

# Layered double hydroxides: matrices for storage and source of boron for plant growth

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**ABSTRACT:** The increase of the absorption efficiency of boron (B) by plants is essential for increasing crop productivity. The intercalation of B in MgAl layered double hydroxides (LDHs) is an alternative to evaluating how these materials can provide B to plants. In this work, a MgAl LDH intercalated with borate ions (Mg<sub>2</sub>Al-B-LDH) was synthesized by the constant pH coprecipitation method, and the material produced was evaluated as a matrix for storage and as a source of B for plants. The Mg<sub>2</sub>Al-B-LDH was characterized by XRD, ATR-FTIR, TGA-DTA, specific surface area, pore size and volume, and SEM. A bioassay was performed to verify the supply of B to plants from the two sources in the forms of H<sub>3</sub>BO<sub>3</sub> and of Mg<sub>2</sub>Al-B-LDH to sunflower plants grown in pots. The LDH basal spacing value of 12.0 Å is characteristic of intercalation of tetraborate octahydrate ions [B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub><sup>2-</sup>].8H<sub>2</sub>O between the layers. There was an increase in the dry matter (DM) and B content of the plants relative to those treatments where no B was added. The lack of statistical difference for plant yield between the two sources of B suggests a lack of stability of the Mg<sub>2</sub>Al-B-LDH structure under the acidic condition of the soil.

**KEYWORDS:** slow-release fertilizer, plant nutrition, LDH matrix, micronutrient, bioassay.

Boron is a micronutrient used in plant growth and development (Marschner, 2012). Some of the B used as fertilizer is highly soluble and easily leached into the soil profile. This is particularly important in very rainy areas. While most clayey soils retain for longer periods the B added, this behaviour is also observed in soils

with more organic carbon and greater ion exchange capacity (Rosolem & Biscaro, 2007). Thus, increase in the adsorption of this nutrient in the soil, for slow and gradual absorption by the plants, is essential for increasing agricultural productivity.

An alternative way to provide B in a sustainable manner includes storage in layered inorganic materials. The intercalation of borate ions in LDH is of interest as a new form of storage and sustained release of B for plants (Benício *et al.*, 2015; Guan *et al.*, 2016).

The LDHs, also called hydrotalcite-type compounds, can be described structurally as the stacking of positively charged layers with hydrated anions in the

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interlamellar domain. To ensure a better understanding of the structure of LDH, it is convenient to start with the brucite structure. In brucite, a  $\text{Mg}(\text{OH})_2$  mineral, the  $\text{Mg}^{2+}$  cations are in the centre of octahedra which have hydroxyl anions at their vertices. These octahedra share their edges, forming flat and neutral layers held together by H bonds. When, in this type of structure, the  $\text{Mg}^{2+}$  cations are replaced isomorphically by trivalent cations, the layer has a positive residual charge. To acquire electroneutrality, the system requires the presence of anions between the layers, which, alongside  $\text{H}_2\text{O}$  molecules, promote the stacking of double hydroxide layers with an orderly interlamellar domain (Cavani *et al.*, 1991; de Roy *et al.*, 1992; Evans & Slade, 2006; Forano *et al.*, 2006). The general formula  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{A^{m-}} \cdot n\text{H}_2\text{O}$  characterizes these materials, in which  $\text{M}^{2+}$  represents a bivalent cation,  $\text{M}^{3+}$  represents a trivalent cation, and  $\text{A}^{m-}$  represents an anion with  $m$ -charge.

In the agricultural field, LDHs have been used in the intercalation of pesticides, herbicides, plant-growth hormones, as well as the intercalation of nutrients such as nitrate, phosphates ( $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ), *etc.*, to obtain matrices that have a sustained release of the intercalated anions (Tronto *et al.*, 2004; Cardoso *et al.*, 2006; Ghormade *et al.*, 2011; da Silva *et al.*, 2014; Benício *et al.*, 2016; Everaert *et al.*, 2016, 2017; Halajnia *et al.*, 2016; Yu *et al.*, 2017).

Woo *et al.* (2011) studied the synthesis, characterization and kinetics of release of phosphate ions intercalated in CaFe-LDH. Those authors suggested the importance of this material as a slow-release phosphate fertilizer and as a soil acidity neutralizer, although they did not conduct any experiments with plants to verify the actual effectiveness of the LDH produced. Everaert *et al.* (2017) noted that, although Mg-Al-LDH has a reduced agronomic potential compared to monoammonium phosphate (MAP) after being incubated with wheat plants, this material has environmental benefits such as P reuse and residue use, thus being attractive for use as a slow-release fertilizer. To compare P-LDH with triple superphosphate in a Neubauer experiment, Benício *et al.* (2016) noted an increase in plant mass and height, as well as the total P content in the DM (the weight of the plant when completely dried). The increase of soil pH in P-LDH treatments was the main contributor to the reduction of soil P adsorption.

Previous work has shown that the treatment of LDH to impart slow release of nutrients is of chemical and mineralogical nature, and suggested its applicability as a source of slow-release nutrients without, however, presenting conclusive bioassay results on this

application (Berber *et al.*, 2014; Imran *et al.*, 2016; Moraes *et al.*, 2016; Ashekuzzaman *et al.*, 2017). The present work thus has the following objectives: (1) to synthesize and characterize a Mg and Al LDH intercalated with borate ions ( $\text{Mg}_2\text{Al-B-LDH}$ ); and (2) to evaluate, by bioassay, the potential of the material produced for use as a matrix for storage and sustained release of B for plants.

## MATERIALS

All reagents used in this work have a degree of analytical purity.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (purity > 98%) was purchased from Vetec;  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (purity > 98%) was purchased from Sigma-Aldrich;  $\text{H}_3\text{BO}_3$  (purity > 99.5%) was purchased from Êxodo Científica, and NaOH (purity = 99%) was purchased from Vetec. The water used in the synthesis reactions was distilled and/or deionized (Milli-Q® system), according to the needs of its use.

### LDH synthesis

The preparation of  $\text{Mg}_2\text{Al-B-LDH}$  was carried out by the constant pH coprecipitation method (De Roy *et al.*, 1992). In this method, 250 mL of a solution containing  $1.0 \text{ mol L}^{-1}$  of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $0.5 \text{ mol L}^{-1}$  of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added dropwise, under vigorous stirring, to 500 mL of a solution containing  $1.25 \text{ mol L}^{-1}$  of  $\text{H}_3\text{BO}_3$ . The synthesis was carried out under  $\text{N}_2$  atmosphere to eliminate the influence of atmospheric carbon dioxide. During the synthesis, a  $2.0 \text{ mol L}^{-1}$  NaOH solution was added to maintain the pH value at  $10.0 \pm 0.5$ . This pH value usually presents highly satisfactory results, obtaining MgAl-LDHs with good structural organization and phase purity (De Roy *et al.*, 1992). After the synthesis, the solid material was washed with  $\text{H}_2\text{O}$  and dried under vacuum in the presence of silica gel.

### Characterization of the sample

To characterize  $\text{Mg}_2\text{Al-B-LDH}$ , the following analysis techniques were used: X-ray powder diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), simultaneous thermogravimetric and differential thermal analysis (TGA-DTA), specific surface area (by the Brunauer Emmet Teller method (BET)), scanning electron microscopy (SEM), and ultraviolet-visible molecular absorption spectrophotometry (UV-Vis).

For the XRD analysis, a sample of  $\text{Mg}_2\text{Al-B-LDH}$  was macerated to obtain particles of uniform size.

A Shimadzu XRD-6000 instrument, with a copper cathode and a graphite monochromator, with a wavelength of 1.5406 Å, was used, at 30 kV and 30 mA. A scanning step of 0.01°, and 10 s per step were used and the scanning range was 4–7°2θ. The same instrument and conditions were used to characterize the soil mineralogy used in the bioassay. The ATR-FTIR spectrum was recorded on a Jasco FTIR 4100 spectrophotometer. The spectrum was obtained with 256 scans, over a wavelength range of 4000 to 400 cm<sup>-1</sup>. Simultaneous TGA-DTA analyses were performed using an SDT 2960 Simultaneous DTA-TGA thermal analyzer (TA Instruments), at a heating rate of 10°C min<sup>-1</sup>, with a dry synthetic air flow (80% N<sub>2</sub> and 20% O<sub>2</sub>) of 100 cm<sup>3</sup> min<sup>-1</sup>, in the temperature range of 30–1000°C. The amount of sample mass used was approximately 10 mg. The BET surface area of the Mg<sub>2</sub>Al-B-LDH was determined with N<sub>2</sub> adsorption using a ChemBET Pulsar TPR/TPD device (Quantachrome Instruments<sup>®</sup>).

The SEM imaging was carried out on a Carl Zeiss EVO 50 microscope. The sample, in powder form, was supported on the sample holder by dispersion on a conductive double-sided adhesive tape. Gold coating was applied to the samples prior to measurement using a Bal-Tec SCD 050 Sputter Coater spray. The concentration of borate in Mg<sub>2</sub>Al-B-LDH was determined with Ultraviolet-Visible Molecular Absorption Spectrophotometry (UV-Vis), λ = 420 nm, in a Thermo Scientific Evolution 300 device. The B available in the soil was determined according to López *et al.* (1993). A soil sample for the bioassay was collected at 0–20 cm depth in a Dystrophic Red Latosol (DRL), an Oxisol (USDA, 1999), with a clay-like texture, in the region of the city of Rio Paranaíba (MG). The sample was air-dried, levelled and sieved with a 4-mm mesh sieve. After drying, the sample was homogenized. A sub-sample of this soil was removed and sieved using a 2-mm mesh sieve, obtaining air-dried fine earth (ADFE). The chemical and physical characteristics of the sample are presented in Table 1 and the mineralogical characterization is presented in Fig. 1a.

### Kinetics of boron adsorption

To evaluate the stability of B adsorption in the soil, an assay was conducted to evaluate the effect of the contact time of increasing doses of this micronutrient on the soil. For this test, 0.00, 10.00 and 20.00 mg dm<sup>-3</sup> of total B were used in the soil, in the forms of H<sub>3</sub>BO<sub>3</sub> and Mg<sub>2</sub>Al-B-LDH. The sources, in their doses, were

TABLE 1. Chemical and physical characteristics of the soil sample.

Attribute	DRL
pH <sub>H<sub>2</sub>O</sub> *	5.04
P (mg dm <sup>-3</sup> )	0.90
K (mg dm <sup>-3</sup> )	22.00
Ca <sup>2+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.23
Mg <sup>2+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.07
Al <sup>3+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	0.50
H + Al (cmol <sub>c</sub> dm <sup>-3</sup> )	9.40
SB (cmol <sub>c</sub> dm <sup>-3</sup> )	0.36
t (cmol <sub>c</sub> dm <sup>-3</sup> )	0.86
T (cmol <sub>c</sub> dm <sup>-3</sup> )	9.76
V (%)	3.70
m (%)	58.10
OM (dag kg <sup>-1</sup> )	4.94
P-rem (mg L <sup>-1</sup> )	6.70
S (mg dm <sup>-3</sup> )	6.80
B (mg dm <sup>-3</sup> )	0.23
Cu (mg dm <sup>-3</sup> )	0.97
Mn (mg dm <sup>-3</sup> )	2.50
Fe (mg dm <sup>-3</sup> )	68.90
Zn (mg dm <sup>-3</sup> )	0.48
Coarse sand (kg kg <sup>-1</sup> )	0.064
Fine sand (kg kg <sup>-1</sup> )	0.058
Silt (kg kg <sup>-1</sup> )	0.109
Clay (kg kg <sup>-1</sup> )	0.769
Textural Classification	Very clayey

\*soil/water ratio 1:2.5; P, K, Cu, Mn, Fe and Zn – Mehlich-1 extractor; Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> – 1.0 mol/L KCl extractor; S-Extractor Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, 500 mg/L of P in HOAc 2 mol/L; B – “Hot water” extractor; H + Al – Calcium Acetate Extractor 0.5 mol/L (pH 7.0); SB = sum of bases; t = effective cation exchange capacity; T = cation exchange capacity at pH = 7; V = base saturation; m = saturation by Al; OM = organic matter; P-rem = remaining phosphorus; DRL = Dystrophic Red Latosol.

homogenized thoroughly with the soil. Plastic bags were filled with treatments (soil + B sources) and received distilled H<sub>2</sub>O in a volume equivalent to soil field capacity (FC). They were then closed to prevent water loss. Every 2 days, checks were made to verify that the plastic bags with the treatments maintained their initial weights; if they had not, they were topped up with distilled H<sub>2</sub>O. The contact times for each soil sample with the B sources were 1, 2, 3, 5, 10, 20 and 40 days. After this contact time, the treatment samples were duly dried, and the available B content in the soil was determined by the hot-water extraction method in

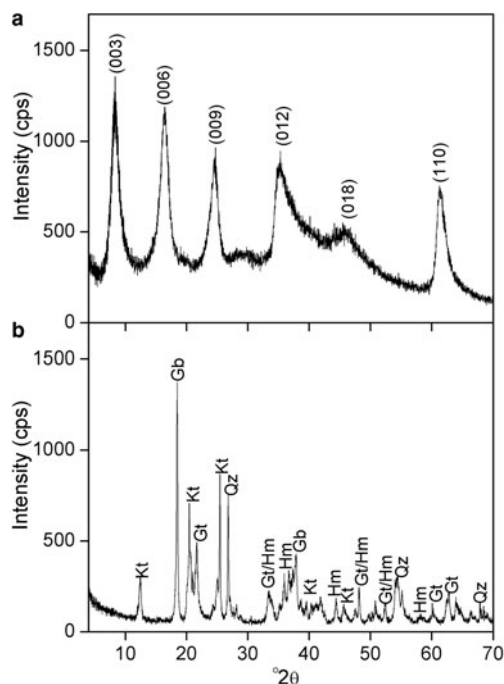


FIG. 1. XRD patterns for (a)  $Mg_2Al$ -B-LDH and (b) soil sample; Kt = kaolinite; Gb = gibbsite; Qz = quartz; Gt = goethite; Hm = hematite.

$5.0 \text{ mmol L}^{-1}$   $CaCl_2$  solution, heated in a microwave oven (Raij *et al.*, 2001). The available B content was analyzed by UV-Vis spectrophotometry according to the method of López *et al.* (1993).

### Bioassay

The bioassay to evaluate the use of  $Mg_2Al$ -B-LDH as a source of B for plants was carried out in a greenhouse from October to November 2016.

The treatments were defined by the combination of  $2 \times 6$  factorial design, using two sources of B ( $Mg_2Al$ -B-LDH and  $H_3BO_3$ ) and six doses of B (0.0, 0.5, 1.0, 2.0, 3.0 and  $5.0 \text{ mg dm}^{-3}$  of total B). The experimental design was performed in randomized blocks (RBD) with four replications. The experimental units consisted of a plastic pot with capacity for  $2.0 \text{ dm}^3$  of soil. Four sunflower plants (*Helianthus annuus* Helio 250 hybrid) were cultivated in each pot. This plant was chosen because of its high B requirement compared to other species.

The liming requirement (LR) calculations were performed with the aim of correcting the acidity and supplying Ca and Mg. These calculations were determined according to the Basal Saturation method,

aiming to raise the saturation to 50% (Alvarez *et al.*, 1999; Caires *et al.*, 2011). The limestone used was composed of a mixture of  $CaCO_3$  and  $MgCO_3$ , with a Ca/Mg ratio of 4:1 and Effective Calcium Carbonate Equivalent (ECCE) = 103%. After the complete homogenization of the limestone with the soil, the samples were packed in plastic bags and the soil moisture was raised to 80% of the field capacity. The incubation period was 25 days, and after 15 days of incubation, humidity was restored to 80% of the FC. After incubation, the soil sample was air-dried again and sieved through a 2-mm mesh sieve.

The sources and respective doses of B were homogenized in the total soil volume of each pot. On the same day N, P, K and S nutrients were applied as a nutrient solution. Fertilization with P and S was defined according to P-rem (Alvarez *et al.*, 2000; Côrrea *et al.*, 2005), and fertilization with N and K as recommended by Novais *et al.* (1991) and Marcatto *et al.* (2005). The nutrient doses applied to the soil were  $450 \text{ mg dm}^{-3}$  of P,  $140 \text{ mg dm}^{-3}$  of K,  $100 \text{ mg dm}^{-3}$  of S and  $100 \text{ mg dm}^{-3}$  of N. The sources used were  $KH_2PO_4$ , MAP,  $CaH_2(PO_4)_2$  and  $(NH_4)_2SO_4$ .

After 5 days of nutrient application, eight sunflower seeds were sown per pot. The seedlings were thinned seven days after emergence, to leave four plants per pot. The cover fertilizations were divided into two applications during the cultivation, in the form of the nutrient solution, as recommended by Novais *et al.* (1991) and Marcatto *et al.* (2005). For this phase, the nutrient doses and sources corresponded to  $200 \text{ mg m}^{-3}$  of N (urea),  $1.32 \text{ mg dm}^{-3}$  of Cu ( $CuSO_4 \cdot 5H_2O$ ),  $1.55 \text{ mg dm}^{-3}$  of Fe ( $FeSO_4 \cdot 7H_2O$ ),  $3.66 \text{ mg dm}^{-3}$  of Mn ( $MnSO_4 \cdot H_2O$ ),  $0.15 \text{ mg dm}^{-3}$  of Mo [ $(NH_4)_6Mo_7O_{24}$ ] and  $4.0 \text{ mg dm}^{-3}$  of Zn ( $ZnSO_4 \cdot 7H_2O$ ).

The plants were cultivated for 45 days. During this period, humidity was maintained at close to 80% of the FC. The irrigations, with distilled water, were made daily in the upper part of the pots; the  $H_2O$  volume and the frequency of irrigations varied according to the average temperature during the cultivation days. The plant material was dried in a forced circulation oven at  $65^\circ C$  for 96 h. After drying, it was weighed, passed through a Wiley mill using a 20-mesh sieve, and stored in paper bags.

The determination of B in plant tissue was performed according to the method described by Embrapa (2000). After determining the total B content in the aerial part of the plants (Bernardi *et al.*, 2010) from the four plants cultivated in each experimental unit, the B content in the aerial part was calculated. A sub-sample of 300 g of soil from each

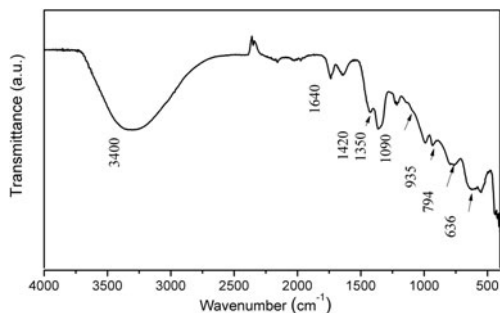


FIG. 2. FTIR/ATR spectrum of  $\text{Mg}_2\text{Al-B-LDH}$ .

experimental unit was taken before and after planting for the determination of available B and soil pH, according to the method described by Raij *et al.* (2001). The results were submitted to analysis of variance and regression.

## RESULTS AND DISCUSSION

### Characterizations

The XRD patterns for the soil and  $\text{Mg}_2\text{Al-B-LDH}$  are shown in Fig. 1. The soil is a typical Latosol consisting of hematite, gibbsite, goethite and kaolinite (Fig. 1a). The XRD pattern of  $\text{Mg}_2\text{Al-B-LDH}$  is presented in Fig. 1b. The pattern is characteristic of hydroxalcite-type compounds, with (003), (006) and (009) basal peaks at  $7.26$ ,  $15.6$  and  $23.6^\circ 2\theta$ , respectively. For this material, the basal spacing calculated by the Bragg equation was  $12.0 \text{ \AA}$ . This value coincides with the values reported in the literature for intercalation of tetraborate octahydrate ions  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-} \cdot 8\text{H}_2\text{O}$  between the layers of LDH (Ay *et al.*, 2011).

The FTIR/ATR spectrum of  $\text{Mg}_2\text{Al-B-LDH}$  is shown in Fig. 2. The presence of the broad band centred at  $3400 \text{ cm}^{-1}$  is attributed to the stretching of

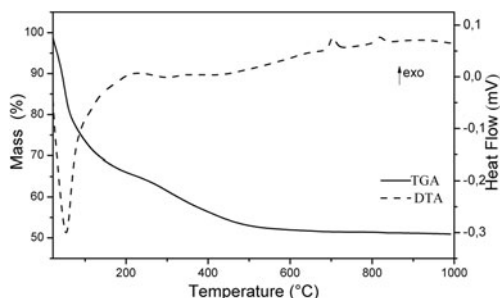


FIG. 3. TGA-DTA of  $\text{Mg}_2\text{Al-B-LDH}$ .

TABLE 2. BET specific surface area, pore volume and pore size for the  $\text{Mg}_2\text{Al-B-LDH}$ .

Sample	Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume ( $\text{cc g}^{-1}$ *)	Pore size ( $\text{\AA}$ )**
$\text{Mg}_2\text{Al-B-LDH}$	89.85	$3.65 \times 10^{-2}$	1.98

\*HK method; \*\*Non-local density functional theory (NDFT).

the O-H bonds of the hydroxyl groups and/or  $\text{H}_2\text{O}$  molecules. Bands in the region between  $1600$  and  $500 \text{ cm}^{-1}$  are attributed to the various modes of vibration related to the presence of borate anions. More specifically, the bands at  $1420$  and  $1350 \text{ cm}^{-1}$ ,  $1090 \text{ cm}^{-1}$ ,  $935 \text{ cm}^{-1}$ ,  $794 \text{ cm}^{-1}$ ,  $636 \text{ cm}^{-1}$  are attributed to the vibrational modes  $\nu_{\text{as}}(\text{B3-O})$ ,  $\nu_{\text{as}}(\text{B4-O})$ ,  $\nu_{\text{s}}(\text{B3-O})$ ,  $\nu_{\text{s}}(\text{B4-O})$ ,  $\nu_{\text{s}}(\text{B3-O})$ , respectively (Ay *et al.*, 2011).

The TGA-DTA curves of  $\text{Mg}_2\text{Al-B-LDH}$  are shown in Fig. 3. The TGA curve presents two events of weight loss. The first event occurs in the temperature range of  $22$ – $230^\circ\text{C}$  (mass loss of 35%). This thermal decomposition is accompanied by an endothermic process, which can be verified by the inflection of the DTA curve at the same temperature range. In this event, the loss of intercalated  $\text{H}_2\text{O}$  and that adsorbed on the surface of the crystallites occurs. The second event of thermal decomposition occurs in the temperature range  $230$ – $670^\circ\text{C}$  (mass loss of 13%) and is attributed to the dehydroxylation of inorganic layers and the thermal decomposition of the borate. The TGA curve shows only a very small mass loss above  $670^\circ\text{C}$ . At  $705^\circ\text{C}$  and  $820^\circ\text{C}$ , the DTA curve presented two exothermic events which are produced by recrystallization of Al

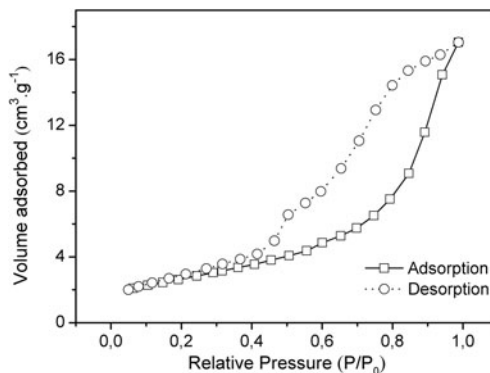


FIG. 4.  $\text{N}_2$  adsorption-desorption isotherm of  $\text{Mg}_2\text{Al-B-LDH}$ .

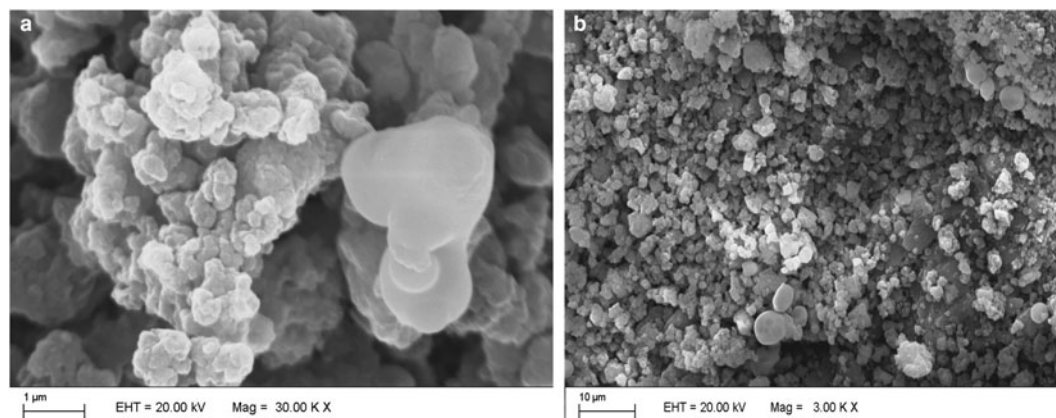


Fig. 5. SEM images of  $\text{Mg}_2\text{Al-B-LDH}$  at two different magnifications.

and Mg borates (Jun *et al.*, 1994; Zhihong *et al.*, 2004; Douy, 2005).

The values of the BET surface area, pore volume and pore size for  $\text{Mg}_2\text{Al-B-LDH}$  are shown in Table 2. The  $\text{N}_2$  adsorption-desorption isotherm of  $\text{Mg}_2\text{Al-B-LDH}$  is shown in Fig. 4. According to the IUPAC classification, this isotherm is of the IV type, typical of mesoporous materials with pore diameters of 2–50 nm.

The morphology of the  $\text{Mg}_2\text{Al-B-LDH}$  was analysed by means of SEM (Fig. 5). The material consists of spherical aggregates with diameters varying between 1 and 5  $\mu\text{m}$ .

The total B content in  $\text{Mg}_2\text{Al-B-LDH}$  as determined by UV-Vis was  $45.23 \text{ mg g}^{-1}$  of B per LDH. Previous work reported  $q_{\text{max}}$  values of 14.0, 37.90 and  $25.5 \text{ mg g}^{-1}$  of B for  $\text{MgAl-CO}_3^{2-}\text{-LDH}$ ,  $\text{MgAl-NO}_3\text{-LDH}$ , and calcined  $\text{MgAl-LDH}$ , respectively (Ferreira *et al.*, 2006; Kentjono *et al.*, 2010; Isaacs-Paez *et al.*, 2014). Therefore, the amount and total B determined for  $\text{Mg}_2\text{Al-B-LDH}$  indicates higher incorporation of B compared to the materials cited in the literature. The chemical formula determined for  $\text{Mg}_2\text{Al-B-LDH}$  was:  $\text{Mg}_2\text{Al}(\text{OH})_6[\text{B}_4\text{O}_5(\text{OH})_4^{2-}]_{0.38}(\text{NO}_3^-)_{0.16}(\text{CO}_3^{2-})_{0.08} \cdot 5.4 \text{ H}_2\text{O}$ .

#### Kinetics of boron release in soil

The results of soil B levels based on the contact time are shown in Fig. 6. The B values for  $\text{Mg}_2\text{Al-B-LDH}$  are lower than those found for  $\text{H}_3\text{BO}_3$ . This suggests that  $\text{Mg}_2\text{Al-B-LDH}$  exhibits greater stability than  $\text{H}_3\text{BO}_3$ . It was thus noted that B intercalated in  $\text{Mg}_2\text{Al-B-LDH}$  is released more slowly than that in  $\text{H}_3\text{BO}_3$ . It was observed that, in the early days,  $\text{Mg}_2\text{Al-B-LDH}$  stabilizes in the soil, following a sustained release profile.

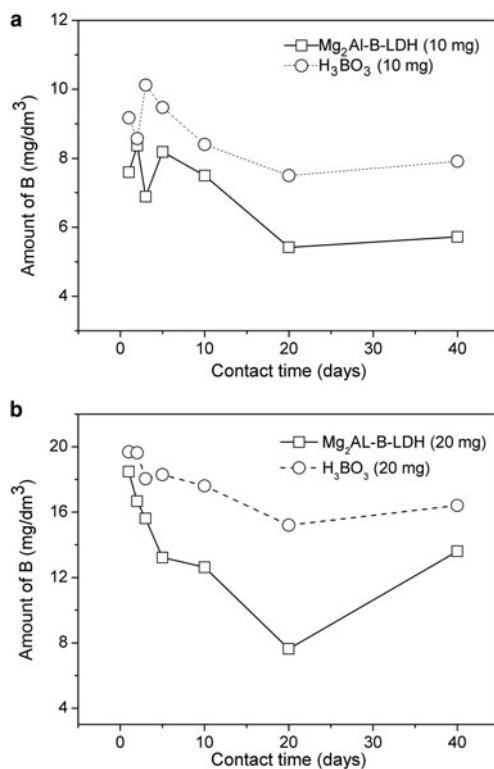


Fig. 6. B available in soil applied in two doses: (a) 10 mg and (b) 20 mg of B, as a function of the equilibrium time for the  $\text{Mg}_2\text{Al-B-LDH}$  and  $\text{H}_3\text{BO}_3$  sources.

#### Bioassay

The levels of B available in the soil indicated that, with increase of the applied doses of  $\text{H}_3\text{BO}_3$  and  $\text{Mg}_2\text{Al-B-LDH}$ , the levels of B increased (Fig. 7). This

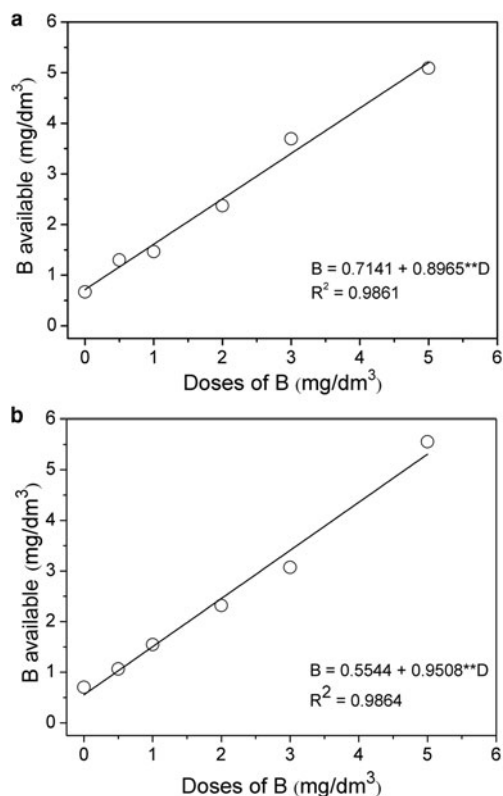


FIG. 7. Simple linear-regression between the available soil B content before the cultivation of sunflower plants as a function of the applied doses of B for: (a) Source of B- $\text{H}_3\text{BO}_3$ ; (b) Source of B- $\text{Mg}_2\text{Al-B-LDH}$ . \*\* = significant at 1%; B = boron available; D = doses of boron applied.

increase in dose, as demonstrated by the regression analysis, followed a significant linear relationship ( $p < 0.01$ ), as expected, as the sunflower plants had not been cultivated yet.

The data for DM production and B content in the aerial parts of the plants are listed in Tables 3 and 4,

respectively. For the plants treated with  $\text{Mg}_2\text{Al-B-LDH}$  and  $\text{H}_3\text{BO}_3$ , there was an increase in the DM and B content in the aerial part of the plants, relative to the treatments that did not receive B. The DM production was not statistically different when comparing the two sources of B used. During the bioassay, it was also noted visually that the sunflower plants showed a similar development for the two sources of B studied. Additionally, it was possible to note plants with symptoms of B deficiency in the treatments without B. The images of the cultivated sunflower plants are presented in Appendices 1 and 2.

The pH values of the soil before and after the cultivation of sunflower plants are presented in Table 5. Before cultivation, the average pH ranged between 5.73 and 6.15. This pH range, ideal for plant cultivation, chemically classifies the soil as having medium to weak acidity (Alvarez *et al.*, 1999; Caires, *et al.*, 2011). This acidity provided destabilization of the lamellar structure of  $\text{Mg}_2\text{Al-B-LDH}$  and the subsequent release of B. Recent work using a  $\text{MgAl-LDH}$  as a matrix for storage and release of phosphorus presented, in a bioassay carried out with maize (*Zea mays*), an increase in the soil pH value based on the dose increase of the P matrix applied (Benício *et al.*, 2016). The release of intercalated anions in LDH depends on the pH value of medium. At acid pH value, the LDH structures are unstable and the release of the intercalated anions occurs due to destruction of the layered material by acid attack, as LDHs are unstable in acid media. Another possibility for the release of intercalated anions is through anion-exchange with the anions in the medium (Tronto *et al.*, 2003, 2004; Benício *et al.*, 2016). In this case, as P is a nutrient required in large quantities for plant growth, the amount of LDH used was greater than the values used for  $\text{Mg}_2\text{Al-B-LDH}$ , which favoured the maintenance of the lamellar structure of LDH intercalated with P. Note that, in this work, a small

TABLE 3. Dry-matter production in the aerial part of the sunflower plants\* as a function of the doses and sources of B added to the soil.

Source	B doses ( $\text{mg dm}^{-3}$ )						Average
	0.0	0.5	1.0	2.0	3.0	5.0	
	$\text{g/pot}$						
$\text{H}_3\text{BO}_3$	24.55	32.56	32.73	32.08	34.53	33.19	31.61
$\text{Mg}_2\text{Al-B-LDH}$	23.59	29.58	33.59	31.76	32.93	33.00	30.74

\*There was no significant difference ( $p < 0.05$ ) between the sources of B.

TABLE 4. B content in the aerial part of the sunflower plants\* as a function of the doses added to the soil.

Source	B doses (mg dm <sup>-3</sup> )						Average
	0.0	0.5	1.0	2.0	3.0	5.0	
	mg/pot						
H <sub>3</sub> BO <sub>3</sub>	1.76	4.27	5.80	6.92	8.65	12.06	6.58
Mg <sub>2</sub> Al-B-HDL	1.92	3.93	6.68	6.95	8.40	10.76	6.44

\*There was no significant difference ( $p < 0.05$ ) between the sources of B.

amount of Mg<sub>2</sub>Al-B-LDH was applied to plant cultivation, as B is a micronutrient and thus required in small amounts only. This small amount was not able to change the pH of the soil (Table 5) to values that might favour the maintenance of the structure of Mg<sub>2</sub>Al-B-LDH, unlike the result presented by Benício *et al.* (2016). In addition, plant cultivation itself may acidify the soils according to post-cultivation pH results (Table 5). Acidification is often associated with the removal of exchangeable bases from the soil (Zinn *et al.*, 2005; Caputo *et al.*, 2016; Zhang *et al.*, 2016), which may favour a lower stability of Mg<sub>2</sub>Al-B-LDH and greater nutrient release compared to H<sub>3</sub>BO<sub>3</sub>.

The expected result for the utilization of Mg<sub>2</sub>Al-B-LDH as a source of B for plants is that there would be a sustainable release (constant concentration of B over a long period of time) of this micronutrient, more pronounced than that presented by normal H<sub>3</sub>BO<sub>3</sub>. However, this work showed that Mg<sub>2</sub>Al-B-LDH, applied in the soil with acid pH values, cannot be characterized as a sustainable release matrix of this micronutrient, as the DM yield and B content in the

aerial part of the plants were statistically the same for both sources.

## CONCLUSIONS

The average results of DM yield and B content in the aerial part of the plants between the two sources of B (Mg<sub>2</sub>Al-B-LDH and H<sub>3</sub>BO<sub>3</sub>) were similar, and not significantly different from each other. The results obtained for Mg<sub>2</sub>Al-B-LDH used as a matrix of sustainable release of B, are probably reflections of the small amount of LDH used in the soil, as B is a micronutrient required in small quantities by the plants. This small amount of Mg<sub>2</sub>Al-B-LDH was not sufficient to increase soil pH, which would allow the stability of the LDH structure and would promote the sustainable release of B by means of anionic exchange. The two sources used were solubilized similarly in the soil and released B equally to the plants. Thus, the Mg<sub>2</sub>Al-B-LDH used in agricultural soils with normal acid pH value can be compared to the commercially available, soluble H<sub>3</sub>BO<sub>3</sub>, not as a slow-release source of B as expected initially. Additional experiments

TABLE 5. Soil pH as a function of the added B doses before and after the first cultivation.

Source	B dose (mg dm <sup>-3</sup> )						Average
	0.0	0.5	1.0	2.0	3.0	5.0	
	mg/pot						
	Before the first cultivation						
H <sub>3</sub> BO <sub>3</sub>	5.73	5.95	5.95	5.98	5.87	6.01	5.91
Mg <sub>2</sub> Al-B-HDL	6.15	6.08	5.95	6.03	6.01	5.85	6.01
	After the first cultivation						
H <sub>3</sub> BO <sub>3</sub>	5.88	5.32	5.08	5.22	5.22	5.27	5.33
Mg <sub>2</sub> Al-B-HDL	5.26	5.11	5.30	5.11	4.89	5.14	5.13



using  $M_2Al$ -B-LDH as stores and sources of B for plant growth in soils at alkaline pH values are being performed by the authors.

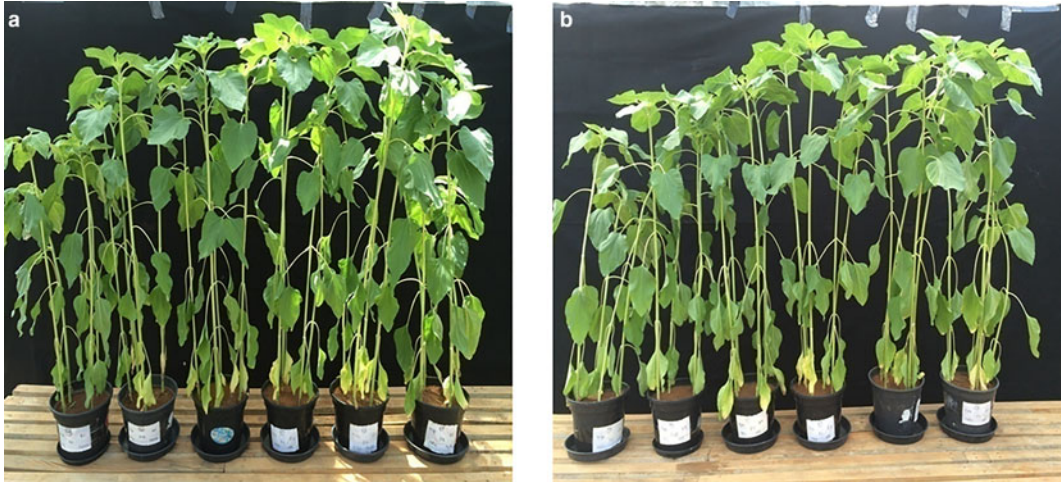
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APPENDIX 1. Response of sunflower plants to increasing doses of B from each of two sources in the soil. From left to right, the pots correspond to doses 0.0, 0.5, 1.0, 2.0, 3.0 and 5.0 mg dm<sup>-3</sup> of B, H<sub>3</sub>BO<sub>3</sub> (a) and Mg<sub>2</sub>Al-B-LDH (b).



APPENDIX 2. Sunflower plant with B deficiency symptom at the floral apex (a) and without that symptom (b).