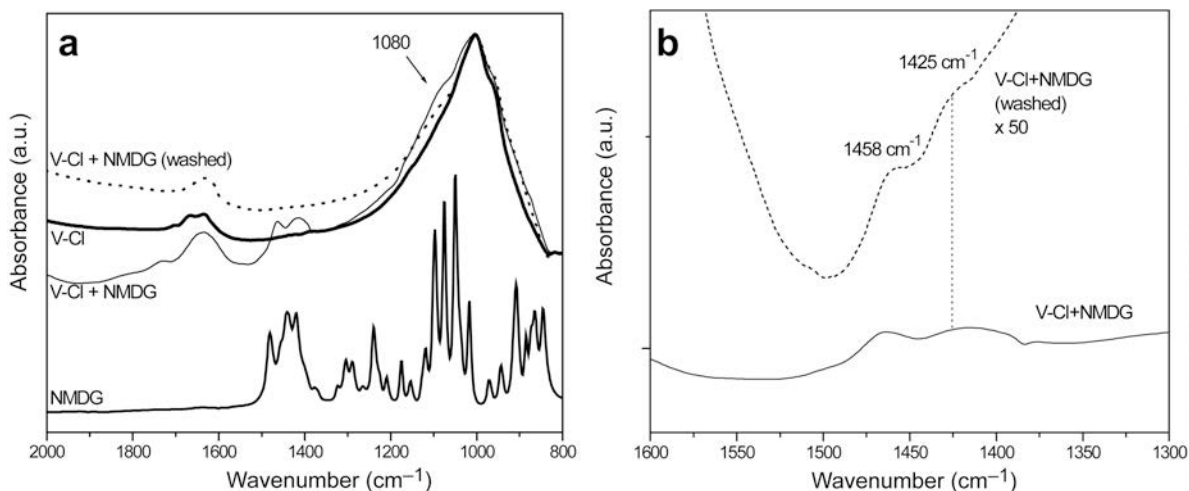

Figure 3. (a) IR spectra of the N-methyl-D-glucamine (NMDG), chlorinated vermiculite (V-Cl), NMDG-grafted vermiculite washed gently (V-Cl + NMDG), NMDG-grafted vermiculite washed extensively with UHQ water (V-Cl + NMDG (washed)). (b) Enlargement of the 1400−1500 cm^{-1} region of the IR spectra of NMDG-grafted vermiculite washed gently (V-Cl + NMDG), and NMDG-grafted vermiculite washed extensively with UHQ water (V-Cl + NMDG (washed)).

developed to describe an outer-sphere complexation mechanism, which was used to interpret B adsorption onto oxides and clays as a function of pH and/or ionic strength (Goldberg, 2005). The ionic strength adsorption dependence suggests an inner-sphere adsorption mechanism onto clays (Goldberg, 2005). The inner-sphere binding occurs on amphoteric layer edge moieties known as SOH groups (Karahan *et al.*, 2006). In clays such as vermiculite, the SOH surface sites are silanol or aluminol groups (Walker, 1961). Both trigonal and tetrahedral B complex species can be formed at the surfaces of minerals, as reported by several authors using IR spectroscopic investigations (Su and Suarez, 1995; Peak *et al.*, 2003).

Effect of pH on sorption

The adsorption of B as a function of pH displays a maximum (Figure 4) close to the pKa value of boric acid (pKa $H_3BO_3/B(OH)_4^- = 9.26$). This behavior is a general trend observed for B adsorption as a function of pH on most adsorbents (Goldberg, 2005; Goldberg and Glaubig, 1986; Karahan *et al.*, 2006). At very acidic pH (pH = 2), the B adsorption capacity approaches zero, due to the main competitive reaction of H^+ ions with SOH groups forming SOH_2^+ instead of a reaction with H_3BO_3. Increasing the pH to basic conditions (pH > pKa), the main B species become borate anions and the basic groups SO^- are formed on the surface of the material. The borate anions are repelled from the negatively charged surface so that the amount of B adsorbed decreases (Karahan *et al.*, 2006).

The clay mineral grafted with NMDG shows a different pH dependence of its B sorption. Indeed, particularly in acidic conditions, the amount of B adsorbed by functionalized vermiculite shows a plateau at 75% in the pH range 3 to 7 (Figure 4), explained by the stability of the hydroxyl groups of grafted molecules in this pH range compared to the SOH surface groups of pristine material. Moreover, the stability of the complexation of the borate ions by the polyol groups of the grafted NMDG is known to be enhanced by the protonation of the tertiary amine (Figure 1) occurring
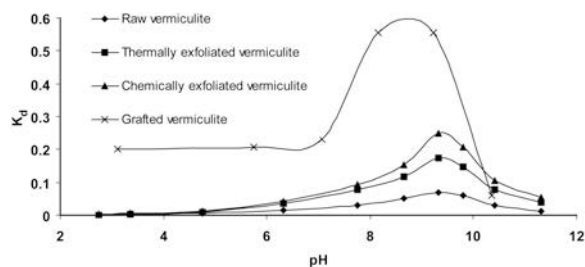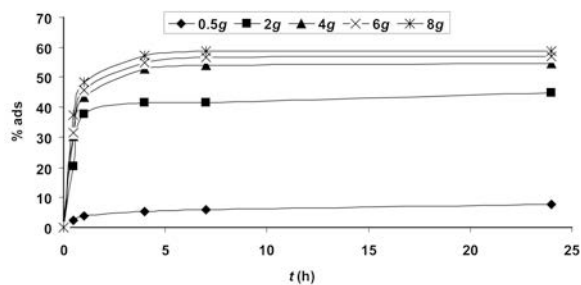

Figure 5. Kinetics of adsorption of B by the raw vermiculite at pH = 9 as a function of adsorbent weight (B concentration: 5 mg L^{-1}, V_{solution} = 200 mL)

in acidic medium (Simonnot *et al.*, 2000; Boncukcoğlu *et al.*, 2004).

Kinetics of adsorption

The kinetics of adsorption at pH $\approx$ pKa (Figure 5) shows that the plateau of adsorption is reached after 4 h, regardless of the amount of substrate. The optimal adsorbent *vs.* adsorbate ratio was obtained for 2 g of vermiculite in 200 mL of a 5 ppm B solution (adsorption percentage: $\approx$ 40%) which corresponds to a weight ratio of 5 g mg^{-1}. Though the amount of vermiculite was increased to 8 g, the adsorption of B was limited and a plateau was attained when 60% of B was adsorbed from the initial solution. The B adsorption limitation can be explained by the pH decrease during adsorption. Indeed, over the course of the adsorption process, the pH decreased as the amount of adsorbed B increased (Figure 6). This means that the surface complexation of boric acid by the SOH groups allows the release of H^+ ions into the solution. The observed pH decrease, concomitant with the adsorption of B, limits the adsorption uptake, as previously observed in the effect of pH on adsorption (Figure 4). This can explain why the maximum limit of adsorption is independent of the weight of vermiculite added in the solution as previously shown (Figure 5). Another proof of the limitation of adsorption
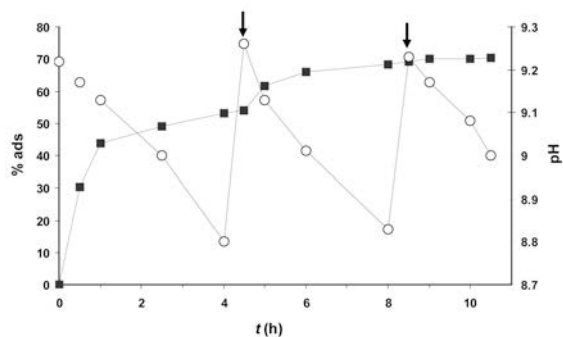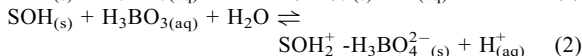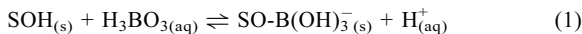

Figure 4. Partition coefficient K_d between adsorbed and aqueous B as a function of pH for the raw, thermally exfoliated (600ºC), chemically exfoliated, and NMDG-grafted vermiculites ($K_d = (m_{Bads}/m_{Ver})/(m_{Baq}/m_{Solution})$, B concentration: 5 mg L^{-1}, 3 g of substrate in 200 mL of solution).

Figure 6. B adsorption by the raw vermiculite ($\blacksquare$), and evolution of pH ($\bigcirc$) as a function of time (B concentration: 5 mg L^{-1}, 3 g of substrate, V_{solution} = 200 mL). The arrows indicate where the pH was adjusted to the pKa value (9.26) by addition of NaOH.

by pH is given in Figure 6: each time a plateau of adsorption was reached, adjusting the pH to the pKa value (9.26) yielded additional adsorption capacity.

From the pH evolution during adsorption, the main reactions of B complexation under fixed pH conditions (pH $\approx$ pKa) can be (1) and (2) for inner- and outer-sphere complexes, respectively:

$$SOH_{(s)} + H_3BO_{3(aq)} \rightleftharpoons SO\text{-}B(OH)^-_{3\,(s)} + H^+_{(aq)} \qquad (1)$$

$$SOH_{(s)} + H_3BO_{3(aq)} + H_2O \rightleftharpoons$$
$$SOH_2^+ \text{-}H_3BO_4^{2-}{}_{(s)} + H^+_{(aq)} \qquad (2)$$

However, as observed by Goldberg (2005), B adsorbs on many clay minerals (*e.g.* kaolinite and montmorillonite) through an inner-sphere complex mechanism.

For kaolinite and montmorillonite minerals, the values of the equilibrium constants for reactions (1) and (2) given by Goldberg (2005) are $\sim 10^{-2}$ and $10^{-4.6}$, respectively, which are smaller than those giving neutral molecular species ($\sim 10^6$ for the formation of SH_2BO_3). This suggests that the adsorption on vermiculite probably follows different complexation mechanisms than on lower-charged clays.

At low B concentration (*e.g.* 5 ppm), the limiting effect of pH on sorption is more pronounced as the boric acid-borate solution has insufficient buffering capacity. In contrast to Figure 5, the adsorption plateau is not observed at high initial B concentrations such as 100 g L^{-1} (Figure 7), as the $H_3BO_3/B(OH)_4^-$ couple buffering capacity overrides the limiting effect of pH.

Adsorption isotherms and desorption

The greater adsorption uptakes are obtained at lower B concentrations (<5 mg L^{-1}, Figure 8) because the interaction energy with adsorbent is greater, thus the efficiency of the vermiculite materials used is limited to low B concentration. The adsorbent becomes saturated at concentrations of >25 mg L^{-1}. The grafting of NMDG on vermiculite improves the adsorption properties slightly (Figure 8) compared to raw materials.

While thermal/chemical exfoliation dramatically increases the vermiculite surface area (Table 1), the uptake of B is only increased slightly (Figure 9). This is due to the location of the adsorption sites in clay
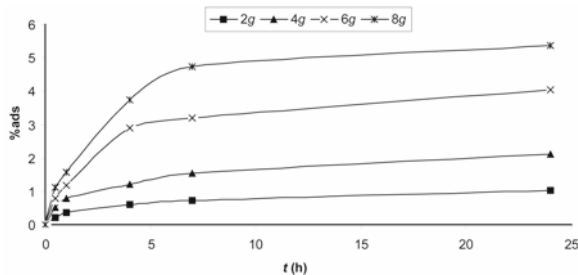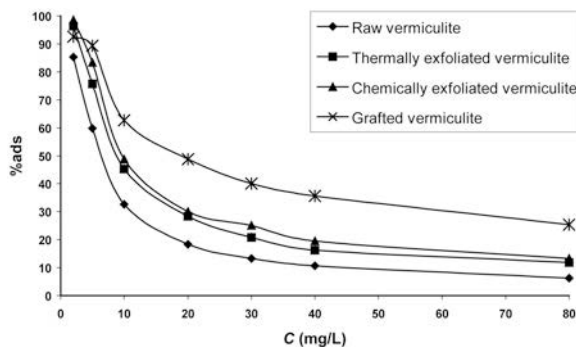

Figure 8. Effect of the concentration of B on the adsorption (pH = 9, 6 g of materials in 200 mL) of raw vermiculite, thermally exfoliated vermiculite (600ºC), chemically exfoliated vermiculite, and functionalized vermiculite.

materials which are at the edges of the layers (Keren and Talpaz, 1984) and not on the basal planes. Thus, the exfoliation only induces layer separation which increases the basal surface while the number of layer edges remains constant. The amount of B adsorbed (0.01 mmol g^{-1} for the raw vermiculite) is roughly of the same order of magnitude as that of SOH groups estimated by acido-basic titration in clay minerals such as montmorillonite, *i.e.* 0.080 mmol g^{-1} (Bayens and Bradbury, 1997). After NMDG grafting, the adsorption of B is almost four times that of pristine material, due to the several possible boric acid complexation sites of the grafted molecule (five $-OH$ groups in NMDG). The adsorption isotherms were fitted with the Freundlich equation ($C_s = kC_e^n$), giving good agreement (correlation coefficient R > 0.94). Among the isotherm types (S, L, and C) reported by Giles *et al.* (1960), the isotherms obtained are classified as L type (n < 1) suggesting chemisorption of B and thus a strong affinity between the adsorbate and adsorbent.

As B is chemisorbed, the desorption which requires the breaking of a coordination bond between boric acid
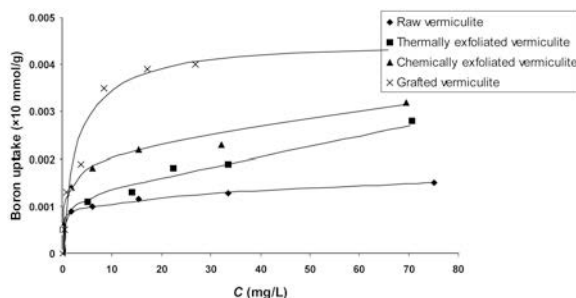

Figure 9. Isotherms of adsorption of B at room temperature for raw vermiculite, thermally exfoliated vermiculite (600ºC), chemically exfoliated vermiculite, and NMDG-grafted vermiculite (pH = 9, 6 g of substrate in 200 mL). The parameters of the Freundlich fit ($C_s = kC_e^n$; adsorption intensity: n; relative adsorption capacity: k, in mmol g^{-1}), are n = 0.179; 0.200; 0.278; and 0.393 and k = 0.011; 0.015; 0.019; and 0.029 mmol g^{-1}; for raw, thermally exfoliated, chemically exfoliated, and grafted vermiculite; respectively.

Figure 7. Kinetics of adsorption of B by the raw vermiculite at pH = 9 as a function of the weight (B concentration: 100 mg L^{-1}, $V_{solution}$ = 200 mL)

and SOH groups can only be carried out in very acidic conditions where the sorption rate is very small (Simonnot *et al.*, 2000; Inukai *et al.*, 2005; Kaftan *et al.*, 2005). Desorption efficiencies (in HCl-acidified UHQ water) from exfoliated vermiculite (or raw vermiculite) loaded with B (at pH = 9.26) are 10% at pH $\approx$ 9 and 15% at pH $\approx$ 5. This confirms that B forms stable complexes with its adsorption at pH $\approx$ 9 being quasi-irreversible. Using nitric acid (HNO_3), desorption of B from the grafted vermiculite depends clearly on the solution acidity. Indeed, desorption efficiencies observed on grafted vermiculite are 16%, 26%, and 95% at pH = 9.5, 5, and 0, respectively.

CONCLUSIONS

The kinetics of adsorption show that the plateau of adsorption is reached after 4 h, regardless of the amount of substrate. The optimal ratio of raw vermiculite *vs.* B is 5 g mg^{-1} in 200 mL of 5 ppm solution. The adsorption of B on vermiculite leads to a release of protons in solution which can hinder the sorption under low concentration conditions (*e.g.* 5 ppm). The exfoliation of vermiculite by heating or by reaction with hydrogen peroxide modifies the B-trapping properties of clays slightly. Indeed, only the SOH groups on the edges of the layers are active sites for the chemisorption of B. Thus, the adsorption cannot theoretically be improved by a simple exfoliation which only induces layer separation.

Synthesis of a new sorbent through the functionalization of exfoliated vermiculite with N-methyl-D-glucamine (NMDG) was described and shown to be an efficient route for the purposes of removal of B for an extended range of pH (3−9.5). The B-trapping uptake of the functionalized vermiculite (grafted or chemically exfoliated) is four times greater (0.04 mmoles g^{-1}) than that of raw vermiculite over a wide range of pH. All adsorption isotherms (fitted with the Freundlich equation) point to a chemisorption-complexation model for B uptake on the SOH groups of the layers edges and thus a strong affinity between the adsorbate and adsorbent. The desorption of B can only be carried out in acidic conditions (1 mol L^{-1} HNO_3). The regeneration of the grafted B sorbent will require further study.

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