GUSTAVO FRANCO DE CASTRO

LAYERED DOUBLE HYDROXIDES INTERCALATED WITH BORATE ANIONS: A NEW SOURCE OF BORON FOR PLANTS

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Solos e Nutrição de Plantas, para obtenção do título de *Doctor Scientiae*.

Orientador: Edson Marcio Mattiello

Coorientadores: Jairo Tronto
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ABSTRACT

CASTRO, Gustavo Franco de, D.Sc., Universidade Federal de Viçosa, September, 2020. **Layered double hydroxides intercalated with borate anions: a new source of boron for plants.** Advisor: Edson Marcio Mattiello. Co-advisors: Jairo Tronto, Lincoln Zotarelli and Leonardus Vergutz.

Boron (B) is generally present in soil as boric acid (H_3BO_3), a non-ionized molecule with weak retention in the soil and very leachable. The B leaching may occur especially when soluble sources are applied in sandy soils in high-rainfall environments and high rates of B may cause toxicity in plants. The use of a slow release source of B, such as layered double hydroxides (LDHs) intercalated with borate can potentially minimize the B leaching in soils, and reduce the plant toxicity. This thesis consists of four chapters with the following objectives: *(i)* synthesize and characterize the magnesium–aluminum LDH intercalated with borate (Mg_2Al-B-LDH) and evaluate the potential of this source as a matrix for storage and sustained release of B for plants in a clayey soil; *(ii)* evaluate the B availability and leaching from Mg_2Al-B-LDH and H_3BO_3 in a sandy soil, and the B bioavailability of these two sources in consecutive cultivations of sunflower; *(iii)* synthesize, characterize, and evaluate the agronomic performance of a new fertilizer produced from alginate microspheres containing Mg_2Al-B-LDH (LDH-B-ALG); and *(iv)* investigate the leaching and bioavailability of B in a sandy soil, in which H_3BO_3, Ulexite, alginate beads containing H_3BO_3 (BA-ALG), and LDH-B-ALG sources were used. The fertilizers synthesized were characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electronic microscopy (SEM). A soil incubation study and single greenhouse experiment with sunflower plants were performed in a clayey soil using H_3BO_3 and Mg_2Al-B-LDH sources. Mg_2Al-B-LDH and H_3BO_3 at two rates of B (10 and 20 mg dm^{-3}) were also incubated (1, 2, 3, 5, 10, 20, and 40 days) in a sandy soil with 81% of sand, and the B availability was evaluated. For the leaching study, 20 mg dm^{-3} of B from Mg_2Al-B-LDH and H_3BO_3 was incorporated into to a sandy soil, and incubated between 1 and 30 days before leaching. Sunflower plants were cultivated in two consecutive seasons (greenhouse experiment) using Mg_2Al-B-LDH and H_3BO_3 sources, and six rates of B (0, 0.5, 1, 2, 3, and 5 mg dm^{-3}). The new slow release fertilizer LDH-B-ALG was synthesized, characterized, and evaluated through the B release and leaching test in soil with 71% of sand. A greenhouse experiment with two responsive species (sunflower and cotton) was carried out using a factorial 2 x (4 + 1) with two soil pH (6.5 and 7.5), four sources of B

(LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite), and a treatment control, without the application of B. Additionally, the leaching study was replicated in a sandy soil with 92% of sand, in which 20 mg/dm^3 of B from LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite were incorporated in the soil and incubated between 1 and 40 days before leaching. A greenhouse experiment with leaching was established with the rate of total B of 2 mg dm^{-3}, four sources of B (LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite), and one treatment without application of B. In the greenhouse experiment with single cultivation of sunflower in the clayey soil, Mg_2Al-B-LDH and H_3BO_3 sources were solubilized similarly and released B equally to the plants. Thus, the profile of B release from Mg_2Al-B-LDH (powder form) used in agricultural soils with normal acid pH value can be compared to the commercially soluble source (H_3BO_3). In the leaching test carried out in a sandy soil (81% of sand), the slow release of B from Mg_2Al-B-LDH resulted in a significant reduction in B leached compared to H_3BO_3. After two consecutive cultivations of sunflower in a sandy soil, the boron rate of 5 mg dm^{-3} applied as H_3BO_3 resulted in plant toxicity, while Mg_2Al-B-LDH promoted a slow release of B to the plants. The chemical characterization by XRD, ATR-FTIR, and SEM analyses for LDH-B-ALG showed that Mg_2Al-B-LDH (powder) was successfully incorporated into to alginate polymer. The B release and leaching were much lower from LDH-B-ALG compared to conventional B sources. The new fertilizer LDH-B-ALG showed be a suitable source in high-rainfall areas, especially for sandy soils, supplying B in a more adjusted way and reducing leaching losses. In the B leaching test in soil with 92% of sand, throughout the incubation period, the percentage of B leached from LDH-B-ALG was significantly lower compared to all B sources. The lower leaching from LDH-B-ALG application in a greenhouse experiment with leaching, resulted in a higher shoot and total B uptake from total cultivation of sunflower and cotton. The LDH-B-ALG application under controlled conditions was the most promising B source to be used in soils prone to B leaching. This study lays a robust platform for future field studies on the validation of these slow-release materials in agricultural settings. Additionally, the alginate beads containing LDHs and fertilizers will serve as foundation for future studies focusing on macro and micronutrients, that it is important to sustainability of agriculture and food security.

Keywords: Slow-release. Micronutrient. Fertilizer. Polymer. Nanotechnology.

RESUMO

CASTRO, Gustavo Franco de, D.Sc., Universidade Federal de Viçosa, setembro de 2020. **Hidróxidos duplos lamelares intercalados com ânions borato: uma nova fonte de boro para plantas.** Orientador: Edson Marcio Mattiello. Coorientadores: Jairo Tronto, Lincoln Zotarelli e Leonardus Vergutz.

O boro (B) é geralmente presente no solo como ácido bórico (H_3BO_3), uma molécula não ionizada com fraca retenção e muito lixiviável. A lixiviação pode ocorrer especialmente quando fontes solúveis são aplicadas em solos arenosos em ambientes de alta pluviosidade, e altas taxas de B podem causar toxicidade nas plantas. O uso de fontes de liberação lenta de B, como os hidróxidos duplos lamelares (HDLs) intercalados com borato, pode potencialmente minimizar a lixiviação de B e reduzir a toxicidade às plantas. Esta tese é composta por quatro capítulos com os seguintes objetivos: *(i)* sintetizar e caracterizar o HDL de Mg-Al intercalado com borato (Mg_2Al-B-HDL) e avaliar o potencial desta fonte como matriz para armazenamento e liberação sustentada de B para plantas em solo argiloso; *(ii)* avaliar a disponibilidade e lixiviação de B de Mg_2Al-B-HDL e H_3BO_3 em solo arenoso, e a disponibilidade de B das fontes em cultivos sucessivos de girassol; *(iii)* sintetizar, caracterizar e avaliar agronomicamente um novo fertilizante produzido a partir de microesferas de alginato contendo Mg_2Al-B-HDL (HDL-B-ALG); e *(iv)* investigar a lixiviação e a disponibilidade de B em solo arenoso, no qual foram utilizadas as fontes H_3BO_3, Ulexita, esferas de alginato contendo H_3BO_3 (AB-ALG) e HDL-B-ALG. Os fertilizantes sintetizados foram caracterizados por difração de raios X (DRX), espectrofotometria de absorção molecular na região do infravermelho com transformada de fourier (FTIR) e microscopia eletrônica de varredura (MEV). Um estudo de incubação de solo e um experimento em casa de vegetação com plantas de girassol foram realizados em solo argiloso usando H_3BO_3 e Mg_2Al-B-HDL. Mg_2Al-B-HDL e H_3BO_3 em duas doses de B (10 e 20 mg dm^{-3}) foram incubados em solo arenoso com 81% de areia, e a disponibilidade de B foi avaliada. Para o estudo de lixiviação, 20 mg dm^{-3} de B de Mg_2Al-B-HDL e H_3BO_3 foram incorporados em um solo arenoso e incubados entre 1 e 30 dias antes da lixiviação. Plantas de girassol foram cultivadas em dois cultivos consecutivos utilizando as fontes Mg_2Al-B-HDL e H_3BO_3, e seis doses de B (0, 0,5, 1, 2, 3 e 5 mg dm^{-3}). O novo fertilizante de liberação lenta HDL-B-ALG foi sintetizado, caracterizado e avaliado por meio de teste de liberação de B e lixiviação em solo com 71% de areia. Um experimento em casa de vegetação com duas espécies responsivas (girassol e algodão) foi conduzido usando um fatorial 2 x (4 + 1) com dois pH do solo

(6,5 e 7,5), quatro fontes de B (HDL-B-ALG, AB-ALG, H_3BO_3 e Ulexita), e um tratamento controle, sem aplicação de B. Adicionalmente, o estudo de lixiviação foi replicado em solo arenoso com 92% de areia, no qual 20 mg dm^{-3} de B (HDL-B-ALG, AB-ALG, H_3BO_3 e Ulexita) foram incorporados ao solo e incubados entre 1 e 40 dias antes da lixiviação. Um experimento em casa de vegetação com lixiviação foi estabelecido com a taxa de B total de 2 mg dm^{-3}, quatro fontes de B (HDL-B-ALG, AB-ALG, H_3BO_3 e Ulexita) e um tratamento sem aplicação de B. No experimento em casa de vegetação com cultivo único de girassol em solo argiloso, as fontes Mg_2Al-B-HDL e H_3BO_3 foram solubilizadas de forma semelhante e o B foi liberado igualmente para as plantas. O perfil de liberação de B do Mg_2Al-B-HDL (em pó) usado em solos agrícolas com valor de pH ácido pode ser comparado com a fonte comercialmente solúvel (H_3BO_3). No ensaio de lixiviação realizado em solo arenoso (81% de areia), a liberação lenta de B do Mg_2Al-B-HDL resultou em uma redução significativa do B lixiviado em relação ao H_3BO_3. Após dois cultivos consecutivos de girassol em solo arenoso, a dose de 5 mg dm^{-3} de boro aplicada como H_3BO_3 resultou em toxicidade para as plantas, enquanto o Mg_2Al-B-HDL promoveu liberação lenta de B para as plantas. A caracterização química por XRD, FTIR e MEV para HDL-B-ALG mostrou que Mg_2Al-B-HDL (pó) foi incorporado com sucesso ao polímero alginato. A liberação e lixiviação de B foram inferiores para HDL-B-ALG em comparação com as fontes de B convencionais. O novo fertilizante HDL-B-ALG mostrou-se uma fonte adequada em áreas de alta pluviosidade, principalmente para solos arenosos, fornecendo B de forma mais adequada e reduzindo as perdas por lixiviação. No teste de lixiviação de B em solo com 92% de areia, durante todo o período de incubação, a porcentagem de B lixiviada de HDL-B-ALG foi significativamente menor em comparação com todas as fontes de B. A menor lixiviação com a aplicação de HDL-B-ALG no experimento em casa de vegetação com lixiviação resultou em maior conteúdo de B na parte aérea e total (raiz e parte aérea) no cultivo total de girassol e algodão somados. A aplicação de HDL-B-ALG sob condições controladas foi a fonte mais promissora para ser usada em solos sujeitos à lixiviação. Este estudo estabelece uma plataforma robusta para futuros estudos de campo para validação desses materiais de liberação lenta em ambientes agrícolas. Além disso, os grânulos de alginato contendo HDL e fertilizantes servirão de base para estudos futuros com foco em macro e micronutrientes, importantes para a sustentabilidade da agricultura e segurança alimentar.

Palavras-chave: Liberação lenta. Micronutriente. Fertilizante. Polímero. Nanotecnologia.

SUMMARY

GENERAL INTRODUCTION

Boron (B) is an important micronutrient used in plant growth and development. B applied in agriculture by means of conventional fertilizers, such as boric acid (H_3BO_3), can easily leach into the soil profile and lead to plant toxicity due to the high solubility of this compound. Areas with high rainfall are more susceptible to leaching, intensifying in sites with sandy soils with low organic matter (OM). B toxicity in seedling and plants can also occur when high doses of soluble sources are applied, particularly in clayey soils with lower B mobility and high availability of B (Degryse, 2017). Therefore, a higher retention of this micronutrient in the soil without leading to plant toxicity can be achieved either by increasing soil OM, or by using slow release sources. Both strategies are important to decrease leaching and improve the synchronization of B release into the soil solution with plant uptake.

Slow- and controlled-release fertilizers were made available since early 1950s and have been extensively studied due to the potential increase of fertilizer use efficiency compared to soluble sources (Morgan et al., 2009). These fertilizers can increase the time of nutrients residency in the top soil, reduce the rates and frequency of fertilizer application, and minimize potential negative effects with overdosage (Al-Zahrani, 2000; Ni et al., 2010). There has been great interest in using nanostructured materials, such as layered double hydroxides (LDHs), as an alternative to provide a gradual release of nutrients to the soil and plants (Benício et al., 2016; Everaert et al., 2016, 2017; Guan et al., 2016; Songkhum et al., 2018).

LDHs, also called hydrotalcite-type compounds, can be structurally described as a stack of positively charged layers with hydrated anions in the interlamellar spaces. These anions, along with water molecules, are responsible for neutralizing the positive charges in their layers. They are also called insertion compounds, given the characteristic of a host matrix for the storage of several species. LDHs have the general formula: $[M^{2+}_{(1-x)} M^{3+}_{x} (OH)_2] (A^{n-})_{x/n}.zH_2O$, in where, M^{2+} is a bivalent metal ion, such as Ca^{2+}, Mg^{2+}, Zn^{2+}; M^{3+} is a trivalent metal ion, such as Fe^{3+}, Al^{3+}, Mn^{3+}; and A^{n} is the interlamellar anion. The LDH structure is similar to the brucita mineral $[Mg(OH)_2]$, with the Mg^{2+} located in the center of octahedra and hydroxyls at the vertices, forming flat and neutral layers held together by hydrogen bonds. When, in this type of structure, bivalent cations are isomorphically replaced by trivalent cations, the lamellae has a positive residual charge. To acquire electroneutrality, the systems requires the presence of anions between the layers, which alongside with H_2O molecules, promote the stacking of the double hydroxide layers with an orderly interlamellar domain (Cavani et al., 1991; De roy et al., 1992). Through the variation of M^{2+} and M^{3+} cations, the proportion between them, and the replacement of the interlamellar anion, a wide range of LDHs can be synthesized. Several cations can make up the lamellar structure, such as Mg^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, and most transition metals of the fourth period in a oxidation state of 2^+ and/or 3^+. It is also possible to synthesize LDH containing more than one divalent and/or trivalent cation, which increase the options of synthesis, composition, chemical properties, and functionality of the inorganic material.

In agriculture, LDHs are used for inclusion of pesticides, herbicides, plant growth regulators, and nutrients such as borate, nitrate, and phosphate, among others, in order to obtain sustained release fertilizers (Benício et al., 2016; Everaert et al., 2016, 2017; Yu et al., 2017). It is observed in general that in several studies conducted, the treatment and characterization of LDHs are of chemical and mineralogical nature, with suggestions as to its use as a source of slow release (Berber et al., 2014; da Silva et al., 2014; Imran et al., 2016; Ashekuzzaman e Jiang, 2017). Studies on the agronomic use of LDHs are still needed for a better understanding of soil nutrient dynamics and their absorption by plants. In addition, there are only a few agronomic studies with LDHs, and most of them were conducted using a single cultivation process (Benício et al., 2016; López-Rayo et al., 2017; Bernardo et al., 2018; Songkhum et al., 2018).

Specifically for the relationship between pH and LDH, the use of LDHs can affect the soil pH when applied in large rates in the soil. Everaert et al. (2016) and Benício et al. (2016), reported an increase in soil pH value with increasing rates of P supply through LDH. The increase in the soil pH can be due to the release of hydroxyls groups through the LDHs fertilizers (Woo et al., 2011). It is noteworthy that the total P applied by LDH, to supply this macronutrient to the plants, is much higher than that applied from LDH for micronutrient supply, which allows significant changes in the soil pH value. The increase in soil pH from application of large amounts of LDH may increase the LDH stability in the soil, allowing a more steady release of the intercalated anions, and even of the cations that make up the lamellar structure (Benício et al., 2016; Imran et al., 2016; López-Rayo et al., 2017). However, the increase in soil pH due to application of high amounts of LDH may decrease the availability of cationic micronutrients in the soil, such as Cu, Fe, Mn, and Zn (Udeigwe et al., 2016; Luna et al., 2017), which constitutes an advantage in using these lamellae materials as a source of micronutrients compared to macronutrients.

It is noteworthy that in all the consulted studies, the nutrient application by LDHs was made in powder form. The hydroxyl groups released from LDHs have an alkaline buffering, which retains the layered structure and decreases the nutrients release rate (Woo et al., 2011; Benício et al., 2016). However, the use of LDHs in powder form can increase the exposure of the fertilizer to the soil acidity and decrease the buffering capacity. In fact, the particle size is closely linked to the contact surface between the fertilizer and the soil. Thus, using powder material there will be a direct influence on the dissolution rate, the atmospheric moisture absorption, and the nutrient use efficiency from fertilizers. Moreover, the use of powder fertilizers impairs accurate applications under field conditions.

Alginate polymer has been reported as a matrice to synthesize microspheres containing nutrients due to its low cost, easiness of manipulation and chemical stability (Ni et al., 2010; Wang et al., 2011; Shan et al., 2016). The alginate polymer can be prepared from a group of anionic polysaccharides extracted from brown algae or produce from by bacteria (Xu et al., 2003). This natural polymer is composed of residues of β-D-mannuronic acid and α-L-guluronic acid in varying proportions from 1-4 linkages (Wang et al., 2011). The concept of microspheres synthesis is to obtain new fertilizers with slower release rate of nutrients than conventional soluble sources. The synthesis of alginate microspheres containing LDHs, as an organic–inorganic hybrid nanomaterial, is still incipient and has not been reported in the literature. In theory, these microspheres can provide physical protection for the LDH, decreasing the contact surface of LDH and soil, which can modify the reactivity, dissolution, and nutrient release from LDHs.

Particularly for B, studies with LDHs as a new B slow-release source are still incipient and have focused on obtaining more efficient synthesis and intercalation of the borate anions, and the characterization of LDHs. Further research is needed focusing in B release and leaching from LDHs, the residual effect of LDHs in the soil, and most importantly the development of granular LDHs forms to ease application. Thus, the aims of this study were to: *(i)* synthesize and characterize the magnesium–aluminum LDH intercalated with borate (Mg_2Al-B-LDH) and evaluate the potential of this source as a matrix for storage and sustained release of B for plants in a clayey soil; *(ii)* evaluate the B availability and leaching from Mg_2Al-B-LDH and H_3BO_3 in a sandy soil, and the B bioavailability of these two sources in consecutive cultivations of sunflower; *(iii)* synthesize, characterize, and evaluate the agronomic performance of a new fertilizer produced from alginate microspheres containing Mg_2Al-B-LDH (LDH-B-ALG); and *(iv)* investigate the leaching and bioavailability of B in a sandy soil, in which H_3BO_3, Ulexite, alginate beads containing H_3BO_3 (BA-ALG), and LDH-B-ALG sources were used.

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CHAPTER 1

LAYERED DOUBLE HYDROXIDES: MATRICES FOR STORAGE AND SOURCE OF BORON FOR PLANT GROWTH

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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_2Al-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_2Al-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_3BO_3 and of Mg_2Al-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 $[B_4O_5(OH)_4{}^{2-}]\cdot 8H_2O$ 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_2Al-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 & Bíscaro, 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 $Mg(OH)_2$ mineral, the 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 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 H_2O 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 $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]A^{m-}_{x/m}\cdot nH_2O$ characterizes these materials, in which M^{2+} represents a bivalent cation, M^{3+} represents a trivalent cation, and 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 (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$), *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 (Mg_2Al-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. $Mg(NO_3)_2\cdot 6H_2O$ (purity > 98%) was purchased from Vetec; $Al(NO_3)_3\cdot 9H_2O$ (purity > 98%) was purchased from Sigma-Aldrich; H_3BO_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 Mg_2Al-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 mol L^{-1} of $Mg(NO_3)_2\cdot 6H_2O$ and 0.5 mol L^{-1} of $Al(NO_3)_3\cdot 9H_2O$ was added dropwise, under vigorous stirring, to 500 mL of a solution containing 1.25 mol L^{-1} of H_3BO_3. The synthesis was carried out under N_2 atmosphere to eliminate the influence of atmospheric carbon dioxide. During the synthesis, a 2.0 mol L^{-1} NaOH solution was added to maintain the pH value at 10.0 ± 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 H_2O and dried under vacuum in the presence of silica gel.

Characterization of the sample

To characterize Mg_2Al-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 Mg_2Al-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^{-1}. 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^{-1}, with a dry synthetic air flow (80% N_2 and 20% O_2) of 100 $\text{cm}^3\ \text{min}^{-1}$, 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_2Al-B-LDH was determined with N_2 adsorption using a ChemBET Pulsar TPR/TPD device (Quantachrome Instruments©).

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_2Al-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.

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

Attribute	DRL
$\text{pH}_{\text{H}_2\text{O}}$*	5.04
P (mg dm^{-3})	0.90
K (mg dm^{-3})	22.00
Ca^{2+} ($\text{cmol}_c\text{dm}^{-3}$)	0.23
Mg^{2+} ($\text{cmol}_c\text{dm}^{-3}$)	0.07
Al^{3+} ($\text{cmol}_c\text{dm}^{-3}$)	0.50
H + Al ($\text{cmol}_c\text{dm}^{-3}$)	9.40
SB ($\text{cmol}_c\text{dm}^{-3}$)	0.36
t ($\text{cmol}_c\text{dm}^{-3}$)	0.86
T ($\text{cmol}_c\text{dm}^{-3}$)	9.76
V (%)	3.70
m (%)	58.10
OM (dag kg^{-1})	4.94
P-rem (mg L^{-1})	6.70
S (mg dm^{-3})	6.80
B (mg dm^{-3})	0.23
Cu (mg dm^{-3})	0.97
Mn (mg dm^{-3})	2.50
Fe (mg dm^{-3})	68.90
Zn (mg dm^{-3})	0.48
Coarse sand (kg kg^{-1})	0.064
Fine sand (kg kg^{-1})	0.058
Silt (kg kg^{-1})	0.109
Clay (kg kg^{-1})	0.769
Textural Classification	Very clayey

*soil/water ratio 1:2.5; P, K, Cu, Mn, Fe and Zn – Mehlich-1 extractor; Ca^{2+}, Mg^{2+} and Al^{3+} – 1.0 mol/L KCl extractor; S-Extractor Ca $(H_2PO_4)_2$, 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.

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^{-3} of total B were used in the soil, in the forms of H_3BO_3 and Mg_2Al-B-LDH. The sources, in their doses, were homogenized thoroughly with the soil. Plastic bags were filled with treatments (soil + B sources) and received distilled H_2O 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_2O. 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

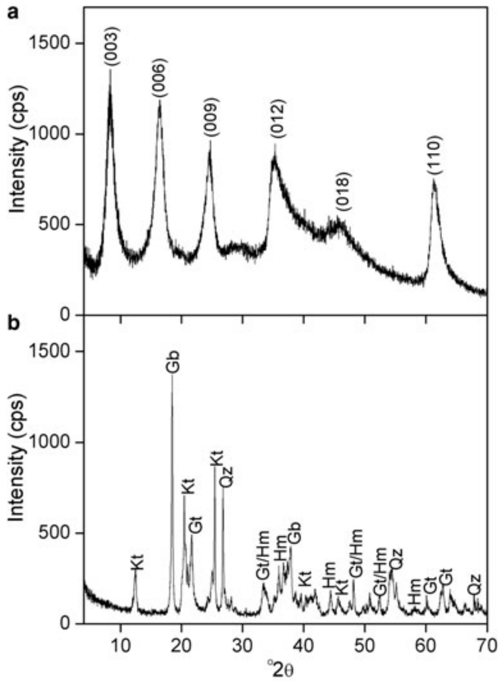

FIG. 1. XRD patterns for (a) Mg_2Al-B-LDH and (b) soil sample; Kt = kaolinite; Gb = gibbsite; Qz = quartz; Gt = goethite; Hm = hematite.

5.0 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 × 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 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 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 Marcato *et al.* (2005). The nutrient doses applied to the soil were 450 mg dm^{-3} of P, 140 mg dm^{-3} of K, 100 mg dm^{-3} of S and 100 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 Marcato *et al.* (2005). For this phase, the nutrient doses and sources corresponded to 200 mg m^{-3} of N (urea), 1.32 mg dm^{-3} of Cu ($CuSO_4{\cdot}5H_2O$), 1.55 mg dm^{-3} of Fe ($FeSO_4{\cdot}7H_2O$), 3.66 mg dm^{-3} of Mn ($MnSO_4{\cdot}H_2O$), 0.15 mg dm^{-3} of Mo [$(NH_4)_6Mo_7O_{24}$] and 4.0 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°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

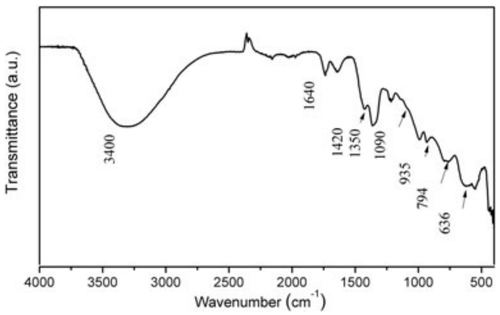

FIG. 2. FTIR/ATR spectrum of Mg_2Al-B-LDH.

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 Mg_2Al-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 Mg_2Al-B-LDH is presented in Fig. 1b. The pattern is characteristic of hydrotalcite-type compounds, with (003), (006) and (009) basal peaks at 7.26, 15.6 and 23.6 °2θ, respectively. For this material, the basal spacing calculated by the Bragg equation was 12.0 Å. This value coincides with the values reported in the literature for intercalation of tetraborate octahydrate ions $[B_4O_5(OH)_4{}^{2-}]\cdot 8H_2O$ between the layers of LDH (Ay *et al.,* 2011).

The FTIR/ATR spectrum of Mg_2Al-B-LDH is shown in Fig. 2. The presence of the broad band centred at 3400 cm^{-1} is attributed to the stretching of the O-H bonds of the hydroxyl groups and/or H_2O molecules. Bands in the region between 1600 and 500 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 cm^{-1}, 1090 cm^{-1}, 935 cm^{-1}, 794 cm^{-1}, 636 cm^{-1} are attributed to the vibrational modes υ_{as}(B3-O), υ_{as}(B4-O), υ_s(B3-O), υ_s(B4-O), υ_s(B3-O), respectively (Ay *et al.,* 2011).

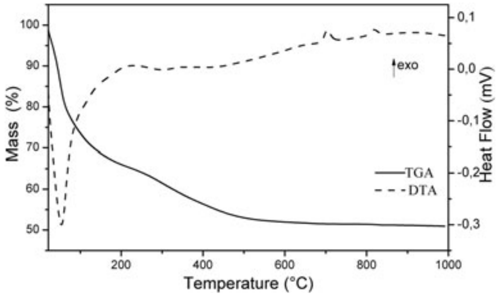

FIG. 3. TGA-DTA of Mg_2Al-B-LDH.

TABLE 2. BET specific surface area, pore volume and pore size for the Mg_2Al-B-LDH.

Sample	Surface area ($m^2\ g^{-1}$)	Pore volume ($cc\ g^{-1*}$)	Pore size (Å)**
Mg_2Al-B-HDL	89.85	3.65×10^{-2}	1.98

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

The TGA-DTA curves of Mg_2Al-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°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 H_2O and that adsorbed on the surface of the crystallites occurs. The second event of thermal decomposition occurs in the temperature range 230–670°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°C. At 705°C and 820°C, the DTA curve presented two exothermic events which are produced by recrystallization of Al

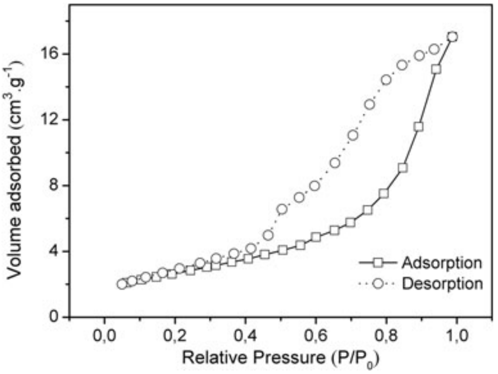

FIG. 4. N_2 adsorption-desorption isotherm of Mg_2Al-B-LDH.

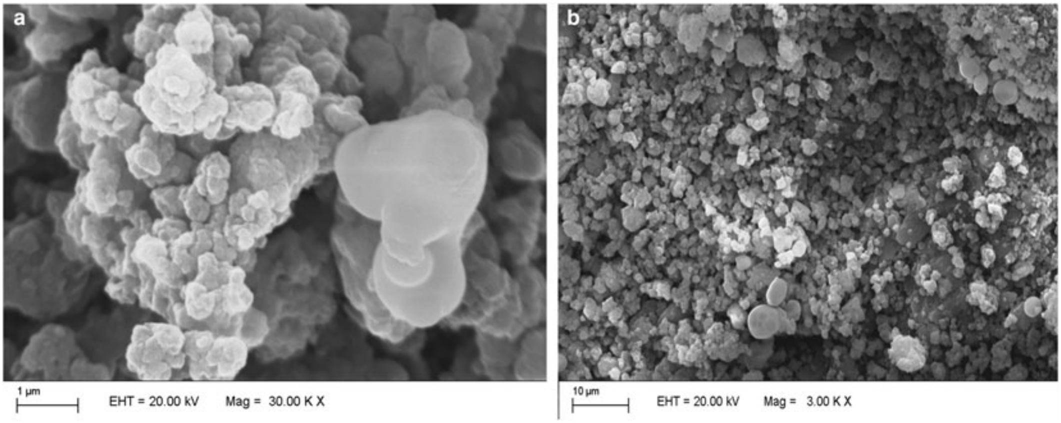

FIG. 5. SEM images of Mg_2Al-B-LDH at two different magnifications.

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 Mg_2Al-B-LDH are shown in Table 2. The N_2 adsorption-desorption isotherm of Mg_2Al-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 Mg_2Al-B-LDH was analysed by means of SEM (Fig. 5). The material consists of spherical aggregates with diameters varying between 1 and 5 µm.

The total B content in Mg_2Al-B-LDH as determined by UV-Vis was 45.23 mg g^{-1} of B per LDH. Previous work reported q_{max} values of 14.0, 37.90 and 25.5 mg g^{-1} of B for MgAl-CO_3^{2-}-LDH, MgAl-NO_3^-LDH, and calcined MgAl-LDH, respectively (Ferreira *et al.,* 2006; Kentjono *et al.,* 2010; Isaacs-Paez *et al.,* 2014). Therefore, the amount and total B determined for Mg_2Al-B-LDH indicates higher incorporation of B compared to the materials cited in the literature. The chemical formula determined for Mg_2Al-B-LDH was: $Mg_2Al(OH)_6[B_4O_5(OH)_4^{2-}]_{0.38}(NO_3^-)_{0.16}(CO_3^{2-})_{0.08}\cdot 5.4\ H_2O$.

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 Mg_2Al-B-LDH are lower than those found for H_3BO_3. This suggests that Mg_2Al-B-LDH exhibits greater stability than H_3BO_3. It was thus noted that B intercalated in Mg_2Al-B-LDH is released more slowly than that in H_3BO_3. It was observed that, in the early days, Mg_2Al-B-LDH stabilizes in the soil, following a sustained release profile.

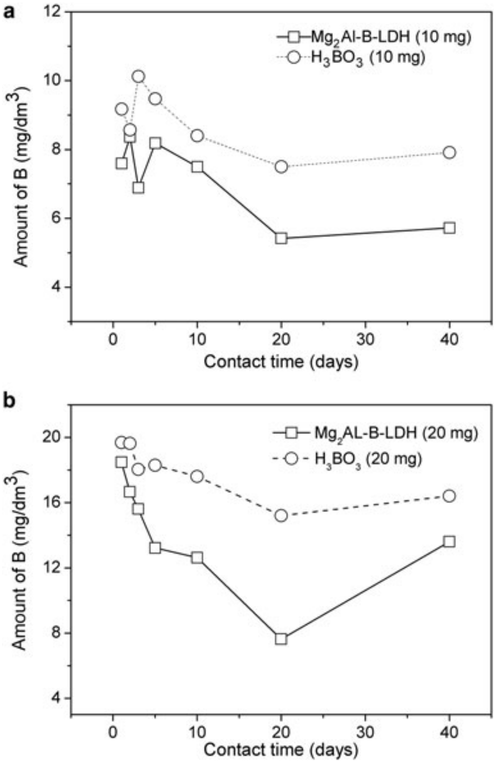

FIG. 6. B available in soil applied in two doses: (a) 10 mg and (b) 20 mg of B, as a function of the equilibrium time for the Mg_2Al-B-LDH and H_3BO_3 sources.

Bioassay

The levels of B available in the soil indicated that, with increase of the applied doses of H_3BO_3 and Mg_2Al-B-LDH, the levels of B increased (Fig. 7). This

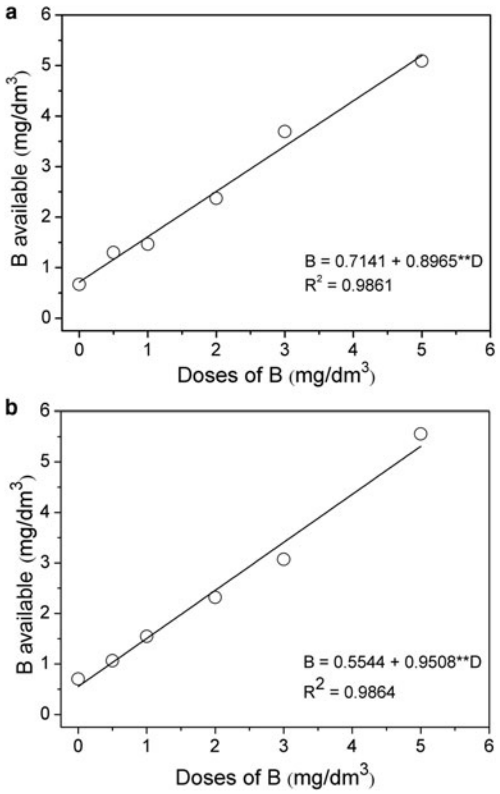

FIG. 7. Simple linear-regression between the available soil B content before the cultivation of sunflower plants as a function of the applied doses of B for: (a) Source of B-H_3BO_3; (b) Source of B-Mg_2Al-B-LDH. ** = significant at 1%; B = boron available; D = doses of boron applied.

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 Mg_2Al-B-LDH and H_3BO_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 Mg_2Al-B-LDH and the subsequent release of B. Recent work using a 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 Mg_2Al-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 (mg dm^{-3})						
	0.0	0.5	1.0	2.0	3.0	5.0	Average
	g/pot						
H_3BO_3	24.55	32.56	32.73	32.08	34.53	33.19	31.61
Mg_2Al-B-HDL	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^{-3})						
	0.0	0.5	1.0	2.0	3.0	5.0	Average
	mg/pot						
H_3BO_3	1.76	4.27	5.80	6.92	8.65	12.06	6.58
Mg_2Al-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_2Al-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_2Al-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_2Al-B-LDH and greater nutrient release compared to H_3BO_3.

The expected result for the utilization of Mg_2Al-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_3BO_3. However, this work showed that Mg_2Al-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_2Al-B-LDH and H_3BO_3) were similar, and not significantly different from each other. The results obtained for Mg_2Al-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_2Al-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_2Al-B-LDH used in agricultural soils with normal acid pH value can be compared to the commercially available, soluble H_3BO_3, 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^{-3})						
	0.0	0.5	1.0	2.0	3.0	5.0	Average
	mg/pot						
	Before the first cultivation						
H_3BO_3	5.73	5.95	5.95	5.98	5.87	6.01	5.91
Mg_2Al-B-HDL	6.15	6.08	5.95	6.03	6.01	5.85	6.01
	After the first cultivation						
H_3BO_3	5.88	5.32	5.08	5.22	5.22	5.27	5.33
Mg_2Al-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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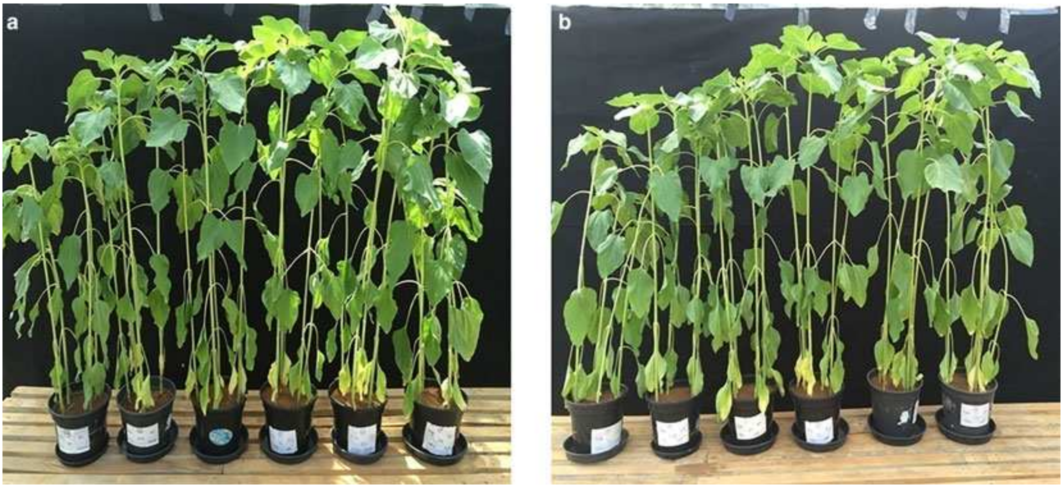

Appendix 1. Response of sunflower plants to increasing doses of B from each of two sources in the soil. From left to right, the pots correspond to doses 0.0, 0.5, 1.0, 2.0, 3.0 and 5.0 mg dm^{-3} of B, H_3BO_3 (a) and Mg_2A1-B-LDH (b).

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

CHAPTER 2

LAYERED DOUBLE HYDROXIDES INTERCALATED WITH BORATE: EFFECT OF FERTILIZATION ON BORON LEACHING AND SUCCESSIVE SUNFLOWER CULTIVATIONS

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Layered double hydroxides intercalated with borate: effect of fertilization on boron leaching and successive sunflower cultivations†

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Boron (B) can easily leach into the soil when added in the form of a soluble fertilizer such as borax or boric acid (H_3BO_3); however, large quantities of B can cause toxicity in plants. The use of a slow release source of B such as layered double hydroxides intercalated with borate may minimize leaching/toxicity of B. The objectives of this study are to evaluate the availability and leaching of B from magnesium–aluminium layered double hydroxides intercalated with borate anions (Mg_2Al-B-LDH) and H_3BO_3 in a sandy soil, and the B bioavailability of these two sources in consecutive cultivations of sunflower. Mg_2Al-B-LDH and H_3BO_3 at two rates (10 and 20 mg dm^{-3} of B) were incubated for 1, 2, 3, 5, 10, 20 and 40 days. After incubation, the soil B availability was evaluated using the hot-water extraction method. For the leaching study, 20 mg dm^{-3} of B from the two sources was incorporated into the top 0.5 cm of soil and incubated for 1, 5, 10, 15, 20, 25 and 30 days before leaching with water volume equivalent to the total soil-pore space. Sunflower plants were cultivated for two consecutive seasons in greenhouse using Mg_2Al-B-LDH and H_3BO_3 and six rates (0, 0.5, 1, 2, 3 and 5 mg dm^{-3}) in a factorial 2 × 6, with four replicates. Plants received a single application of B before sowing at the first cultivation. H_3BO_3 had greater availability of B in the soil than Mg_2Al-B-LDH regardless of the applied rate or time of incubation. The slow release of B by Mg_2Al-B-LDH resulted in a significant reduction in B leached compared to H_3BO_3. There was a quadratic and linear response of sunflower aboveground biomass and B accumulation with increasing rates of H_3BO_3 and Mg_2Al-B-LDH, respectively, in the second cultivation only. A boron rate of 5 mg dm^{-3} applied as H_3BO_3 resulted in plant toxicity, while Mg_2Al-B-LDH promoted a slow release of B to the plants throughout the cultivation period.

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1 Introduction

Boron (B) applied in agriculture by means of conventional fertilizers, such as boric acid (H_3BO_3), can easily leach into the soil profile and lead to plant toxicity due to the high solubility of this compound. Areas with high rainfall are more susceptible to leaching, intensifying in sites with sandy soils with low organic matter (OM). B toxicity in seedling and plants can occur when high doses of soluble sources are applied, particularly in soils with lower mobility and high availability of B. Therefore, a higher retention of this micronutrient in the soil without leading to plant toxicity can be achieved either by increasing soil OM, or by using slow release sources. Both strategies are important to decrease leaching and improve the synchronization of B release into the soil solution with plant uptake. There has been great interest in using nanostructured materials, such as layered double hydroxides (LDHs), as an alternative to provide a gradual release of nutrients to the soil and plants.[1–6] LDHs act as host matrices of negative species (anions) in their interlamellar spaces. These anions, along with water molecules, are responsible for neutralizing the positive charges in their layers. They are therefore also called insertion compounds, given the characteristic of a host matrix for the storage of several species. LDHs have the general formula: $[M_{(1-x)}{}^{2+}M_x{}^{3+}(OH)_2]\,(A^{n-})_{x/n}\cdot zH_2O$, in which M^{2+} = bivalent metal ions, such as Ca^{2+}, Mg^{2+}, Zn^{2+}, *etc.*; M^{3+} = trivalent metal ions, such as Fe^{3+}, Al^{3+}, and Mn^{3+}, and A^{n-} = interlamellar anions, in a structure similar to the Brucite mineral [$Mg(OH)_2$], with the Mg^{2+} located in the center of the octahedra with hydroxyls at the vertices, forming flat and neutral layers remain stacked by means of hydrogen bonds.

In agriculture, the main use of LDHs is for inclusion in pesticides, herbicides, plant growth regulators and, as in the

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case of interest in this study, the inclusion of nutrients such as borate, nitrate, and phosphate, among others, is done in order to obtain sustained release fertilizers.[2–4,7,8]

Songkhum and coworkers investigated the use of zinc (Zn) and aluminum (Al) LDH intercalated with borate (ZnAl-LDH) in association with a conventional fertilizer blend of nitrogen, phosphorus and potassium (NPK).[6] The application of ZnAl-LDH in association with NPK increased the plant growth as a consequence of the controlled and sustained release of Zn and B. The authors evaluated the application of NPK with and without ZnAl-LDH, however there was no control treatment when combining NPK with a soluble source of B and Zn (*e.g.* H_3BO_3 and $ZnSO_4$) with a similar rate of this micronutrient compared to ZnAl-LDH. Thus, their results indicated an additive effect of micronutrient application due to the release of Zn and B from ZnAl-LDH, and not the effect of sustained release of Zn and B.

Magnesium (Mg) and aluminum (Al) LDH intercalated with borate anions (Mg_2Al-B-LDH) have been successfully used as a matrix for the sustained release of B in a clayey soil with high retention of nutrients and they are not prone to B leaching.[8] The application of Mg_2Al-B-LDH and H_3BO_3 resulted in similar B availability in the soil and similar growth and uptake of B by sunflower plants.

It is observed in general that in several studies conducted, the treatment and characterization of LDHs are of chemical and mineralogical nature, with suggestions as to its use as a source of slow release.[9–12] However, studies on the agronomic use of LDHs are still needed for a better understanding of soil nutrient dynamics and their absorption by plants. In addition, there are only a few agronomic studies with LDHs and most of them were conducted using a single cultivation process,[3,5,6,8,13] not factoring the residual effect of LDHs on the release of nutrients to successive crops. Bernardo and coworkers suggested a higher residual P effect in soil using Mg–Al–PO_4-LDH compared to monoammonium phosphate (MAP) after plant cultivation.[5] However, the authors did not evaluate the availability of P for the second crop regarding plant dry matter (DM) and P uptake. These methodologies make it difficult to evaluate the residual effect of fertilizers on the soil, and cultivation is necessary without replenishing the nutrients to prove the efficiency of the layered materials.

Particularly for B, borate intercalated in LDHs is usually studied in order to obtain more efficient methods for intercalation with anions and also their use as borate adsorbents in solution.[14,15] Studies of B leaching in the soil using LDHs as matrices, their residual effect and availability of B to plants in successive crops are still incipient. Thus, the present work aims to evaluate: (i) the dynamics of B availability and leaching by Mg_2Al-B-LDH and H_3BO_3 in sandy soil; (ii) B release by Mg_2Al-B-LDH and H_3BO_3 in successive crops of sunflower in sandy soil without replenishing the micronutrient.

2 Experimental section

2.1 Materials and methods

2.1.1 Synthesis and characterization of LDH. The synthesis of magnesium–aluminum layered double hydroxides intercalated with borate (Mg_2Al-B-LDH) was carried out by the coprecipitation method at a constant pH value. 250 mL of the solution of containing 1.0 mol L^{-1} of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.5 mol L^{-1} of $Al(NO_3)_3{\cdot}9H_2O$ was added dropwise, under vigorous stirring, into a 500 mL solution containing 1.25 mol L^{-1} of H_3BO_3. The pH value of the solution was maintained at 10.0 during the synthesis using 2.0 mol L^{-1} of NaOH solution. The synthesis was carried out in a N_2 atmosphere. The solid material was washed with H_2O (deionized-Milli-Q® system) and dried at 25 °C under vacuum in the presence of silica gel.

Mg_2Al-B-LDH was characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electronic microscopy (SEM). XRD analysis was performed using a graphite crystal monochromator to select Cu-Kα_1 radiation with λ = 1.5406 Å and a step away from 0.02° s^{-1}, with 2θ between 4° and 70°. The ATR-FTIR spectra were recorded in the range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution and 256 scanning. A Shimadzu XRD-6000 diffractometer and a Jasco spectrometer FT/IR-4100 were used for XRD and ATR-FTIR analyses, respectively. For SEM analysis, Mg_2Al-B-LDH was supported on conductive double-sided adhesive tape and a Zeiss EVO 50 scanning electron microscope was used.

The content of B in Mg_2Al-B-LDH was evaluated by Ultraviolet-Visible Molecular Absorption Spectrophotometry (UV-Vis), λ = 420 nm, using a Thermo Scientific Evolution 300 device. The sample was solubilized in 5 mol L^{-1} of HNO_3 using a 1 : 60 ratio of fertilizer : solution (w/v).

2.1.2 Kinetics of B availability in soil. A soil sample of 0–20 cm depth of a Dystrophic Yellow Red Latosol (DYRL), an Oxisol,[16] with 81.3% of sand, was collected from the Serra do Salitre region. The soil was air-dried and sieved with a 2 mm mesh. The results of the chemical and physical characterization of the soil sample are shown in Table 1. The same soil was used in the leaching tests in soil columns and consecutive cultivations in greenhouse, which will be presented later.

Table 1 Chemical and physical characterization of a typical dystrophic yellow red latosol sampled from the 0–20 cm soil depth layer in Serra de Salitre, MG, Brazil

Attribute	DYRL	Attribute	DYRL
pH_{H_2O}	5.35	OM (dag kg^{-1})	1.14
P (mg dm^{-3})	9.50	P-rem (mg L^{-1})	31.80
K (mg dm^{-3})	9.00	S (mg dm^{-3})	19.40
Ca^{2+} ($cmol_c$ dm^{-3})	1.51	B (mg dm^{-3})	0.13
Mg^{2+} ($cmol_c$ dm^{-3})	0.12	Cu (mg dm^{-3})	0.28
Al^{3+} ($cmol_c$ dm^{-3})	0.00	Mn (mg dm^{-3})	1.80
H + Al ($cmol_c$ dm^{-3})	4.00	Fe (mg dm^{-3})	98.30
SB ($cmol_c$ dm^{-3})	1.65	Zn (mg dm^{-3})	1.47
t ($cmol_c$ dm^{-3})	1.65	Coarse sand (g kg^{-1})	195
T ($cmol_c$ dm^{-3})	5.65	Fine sand (g kg^{-1})	618
V (%)	29.20	Silt (g kg^{-1})	28
m (%)	0.00	Clay (g kg^{-1})	160

DYRL = Dystrophic Yellow Red Latosol; pH – soil/water ratio of 1 : 2.5; P, K, Cu, Mn, Fe and Zn – Mehlich-1 extractor; Ca^{2+}, Mg^{2+} and Al^{3+} – 1.0 mol L^{-1} KCl extractor; S – extractor $Ca(H_2PO_4)_2$, 500 mg L^{-1} of P in HOAc 2.0 mol L^{-1}; B – "Hot water" extractor; H + Al – calcium acetate extractor 0.5 mol L^{-1} (pH = 7.0); SB = sum of bases; t = effective cation exchange capacity; T = cation exchange capacity at pH = 7.0; V = base saturation; m = saturation by aluminum; OM = organic matter; P-rem = remaining phosphorus.

The release of B from two sources (Mg_2Al-B-LDH and H_3BO_3) over time was evaluated under laboratory conditions *via* incubation between the sources and soil. The doses of 10 and 20 mg dm^{-3} of total B were utilized and the B availability was evaluated at different incubation times (1, 2, 3, 5, 10, 20, and 40 days) with four replicates. The sources of B were homogenized with soil using plastic bags, and soil moisture was maintained at field capacity (FC) throughout the experiment. At the pre-established incubation times, the soil samples were dried, and the B availability was evaluated according to the methodology described by Raij and cowokers.[17]

2.1.3 B leaching in soil columns. The B leaching test was performed and adapted from the method described by Abat and coworkers,[18] and is summarized below. The columns with 3 cm diameter and 12 cm height were filled with 60 cm^3 of sandy soil (Table 1). Before applying the fertilizers, a volume of distilled water corresponding to once the volume of pores (30 mL) was applied on top of the soil column and drained using a syringe system. After drainage, the fertilizers were applied 0.5 cm from the surface of soil in the center of the column and covered with soil. A rate of 20 mg dm^{-3} of total B from Mg_2Al-B-LDH and H_3BO_3 sources was used. Leachate was collected after the application of distilled water corresponding to the volume of pores (30 mL) after 1, 5, 10, 15, 20, 25, and 30 days. The experiment was performed with four replicates. The determination of the B concentration in the leachate was done according to the method described by López and coworkers.[19]

2.1.4 Greenhouse experiment. The release of B into plants from Mg_2Al-B-LDH was evaluated using successive cultivations of sunflowers in greenhouses without replenishing B. A factorial 2 × 6 was established with two sources of B (Mg_2Al-B-LDH and H_3BO_3) and six doses of total B (0.0, 0.5, 1.0, 2.0, 3.0 and 5.0 mg dm^{-3}). The experiment was conducted using a randomized complete block design with four replicates, using pots with 2.0 dm^{-3} soil capacity.

The lime requirement calculation was carried out to correct the soil acidity and to supply calcium (Ca) and magnesium (Mg) to the plants, increasing the soil saturation to 50%. For this purpose, $CaCO_3$ and $MgCO_3$ were used as sources. Then, the soil was wetted to 80% of FC and incubated for 30 days in greenhouse.

Before sowing, the B sources were homogenized in the soils and immediately afterwards 300 mg dm^{-3} of P, 140 mg dm^{-3} of K, 60 mg dm^{-3} of S, and 100 mg dm^{-3} of N were applied, where KH_2PO_4, $NH_4H_2PO_4$, $CaH_2(PO_4)_2$, and $(NH_4)_2SO_4$ were used as sources.

Eight sunflower seeds (*Helianthus annuus* – Helio 250 hybrid) were sown per pot. Sunflower plants were chosen because they are sensitive to B. After five days, the seedlings were thinned to the four most uniform ones in each pot. Further liquid basal nutrients were added twice in 10 mL of the solution per pot, resulting in a total basal nutrient dose per dm^3 soil of 200 mg of N as urea, 1.32 mg of Cu as $CuSO_4{\cdot}5H_2O$, 1.55 mg of Fe as $FeSO_4{\cdot}7H_2O$, 3.66 mg of Mn as $MnSO_4{\cdot}H_2O$, 0.15 mg of Mo as $(NH_4)_6Mo_7O_{24}$, and 4.0 mg of Zn as $ZnSO_4{\cdot}7H_2O$. The pots were watered with distilled water every day to 80% of FC.

After 45 days of cultivation, the plants were harvested by cutting the stems at the soil surface. The plant biomass was dried at 65 °C for 96 h and weighed to obtain DM. Samples of 100 g of soil from each experimental unit were collected before and after the first cultivation to determine the soil pH and B availablity.[17] The samples were air dried and sieved with 2 mm mesh for further analysis.

After harvesting the first cultivation, the pots were left undisturbed for 60 days until the second cultivation started. No B fertilizers were applied, enabling the plants to use residual B. The other nutrients were applied at the same rate and sources as in the first crop. Eight seeds of sunflower of the same cultivar were sown in and after five days, and each pot was thinned to four plants. The pots were watered with distilled water to maintain a water content of 80% FC. At 40 days after seeding, the shoot was harvested. The plant biomass and soil were analyzed following the same methodology described for the first cultivation. The plant biomass samples were ground and the B concentration in the plant tissue was determined according to the methodology described by Embrapa.[20] This sequential cultivation resulted in 45 and 145 days from B application.

2.2 Statistical analysis

Data were submitted to analysis of variance. For the B soil incubation and leaching in soil column experiments the differences between treatment (B fertilizers) means were evaluated using the Tukey's and least significant difference (LSD) adjustment at $p \leq 0.05$. For the greenhouse experiment, regression analysis and identity test for regression models were performed. The R environment (R Core Team, 2016) was used in the statistical analysis.[21]

3 Results

3.1 Chemical and structural characterization of Mg_2Al-B-LDH

The results and discussion of XRD, ATR-FTIR, and SEM, and the total content of B in Mg_2Al-B-LDH are presented in the ESI.†

3.2 Kinetics of B availability in soil

The results of soil B availability as a function of incubation time after application of Mg_2Al-B-LDH and H_3BO_3 are shown in Fig. 1. The point of maximum release of B occurred within two days of incubation between the two sources and soil for both doses applied (10 and 20 mg dm^{-3} of B). After the peak of maximum B release, the soil B availability was stabilized at 20 and 40 days of incubation for both sources at a dose of 10 mg dm^{-3} of B (Fig. 1). For 20 mg dm^{-3} of B, there was a significant decrease of soil B availability at 40 days of incubation compared to the concentration at 20 days of incubation (Fig. 1). Comparing the two sources applied at doses 10 and 20 mg dm^{-3} of B, the soil availability of micronutrients for Mg_2Al-B-LDH was lower than that for H_3BO_3 for most incubation times analyzed.

3.3 B leaching in soil columns

The B leaching test in soil columns indicated a linear increase in micronutrient release with increasing incubation times between the sources (Mg_2Al-B-LDH and H_3BO_3) and soil (Fig. 2). Throughout the incubation period, the percentage of B leached was lower

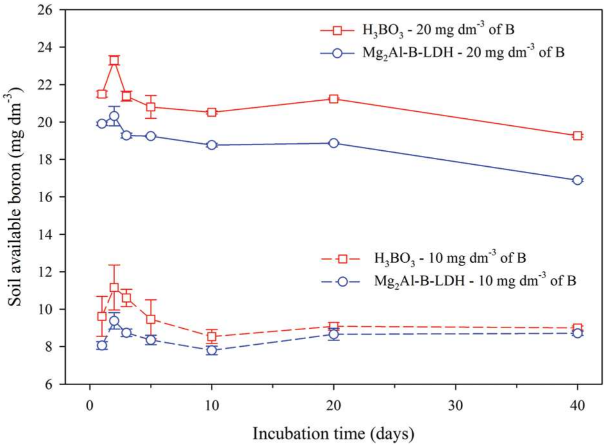

Fig. 1 Soil boron availability as a function of incubation time from the application of 10 mg dm^{-3} of B and 20 mg dm^{-3} of B as Mg_2Al-B-LDH and H_3BO_3.

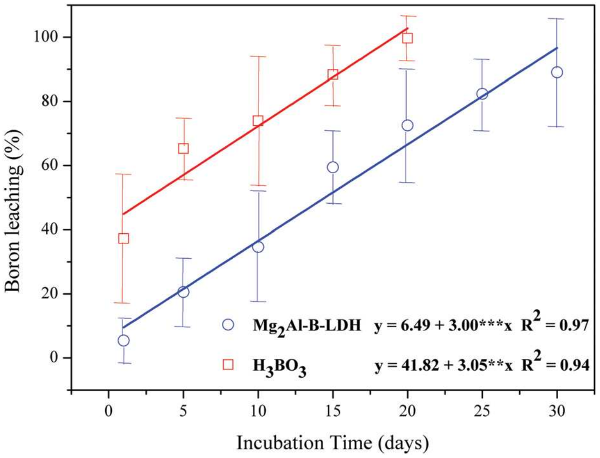

Fig. 2 Boron leaching in soil columns as a function of incubation time from the application of 20 mg dm^{-3} of B as Mg_2Al-B-LDH and H_3BO_3. ** and *** Significant at $p < 0.01$ and $p < 0.001$ by t test, respectively.

for Mg_2Al-B-LDH than that for H_3BO_3. According to linear regression analysis, at the first leaching collection (after 1 day of incubation), the leached percentage was 44.9% and 9.50% of B for H_3BO_3 and Mg_2Al-B-LDH, respectively. When the fifth leaching was carried out, after 20 days of incubation, 100% of the B availability as H_3BO_3 was recovered in the leachate, while only 66.5% of B from Mg_2Al-B-LDH was recovered. At 30 days of incubation, the leached percentage was 96.5% for Mg_2Al-B-LDH.

3.4 Greenhouse experiment

The soil B availability as a function of doses applied before the first cultivation is shown in Fig. 3a. The soil B availability increased linearly with the increase of the applied dose regardless of the B source (H_3BO_3 or Mg_2Al-B-LDH). An identity test performed to compare the similarities between the two linear regression equations revealed that both equations were significantly similar. The recovery rate of B by the extractor was 85% of the B applied to the soil in accordance with the identity test for linear regression.

The soil pH value was analyzed before the first cultivation to evaluate the eventual change in the pH value due to the application of Mg_2Al-B-LDH and H_3BO_3 sources. Considering the applied doses, the sources and the interaction between the sources and doses, the results of the soil pH value were statistically equal ($p < 0.01$) (Table 2).

Sunflower DM accumulation was not influenced by the applied doses at 1% of significance by any B sources in the first cultivation (Fig. 4a). The average DM production across the doses was 23.66 g pot^{-1} for the plants supplied with H_3BO_3, which was significantly higher than 20.20 g pot^{-1} for the plants supplied with Mg_2Al-B-LDH. However, the plant B uptake in the first cultivation was statistically the same for the two sources at all applied doses (Fig. 4c). The B uptake responded quadratically to increasing doses of B for both sources.

The identity test compared the regression fitting for the B uptake as a function of increasing doses of B and revealed that the two models used were similar for the two B sources (Fig. 4c).

The B availability in the residual soil was determined from the first cultivation. Before the second cultivation, B in the soil was determined and there was a linear increase as a function of the applied doses of B as it was presented before the first cultivation (Fig. 3b). It is noteworthy that Mg_2Al-B-LDH at a dose of 5 mg dm^{-3} in the first cultivation resulted in 2.21 mg dm^{-3} of B availability in the soil, which was significantly higher than the residual B from H_3BO_3 (1.67 mg dm^{-3}). For all other doses, there was no significant difference between the residual B in the soil between the sources within each applied dose. Regarding the soil pH value before the second cultivation, it was observed that there was a slight acidification occurred in all treatments (Table 2). As before the first cultivation, the soil pH value was not altered by the sources and the applied doses ($p < 0.01$).

The DM accumulation from the second cultivation is shown in Fig. 4b. The interaction between the B sources and the doses was significant ($p < 0.01$). The DM of sunflower responded quadratically and linearly to the increasing B doses of H_3BO_3 and Mg_2Al-B-LDH, respectively (Fig. 4b). At 3 mg dm^{-3} dose of B, the DM accumulation using H_3BO_3 and Mg_2Al-B-LDH was 29.4 and 28.8 g pot^{-1}, according to the quadratic and linear regression, respectively. For the highest dose (5 mg dm^{-3} of B), the DM was 31.76 and 29.16 g pot^{-1} for Mg_2Al-B-LDH and H_3BO_3, respectively.

The B uptake of sunflower during the second cultivation followed a similar response observed in the DM accumulation (Fig. 4d). The models that best fit the data were quadratic for H_3BO_3 and linear for Mg_2Al-B-LDH. The B uptake for the highest applied dose (5 mg dm^{-3} of B) was 9.4 and 8.91 mg pot^{-1} for Mg_2Al-B-LDH and H_3BO_3, according to linear and quadratic regression, respectively.

4 Discussion

One of the properties of LDHs is the slower release of nutrients than soluble conventional sources.[2,3,6] The results of the soil B availability after different incubation times were lower for

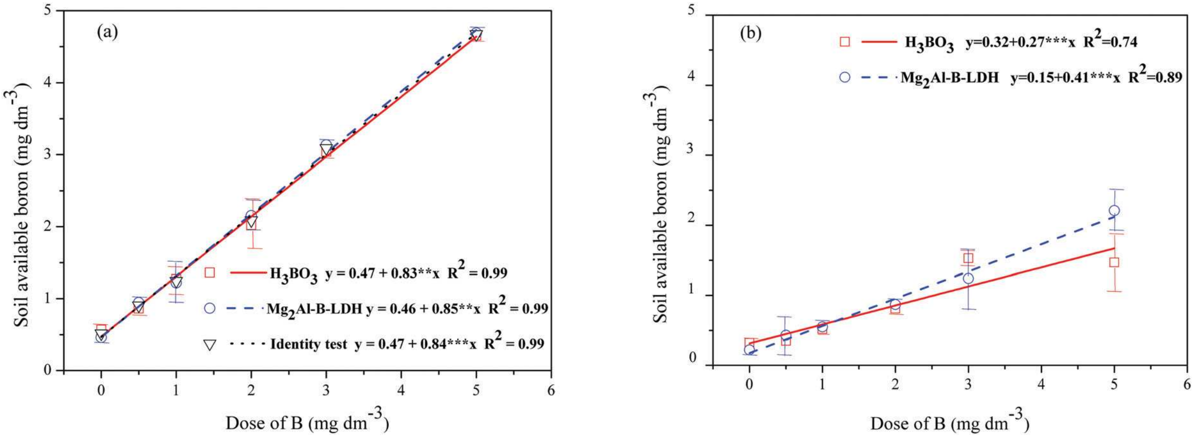

Fig. 3 Soil boron availability as a function of the applied doses of B as Mg_2Al-B-LDH and H_3BO_3 before the first (a) and second (b) sunflower cultivation. **, *** significant at $p < 0.01$ and $p < 0.001$ by t test, respectively.

Table 2 Soil pH value as a function of applied doses of B (Mg_2Al-B-LDH and H_3BO_3) before the first and second cultivation

	Dose of B (mg dm^{-3})						
Source	0.0	0.5	1.0	2.0	3.0	5.0	Medium
	Soil pH value before the first cultivation						
H_3BO_3	5.64	5.87	5.81	5.69	6.09	6.02	5.85
Mg_2Al-B-LDH	5.92	5.95	5.94	5.89	5.92	6.06	5.95
	Soil pH value before the second cultivation						
H_3BO_3	5.46	5.44	5.74	5.67	5.86	5.81	5.66
Mg_2Al-B-LDH	5.93	5.79	5.77	5.72	5.73	5.86	5.80

The results of the soil pH value were statistically equal ($p < 0.01$) for sources, doses and interaction between the sources and doses.

Mg_2Al-B-LDH than for H_3BO_3 (Fig. 1), confirming the slow release profile of B in the soil for Mg_2Al-B-LDH. Bernardo and coworkers compared the soil P availability using multiple incubation times and two P sources (Mg–Al–PO_4-LDH and MAP).[5] The P availability for Mg–Al–PO_4-LDH was much lower than that for MAP (soluble source) at all incubation times. The authors attributed the lowest availability to the protection of phosphate anions in the interlamellar spaces of LDHs.[5] The results presented in our paper and corroborated by Bernardo and coworkers are particularly important for sandy soils with low OM and low ion retention capacity.[5] Thus, LDHs can minimize the losses of nutrients in the soil by leaching and increase the time of residence of nutrients in the soil, consequently increasing the absorption by plants.

In this sense, the research carried out had the proposal to present B leaching using Mg_2Al-B-LDH, which in principle, to the best of our knowledge, has not been reported in the literature. The B leaching profile for Mg_2Al-B-LDH was lower than that for H_3BO_3 (Fig. 2). The initial B leaching of 44.9% from H_3BO_3 compared to 9.5% from Mg_2Al-B-LDH is an important fertilizer property to increase the time of B residence in the root zone that can result in a higher B uptake by plants. It is noteworthy that all B supplied by H_3BO_3 was recovered in the leachate within 20 days of incubation (100% leached), which could have resulted in insufficient B availability to the plants. Conversely, after 20 days of incubation, the B leached from Mg_2Al-B-LDH was 66.5% (Fig. 2), which represents the residual effect of the fertilizer and the consequent B availability in the soil for plants. In regions with high leaching in the soils, combined with high rainfall, the results indicate the advantage of using Mg_2Al-B-LDH as a new B fertilizer for plants.

Some studies in the literature, in which increasing doses of LDH (source of P) were applied, indicated an increase in P availability in the soil.[2,3] The finding from the present study regarding to use of LDH as a source of B corroborated with the studies using LDH as a source of P (Fig. 3a). There was a linear response of B availability in the soil as a function of increasing doses of Mg_2Al-B-LDH. In another context, the recovery rate of applied B in the soil by the extraction method used ("hot water") was 85%, indicating a good sensitivity to evaluate the availability of the micronutrient.[17] Therefore, the availability of B in the soils with the application of Mg_2Al-B-LDH can be evaluated by means of conventional techniques that are used in routine laboratories.

It is noteworthy that the borate intercalated in LDH could be released into the soil through two different mechanisms: (i) by ion exchange reactions between intercalated borate and the anions usually present in the soil, such as carbonates, phosphates, nitrates, *etc.*, since the ion replacement can promote better structural stability of the LDH layers; (ii) dismantling of the LDH structure due to the "acid attack" promoted by the H^+ ions present in the acidic soil, with the subsequent release of borate. The soil used in our study presented H + Al = 4 $cmol_c$ dm^{-3} and soil pH = 5.95 before the first cultivation. The separation of LDH from the soil after cultivation is not possible under the conditions in which we conducted our study, therefore hindering the chemical analysis of the material. Thus, according to the soil chemical properties presented, we suggest that the release of boron from LDH was by acid dissolution due to the "acid attack".

In addition to soil nutrient availability, the use of LDHs can also directly affect the soil pH. Everaert and coworkers and Benício and coworkers reported a linear increase of soil pH

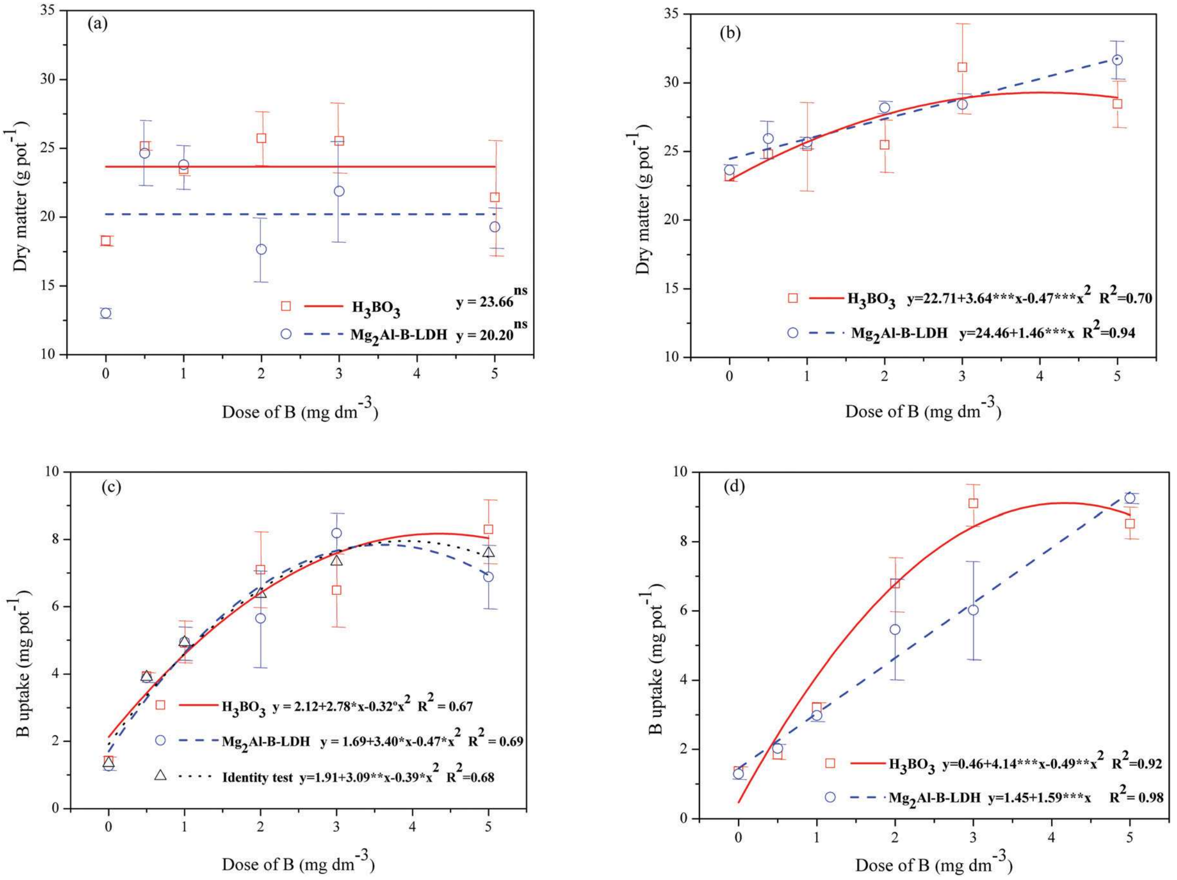

Fig. 4 Dry matter (a and b) and boron uptake (c and d) in the shoot of the sunflower plants as a function of the applied B (Mg_2Al-B-LDH and H_3BO_3) in the first (a and c) and second (b and d) cultivation. °, *, **, and *** significant at $p < 0.1$, $p < 0.05$, $p < 0.01$ and $p < 0.001$ by *t* test, respectively; ns = not significant.

with the increasing doses of LDH for P supply.[2,3] This increase in the soil pH value can be attributed to the release of hydroxyls through the LDHs.[22] The change in the soil pH can also contribute to the formation of microsites with higher pH values, which also increased the stability of LDHs in the soil, presenting an improvement in the nutrient absorption by plants.[3] In the present study, soil pH was not influenced by increasing the doses of Mg_2Al-B-LDH (Table 2). The difference found in this study compared to those cited above is due to the use of Mg_2Al-B-LDH as a source of micronutrient (B). Thus, the total P applied by LDH to supply this macronutrient to the plants[2,3] is much higher than that applied for B supply (micronutrient), which allows significant changes in the soil pH. The increase in soil pH caused by large amounts of LDH may favor its stability in the soil, allowing a more steady release of the intercalated anions, and even of the cations that make up the lamellar structure.[3,11,13] However, application of high amounts of LDH may decrease the availability of cationic micronutrients in the soil, such as Cu, Fe, Mn and Zn.[23,24] Thus, the use of LDH for the application of macronutrients may present an undesirable elevation of soil pH due to the large quantities of LDH required. Conversely, alterations of soil pH were not observed using LDH to supply micronutrients.

Sunflower DM production in the first cultivation was not influenced by the increase of the fertilizer doses (Fig. 4a). Benício and coworkers, applying LDH-P for maize cultivation, showed similar results with doses varying from 0 to 60 mg kg^{-1} of P in a sandy soil.[3] Although a higher DM was reported for sunflower fertilized with H_3BO_3 compared to Mg_2Al-B-LDH in the first cultivation, the dynamics of the plant B uptake was similar between B fertilizers as a function of increasing doses of B (Fig. 4c). In annual crops, which require an immediate availability of nutrients in the soil, these results confirm that the release profile of B by Mg_2Al-B-LDH did not affect the accumulation of B by plants. Thus, the results of the first cultivation validated the use of Mg_2Al-B-LDH as an alternative source of B for plants with micronutrient release adjusted according to plant requirements. The results from this study were in agreement with the research findings from Bernardo and coworkers, in which Mg–Al–PO_4-LDH and MAP sources were used to supply P to wheat (*Triticum aestivum*).[5] Wheat P uptake was similar for the sources applied, making Mg–Al–PO_4-LDH a viable P source to be supplied in a short period of time similarly to MAP.

The soil B availability before the second cultivation without micronutrient replenishing was linear according to the increasing applied doses, similarly to the response observed before the first cultivation (Fig. 3b). However, at a dose of 5 mg dm^{-3} of B, soil B availability from Mg_2Al-B-LDH was higher than that from H_3BO_3. This result confirms the slower release properties of B by Mg_2Al-B-LDH with a residual effect enabling B availability in the soil for successive crops. A similar result was presented by

Bernardo and coworkers by comparing the release of P from Mg–Al–PO_4-LDH and MAP after 30 days of cultivation of wheat.[5] The P availability in the soil after cultivation was higher for Mg–Al–PO_4-LDH. The authors attributed the higher P availability presented by Mg–Al–PO_4-LDH to the smaller fraction of P that was released during the cultivation.[5] Furthermore, even with the less P being released by Mg–Al–PO_4-LDH, the wheat DM and P uptake were the same between the P sources, not hampering plant development.[5]

The soil pH value after the first cultivation was slightly acidic (Table 2), which is common due to the removal of exchangeable bases from the soil by plant uptake.[25,26] The slightly acidic soil pH can influence the stability of the LDH structure in the soil due to the ''attack'' of the protons to the LDH layers.[3,8] At acidic soil pH, there is a greater release of the intercalated nutrients and cations that make up the layers due to the dismantling of the structure.[3,11,13] Conversely, Bernardo and coworkers obtained higher soil pH values after plant cultivation using Mg–Al–PO_4-LDH as a source of P.[5] However, the doses of LDH used for P supply were much higher than those used for the supply of B in this study. In this way, the increase in the soil pH directly depends on the amount of LDH applied, that is, on the purpose of using the LDH as a source of macronutrients or micronutrients. It is noteworthy that the increase in soil pH, despite improving soil LDH stability, can decrease the availability of Cu, Fe, Mn, and Zn in the soil to plant uptake, as previously described in this study.

At a dose of 3 mg dm^{-3} of B the DM of sunflower was higher for H_3BO_3, however the application of 5 mg dm^{-3} of B resulted in a significantly higher DM production for Mg_2Al-B-LDH. The quadratic response of DM for H_3BO_3 and the linear response for Mg_2Al-B-LDH confirmed the slower and gradual release of B for Mg_2Al-B-LDH, avoiding any potential toxic effect of B at the highest applied dose (5 mg dm^{-3} of B). These results were confirmed by the B uptake obtained in the aerial part of the plants in the second cultivation. As for DM, the uptake of B followed a quadratic response for H_3BO_3 and a linear response for Mg_2Al-B-LDH.

The recommendation of B fertilization for sunflower is between 0.5–1.5 mg dm^{-3} of B.[27,28] According to Gormus and coworkers and Anderson and coworkers,[28,29] B availability in the soil varying from 2.5 to 5 mg dm^{-3} is excessive and toxic to the plants. Therefore, the application of 5 mg dm^{-3} of B, which was used in this study, exceeded the recommended limits for the sunflower, which in theory should have resulted in a toxic effect in the plants. Plant toxicity symptoms occurred only when H_3BO_3 was applied as a result of the decrease in the DM and B uptake in the aerial part of the plants at 5 mg dm^{-3} of B applied. For Mg_2Al-B-LDH, the process of B release slowly and gradually resulted in no B toxicity, since the amount of DM and B uptake responses was linear as a function of the applied doses.

5 Conclusions

The B availability in the soil after the application of Mg_2Al-B-LDH was lower than that for H_3BO_3 for most incubation times as a result of the slower release of B from LDH compared to the soluble source of B. In the B leaching experiment in soil columns, the slower and gradual release profile of Mg_2Al-B-LDH significantly decreases the amount of B leached compared to H_3BO_3. Regions with predominant sandy soil with high precipitation rates and nutrient leaching are a concern, and the results of this study highlight the use of Mg_2Al-B-LDH as a promising slow release B fertilizer. The slow release of B promoted by Mg_2Al-B-LDH is an important fertilizer property to increase the time of residence of B in the root zone and increase the likelihood of B uptake by plants.

In annual crops with immediate nutrient requirement, the results presented confirm that the B released from Mg_2Al-B-LDH did not impair the development of plants. Thus, results from only one cultivation confirmed that Mg_2Al-B-LDH can be used as an alternative source of B for plants providing enough B release that matches the plant requirements. The second cultivation without replenishing B showed a toxic effect on the plants when the soluble source of B (H_3BO_3) was used. For Mg_2Al-B-LDH the release profile of B was slow and continuous, even for doses above the recommendation such as 5 mg dm^{-3} of B. These results suggested that Mg_2Al-B-LDH can be safely used as a source of B to supply this micronutrient to the plants for an extended period of time compared to conventional soluble sources.

The maintenance of the soil pH value in ideal ranges is a basic requirement to promote greater availability of other macronutrients and micronutrients in high production agricultural systems. The use of Mg_2Al-B-LDH as a source of micronutrient, specifically B, did not affect the soil pH, which constitutes an advantage in using these lamellae materials as a source of micronutrients compared to macronutrients.

Conflicts of interest

There are no conflicts to declare.

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Electronic Supplementary Information: LAYERED DOUBLE HYDROXIDE INTERCALATED WITH BORATE: EFFECT OF FERTILIZATION ON BORON LEACHING AND SUCCESSIVE SUNFLOWER CULTIVATIONS

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X-ray diffraction (XRD)

The XRD pattern of Mg_2Al-B-LDH is regarding of hydrotalcite-type compounds with basal peaks (00l) [(003), (006) and (009)] at 7.2, 15.6 and 23.6 2θ (degree), respectively (Fig. 1). The basal spacing for Mg_2Al-B-LDH, calculated by Bragg's equation ($n\lambda = 2dhk\ell sen\theta$), was 12.0 Å, and it is related to intercalation of tetraborate ions $[B_4O_5(OH)_4]^{2-}$ between the layers of LDH.[1]

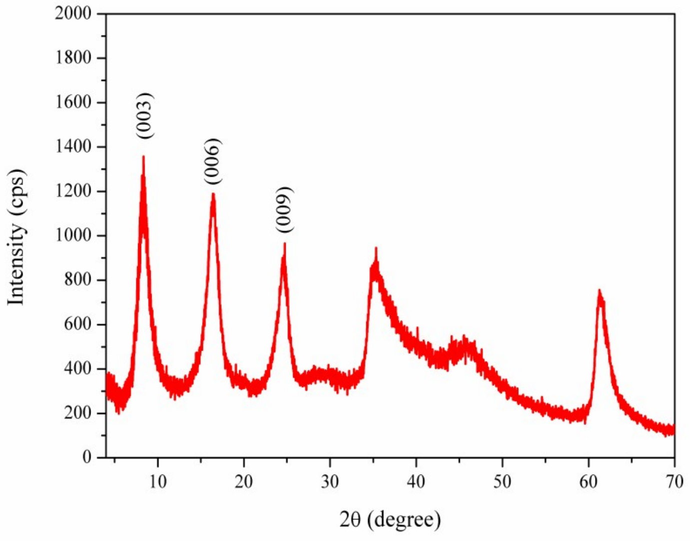

Fig. 1: Diffractogram of Mg_2Al-B-LDH.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

The presence of the broad band in the wavenumber range from 3600 cm^{-1} to 3200 cm^{-1} are due to the O-H stretching of the hydroxyl groups and/or H_2O molecules (Fig. 2).[2,3] The O-H stretching of the hydroxyl groups and/or H_2O

molecules is also observed at 1640 cm^{-1} in the spectrum of Mg_2Al-B-LDH (Fig. 2).[4] Bands in the wavenumber range from 1600 to 500 cm^{-1} are attributed to the various vibration modes related to the presence of borate anions. More specifically, the bands at 1350 cm^{-1}, 1020 cm^{-1}, 935 cm^{-1}, 790 cm^{-1}, and 667 cm^{-1} are attributed to the vibrational modes υ_{as}(B3-O), υ_{as}(B4-O), υ_{s}(B3-O), υ_{s}(B4-O), υ_{s}(B3-O), respectively (Fig. 2).[1]

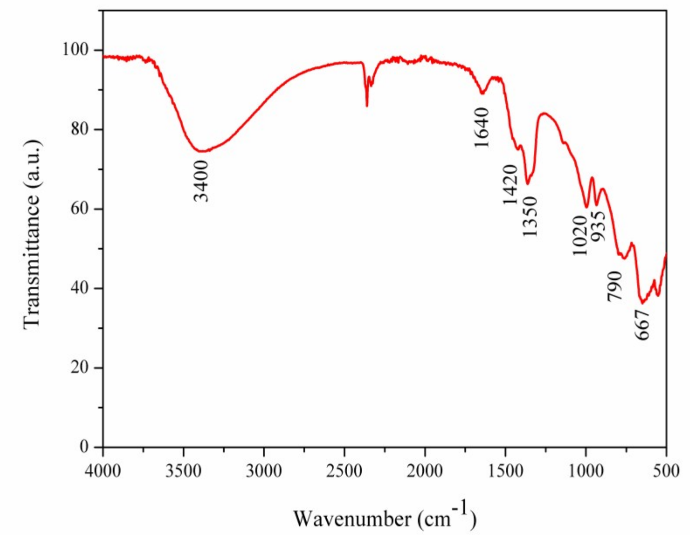

Fig. 2: Attenuated total reflectance Fourier transform infrared spectroscopy spectra of Mg_2Al-B-LDH.

Scanning electronic microscopy (SEM)

The morphology of the Mg_2Al-B-LDH was analyzed by SEM (Fig. 3). The Mg_2Al-B-LDH presented spherical aggregates particles with diameters varying between 1 and 5 µm.

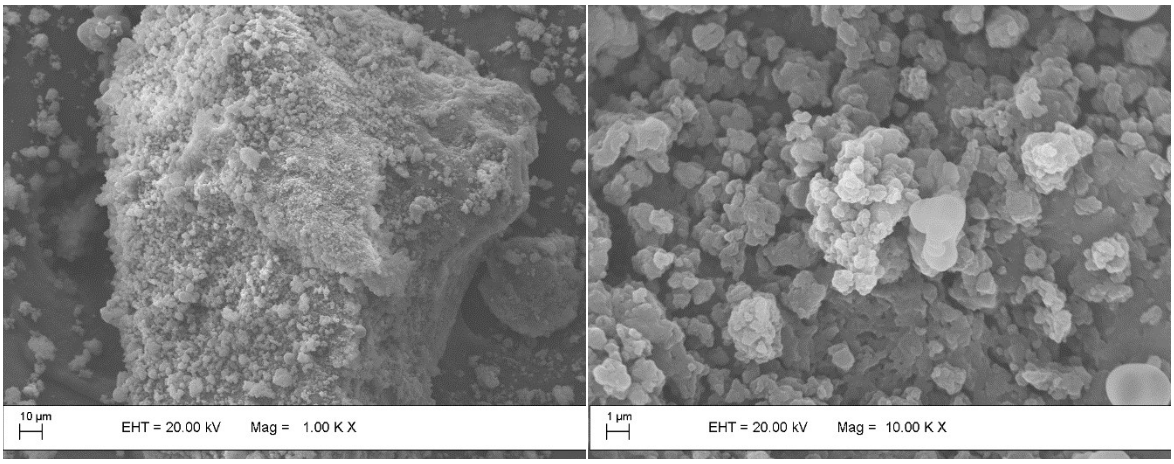

Fig. 3: Scanning electronic microscopy images of the surface morphology of Mg_2Al-B-LDH.

B total concentration in the Mg_2Al-B-LDH

The B total content in the Mg_2Al-B-LDH was 50.60 g kg^{-1} of B per LDH, corresponding to 5.06 % of B. Previous researchs reported values of 14.00, 37.90, 25.50, and 45.23 g kg^{-1} of B for MgAl-CO_3-LDH, MgAl-NO_3-LDH, calcined MgAl-LDH, and non-calcined MgAl-LDH, respectively.[5,6,7] The total of B determined for Mg_2Al-B-LDH indicated higher incorporation of B, which is important condition when studies are conducted with micronutrients (required in small quantities by plants).

Statistical Analysis

Table 1 - Summary of variance analysis from soil available boron as a function of incubation time from Mg_2Al-B-LDH and H_3BO_3 application of 10 mg dm^{-3} and 20 mg dm^{-3} of B

Source of Variation	^{2}DF	------------------Mean Square----------------- ^{3}10 mg dm^{-3}	^{4}20 mg dm^{-3}
Source	1	14.8526^{***}	61.992^{***}
Incubation time	6	3.9680^{***}	10.163^{***}
Source x Incubation time	6	0.9353^{***}	0.527^{***}
^{1}CV %		5.44	1.23

*** 0.1 % of significance by F test. ^{1}Coefficient of variation; ^{2}Degrees of freedom; ^{3}Soil available boron as a function of incubation time from application of 10 mg dm^{-3} of B; ^{4}Soil available boron as a function of incubation time from application of 20 mg dm^{-3} of B.

Table 2 - Summary of variance analysis from boron leaching in soils columns as a function of incubation time from Mg_2Al-B-LDH and H_3BO_3

Source of Variation	^{2}DF	Mean Square
Source	1	0.1^{o}
Incubation time	6	3789.8^{***}
Source x Incubation time	6	6948.9^{***}
^{1}CV %		6.55

*** 0.1 % of significance; ^{o} 10 % of significance by F test. ^{1}Coefficient of variation; ^{2}Degrees of freedom

Table 3 - Summary of variance analysis from dry matter, boron uptake, soil available boron, and soil pH as a function of the applied doses of B (Mg_2Al-B-LDH and H_3BO_3) in first cultivation

		-----------------------Mean Square---------------------			
Source of Variation	^{2}DF	Dry matter	B uptake	Available B^3	pH^3
Source	1	143.037^{**}	0.622^{ns}	0.0018^{ns}	0.1764^{ns}
Dose	5	95.736^{*}	45.248^{*}	19.6654^{*}	0.0791^{ns}
Source x Dose	5	17.381^{ns}	2.694^{ns}	0.0157^{ns}	0.0555^{ns}
^{1}CV %		20.63	28.04	5.7	1.98

* 1 % of significance; ** 5 % of significance; ns: not significant by F test. ^{1}Coefficient of variation; ^{2}Degrees of freedom; ^{3} Soil available boron and soil pH value as a function of the applied doses of B (Mg_2Al-B-LDH and H_3BO_3) before the first cultivation.

Table 4 - Summary of variance analysis from dry matter, boron uptake, soil available boron, and soil pH as a function of the applied doses of B (Mg_2Al-B-LDH and H_3BO_3) in second cultivation

		------------------------Mean Square----------------------			
Source of Variation	[2]DF	Dry matter	B uptake	Available B[3]	pH[3]
Source	1	5.549^{ns}	16.020^{ns}	0.1173^{ns}	0.2976^{ns}
Dose	5	60.296*	84.119*	3.15345*	0.1153^{ns}
Source x Dose	5	11.937**	5.272^{o}	0.3230*	0.2189^{ns}
[1]CV %		7.41	32.16	26.45	2.87

* 1 % of significance; ** 5 % of significance; ^{o} 10 % of significance; ns: not significant by F test. [1]Coefficient of variation; [2]Degrees of freedom; [3] Soil available boron and soil pH value as a function of the applied doses of B (Mg_2Al-B-LDH and H_3BO_3) before the second cultivation.

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CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND AGRONOMIC USE OF ALGINATE MICROSPHERES CONTAINING LAYERED DOUBLE HYDROXIDES INTERCALATED WITH BORATE

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Synthesis, characterization and agronomic use of alginate microspheres containing layered double hydroxides intercalated with borate

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Boron (B) is generally present in soil as boric acid (H_3BO_3), a non-ionized molecule with weak retention in the soil and very leachable. Boron leaching may occur especially when soluble sources are applied in sandy soils in high-rainfall environments. Slow release fertilizers are important for the management of B fertilization and to obtain a desirable residual effect. We produced and evaluated the performance of a new slow release fertilizer made from alginate microspheres containing magnesium–aluminum layered double hydroxide intercalated with borate (LDH-B-ALG). LDH-B-ALG microspheres and alginate microspheres containing H_3BO_3 (BA-ALG) were produced using the modified complex coacervation method. The fertilizers were characterized by X-ray diffraction, attenuated total reflectance Fourier transform infrared spectroscopy, and scanning electronic microscopy. The B release test and leaching in soil columns were performed for synthetized fertilizers, H_3BO_3, and Ulexite. A greenhouse experiment with two responsive species (sunflower and cotton) was carried out using a factorial 2 × (4 + 1) with two soil pH (6.5 and 7.5), four sources of B (LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite), and a treatment control, without the application of B. The chemical characterization of LDH-B-ALG showed that LDH (powder) was successfully incorporated into the alginate polymer. The B release and leaching were much lower from LDH-B-ALG compared to conventional B sources. LDH-B-ALG was solubilized into the soil similarly to the other B sources in the greenhouse experiment. The lower release and leaching from LDH-B-ALG improved the accumulation of B in the root zone, consequently increasing the fertilizer efficiency and plant's B uptake. The new fertilizer showed be a suitable source in high-rainfall areas, especially for sandy soils, supplying B in a more adjusted way and reducing leaching losses.

1 Introduction

Boron (B) is an important micronutrient used for plant growth and development. B is generally present in the soil as boric acid (H_3BO_3), a non-ionized molecule with weak retention in the soil and very leachable. The B leaching and plant deficiency may occur when soluble sources (*e.g.* H_3BO_3 and borax) are applied to sandy soils with low organic matter and in areas with high precipitation.[1] Plant B toxicity can also occur when using high rates of B from soluble sources, particularly in clayey soils in which there is a lower B mobility and high availability of B.[1] Thus, new technologies of borated fertilizers are important to synchronize the B release in the soil, the time of B residency in the root zone, and the B absorption by the plants.

The use of nanomaterials in agriculture can optimize nutrient use efficiency due to a slow and controlled release of nutrients. There has been great interest in using nanostructured materials, such as Layered Double Hydroxides (LDHs), as an alternative to provide a sustained nutrient release.[2–8] LDHs act as host matrices with negative species (anions) placed in their interlamellar spaces. These anions, along with water molecules, are responsible for neutralizing the positive charges in their layers. They are also called insertion compounds, given the characteristic of a host matrix for the storage of several species. LDHs have the general formula: $[M_{(1-x)}{}^{2+}\ M_x{}^{3+}\ (OH)_2]\ (A^{n-})_{x/n}{\cdot}zH_2O$, in which M^{2+} = bivalent metal ion, such as Ca^{2+}, Mg^{2+}, Zn^{2+}, *etc.*; M^{3+} = trivalent metal ion, such as Fe^{3+}, Al^{3+}, Mn^{3+}, *etc.*, and A^{n-} = interlamellar anion. The LDH structure is similar to the brucite mineral $[Mg(OH)_2]$, with the Mg^{2+} located in the center of the octahedra and the hydroxyls at the vertices, so forming flat and neutral layers which are kept stacked by means of hydrogen bonds.

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In agriculture, LDHs have been used to obtain slow release matrices intercalated with herbicides, pesticides, plant growth regulators, and nutrients such as nitrates, phosphates and borates.[3–6,9–12] Specifically for B fertilizers, studies have focused on obtaining more efficient synthesis and intercalation of the borate anions, and characterization of LDHs.[6,7] In a single greenhouse cultivation of sunflowers, the rates of 0.0 to 5.0 mg dm^{-3} of total B, and two sources H_3BO_3 and LDH intercalated with borate, were applied in a clayey soil.[6] The sources were similarly solubilized in the soil and the sunflower B uptake was statistically equal. According to Castro and coworkers, the use of powdered LDHs in agricultural acidic pH soil, can destabilize the layered structure of LDH and increase the nutrient release in the soil.[6] LDH intercalated with borate (Mg_2Al-B-LDH) in powder form was used in a sandy soil and resulted in lower B leaching compared to H_3BO_3 and Ulexite, which are commercial sources of B with high and low solubility, respectively.[13] Additionally, during successive cultivations of sunflower in the same soil, Mg_2Al-B-LDH released sufficient B into the soil solution to support plant growth without B deficiency compared to H_3BO_3 and Ulexite.[13] The use of zinc (Zn) and aluminum (Al) LDH intercalated with borate (ZnAl-LDH) was investigated by Songkhum and coworkers.[7] The use of ZnAl-LDH increased plant growth in association with a conventional fertilizer of nitrogen, phosphorus, and potassium (NPK), but the authors did not evaluate the application of a control treatment, combining NPK and a soluble source of B (*e.g.* H_3BO_3).

It is noteworthy that in all the consulted studies, the nutrient application by LDHs was made in powder form. The hydroxyl groups released from LDHs have an alkaline buffering, which retains the layered structure and decreases the nutrients release rate.[5,6,14] However, the use of LDHs in powder form can increase the exposure of the fertilizer to the soil acidity and decrease the buffering capacity. In fact, the particle size is closely linked to the contact surface between the fertilizer and the soil. Thus, using powder material there will be a direct influence on the dissolution rate, the atmospheric moisture absorption, and the nutrient use efficiency from fertilizers. Moreover, the use of powder fertilizers impairs accurate applications under field conditions.

Biodegradable natural polymers such as starch, ethylcellulose, cellulose acetate, lignin, chitosan, and alginate, have been suggested as matrices to synthesize granular fertilizers.[15–18] Alginate is a low-cost polymer that could be prepared from a group of anionic polysaccharides extracted from brown algae. This natural polymer is composed of residues of β-D-mannuronic acid and α-L-guluronic acid in varying proportions from 1-4 linkages.[18] Alginate has been reported as a matrix for the formation of microspheres to be used in the sustained release of nutrients.[17–19] In a solution containing Ca^{2+} or other polyvalent cations, there is a strong interaction between the cations and the carboxylate groups from the base residual of guluronic acid from alginate. The cations are trapped in a continuous, stable, and thermo-irreversible three dimensional network, whose configuration is like an egg-box.[20,21] Usually, the microspheres are formed by dripping an alginate solution into a Ca^{2+} solution,[17,18] but fertilizer blends can be conveniently obtained by replacing the alginate solution with a homogeneous suspension of alginate/clays, alginate/polymers, and alginate/fertilizers.

The synthesis of alginate microspheres containing LDHs, as an organic–inorganic hybrid nanomaterial, is still incipient and has not been reported in the literature. In theory, these microspheres can provide physical protection for the LDH decreasing the contact surface of LDH and soil, which can modify the LDH chemical characteristics such as reactivity, dissolution, and nutrient release. Thus, the present work aims to: (i) synthesize and chemically characterize alginate microspheres containing magnesium–aluminum LDH intercalated with borate (LDH-B-ALG); (ii) evaluate the "*in vitro*" release and leaching of B; (iii) evaluate, by greenhouse plant cultivations, the potential of the microspheres as B slow release in sandy soil, and compare the results with commercial sources of B such as H_3BO_3 and Ulexite ($NaCaB_5O_6(OH)_6 \cdot 5(H_2O)$).

2 Experimental section

2.1 Materials and methods

2.1.1 Synthesis of magnesium–aluminum layered double hydroxide intercalated with borate. The synthesis of the Mg-Al LDH intercalated with borate (Mg_2Al-B-LDH) was carried out by the constant pH coprecipitation method.[22] A solution of 250 mL containing 1.0 mol L^{-1} of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.5 mol L^{-1} of $Al(NO_3)_3 \cdot 9H_2O$ was added dropwise, under vigorous stirring, into a 500 mL solution of 1.25 mol L^{-1} of H_3BO_3. The solution pH was maintained at 10.0 during the synthesis using a 2.0 mol L^{-1} of NaOH solution. The synthesis was carried out under a N_2 atmosphere to eliminate the influence of atmospheric carbon dioxide. After the synthesis, the solid material was washed with H_2O and dried at 25 °C under vacuum in the presence of silica gel. The H_2O used in the synthesis reactions was deionized (Milli-Q$^{®}$ system).

2.1.2 Synthesis of alginate microspheres containing Mg_2Al-B-LDH. The synthesis of alginate microspheres and Mg_2Al-B-LDH was performed by the complex coacervation method, adapted from Zhang and coworkers.[23] The solution of alginate in water (2% w/v) was prepared under constant stirring for 30 minutes at 25 °C. Immediately afterwards, the powder Mg_2Al-B-LDH was added in a 10 : 1 (w/w) ratio of Mg_2Al-B-LDH:Alginate and stirred for 1 hour at 25 °C. The obtained suspension was then transferred to a burette and dripped (1 drop per second) in a solution containing 5% of $Ca(NO_3)_2$ in water (w/v). Subsequently, the material was filtered, and oven dried at 30 °C for 48 hours. The alginate microspheres containing Mg_2Al-B-LDH was labeled LDH-B-ALG.

With the aim of producing materials with different reactivity and release of B, two different kinds of alginate microspheres containing H_3BO_3 were synthesized. The first one was produced using the same methodology as described above for LDH-B-ALG, using a 10 : 1 (w/w) ratio of H_3BO_3 : Alginate. The alginate microspheres containing H_3BO_3 was labeled BA-ALG. The second one was synthesized with the same ratio between H_3BO_3 and alginate (10 : 1-w/w), but a solution containing 10% of $Ca(NO_3)_2$

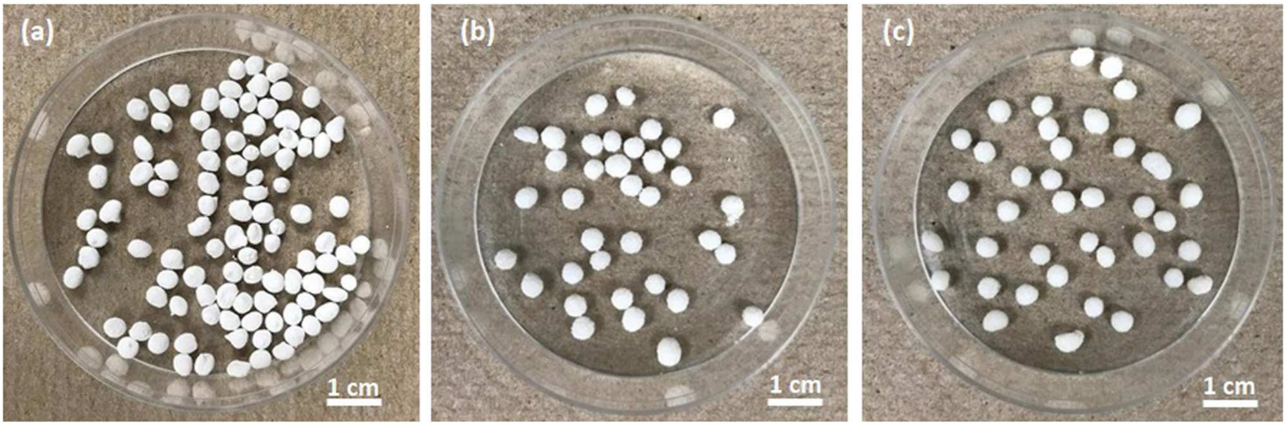

Fig. 1 Images of LDH-B-ALG (a); BA-ALG (b); and BA-ALG2 (c) microspheres. The medium diameter of LDH-B-ALG, BA-ALG, and BA-ALG2 microspheres are 3.40 ± 0.08 mm, 3.42 ± 0.08 mm, and 3.67 ± 0.09 mm, respectively.

in water (w/v) was used. This product was labeled BA-ALG2. The images of the synthesized microspheres (LDH-B-ALG, BA-ALG, and BA-ALG2) are presented in Fig. 1. The size of the microspheres was obtained by the average of twenty microspheres using a digital caliper electronic.

2.1.3 Characterization of materials. Mg_2Al-B-LDH, H_3BO_3, alginate, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite were characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electronic microscopy (SEM). Additionally, the total concentrations of elements were analyzed.

The XRD analyses were performed in a Shimadzu XRD-6000 diffractometer, using a graphite crystal monochromator to select Cu Kα_1 radiation with λ = 1.5406 Å and a step rate from 0.02° s^{-1}, with 2θ angle between 4° and 70°. The ATR-FTIR spectra were recorded with a Jasco spectrometer, model FT/IR-4100, in the range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution and 256 scanning. For SEM analyses, the microspheres were supported on conductive double-sided adhesive tape and a Zeiss EVO 50 scanning electron microscope was used.

The concentrations of B, Ca, Mg, and Al in the Mg_2Al-B-LDH, LDH-B-ALG, BA-ALG, and BA-ALG2 were evaluated by optical emission spectrometer, model Optima 8300. The samples were solubilized in a solution of HNO_3 5 mol L^{-1} using a 1 : 60 ratio of fertilizer:solution (w/v). The concentrations of C, N, and H, in the LDH-B-ALG, BA-ALG, and BA-ALG2 were evaluated by the ignition method in an elemental analyzer, model PerkinElmer Series II 2400.

2.1.4 Boron release test. The B release test was performed and adapted from the ''*in vitro*'' release method, described by Bin Hussein and coworkers.[24] A factorial 2 × 7 × 5 was established with two water buffer solutions (pH value at 6.5 and 7.5), seven collection times (0, 1, 2, 4, 6, 12, and 24 hours), and five B sources (LDH-B-ALG, BA-ALG, BA-ALG2, H_3BO_3, and Ulexite). The experiment was conducted in a randomized complete block design with four replicates. The H_3BO_3 (17.5% of B) and Ulexite (10% of B) were chosen because they are commercial sources of B with high and low solubility, respectively. The buffer solution pH value was adjusted using 0.14 mol L^{-1} of HNO_3 or 0.1 mol L^{-1} of NaOH. The water used in the boron release test was H_2O deionized-Milli-Q system.

Using an Erlenmeyer's flask with 250 mL of capacity, 45 mg L^{-1} of total B from the B sources and 100 mL of the water buffer solution (pH 6.5 and 7.5) were added. At pre-established times (0, 1, 2, 4, 6, 12, and 24 hours), a slight agitation was performed to homogenize the solution and aliquots of 5 mL were withdrawn. Immediately afterwards, 5 mL of the buffer solutions (pH 6.5 and 7.5) were added in order to keep the volume constant. The internal temperature of the incubator was kept at 25 °C. The analyses of B concentration were performed according to the method described by López and coworkers.[25]

2.1.5 Boron leaching in soil columns. A soil sample from a 0–20 cm depth layer of a Dystrophic Yellow Red Latosol, a sandy oxisol,[26] was collected in the region of Três Marias, Minas Gerais, Brazil. The soil samples were homogenized, sieved (<2 mm) and air-dried. The soil had the following physical and chemical properties: clay 270 g kg^{-1}; silt 14 g kg^{-1}; fine sand 470 g kg^{-1}; coarse sand 240 g kg^{-1}; soil bulk density 1.34 g cm^{-3}; total porosity 0.49 m^3 m^{-3}; pH (H_2O) 4.36; B 0.1 mg dm^{-3}; cation exchange capacity 3.99 $cmol_c$ dm^{-3}, and organic carbon total 1%. Lime was applied to the soil in order to reach soil pH values of 6.5 and 7.5. For this purpose, $CaCO_3$ and $MgCO_3$, in the ratio Ca : Mg of 4 : 1 were used. After 30 days of incubation with soil moisture at the field capacity, the soil samples were air-dried and sieved (<2 mm).

The B leaching test, adapted from the method described by Abat and coworkers,[27] was carried out. Syringes (columns) with a diameter of 3 cm and a height of 12 cm were filled with 60 cm^3 of soil. At the bottom of the syringe, glass wool was used to prevent loss of soil. In order to settle the soil sample in the columns, water in an amount corresponding to the volume of soil pores (30 mL) was added and drained from the bottom by a syringe system.

After drainage, a rate of 20 mg dm^{-3} of B was incorporated in the top 0.5 cm of soil in the center of the column. A factorial 2 × 7 × 5 scheme was established with two soil pHs (6.5 and 7.5), seven incubation times (1, 5, 10, 15, 20, 25, and 30 days before leaching) and five B sources (LDH-B-ALG, BA-ALG, BA-ALG2, H_3BO_3, and Ulexite), and a control treatment without the application of B. The experiment was conducted in a randomized complete block design with four replicates.

At 1, 5, 10, 15, 20, 25, and 30 days of incubation, water corresponding to the volume of pores (30 mL) was applied and the leachate was collected. During the leaching test, the soil columns were maintained at 25 °C. The analyses of the B concentrations in the leachate were performed according to the method described by López and coworkers.[25]

2.1.6 Greenhouse experiment. A sequential crop cultivation using responsive B species (sunflower and cotton) was performed to evaluate the efficiency and the residual effect of B sources. The soil was the same used in the leaching test, which was a B-deficient soil (0.1 mg dm^{-3} of B by hot water extraction). A basal fertilization was added for all treatments, giving a total dose per dm^3 of 200 mg of P, 150 mg of K, 60 mg of S, and 100 mg of N. The sources used were KH_2PO_4, $NH_4H_2PO_4$, and $(NH_4)_2SO_4$. At the same time, boron fertilizer treatments were applied at rate of 2 mg dm^{-3} of B. Soil and fertilizers were homogenized and plastic pots were filled with 2 dm^3 of soil.

A factorial 2 × (4 + 1) scheme was established with two soil pHs (6.5 and 7.5), four sources of B (LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite), and a control without application of B. The experimental design was a randomized complete block with four replicates. The BA-ALG2 source was not used in the greenhouse experiments because previous results of "*in vitro*" release and leaching of B showed a similar release to H_3BO_3.

Eight seeds of sunflower (*Helianthus annuus* – ALTIS 99 hybrid) were sown per pot. After seven days, the seedlings were thinned to the four most uniform ones in each pot. Further liquid basal nutrients were added twice, in 20 mL of solution per pot, resulting in a total basal nutrient dose per dm^3 soil of 100 mg of N as urea, 1.32 mg of copper (Cu) as $CuSO_4 \cdot 5H_2O$, 1.55 mg of iron (Fe) as $FeSO_4 \cdot 7H_2O$, 3.66 mg of manganese (Mn) as $MnSO_4 \cdot H_2O$, 0.15 mg of molybdenum (Mo) as $(NH_4)_6Mo_7O_{24}$, and 4.0 mg of Zn as $ZnSO_4 \cdot 7H_2O$. Ten days after emergence, plants cultivated in treatments at soil pH 7.5 presented visual symptoms of cationic micronutrient deficiency (Cu, Fe, Mn and Zn). Thus, the treatments at soil pH 7.5 received an extra application of cationic micronutrients (1.32 mg dm^{-3} of Cu, 1.55 mg dm^{-3} of Fe, 3.66 mg dm^{-3} of Mn, and 4.0 mg dm^{-3} of Zn). Pots were watered daily with distilled water to 80% of soil field capacity. After 30 days of cultivation, sunflower plants were harvested by cutting the stems at the soil surface. Plant biomass was dried at 65 °C for 96 hours and weighed to obtain the dry matter (DM). Samples of 50 g of soil from each experimental unit were collected after the first cultivation to determine the availability of B.[28]

Rates of 1.0 and 2.0 ton ha^{-1} of lime were applied before the second cultivation to keep the soil pH values at 6.5 and 7.5, respectively. The lime used was the same described in the B leaching test. The soil was wetted to 80% of field capacity and incubated for 30 days in plastic bags at 25 °C. At 45 days after harvesting of the sunflower, eight seeds of cotton (*Gossypium vitifolium* – TMG 47 B2RF hybrid) were sown per pot. Five days after plant emergence, each pot was thinned to two plants. No B fertilization was applied, requiring the plants to use the soil residual B. The other nutrients were applied at the same rate and sources as in the first cultivation. Pots were watered with distilled water to maintain 80% of soil field capacity. At 50 days after seeding, the plants were harvested, and the plant biomass was dried at 65 °C for 96 hours and weighed. This sequential cultivation produced results at 30 and 125 days from the B application.

The plant biomass was ground and the B concentration in the plant tissue was analyzed according to the method described by Embrapa.[29]

2.2 Statistical analysis

Data were submitted to a one-way analysis of variance. The differences between the treatment means were evaluated using the Tukey's and least significant difference adjustment at $p \leq 0.05$. The *R* environment was used in the statistical analysis.[30]

3 Results and discussion

3.1 Characterization of materials

The XRD patterns of Mg_2Al-B-LDH, H_3BO_3, alginate, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite are presented in Fig. 2. The XRD pattern of Mg_2Al-B-LDH is characteristic of the hydrotalcite-type compounds with basal peaks (00*l*) [(003), (006) and (009)] at 7.2, 15.6 and 23.6 2θ (degrees), respectively (Fig. 2a). The basal spacing for Mg_2Al-B-LDH, calculated by Bragg's equation ($n\lambda = 2dhkl\sin\theta$), was 12.0 Å, and is related to the intercalation of tetraborate ions $[B_4O_5(OH)_4]^{2-}$ between the layers of LDH.[31] The XRD patterns from the commercial sources (H_3BO_3 and Ulexite) showed well-defined peaks due to the crystallinity of the materials (Fig. 2b and g). Conversely, in the XRD pattern of the alginate, the weak and broad peak 2θ (degrees) at 13.3 indicates the amorphous structure of this polymer (Fig. 2c).[32] The diffractogram of LDH-B-ALG presented the same (*hkl*) basal peaks as Mg_2Al-B-LDH [(003), (006) and (009)], confirming that the powder LDH was successfully incorporated into the alginate (Fig. 2d). In Fig. 2d, the additional basal peaks marked as *(003) and *(006) in the diffractogram, are quite possibly due to a new phase originating from the partial ion-exchange reaction between borate intercalated into the LDH and nitrate anions, since the $Ca(NO_3)_2$ is used to synthesize the microspheres. For this phase, the basal spacing value (*d*) of 8.7 Å was determined using Bragg's equation ($n\lambda = 2dhkl\sin\theta$), and the average values of 2θ of the basal peaks *(00*l*). This result corresponds with the previous literature published on the intercalation of nitrate anions into LDH.[33,34] The XRD patterns for BA-ALG and BA-ALG2 showed the same peaks as H_3BO_3, indicated by # in Fig. 2e and f. It is noteworthy that the XRD patterns showed that Mg_2Al-B-LDH (powder) and H_3BO_3 (acid), were successfully incorporated into the alginate. However, the produced blends (LDH-B-ALG, BA-ALG, and BA-ALG2) presented a lower crystallinity and phase purity than Mg_2Al-B-LDH and H_3BO_3, which can be explained by the amorphous structure of the alginate.

The ATR-FTIR spectra of Mg_2Al-B-LDH, H_3BO_3, alginate, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite are shown in Fig. 3.

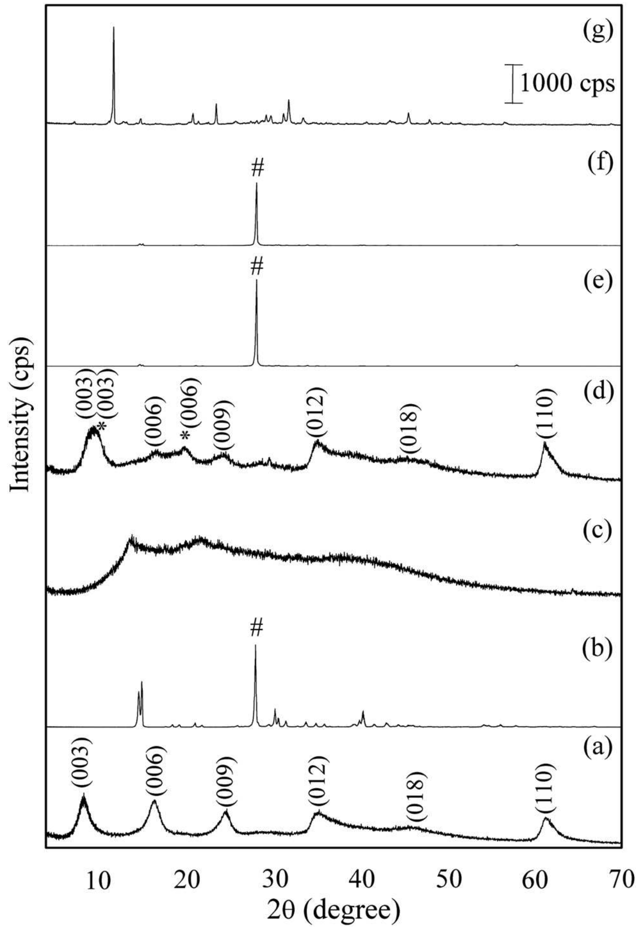

Fig. 2 Diffractograms of Mg_2Al-B-LDH (a); H_3BO_3 (b); alginate (c); LDH-B-ALG (d); BA-ALG (e); BA-ALG2 (f); and Ulexite (g). #: peaks refer to the crystallinity of H_3BO_3 and the presence of H_3BO_3 into the alginate. *(003) and *(006): peaks refer to the intercalation of nitrate ions in the Mg_2Al-B-LDH.

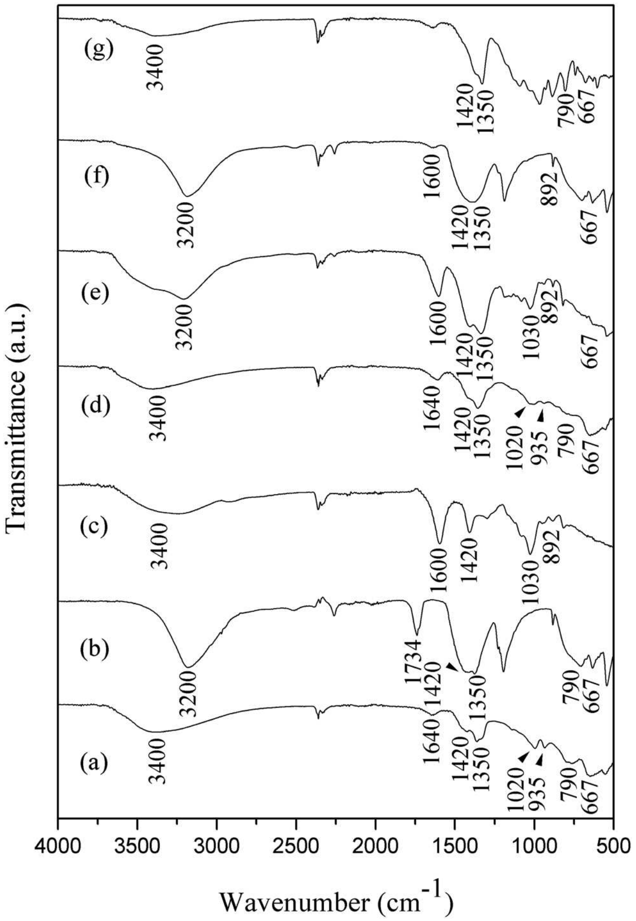

Fig. 3 Attenuated total reflectance Fourier transform infrared spectroscopy spectra of Mg_2Al-B-LDH (a); H_3BO_3 (b); alginate (c); LDH-B-ALG (d); BA-ALG (e); BA-ALG2 (f); and Ulexite (g).

The presence of the broad band in the wavenumber range from 3600 cm^{-1} to 3200 cm^{-1} is due to the O–H stretching of the hydroxyl groups and/or H_2O molecules (Fig. 3a–g).[5,35] The O–H stretching of the hydroxyl groups and/or H_2O molecules is also observed at 1640 cm^{-1} in the spectra of Mg_2Al-B-LDH and LDH-B-ALG (Fig. 3a and d).[7] Bands in the wavenumber range between 1600 and 500 cm^{-1} are attributed to the various vibration modes related to the presence of borate anions. More specifically, the bands at 1350 cm^{-1}, 1020 cm^{-1}, 935 cm^{-1}, 790 cm^{-1}, and 667 cm^{-1} are attributed to the vibrational modes ν_{as}(B3–O), ν_{as}(B4–O), ν_s(B3–O), ν_s(B4–O), and ν_s(B3–O), respectively (Fig. 3a, b, d, e, f and g).[31] It is noteworthy that these specifics bands were not observed in the ATR-FTIR spectra of the alginate (Fig. 3c). The ATR-FTIR spectra of alginate, BA-ALG, and BA-ALG2 showed peaks at 1600 cm^{-1}, 1030 cm^{-1}, and 892 cm^{-1}, which are due to the symmetric COO^- stretching vibration of the carboxylate group, the C–O(H) stretching vibration, and the glycosides bonds stretching vibration, respectively (Fig. 3c, e and f).[19,32] The characteristic absorption band observed at 1734 cm^{-1} for H_3BO_3 is due to the C=O stretching of the –COOH group (Fig. 3b).[19] The spectra also showed peaks at 1420 cm^{-1} for all materials which are attributed to the $-COO^-$ symmetric stretching vibrations.[19] According to the ATR-FTIR spectra, it is possible to conclude that Mg_2Al-B-LDH and H_3BO_3 are present in the LDH-B-ALG, BA-ALG and BA-ALG2, since there are similar bands between the precursor and synthesized materials.

The morphologies of the Mg_2Al-B-LDH, H_3BO_3, alginate, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite were analyzed by SEM (Fig. 4). The Mg_2Al-B-LDH presented spherical aggregate particles with diameters varying between 1 and 5 μm (Fig. 4a). SEM images from H_3BO_3 and Ulexite showed a crystalline morphology (Fig. 4b and d). Conversely, the surface of the alginate displays a smooth morphology with non-crystalline aggregate particles (Fig. 4c). SEM images from LDH-B-ALG, BA-ALG, and BA-ALG2 showed microspheres with diameters varying between 2500 and 3000 μm (Fig. 4e, g, and i). There are cracks in the LDH-B-ALG microspheres, in contrast with those of BA-ALG and BA-ALG2. This may indicate the possibility of different interactions between the alginate/H_3BO_3 and alginate/Mg_2Al-B-LDH. Future studies should be performed to clarify the different interactions between alginate and LDHs. The Mg_2Al-B-LDH and H_3BO_3 were also seen in the images obtained from the

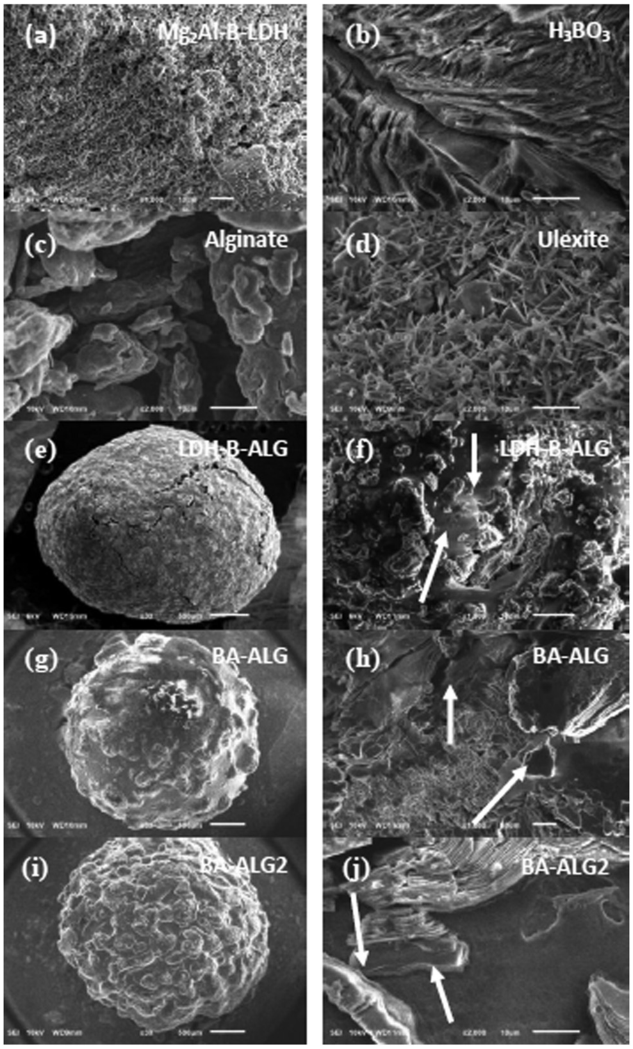

Fig. 4 SEM images of the surface morphology of Mg_2Al-B-LDH (a); H_3BO_3 (b); alginate (c); Ulexite (d); LDH-B-ALG (f); BA-ALG (h); and BA-ALG2 (j); and intact microspheres of LDH-B-ALG (e); BA-ALG (g); and BA-ALG2 (i). Arrows indicated a coating and distribution of Mg_2Al-B-LDH and H_3BO_3 in the alginate matrix.

Table 1 Total concentration of boron, calcium, magnesium, aluminum, carbon, nitrogen, and hydrogen in the Mg_2Al-B-LDH, LDH-B-ALG, BA-ALG, and BA-ALG2

	B	Ca	Mg	Al	C	N	H
Fertilizer	%						
Mg_2Al-B-LDH	5.06	—	14.99	8.68	—	—	—
LDH-B-ALG	4.20	2.85	12.77	7.49	2.68	1.80	1.39
BA-ALG	13.82	2.42	—	—	1.05	0.82	1.43
BA-ALG2	9.40	6.10	—	—	0.71	1.17	1.50

The B total concentration in the H_3BO_3 and Ulexite (commercial sources) are 17.5 and 10% of B, respectively.

surface morphology of LDH-B-ALG, BA-ALG, and BA-ALG2 (Fig. 4f, h and j). The Fig. 4f, h and j showed a coating and distribution of Mg_2Al-B-LDH and H_3BO_3 in the alginate matrix (indicated by arrows). The SEM of microspheres indicates a physical protection of Mg_2Al-B-LDH and H_3BO_3 by an alginate polymeric net. The physical protection can produce a barrier to reduce the rate of water diffusion into to the microspheres and decrease the release of B to outside of the microspheres, indicating good slow-release properties.

The total concentration of B in the Mg_2Al-B-LDH was 50.60 g kg^{-1} of B per LDH, corresponding to 5.06% of B (Table 1). Previous research has reported values of 14.00, 37.90, 25.50, and 45.23 g kg^{-1} of B for MgAl-CO_3-LDH, MgAl-NO_3-LDH, calcined MgAl-LDH, and non-calcined MgAl-LDH, respectively.[6,36–38] The total of B determined for Mg_2Al-B-LDH indicated a higher incorporation of B, which is an important consideration when studies are conducted with micronutrients due to the small quantities required by plants. The LDH-B-ALG presented 4.20% of B, indicating that the formation of the microspheres did not significantly decrease the total concentration of B in the fertilizer. In addition, this fertilizer has in its composition three other nutrients (2.85% of Ca, 12.77% of Mg, and 1.80% of N), which can also benefit plant development (Table 1). The total B concentration in H_3BO_3 used for the synthesis of microspheres was 17.50%. The BA-ALG and BA-ALG2 presented 13.85 and 9.40% of B, respectively (Table 1), indicating the lowest and highest decrease of the total concentration of B in the fertilizers. The differences in Ca and B concentrations between BA-ALG and BA-ALG2 can be attributed to process of synthesis, in which required solutions containing 5 and 10% of $Ca(NO_3)_2$ in water (w/v), respectively (Table 1).

3.2 Boron release test

The cumulative release of B from H_3BO_3, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite in buffer solution at pH values of 6.5 and 7.5 are shown in Fig. 5. In the first collection, the total B released at pH 6.5 from H_3BO_3, BA-ALG, BA-ALG2, Ulexite, and LDH-B-ALG were equivalent to 4.0, 5.0, 3.7, 0.7, and 0.6%, respectively of the total B. At pH 7.5, in the first collection, the total B released was 2.8, 4.9, 4.4, 0.9, and 0.7% from H_3BO_3, BA-ALG, BA-ALG2, Ulexite, and LDH-B-ALG, respectively. In the buffer solution at pH value 6.5, with the use of BA-ALG2 and H_3BO_3, 100% of B was released after 1 hour, and with the application of BA-ALG, Ulexite, and LDH-B-ALG, 100% of B was released after 2, 6, and 24 hours, respectively. In the buffer solution at pH value 7.5, with the use of BA-ALG and H_3BO_3, 100% of B was released after 2 hours, and after 1, 6, and 24 hours with the application of BA-ALG2, Ulexite, and LDH-B-ALG, respectively.

There was no effect of the pH value on the B release for the H_3BO_3, BA-ALG, BA-ALG2, and Ulexite sources (Fig. 5). However, the pattern of B release by LDH-B-ALG was lower at pH 7.5. After 12 hours of LDH-B-ALG application, 91% and 84% of the B at pH 6.5 and 7.5 were released, respectively. The pH increase in the buffer solution contributes to the stability of LDHs structure, allowing a more slow release of the intercalated anions, and even of the cations that make up the layered structure.[5,39,40]

LDH-B-ALG presented a cumulative B release much lower than all the other sources of B used in this study (Fig. 5). Benício and coworkers compared a cumulative release of P using multiple

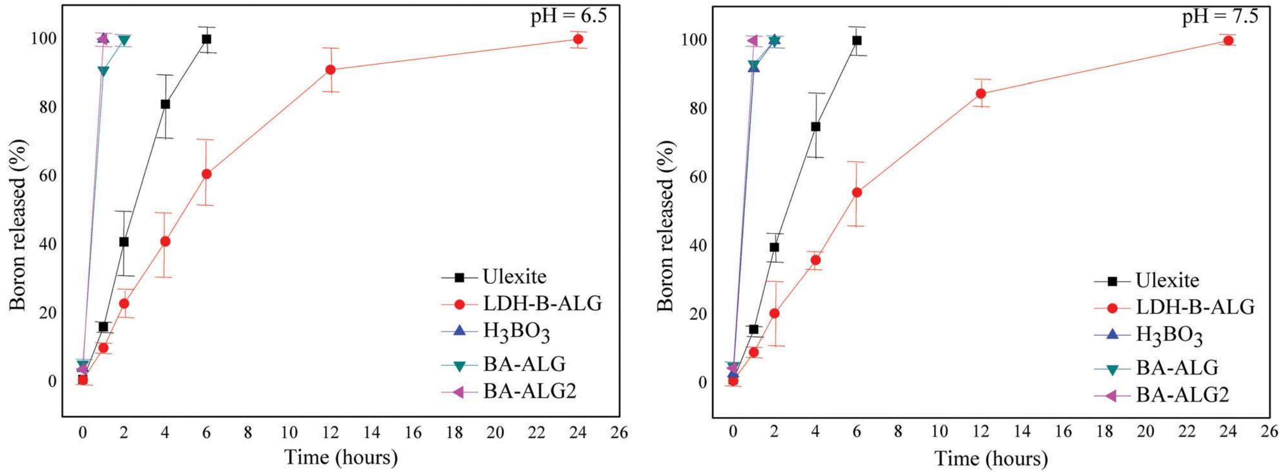

Fig. 5 Cumulative release of B from H_3BO_3, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite in water buffer solution at pH 6.5 and 7.5.

collection times and two P sources (LDH-P and triple superphosphate-TSP).[5] The P released from LDH-P was much lower than TSP (soluble source) at all collection times. The authors attributed the lower release due to the protection of phosphate anions in the interlamellar spaces of LDHs.[5]

Alginate polymers can also present slow release properties when combined with other materials such as starch or clay.[18,19] Thus, the results presented by LDH-B-ALG in our study are attributed to both the protection of borate anions found in the interlamellar spaces of LDHs and also to the LDH physical protection by the alginate polymer.

3.3 Boron leaching in soil columns

As expected, the leachate had more B when H_3BO_3 was applied. For the first leaching event, about 37% and 19% of the total B applied as H_3BO_3 was leached into the soil pH 6.5 and 7.5, respectively. However, after 10 and 15 days of incubation time, BA-ALG2 had similar amount leached to H_3BO_3 in soil pH values at 6.5 and 7.5, respectively (Fig. 6). These results showed a higher B leaching profile from H_3BO_3 and BA-ALG2, which can decrease the B accumulation in the soil, consequently reducing the plants B absorption and fertilizer efficiency.

There was an effect of soil pH on B release (Fig. 6). The percentage of B leached from H_3BO_3, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite were lower for soil pH 7.5. After 15, 20, and 25 days from the respective application of BA-ALG2, H_3BO_3, and BA-ALG in soil pH 6.5, 100% of the B was recovered in the leachate. For Ulexite and LDH-B-ALG, after 30 days of application at soil pH 6.5, 90% and 74% of B was recovered, respectively. At soil pH 7.5, 100% of B from BA-ALG2 and H_3BO_3 were leached after 25 and 30 days of source application, respectively. At 30 days after source application at soil pH 7.5, 95%, 74%, and 59% of B from BA-ALG, Ulexite, and LDH-B-ALG was leached, respectively. These results suggest a higher formation of borate anions at an alkaline soil pH, which results in a higher affinity with the solid phase of the soil,[1,41] decreasing the B leaching.

Mg and Al LDH intercalated with Borate anions (Mg_2Al-B-LDH) in powder form has been successfully used as a matrix for sustained release of B in a sandy soil with lower mobility of nutrient and that are prone to B leaching.[13] The application of

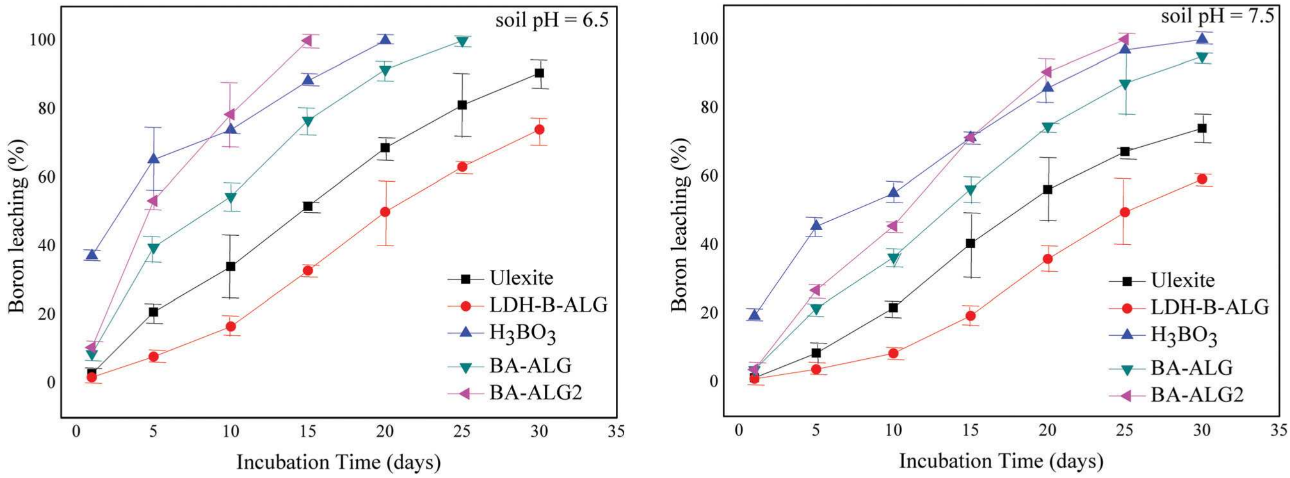

Fig. 6 Cumulative leaching of boron from H_3BO_3, LDH-B-ALG, BA-ALG, BA-ALG2, and Ulexite at soil pH 6.5 and soil pH 7.5.

Mg_2Al-B-LDH resulted in a B leaching much lower compared to H_3BO_3 and the authors highlighted the use of Mg_2Al-B-LDH as a promising slow release B fertilizer. Comparing the results of Castro and coworkers and the present study at soil pH 6.5, in the first incubation time (1 day), Mg_2Al-B-LDH and LDH-B-ALG leached 9.5% and 2% of B, respectively.[13] After 30 days from the respective application of Mg_2Al-B-LDH and LDH-B-ALG, 96% and 74% of B were recovered in the leachate. These results suggested a lower leaching pattern by LDH-B-ALG compared Mg_2Al-B-LDH, showing an advantage in producing LDH microspheres compared to the LDH in powder form.

The slow release profile of B from LDH-B-ALG resulted in a significant reduction in the leached B compared with all the sources of B for both soil pHs. The low leaching potential of LDH-B-ALG is an important fertilizer property to increase the time of B residency in the root zone, consequently increasing the likelihood of B uptake by plants. According to Degryse and coworkers, the slow release sources can prolong the B availability and reduce leaching losses in the soil, thus allowing the use of lower rates or a decrease in the frequency of fertilizer applications.[1] In regions with sandy soils, such as the one used in our study, combined with high rainfall, the results indicate the advantage of LDH-B-ALG as a new fertilizer to supply B to plants.

3.4 Greenhouse experiment

There was no significant effect of B sources on shoot dry matter of sunflower, cotton and total (sunflower + cotton) (Table 2 and Fig. 7a–d). There were significant effect of B fertilizer treatments on the B uptake in the shoot of sunflower and cotton (Table 2). Applying B as H_3BO_3, LDH-B-ALG, BA-ALG, and Ulexite resulted in a higher shoot uptake of B in sunflower and cotton compared with the control treatment with no added B and on the total B uptake in the soil pH 6.5.

Table 2 Dry matter and boron uptake in the plant shoots as a function of the applied B sources in first (sunflower), second (cotton), and total cultivation

	Dry matter (g pot^{-1})		B uptake (mg pot^{-1})	
Source	Soil pH 6.5	Soil pH 7.5	Soil pH 6.5	Soil pH 7.5
First cultivation (sunflower)				
H_3BO_3	10.68aA	3.18aB	2.79aA	0.78aB
LDH-B-ALG	10.62aA	3.03aB	3.37aA	0.84aB
BA-ALG	10.83aA	3.20aB	2.95aA	0.81aB
Ulexite	10.40aA	2.46aB	3.48aA	0.55aB
Control	10.83aA	2.27aB	1.46bA	0.56aB
Second cultivation (cotton)				
H_3BO_3	11.60aB	12.68aA	2.49bA	2.12bcB
LDH-B-ALG	12.27aB	12.36aA	2.97aA	3.03aA
BA-ALG	11.76aB	12.72aA	2.61abA	1.87cB
Ulexite	12.22aB	12.77aA	2.65abA	2.32bB
Control	11.91aB	13.38aA	1.37cA	1.33dA
Total				
H_3BO_3	22.28aA	15.86aB	5.28bA	2.90bB
LDH-B-ALG	22.89aA	15.39aB	6.34aA	3.87aB
BA-ALG	22.59aA	15.92aB	5.56abA	2.68bcB
Ulexite	22.62aA	15.23aB	6.13abA	2.87bcB
Control	22.74aA	15.65aB	2.83cA	1.89cB

Lowercase letters compare the effect of B sources in each soil pH. Uppercase letters compare the effect of the soil pH in each B source. Equal letters do not differ statistically at the level of 5% by Tukey test.

There was an effect of soil pH on the sunflower total dry matter and B uptake (Table 2). Total dry matter and B uptake from B sources were lower at soil pH 7.5 than 6.5 (Fig. 7a and b). This effect can be attributed to a decrease in the availability of cationic micronutrients in the soil, such as Cu, Fe, Mn and Zn.[42,43] After 10 days of emergence, the plants cultivated in treatments at soil pH 7.5 presented visual symptoms of a deficiency of Cu, Fe, Mn, and Zn.

The total B uptake of plants supplied with LDH-B-ALG at soil pH 7.5 was significantly higher than that of the plants supplied with other sources, and can be attributed to a slower nutrient release by LDHs in an alkaline pH.[5,6,14,39,40] The increase in the soil pH can contribute to the formation of micro sites with higher pH values, which also increase the structural stability of LDHs in the soil.[5] The increase in the stability of LDHs, can lead to a gradual release of nutrients from LDHs and increase the nutrient absorption by plants in successive cultivations.

The availability of B in the soil after the first cultivation without micronutrient replenishment was not significant among H_3BO_3, LDH-B-ALG, BA-ALG, and Ulexite, and significantly higher than the control treatment. The available B at soil pH 6.5 was 1.51, 1.79, 1.89, 1.48, and 0.09 mg dm^{-3} for H_3BO_3, LDH-B-ALG, BA-ALG, Ulexite, and the control treatment, respectively. For soil pH 7.5 the available B was 1.70, 1.83, 1.72, 1.70, and 0.16, for H_3BO_3, LDH-B-ALG, BA-ALG, Ulexite, and the control treatment, respectively. Castro and coworkers applied a powdered LDH intercalated with borate (LDH-B) and H_3BO_3 into a clayey soil.[6] The sources resulted in a similar soil B availability, growth, and B uptake by sunflower plants.[6]

The results of the soil B availability suggest that LDH-B-ALG has a similar solubilization to the other sources in the greenhouse experiments where soil moisture is maintained every day in field capacity. In annual crops, which require an immediate availability of nutrients in the soil, these results confirm that the release profile of B from LDH-B-ALG did not affect the accumulation of B by plants. The results from our study corroborated with research from Bernardo and coworkers, in which Mg-Al-PO_4-LDH and monoammonium phosphate (MAP) sources were used to supply P to wheat (*Triticum aestivum*).[8] The wheat P uptake was similar for the applied sources, making the Mg-Al-PO_4-LDH a viable source to supply P in a short period of time, similarly to MAP.

According to Degryse and coworkers, the release of nutrients from slow-release sources should be slow enough to decrease leaching losses and plant toxicity, but fast enough to provide nutrients when the plants are in need.[1] The slow release of B from LDH-B-ALG, compared with all the sources applied in the B release and leaching tests (Fig. 5 and 6), suggests a potential increase in the B accumulation in the root zone and fertilizer use efficiency from LDH-B-ALG. At the same time, LDH-B-ALG showed a release of B into the soil and uptake by plants similar to other sources. Thus, the results from our study corroborate with the assumptions proposed by Degryse and coworkers to obtain the ideal slow-release fertilizer.[1]

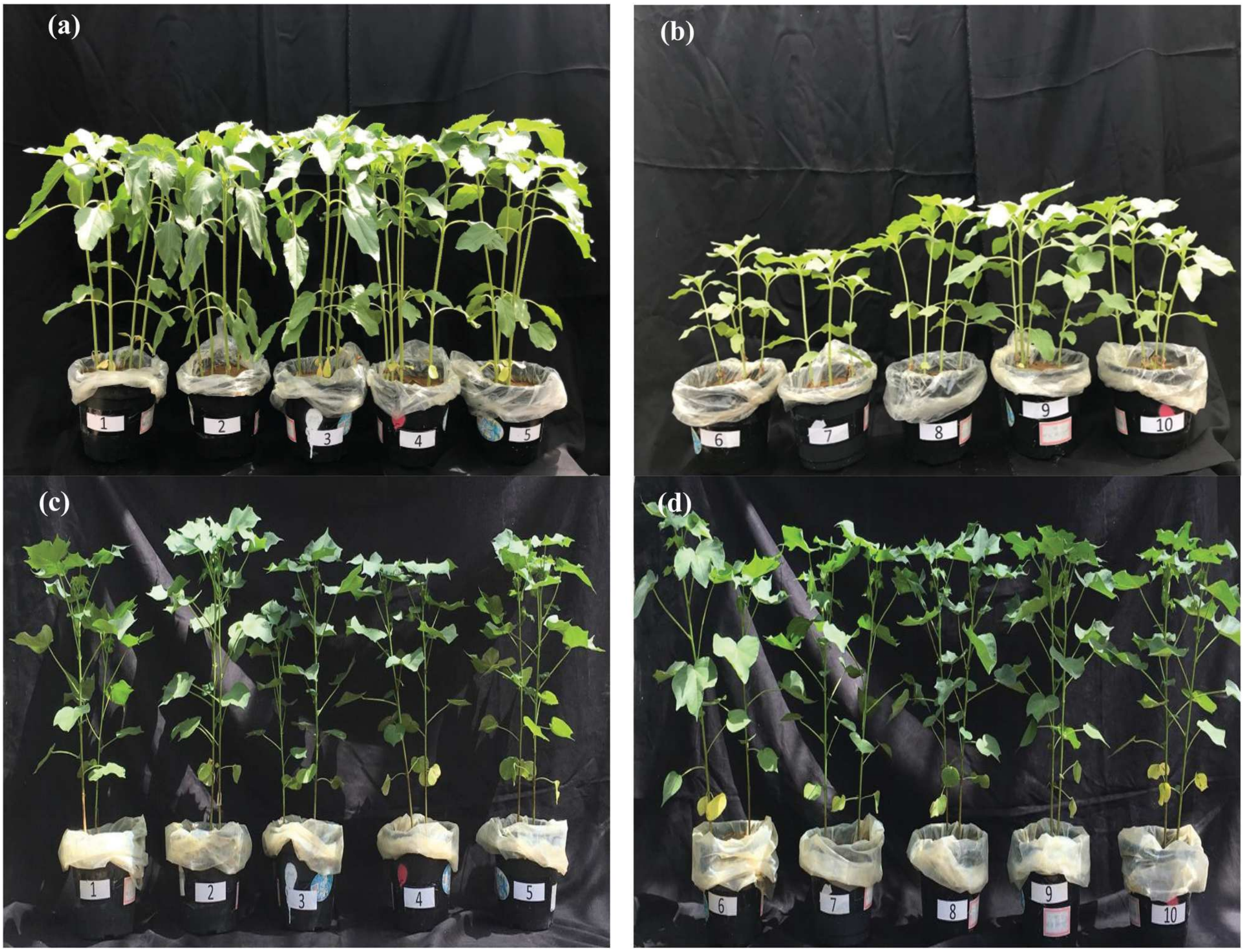

Fig. 7 Response of the sunflower (a and b) and cotton (c and d) plants as a function of the applied B sources at soil pH 6.5 (a and c) and 7.5 (b and d). From left to right, the pots correspond to Ulexite, H_3BO_3, LDH-B-ALG, BA-ALG and control treatments.

It is noteworthy that Ulexite is the commercial borate fertilizer with a slow release of B, which is recommended for soils prone to leaching. The results from the B release and leaching tests showed a lower release and leaching of B from LDH-B-ALG compared to Ulexite. At the same time, LDH-B-ALG provided B to plants with the same efficiency as Ulexite in soil of pH 6.5, and with superior efficiency in soil of pH 7.5. Thus, our results showed that LDH-B-ALG would be the most recommended fertilizer for areas with high leaching where slow release sources are required.

4 Conclusions

LDH-B-ALG, BA-ALG, and BA-ALG2 microspheres were successfully synthesized and characterized by XRD, ATR-FTIR, and SEM. The chemical characterization for LDH-B-ALG, BA-ALG, and BA-ALG2, showed that Mg_2Al-B-LDH (powder) and H_3BO_3 were successfully incorporated into the alginate polymer.

The B release and leaching were much lower from LDH-B-ALG compared to H_3BO_3, BA-ALG, and BA-ALG2. LDH-B-ALG was solubilized similarly in the soil compared to the other B sources in greenhouse experiments. In annual crops, which require an immediate availability of nutrients in the soil, these results confirm that the release profile of B from LDH-B-ALG did not affect the accumulation of B by plants.

The lower release and leaching from LDH-B-ALG improved the accumulation of B in the root zone, consequently increasing the fertilizer efficiency and the plant's B uptake. In sandy soils with low organic matter combined with high precipitation, the results validated the use of LDH-B-ALG as a new slow release fertilizer of B for plants with the micronutrient release adjusted according to the plant's requirements.

Conflicts of interest

There are no conflicts to declare.

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CHAPTER 4

ALGINATE BEADS CONTAINING LAYERED DOUBLE HYDROXIDE INTERCALATED WITH BORATE: A POTENTIAL SLOW-RELEASE BORON FERTILIZER FOR APPLICATION IN SANDY SOILS

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Alginate beads containing layered double hydroxide intercalated with borate: a potential slow-release boron fertilizer for application in sandy soils†

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Boron (B) is very soluble and mobile in soil, and for this reason, it can be easily leached when applied as boric acid (H_3BO_3), particularly in sandy soils. High application rates of B may be toxic to plants. Alginate beads containing layered double hydroxides intercalated with borate (LDH-B-ALG) can potentially minimize the B leaching in soils and reduce the toxicity to plants. The aims of this work were to evaluate the leaching of B in sandy soils from different B sources such as H_3BO_3, Ulexite, and alginate beads containing H_3BO_3 (BA-ALG), and LDH-B-ALG, and investigate the bioavailability of B from these sources in consecutive cultivations of plants. The LDH-B-ALG was synthesized, characterized, and evaluated through the B leaching test in sandy soil. For the leaching column study, the B sources were homogenized with the soil, and incubated before leaching. Sunflower and cotton were cultivated for two seasons in a greenhouse experiment without leaching. Additionally, a greenhouse experiment with leaching was carried out, in which sunflower and cotton were sequentially cultivated after B leaching. In the leaching tests, throughout the incubation time, the percentage of B leached from LDH-B-ALG was significantly lower compared to other B commercial sources. In a greenhouse experiment with leaching, the residual concentration of B in the soil after first cultivation was 1.57, 0.73, 0.66, and 0.61 mg dm^{-3} of B for LDH-B-ALG, Ulexite, H_3BO_3, and BA-ALG treatments, respectively. The residual B in the soil was significantly higher for LDH-B-ALG compared to the other B sources after first cultivation, and, resulted in a higher B uptake in shoots and total (shoots and roots) for the cotton (second cultivation) and for the sum of sunflower and cotton (total cultivation). These results suggest that LDH-B-ALG can improve the B accumulation in topsoil, the fertilizer efficiency, and also B uptake by plants.

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1 Introduction

Boric acid (H_3BO_3) and sodium borate ($B_4O_7Na_2{\cdot}10H_2O$) are fertilizers commonly used to supply boron (B) to crops. The high solubility of these sources can increase the B toxicity in seedling and plants and lead to leaching losses in the soil, consequently decreasing the time of B residency in the root zone.[1] In the specific case of sandy soils with low organic matter, these soils are prone to B leaching which can result in B deficiency in plants.[1] This problem is exacerbated when soluble sources of B are used. Thus, new formulations of borated fertilizers with moderate or low solubility can potentially increase the B retention in the soil and improve the synchronization between the B release into the soil solution and B uptake by plants.

Slow- and controlled-release fertilizers were made available since the early 1950s and have been extensively studied due to the potential increase of fertilizer use efficiency when compared to soluble sources.[2] These fertilizers can increase the time of nutrient residency in the topsoil, reduce the rates and frequency of fertilizer application and minimize potential adverse effects with overdosage.[3,4] In recent years, the development of nanomaterials, such as the layered double hydroxides (LDHs), expanded the alternatives to obtain new formulations of slow-release fertilizers.[5–11] LDHs, also called hydrotalcite-type compounds, can be structurally described as a stack of positively charged layers with hydrated anions in the interlamellar domain. These anions, along with water molecules, are responsible for neutralizing the positive charges in their layers.

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They are also called insertion compounds, given the characteristic of a host matrix for the storage of several species. LDHs have the general formula $[M^{2+}{}_{(1-x)}\ M^{3+}{}_x(OH)_2](A^{n-})_{x/n}\cdot zH_2O$, where, M^{2+} is a bivalent metal ion, such as Ca^{2+}, Mg^{2+}, and Zn^{2+}, M^{3+} is a trivalent metal ion, such as Fe^{3+}, Al^{3+}, and Mn^{3+}, and A^n is the interlamellar anion. The LDH structure is similar to the brucita mineral $[Mg(OH)_2]$, with the Mg^{2+} located in the center of octahedra with hydroxyls at the vertices, forming flat and neutral layers, kept stacked by means of hydrogen bonds.[12]

LDH-based materials and micro/nanostructures are important topics in materials and applied chemistry fields and attract broad attention in this field, in which several strongly related studies have been published.[13–18] LDHs have received attention because of their ability to intercalate a wide range of species. LDHs have been used to intercalate isophthalic acid as the guest into the interlayer gallery of Zn–Al-LDH, a new type of high-efficiency light energy transfer system, in which the new material showed an ultrathin-nanosheet morphology and also exhibited well-defined up-conversion phosphorescence and reversible temperature-responsive emission.[14] In the same type of Zn–Al-LDH matrix, Gao and coworkers intercalated different organic carboxylic molecules (namely benzoic acid, isophthalic acid, trimesic acid, pyromellitic acid, and mellitic acid) in order to achieve a confined triplet exciton for high-efficiency $^1O_2$ generation.[17] Due to the combination of the effective $^1O_2$ generation and 2D ultrathin nanosheets, *in vitro* tests were used to verify the superior anti-cancer properties of isophthalic acid/LDH with an inhibitory concentration (IC_{50}) of 0.153 μg mL^{-1}.[17] Also, LDHs were synthesized for different purposes such as nickel–chromium layered double hydroxide nanosheets as a new system more efficient for bifunctional water splitting electrocatalysts,[18] and long-afterglow thin films produced by a hydrogen-bonding layer-by-layer assembly process (*via* the alternating deposition of a 1,2,4,5-benzenetetracarboxylic acid/LDH nanosheet suspension and the polyacrylic acid solution for *n* cycles), which demonstrated high polarization and up-conversion room-temperature phosphorescence, as well as enhanced quantum yields and luminescence lifetimes.[15] In the environment field, the serious air-pollution problem with volatile organic compounds (one of the major pollution sources of air contamination) stimulated Gao and Yan to synthesize 2D LDH materials as the basic building blocks to obtain inorganic/organic hybrid room-temperature phosphorescence films.[16] The LDH-based hybrid thin films were synthesized by incorporating trimellitic acid into a LDH 2D gallery and then using layer-by-layer assembly with polyacrylic acid. The room-temperature phosphorescence systems showed reversible responses to volatile organic compounds (such as pyridine and nitrobenzene) with high sensitivity and selectivity.[16] In recent work, Arif and coworkers, aiming to obtain a substitute synthesis for the Haber Bosch process, produced nanotubes of CoVP@NiFeV-LDHs heterostructures as an electrocatalyst for the nitrogen reduction reaction.[13] This new material provided highly rich surface-active sites for the adsorption and reduction of nitrogen to NH_3. The authors highlight that CoVP@NiFeV-LDHs presented an excellent electrocatalytical nitrogen reduction reaction conversion efficiency, high average NH_3 yield rate and good selectivity and stability under ambient conditions.[13]

In agriculture, LDHs are used for the inclusion of herbicides, plant growth hormones, pesticides and nutrients such as nitrate, phosphate, and borate.[7,8,19–22] The release profile of the nutrients intercalated in LDHs is highly dependent on the pH value of the soil solution. Thus the decrease in the pH value can increase the nutrient release.[8,21] Most of the studies reported in the scientific literature describe the use of LDHs in the soil exclusively in powder form. The application of LDHs in powder form can increase the specific surface area and consequently the exposure of the fertilizer to soil acidity, accelerating the solubility and release of nutrients at rates similarly to soluble sources.[5,21] In addition, achieving an uniform distribution of powdered fertilizers under field conditions can be challenging and requires appropriate fertilizer applicators.

Hybrid inorganic–organic materials are promising systems to obtain structures for a range of applications due to the improved properties based on the combination of different species. Biodegradable natural polymers such as ethylcellulose, cellulose acetate, starch, lignin, chitosan, and alginate have been suggested as matrices to synthesize hybrid inorganic–organic granular fertilizers and to obtain blends with slow-release properties.[23–26] Alginate polymers have been reported as a matrix to synthesize beads containing nutrients due to their relatively low cost (US$ 0.06 per g), easiness of manipulation and chemical stability.[3,25,26] The concept of synthesis of microspheres is to obtain new fertilizers with a slower release rate of nutrients than conventional soluble sources. The synthesis of alginate microspheres containing LDHs may be an alternative to provide physical protection for the LDH structure. Alginate microspheres can decrease the specific surface area of powdery LDH and exposure of the LDH to soil charges, leading to a decrease in the rate of nutrient release from LDHs into the soil.

Particularly for B, studies with LDHs as a new B slow-release source are still incipient. Our previous studies with layered materials led to the development of slow-release B fertilizers using LDHs intercalated with B as matrices or mixing them with the alginate polymer to form beads. Magnesium (Mg) and aluminum (Al) LDH intercalated with borate anions (Mg_2Al-B-LDH) was used as a matrix for the release of B in clayey soil, and resulted in a similar availability of B in the soil and B uptake by sunflower plants compared to H_3BO_3 (soluble source).[21] Mg_2Al-B-LDH was also applied in sandy soil to minimize the B leaching.[22] The source Mg_2Al-B-LDH resulted in lower leaching of B compared to H_3BO_3 and Ulexite (commercial sources of B with high and low solubility, respectively). Besides, the successive cultivations of sunflower without replenishment of B resulted in similar growth and B uptake by plants compared to Mg_2Al-B-LDH, H_3BO_3 and Ulexite sources.[22] Alginate beads containing LDH intercalated with borate (LDH-B-ALG) in a sandy soil resulted in lower B leaching compared to H_3BO_3 and Ulexite.[27] During the successive cultivation of sunflower and cotton in the same substrate, LDH-B-ALG released sufficient B into the soil solution to support plant growth without B deficiency compared to H_3BO_3 and Ulexite.[27]

The development of new fertilizers requires a sequence of experiments with results for efficacy validation under multiple environments and conditions, such as different types of soil texture, organic matter, leaching soil sceneries, sensitive crops to nutrients, *etc.* Thus, in the particular case of LDH-fertilizers, additional research studies need to be conducted with focus on B release and leaching from the layered matrix, the residual effect of LDHs in the soil, and also the development of granular LDH forms to better application and to improve the uptake by plants. In this sense, giving continuity to our studies encompassing alginate beads containing LDH-B, the aims of this study were to: (i) evaluate the effect of LDH-B-ALG on the dynamics of B leaching and B uptake by plants during successive crops in sandy soil subjected to leaching and (ii) the B release and B uptake by plants in successive crops in sandy soil with increasing rates of B.

2 Materials and methods

2.1 Synthesis and characterization of alginate beads containing Mg–Al-LDH intercalated with borate anions, and alginate beads containing H_3BO_3

The Mg–Al-LDH intercalated with borate (Mg_2Al-B-LDH), pristine LDH, was synthesized using the constant pH coprecipitation method. The solutions containing 1.0 mol L^{-1} of $Mg(NO_3)_2 \cdot 6H_2O$, 0.5 mol L^{-1} of $Al(NO_3)_3 \cdot 9H_2O$, and 1.25 mol L^{-1} of H_3BO_3 were used.[21,28] The pH value was maintained at 10.0 during the synthesis using a 2.0 mol L^{-1} of NaOH solution.

The synthesis of the LDH-B-ALG and alginate beads containing H_3BO_3 (BA-ALG) was carried out using the complex coacervation method,[29] and in accordance with the methodology described by Castro and coworkers.[27] The alginate beads containing Mg_2Al-B-LDH (LDH-B-ALG) were synthesized using solutions of alginate in water of 2% w/v, 5% of $Ca(NO_3)_2$ in water (w/v), and Mg_2Al-B-LDH : alginate in the ratio of 10 : 1 (w/w).[27] BA-ALG was synthesized according to the same methodology described for LDH-B-ALG, in which Mg_2Al-B-LDH powder was replaced by H_3BO_3.

LDH-B-ALG and BA-ALG were characterized by the following techniques: X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM). XRD analyses were performed using a graphite crystal monochromator to select Cu-Kα_1 radiation with λ = 1.5406 Å and a step rate from 0.02° s^{-1}, with 2θ angle between 4° and 70°. A Shimadzu XRD-6000 diffractometer was used for XRD analyses. The ATR-FTIR spectra were recorded in the range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution and 256 scanning, using a Jasco spectrometer, model FT/IR-4100. LDH-B-ALG and BA-ALG were macerated to perform XRD and ATR-FTIR analyses. For SEM analyses, the microspheres were supported on conductive double-sided adhesive tape and a Zeiss EVO 50 scanning electron microscope was used.

The total amount of B in the Mg_2Al-B-LDH, LDH-B-ALG and BA-ALG was evaluated by using an optical emission spectrometer, model Optima 8300. The fertilizers were solubilized in a solution of HNO_3 5 mol L^{-1} using a 1 : 60 ratio of sample : solution (w/v).

The total concentration of nitrogen (N) in the LDH-B-ALG and BA-ALG was analyzed by the ignition method in an elemental analyzer PerkinElmer Series II 2400. The results are presented in the ESI.†

A preliminary experiment of "cumulative release and leaching of boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3, and BA-ALG" is presented in the ESI.† The results showed a lower release and leaching of B from LDH-B-ALG and BA-ALG, compared to Mg_2Al-B-LDH and H_3BO_3, respectively. Thus, the following studies of leaching and greenhouse cultivations were carried out using sources with different release rates of B, such as LDH-B-ALG, BA-ALG (less solubility than H_3BO_3), H_3BO_3 (commercial source with higher release of B), and Ulexite (commercial source with lower release of B).

2.2 Boron leaching in soil columns

The study was conducted with soil from a potato cultivated area from the University of Florida, Hastings Agricultural Extension Center (HAEC) research farm located in Hastings, FL, USA. A soil sample was collected from the 0–20 cm depth layer of sandy (91.6% of sand), siliceous, active, hyperthermic Alfic Alaquods belonging to Wabasso Fine Sand Series.[30] The soil was homogenized, sieved (2 mm), and air-dried. The general soil physical and chemical properties were: clay 2 g kg^{-1}, silt 6.4 g kg^{-1}, sand 91.6 g kg^{-1}, soil bulk density 1.49 g cm^{-3}, pH (H_2O) = 6.3, B 0.16 mg dm^{-3}, cation exchange capacity 3.1 $cmol_c$ dm^{-3}, and soil organic carbon 5 g kg^{-1}. This available B in the soil is below all the B critical levels reported in the literature for sunflower and cotton in soils of different textures.[31–34]

The leaching study was conducted under laboratory conditions at the Horticultural Sciences Department of the University of Florida in Gainesville, FL. The B leaching test was performed and adapted from the method described by Abat and coworkers, and is summarized below.[35] Columns of polyvinyl chloride with 3 cm diameter and 12 cm height were filled with 60 cm^3 of soil. The fertilizers used in the B leaching test were LDH-B-ALG, H_3BO_3, Ulexite and BA-ALG. The H_3BO_3 and Ulexite were chosen because they are commercial sources with high and low solubility, respectively.

Before the fertilizer application, a volume of deionized distilled (DDI) H_2O equivalent to one volume of pores (20 mL) was applied on top of the soil column. The water was drained using vacuum with a syringe system. After drainage, each fertilizer was applied at 0.5 cm from the surface of the soil in the center of the column and covered with soil. A rate of 20 mg dm^{-3} of total B from LDH-B-ALG, H_3BO_3, Ulexite and BA-ALG sources was used. The leachate was collected after the application of DDI H_2O corresponding to the volume of pores (20 mL) after 1, 5, 10, 15, 20, 25, 30, 35, and 40 days. The ambient temperature of the laboratory was maintained at 25 °C. The experiment was conducted in a randomized complete block design with four replications. The concentrations of B in the leachate were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).[36]

2.3 Greenhouse experiment without leaching

The availability of B to plants was evaluated in successive cultivations of sunflower and cotton without replenishment of B. The experiment was conducted in a greenhouse located at the University of Florida, HAEC in Hastings, FL. Plastic pots of 2.0 dm^{-3} capacity without holes at the bottom were filled with the soil described in item 2.2. A factorial 4 × 5 was established with four sources of B (LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite) and five doses of total B (0.0, 0.5, 1.0, 3.0, and 5.0 mg dm^{-3}). The experimental design was a randomized complete block with four replicates.

Before sowing, the B sources were homogenized with the soil and placed in the pots. Immediately after that, the soil was fertilized with 60 mg dm^{-3} of P, 75 mg dm^{-3} of K, 30 mg dm^{-3} of S, and 100 mg dm^{-3} of N. The fertilizer sources homogenized with the soil were KH_2PO_4, $NH_4H_2PO_4$, $CaH_2(PO_4)_2$, $(NH_4)_2SO_4$, and urea. Eight seeds of sunflower (*Helianthus annuus*) were sown per pot. After five days, the seedlings were thinned to the four most uniform ones in each pot. Further liquid basal nutrients were added three times in 10 mL of solution per pot, resulting in a nutrient rate per dm^3 soil of 100 mg of N as urea, 1.32 mg of Cu as $CuSO_4{\cdot}5H_2O$, 1.55 mg of Fe as $FeSO_4{\cdot}7H_2O$, 3.66 mg of Mn as $MnSO_4{\cdot}H_2O$, 0.15 mg of Mo as $(NH_4)_6Mo_7O_{24}$, and 4.0 mg of Zn as $ZnSO_4{\cdot}7H_2O$. Pots were watered daily to 80% of field capacity (FC) with irrigation water from the farm well. The results of the chemical characterization of the water samples are shown in Table S1 of the ESI.†

After 45 days of cultivation, the plants were harvested by cutting the stems at the soil surface. Additionally, roots were carefully separated from the soil using a 2 mm sieve and roots were washed using deionized water. Plant biomass and roots were dried at 65 °C for 96 h and weighed to obtain dry matter (DM). Plant biomass and roots samples were milled using a Wiley mill (Model 4, Thomas Scientific, Swedesboro, NJ, USA) and passed through a 1 mm screen, and the concentration of B in plant tissues was determined. The whole soil from each pot (experimental unit) was homogenized and a sub-sample of 100 g of soil was collected after the first cultivation to determine soil B availability. The amount of B contained in the tissue samples was analyzed by the dry method and the extractant used was HCl 0.1 mol L^{-1}.[37] The Mehlich-1 extractant was used for the soil samples.[38]

After the harvest of sunflower, pots were maintained undisturbed for 15 days in the greenhouse. Lime was applied at a rate of 1000 kg Ha^{-1} to maintain the soil pH value in the 6.0–6.5 range. The lime was composed of a mixture of $CaCO_3$ and $MgCO_3$, with Ca : Mg = 4 : 1. Then, soil was wetted to 80% of FC and incubated in plastic bags for 20 days in the greenhouse. After the incubation, the soil was air dried and before sowing, 200 mg dm^{-3} of P, 150 mg dm^{-3} of K, 60 mg dm^{-3} of S, and 100 mg dm^{-3} of N were applied. The sources of fertilizer used were KH_2PO_4, $NH_4H_2PO_4$, $CaH_2(PO_4)_2$, $(NH_4)_2SO_4$, and urea. At the same day, eight seeds of cotton (*Gossypium vitifolium*) were sown per pot. Five days after plant emergence, each pot was thinned to four plants. No B fertilization was applied, requiring the plants to use residual B. Further liquid basal nutrients were applied at the same rate and sources as in the first cultivation of sunflower. Pots were watered with distilled H_2O to maintain 80% of FC. At 60 days after seeding, the plants were harvested by cutting the stems at the soil surface and the roots were separated from the soil and washed. Plant biomass and roots were oven dried at 65 °C for 96 hours and weighed. The B concentration in plant biomass, roots and soil samples were determined according to the methodology previously described.

2.4 Greenhouse experiment with leaching

The study was established with four sources of B (LDH-B-ALG, BA-ALG, H_3BO_3, and Ulexite), and one treatment without application of B. The experimental design was a randomized complete block with four replicates, using pots with 2.0 dm^{-3} soil capacity. A 5 mm layer of glass wool was placed at the bottom of the pots to prevent soil losses during leaching events. Each pot was filled with sandy soil described in item 2.2 and a total rate of 2 mg dm^{-3} of B from each source was applied and homogenized in the soil.

After the application of fertilizers, a volume of distilled H_2O corresponding to 20 mm of precipitation was applied on top of the soil and drained. The leachate was collected and the B concentration in the leachate was determined according to the method described by USEPA-ICP.[39] After leaching, the residual effect of the B sources was evaluated in successive sunflower and cotton cultivations without replenishment of B. The crop management performed on successive sunflower and cotton cultivations was the same as described in Section 2.3, except for the first sunflower cultivation, in which pots were fertilized with 200 mg dm^{-3} of P, 150 mg dm^{-3} of K, 60 mg dm^{-3} of S, and 100 mg dm^{-3} of N before sowing, with the same fertilizer sources described in Section 2.3.

2.5 Statistical analysis

Data were submitted to analysis of variance and regression. The differences between the treatment means were evaluated using the Tukey's and least significant difference adjustment at $p \leq 0.05$. The *R* environment was used in the statistical analysis.[40]

3 Results

3.1 Characterization of LDH-B-ALG and BA-ALG

The diffractograms of LDH-B-ALG and BA-ALG are presented in Fig. 1. The diffractogram of LDH-B-ALG (Fig. 1a) shows diffraction basal peaks (00*l*) marked as (003), (006), and (009), with 2θ degree values at 9.3, 16.7, and 24.6. This diffractogram also shows diffraction peaks marked as #(003), #(006), and #(009), with 2θ degree values at 9.8, 19.8, and 28.9. The diffractogram of the BA-ALG (Fig. 1b) presents one well-defined peak with a 2θ degree value at 28.1.

The ATR-FTIR spectra of LDH-B-ALG and BA-ALG are shown in Fig. 2. LDH-B-ALG and BA-ALG presented bands in the wavenumber range between 3600 cm^{-1} and 3200 cm^{-1} (Fig. 2a and b). The spectra of LDH-B-ALG also showed peaks at 1640 cm^{-1}, 1360 cm^{-1}, 1350 cm^{-1}, 1020 cm^{-1}, 935 cm^{-1}, 827 cm^{-1}, and

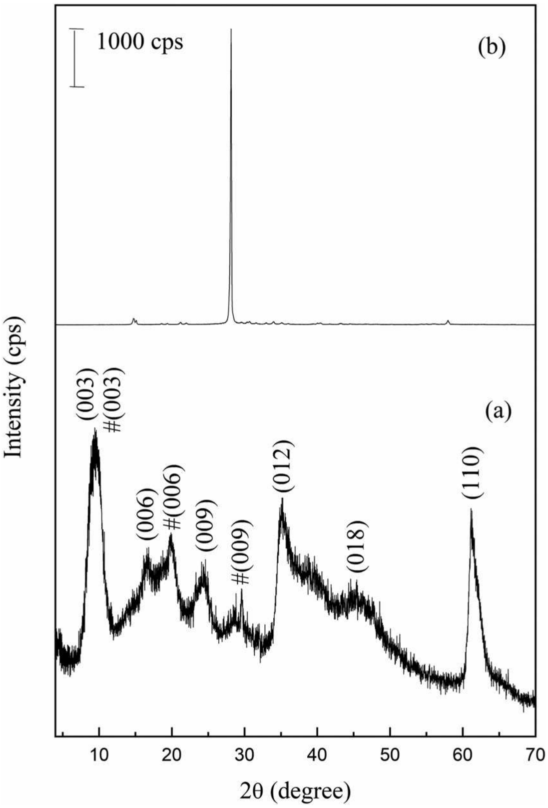

Fig. 1 Diffractograms of LDH-B-ALG (a), and BA-ALG (b). #(003), #(006) and #(009): peaks refer to the intercalation of nitrate ions into the LDH.

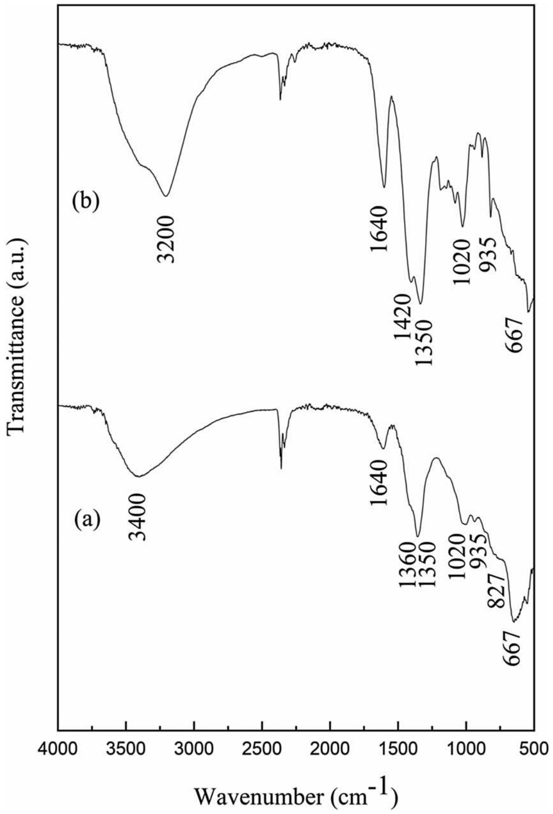

Fig. 2 Attenuated total reflectance Fourier transform infrared spectroscopy spectra of LDH-B-ALG (a), and BA-ALG (b).

667 cm^{-1}. Similarly to LDH-B-ALG, the BA-ALG presented bands in the wavenumbers of 1640 cm^{-1}, 1350 cm^{-1}, 1020 cm^{-1}, 935 cm^{-1}, and 667 cm^{-1}. Additionally, the ATR-FTIR spectra of BA-ALG presented a peak at 1420 cm^{-1}.

The morphologies of the LDH-B-ALG and BA-ALG beads were analyzed by SEM images (Fig. 3). LDH-B-ALG and BA-ALG presented beads with diameters varying between 2500 μm and 3000 μm (Fig. 3a and f). The interaction between alginate/Mg_2Al-B-LDH (Fig. 3b–e) and alginate/H_3BO_3 (Fig. 3g–i) showed the simultaneous presence of alginate, H_3BO_3, and Mg_2Al-B-LDH phases in the synthesized LDH-B-ALG and BA-ALG fertilizers.

The B concentrations in the Mg_2Al-B-LDH, LDH-B-ALG, and BA-ALG were 50 g kg^{-1}, 40 g kg^{-1}, and 139 g kg^{-1} of the material, respectively. These values correspond to 5% of B in the Mg_2Al-B-LDH, 4% of B in the LDH-B-ALG, and 13.9% of B in the BA-ALG.

3.2 Boron leaching in soil columns

The incubation period started with the application of B fertilizers and was carried out for 40 days. The first leaching event occurred one day after the fertilizer application, followed by successive leaching events every 5 days. The B leaching test in soil columns showed different patterns of B release and leaching among the different sources of B throughout the incubation period. At the first leaching event, 58.3%, 11.8%, 11.2%, and 4.1% of the total B applied as H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG were recovered in the leachate, respectively (Fig. 4).

After 10 days of incubation, 100.0% and 91.9% of the B applied as H_3BO_3 and BA-ALG, respectively, were recovered in the leachate, while, Ulexite and LDH-B-ALG, both sources with lower solubility of B, resulted in 31.6%, and 19.5% of B leaching, respectively. At 35 days of incubation, 100.0% and 57.5% of total B applied as Ulexite and LDH-B-ALG were recovered in the leachate, respectively. Throughout the incubation period, the percentage of B leached from LDH-B-ALG was significantly lower compared to other B sources, except for Ulexite at 20, 25, and 30 days of incubation (Fig. 4).

3.3 Greenhouse experiment without leaching

Sunflower and cotton shoots, roots and total DM accumulation were not influenced by the applied rates or sources of B at $p < 0.05$ in the first and second cultivations (Fig. S1 of the ESI†).

The sunflower shoot, root, and total B uptake as a function of B rates in the first cultivation are presented in Fig. 5a–c, respectively. There was a linear increase of B uptake for sunflower in shoots, roots, and overall total with the increasing B rates regardless of the B sources. A similar linear response of B uptake to the increasing B rates across B fertilizer sources was observed for cotton (Fig. 5d–f). Since the leaching losses were prevented during this trial, the total B uptake for sunflower and cotton were summed. There was a linear increase in the total plant B uptake with the increasing rates of B, and the coefficients of the equations describing each B source were similar (Fig. 6).

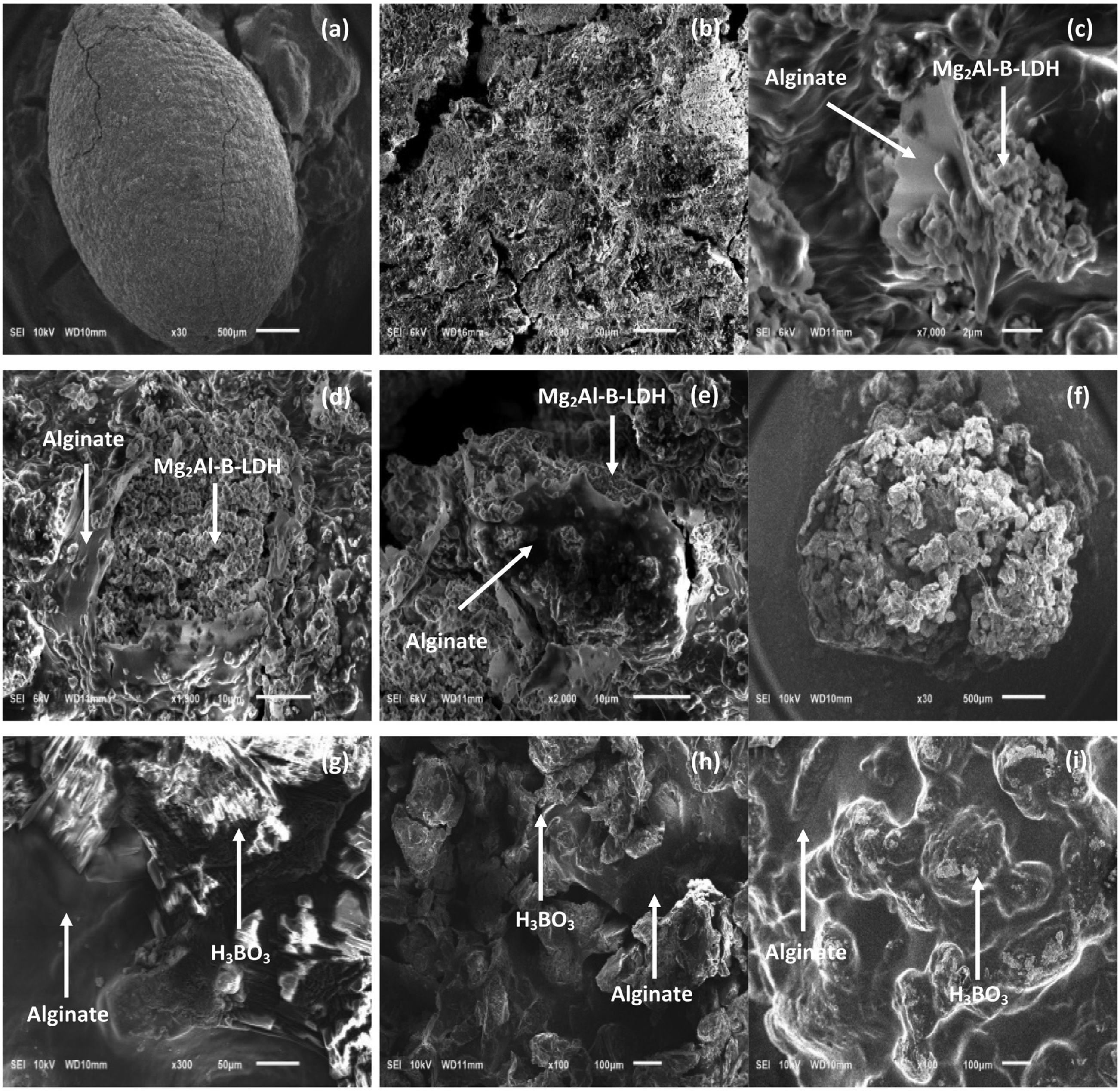

Fig. 3 Representative images of SEM of the surface morphology of LDH-B-ALG (a–e), and BA-ALG (f–i). Arrows indicated the alginate, H_3BO_3, and Mg_2Al-B-LDH distribution in the fertilizer.

The amount of B available in soil as a function of applied B rates, evaluated using the Mehlich-1 extractant, is presented in Fig. 7. After the sunflower and cotton cultivations, the amount of B available in soil increased linearly with increasing B rates regardless of the B sources (Fig. 7).

3.4 Greenhouse experiment with leaching

In this study, sunflower plants were fertilized with a single rate of B at 2 mg dm^{-3} using four different sources H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG. Right after the application of B fertilizer and before sunflower sowing, pots were subjected to the first leaching procedure. After the sunflower cultivation, cotton plants were grown in the same soil without any additional application of B.

There was an effect of B sources on the total leached B before the sunflower cultivation. The B concentration in the leachate of H_3BO_3 was 3.01 mg L^{-1} of B, which was significantly higher than 1.6 mg L^{-1} of B from the BA-ALG source, while, the B concentration in the leachate was 0.7, 0.6, and 0.4 mg L^{-1} of B for LDH-B-ALG, Ulexite, and control treatment, respectively, and they were significantly lower compared to those of H_3BO_3 and BA-ALG.

There were no differences in DM and B uptake of sunflower shoots, roots, and total as a function of B fertilizer sources (Table 1).

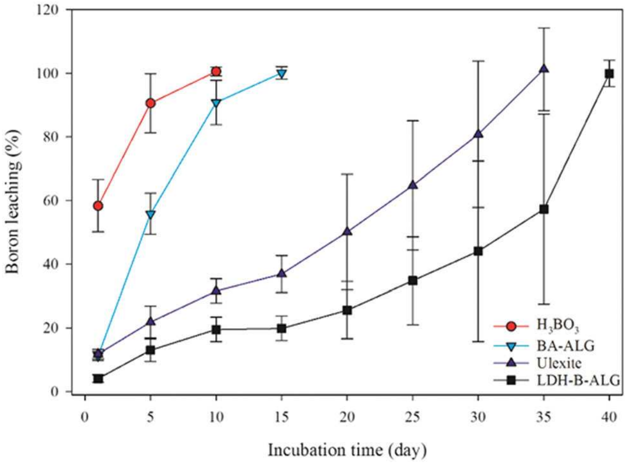

Fig. 4 Boron leaching in soil columns as a function of incubation time from application of 20 mg dm^{-3} of B as H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG.

After the cultivation of sunflower, the residual amount of B in the soil was determined using the Mehlich-1 extractant. The residual concentration of B was 1.57, 0.82, 0.73, 0.66, and 0.61 mg dm^{-3} of B for LDH-B-ALG, control, Ulexite, H_3BO_3, and BA-ALG treatments, respectively. The residual B in the soil was significantly higher for LDH-B-ALG compared to the other B sources, and there were no significant differences among control, Ulexite, BA-ALG, and H_3BO_3 treatments.

There were also no differences in cotton DM accumulation as a function of B sources in the second cultivation (Table 1). However, cotton shoot and total B uptake were significantly higher for LDH-B-ALG compared to H_3BO_3, Ulexite, BA-ALG, and control treatments. A similar response was observed for the total DM and B uptake as a sum of sunflower and cotton cultivation (Table 1).

4 Discussion

The diffractogram of LDH-B-ALG in Fig. 1a presents the characteristic profile of the hydrotalcite-like compounds with basal peaks (003), (006), and (009) with 2θ degrees values at 9.3, 16.7, and 24.6, respectively. The basal spacing calculated by Bragg's equation ($n\lambda = 2dhk\ell \sin\theta$) was 10.33 Å. In previous studies, MgAl-LDH intercalated with borate was synthesized in pH value 9.0 and the calculated d spacing value was 10.78 Å, in which monoborate anion ($B(OH)_4{}^-$) and/or triborate anion ($B_3O_3(OH)_4{}^-$) were proposed as interlayer anions.[41,42] Conversely from our method, Ay and coworkers synthesized the LDH intercalated with borate anions through ion-exchange reactions with nitrate-LDH, adipate-LDH, and terephthalate-LDH, in pH value solutions of 9 and 12.[43] The authors found different basal spacing $d(003)$ values between 7.69 and 11.05 Å, in which a tetraborate ($B_4O_5(OH)_4{}^{2-}$) was intercalated.[43] In addition, the diffraction peaks #(003), #(006), and #(009) in Fig. 1a can be due to the partial ion-exchange reaction between borate intercalated into the LDH and nitrate anions of the solution, since that $Ca(NO_3)_2$ is used to synthesize the beads. These basal peaks are similar to the powder diffraction pattern of the nitrate/MgAl-LDH presented by Berber and coworkers.[44] The diffractogram of H_3BO_3, the precursor material for the production of BA-ALG, was previously described by Bingöl and coworkers and showed well-defined peaks due to the crystallinity of this material.[45] The diffractogram of the BA-ALG, produced from H_3BO_3, shows one well-defined peak due to the presence of this acid in the hybrid material, matching with findings of Bingöl and coworkers.[45]

The presence of the broad band in the ATR-FTIR spectra of the LDH-B-ALG and BA-ALG in the wavenumber range from 3600 cm^{-1} to 3200 cm^{-1} is due to the O–H stretching of the hydroxyl groups and/or H_2O molecules (Fig. 2a and b).[19,22,46] The characteristic absorption band observed at 1640 cm^{-1} for LDH-B-ALG and BA-ALG is also due to the O–H stretching of the hydroxyl groups and/or H_2O molecules.[10] The vibration modes related to the presence of borate anions have been reported at the bands 1350 cm^{-1}, 1020 cm^{-1}, and 935 cm^{-1}, and are attributed to the vibrational modes $\nu_{as(B3-O)}$, $\nu_{as(B4-O)}$, and $\nu_{s(B3-O)}$, respectively.[43] Additionally, Kloprogge and coworkers showed a very strong ν_3 mode at 1360 cm^{-1}, with a very weak ν_2 mode at 827 cm^{-1}, and the ν_4 mode at 667 cm^{-1}, due to the presence of nitrate anions in hydrotalcite compounds.[47] These results suggested the presence of both borate and nitrate anions in the LDH-B-ALG. The ATR-FTIR spectra of BA-ALG showed a peak at 1420 cm^{-1}, which is due to the $-COO^-$ symmetric stretching vibrations.[26]

The morphologies of the LDH-B-ALG and BA-ALG showed an effective formation of beads (Fig. 3a and f) and also the presence of alginate, Mg_2Al-B-LDH powder, and H_3BO_3 in synthesized fertilizers (Fig. 3). The physical interaction of LDH, fertilizers, and alginate can produce a barrier to reduce the rate of water diffusion into the beads and also decrease the release of nutrients and other compounds, indicating the desirable slow-release fertilizer properties.[26,27] These results agreed with the previous results from "cumulative release and leaching of boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3, and BA-ALG" presented in the ESI† (Fig. S2). LDH-B-ALG and BA-ALG presented a slow release profile, in which the release and leaching of B was lower compared to Mg_2Al-B-LDH and H_3BO_3, respectively. These results demonstrated the advantage for the release and protection of B in the beads compared to the Mg_2Al-B-LDH in powder form and H_3BO_3.

Previous research reported concentrations of 14.00, 37.90, 25.50, 45.23, and 50.60 g kg^{-1} of B for MgAl-CO_3-LDH, MgAl-NO_3-LDH, calcined MgAl-LDH, non-calcined MgAl-LDH, and Mg_2Al-B-LDH, respectively.[21,27,48–50] The total amount of B determined for Mg_2Al-B-LDH indicated higher incorporation of B compared to MgAl-CO_3-LDH, MgAl-NO_3-LDH, calcined MgAl-LDH, and non-calcined MgAl-LDH. This is an important result because B is required in small quantities by plants, and small rates applied to the soil through fertilizers can increase the crop productivity. The usual recommendation for B fertilization for sunflower ranges from 0.5 to 1.5 mg dm^{-3} for soils with B concentration in the soil below the B critical level.[31–34,51–53]

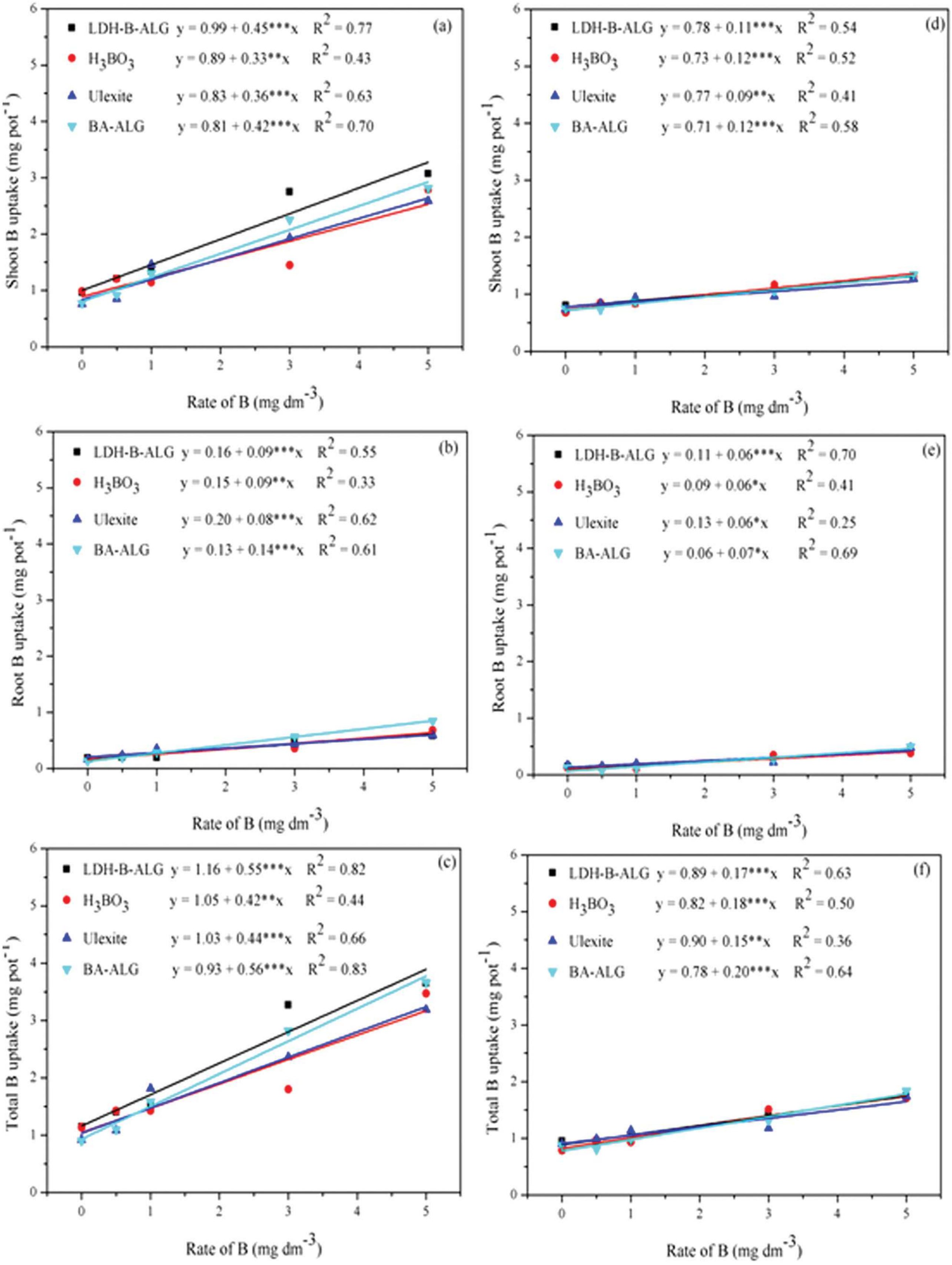

Fig. 5 Shoot, root and total plant B uptake as a function of B rates as H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG of sunflower and cotton, in first (a–c) and second (d–f) cultivation, respectively. *, **, *** Significant at $p < 0.05$, $p < 0.01$ and $p < 0.001$ by t test, respectively.

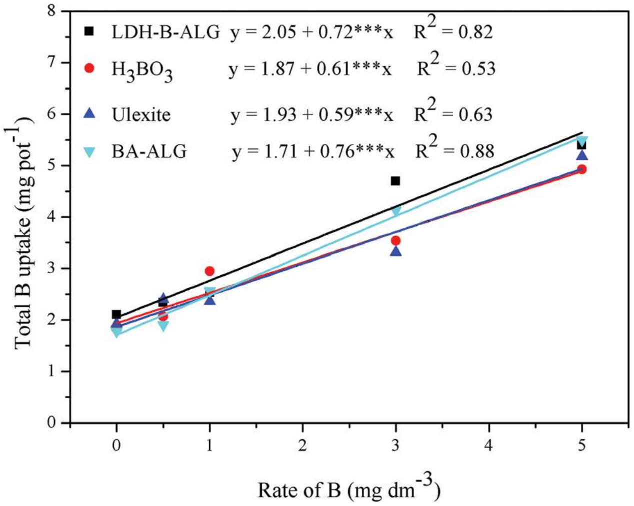

Fig. 6 Total plant B uptake of sunflower and cotton calculated from the sum of first and second cultivations as a function of the B rates as H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG. ***Significant at $p < 0.001$ by t test, respectively.

Table 1 Shoot, root and total (shoot + root) dry matter and B uptake of sunflower and cotton as a function of the applied B sources in the first (sunflower), second (cotton) and combined cultivations

	Dry matter (g pot^{-1})			B uptake (mg pot^{-1})		
Source	Shoot	Root	Total	Shoot	Root	Total
First cultivation (sunflower)						
H_3BO_3	15.66a	4.25a	19.91a	2.09a	0.31a	2.40a
LDH-B-ALG	15.89a	5.03a	20.92a	3.14a	0.51a	3.65a
BA-ALG	15.09a	3.80a	18.89a	2.11a	0.26a	2.37a
Ulexite	17.66a	3.99a	21.65a	2.58a	0.34a	2.92a
Control	17.78a	4.25a	22.03a	2.17a	0.26a	2.43a
Second cultivation (cotton)						
H_3BO_3	49.66a	6.00a	55.66a	1.01bc	0.20ab	1.21bc
LDH-B-ALG	53.20a	5.89a	59.09a	1.74a	0.31a	2.05a
BA-ALG	49.27a	6.35a	55.62a	1.05b	0.15ab	1.20bc
Ulexite	48.24a	6.15a	54.39a	1.14b	0.26ab	1.40b
Control	47.24a	5.45a	52.69a	0.71c	0.09b	0.80c
Sunflower + cotton (combined cultivations)						
H_3BO_3	65.32a	10.25a	75.57a	3.10bc	0.51ab	3.61c
LDH-B-ALG	69.09a	10.92a	80.01a	4.88a	0.82a	5.70a
BA-ALG	64.36a	10.15a	74.51a	3.16bc	0.41ab	3.57c
Ulexite	65.90a	10.14a	76.04a	3.72b	0.60ab	4.32b
Control	65.02a	9.70a	74.72a	2.88c	0.35b	3.23c

Values followed by the same lowercase letter within columns and within each cultivation indicate that the mean of dry matter and plant B uptake of shoot, root and total is not significantly different at $p < 0.05$ according to the Tukey test between B fertilizer sources. There were four replicates (pots) for treatment with four plants per pot.

Conversely, B concentrations in soils in the range of 2.5 to 5.0 mg dm^{-3} can be excessive and toxic to plants.[52,53] The total amount of B in the Mg_2Al-B-LDH, LDH-B-ALG, and BA-ALG presented by Castro and coworkers was 5.06, 4.20 and 13.85% of B, respectively, compared to 5.0, 4.0, and 13.9% in our research for the same fertilizers.[27] It is noteworthy that the total amount of B concentration in the fertilizers was statistically similar compared to fertilizers from research conducted by Castro and coworkers due to the same methodology used in both studies.[27]

LDHs are presented in the literature as slow-release sources of nutrients compared to other conventional soluble sources.[7,10,22] The total amount of B leaching in soil columns throughout the incubation time was lower for LDH-B-ALG than H_3BO_3, Ulexite, and BA-ALG. These results confirm that LDH-B-ALG can be classified as a slow-release fertilizer source of B. Castro and coworkers investigated the dynamics of B leaching and availability in sandy soil from MgAl-LDH intercalated with borate (Mg_2Al-B-LDH) compared to H_3BO_3 as a soluble source.[22] The slower and gradual release profile of Mg_2Al-B-LDH significantly decreased the amount of B in the soil solution and B leached compared to H_3BO_3. The reduced B release into the soil and leaching of B can be attributed to the ''protection'' of borate anions in the interlamellar spaces of LDHs. Also, alginate polymers combined with materials such as starch, clay, and LDHs can produce physical protection and reduce the rate of H_2O diffusion into to the beads.[3,26,27] Thus, the slow-release

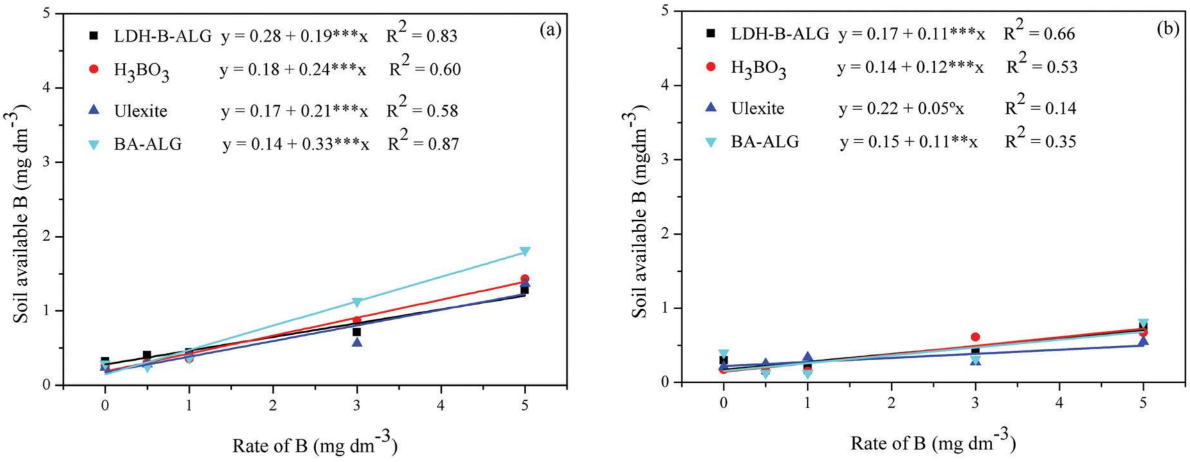

Fig. 7 The amount of boron available in the soil from the Mehlich-1 extractant as a function of B rates as H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG after the first (a) and second (b) cultivation. ○, **, *** Significant at $p < 0.1$, $p < 0.01$ and $p < 0.001$ by t test, respectively.

profile presented by LDH-B-ALG can be attributed to the physical interaction of LDH and the alginate polymers, and also to the protection of borate anions intercalated between the layers of LDHs. Under agricultural conditions, the reduced susceptibility of B leaching from LDH-B-ALG can increase the time of residency of B in the root zone, benefiting B absorption for plants and fertilizer efficiency. According to Degryse,[1] sources with slow-release properties can allow the use of lower rates of nutrients and decrease the frequency of fertilizer application. Thus, LDH-B-ALG can be indicated as a new B fertilizer for environments with high rainfall incidence, and sandy soils with low organic matter and prone to leaching.

The application of B sources in the greenhouse experiment with increased rates of B resulted in similar DM and B uptake of sunflower and cotton plants. These results corroborate with many other studies that evaluated the bioavailability of LDH to crops.[8,9,22,27] Benício and coworkers applying LDH intercalated with phosphate (LDH-P) in maize reported similar results with rates from 0 to 60 mg kg^{-1} of P in a sandy soil.[19] The shoot dry matter mass was not influenced by the applied rates and sources of P (super triple phosphate and LDH-P) in a single cultivation.[19] In another study with wheat (*Triticum aestivum*), DM and P uptake were similar when the same rate of P was applied as LDH-P, struvite, and monoammonium phosphate (MAP).[8] Bernardo and coworkers reported that the wheat P uptake response was similar for Mg–Al–PO_4-LDH and MAP, which indicated that Mg–Al–PO_4-LDH was a feasible source of P in a short period of time.[9] The application of 2.0 mg dm^{-3} of B as LDH-B-ALG in sandy soil resulted in a similar release of B into the soil solution, plant growth and B uptake in successive cultivations of sunflower and cotton compared to the same rate of B applied as H_3BO_3 and Ulexite.[27] These studies illustrate that there was an increase in P and B availability in the soil with increasing rates of LDHs.[7,19,22] In the present study, a similar response of B availability from LDH-B-ALG application was observed. Under no leaching conditions and soil moisture maintained at field capacity, LDH-B-ALG solubilized in the soil at a similar rate compared to the other B sources, supplying enough B to match plant requirements. Moreover, under slightly acidic soil pH conditions, the release of nutrients from LDHs is similar to other soluble sources.[21] In this study, the release profile of B from LDH-B-ALG did not reduce the B plant accumulation compared to the other sources.

Previous studies only reported the B leaching tests in soil columns without analyzing the B leaching and subsequent plant cultivation in the same substrate.[22,27] In the greenhouse experiment with leaching, there was a lower B concentration in the leachate before the first cultivation from LDH-B-ALG, Ulexite, and control treatments compared to H_3BO_3 and BA-ALG sources. After the first cultivation of sunflower, there was a higher residual amount of B available in the soil from LDH-B-ALG compared to other treatments. These results were also confirmed during the second cultivation of cotton and combined cultivation of sunflower and cotton, in which the LDH-B-ALG application resulted in a higher B uptake in shoots and total (shoots and roots) compared to H_3BO_3, Ulexite, BA-ALG, and control treatment. Thus, the application of soluble sources (*e.g.*, H_3BO_3) and even sources with lower solubility (*e.g.*, Ulexite) in sandy soils with low organic matter and prone to B leaching can result in lower B uptake compared to LDH-B-ALG.

It is noteworthy that the borate and other anions intercalated in LDH could be released into the soil by two different mechanisms: (i) ion exchange reactions between intercalated borate and the anions usually present in the soil, such as carbonates, phosphates, nitrates, etc, since the ion replacement can promote the structural stability of the LDH layers;[54,55] and (ii) dismantling of the LDH structure due to the ''acid attack'' promoted by the H^+ ions present in the acid soil solution, and subsequent release of the anions intercalated between LDH layers.[11,56] The soil used in this work presented a pH value of 6.3 before the first cultivation. The separation of LDH from the soil after two cultivations is not possible to be achieved under the conditions that the experiments were conducted, thereby hindering the chemical analysis of the material. Thus, according to the chemical properties of the soil presented, the release of boron from LDH might be due to the acid dissolution due to the ''acid attack'' and ion exchange reactions.

Regarding the influence of pH on the B release, Theiss and coworkers presented the B speciation as a function of pH.[41] According to the authors, the $B(OH)_4{}^-$, $B_4{}^{2-}$, $B_3{}^-$, and $B_3{}^{2-}$ anions are predominant in aqueous solution with pH values between 9 and 11.[41] The H_3BO_3 is not the predominant species during the LDH synthesis process, since the synthesis was carried out in aqueous solution with a pH value of 10 (''Materials and methods'' section). Thus, the H_3BO_3 cannot influence the B release performance from LDH-B-ALG. Specifically for the relationship between pH and LDH, the use of LDHs can affect the soil pH when applied in large rates in the soil. Everaert and coworkers and Benício and coworkers reported an increase in the soil pH value with increasing rates of P supply through LDH.[7,19] The increase in the soil pH can be due to the release of hydroxyls groups through the LDH fertilizers.[57] It is noteworthy that the total P applied by LDH, to supply this macronutrient to the plants, is much higher than that applied from LDH-B-ALG for B supply, which allows significant changes in the soil pH value. The increase in soil pH from application of large amounts of LDH may increase the LDH stability in the soil, allowing a more steady release of the intercalated anions, and even of the cations that make up the lamellar structure.[11,19,58] However, the increase in soil pH due to the application of high amounts of LDH may decrease the availability of cationic micronutrients in the soil, such as Cu, Fe, Mn, and Zn.[59,60] In this way, the increase in the soil pH directly depends on the amount of LDH applied, that is, on the purpose of using the LDH as a source of macronutrients or micronutrients. Thus, the use of LDH for the application of macronutrients may present an undesirable elevation of soil pH due to the large quantities of LDH required. Conversely, alterations of soil pH are not observed when using LDHs to supply micronutrients (*e.g.* B), which helps in maintaining the pH value in the realistic situation of agricultural soils under proper management.

The functionality of the hybrid organic–inorganic material systems depends on the substrate materials to be coated/synthesized and their physical properties and characteristics, such as antisoiling, antistatic or diffusion-inhibiting properties, leading to smart multifunctional hybrid structures.[61] Through the results of SEM analysis, *in vitro* release, leaching, and greenhouse cultivation with leaching presented in this work, that compared LDH-B-ALG with others B sources, the physical interactions between alginate and LDH can be correlated with the increase of the physical barrier in the fertilizer and consequently less diffusion of water and less release of the nutrient out of the granule. In addition, a granular material has a lower specific surface area compared to materials in powder form, which certainly decreases the exposure of the material to soil reaction (chemically, biologically, and physically), which is important to decrease the rate of nutrient release through the fertilizer into the soil. Also, the granular fertilizer synthesized, LDH-B-ALG, allows farmers to accurately apply it under field conditions. The interest in hybrid materials as barrier systems has been increasing with the aim to synthesize more sophisticated materials in many fields,[61] such as the ''soil and plant nutrition'' field, presented in this work. New materials with a physical interaction barrier can lead to enough protection and guarantee a sustainable release of nutrients, which was shown in the B release and leaching tests, and greenhouse cultivation with leaching, presented in this manuscript. The new organic–inorganic hybrid fertilizer material, LDH-B-ALG, represents a whole granulation system, since apart from the physical interaction between precursors materials, it acts as a slow-release fertilizer. LDH-B-ALG can be considered a new fertilizer that releases B slow enough to decrease leaching losses and fast enough to provide sufficient B into the soil solution to support plant growth without B deficiency or toxicity.

5 Conclusions

To conclude, the characterization of LDH-B-ALG and BA-ALG by XRD, ATR-FTIR, and SEM analysis, showed that Mg_2Al-B-LDH and H_3BO_3 were both presented into the alginate beads. The results from XRD, ATR-FTIR, and SEM analyses served as preliminary information on the slow-release properties of these materials and can be used as a predictor of the agronomic performance of these compounds. The overall B leaching from LDH-B-ALG was significantly lower compared to the other B sources during the soil column study, showing a slow-release property for this material. Under the absence of leaching conditions in greenhouse experiments, LDH-B-ALG was able to supply enough B for two consecutive cultivations performing comparatively to the more soluble sources. Under plant growing conditions in which the pots were subjected to leaching, the use of LDH-B-ALG resulted in a higher B uptake in shoots and total (sum of shoots and roots) in cotton (second cultivation) and for the sunflower and cotton combined cultivations. The use of LDH-B-ALG improves the overall time of residency of B in topsoil and B uptake by plants compared to H_3BO_3, Ulexite, and BA-ALG sources. In conclusion, the LDH-B-ALG application under controlled conditions was the most promising B source to be used in soils prone to B leaching. This study lays a robust platform for future field studies on the validation of these slow-release materials in agricultural settings. The alginate beads containing LDHs and fertilizers will serve as foundation for future studies focusing on macronutrients and micronutrients, which are important for the sustainability of agriculture and food security.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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ALGINATE BEADS CONTAINING LAYERED DOUBLE HYDROXIDE INTERCALATED WITH BORATE: A POTENTIAL SLOW-RELEASE BORON FERTILIZER FOR APPLICATION IN SANDY SOILS

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Table S1: Chemical characterization of the irrigation water collected in Hastings Agricultural Extension Center research farm located in Hastings, FL, U.S.

Element	Level	Element	Level
Nitrate (mg L^{-1})	0.28	Iron (mg L^{-1})	0.05
Phosphorus (mg L^{-1})	0.04	Manganese (mg L^{-1})	0.01
Potassium (mg L^{-1})	2.8	Sulfate (mg L^{-1})	0.02
Magnesium (mg L^{-1})	12.4	pH	8
Calcium (mg L^{-1})	96.47	Chloride (mg L^{-1})	23
Sodium (mg L^{-1})	15.27	Carbonate (mg L^{-1})	48
Boron (mg L^{-1})	0.12	Bicarbonate (mg L^{-1})	448.35

Total concentration of nitrogen (N) in the LDH-B-ALG and BA-ALG fertilizers:

LDH-B-ALG and BA-ALG presented a low fraction of N in their compositions. Nitrogen is a macronutrient required in relatively large amounts, and it is directly related to plant growth and development. The total N concentration was 15.0 g kg^{-1} in LDH-B-ALG (1.50% of N) and 6.0 g kg^{-1} in BA-ALG (0.60% of N). In the present study, the total N applied from LDH-B-ALG and BA-ALG was considered negligible. The total amount of LDH-B-ALG and BA-ALG was calculated to supply B, considering the plant's relatively low B requirement. The B rates applied in this study were 0, 0.5, 1.0, 3.0, and 5.0 mg dm^{-3} of B in the “Greenhouse experiment without leaching” and 2.0 mg dm^{-3} of B in the “Greenhouse experiment with leaching”. Under the highest B rate (5.0 mg dm^{-3}), the total N applied as LDH-B-ALG and BA-ALG corresponded to less than 1% of the total N supplied (200 mg dm^{-3} of N as urea source) in the first and second cultivations at pre-planting and sidedress. Therefore, the contribution of N from LDH-B-ALG and BA-ALG was not considered.

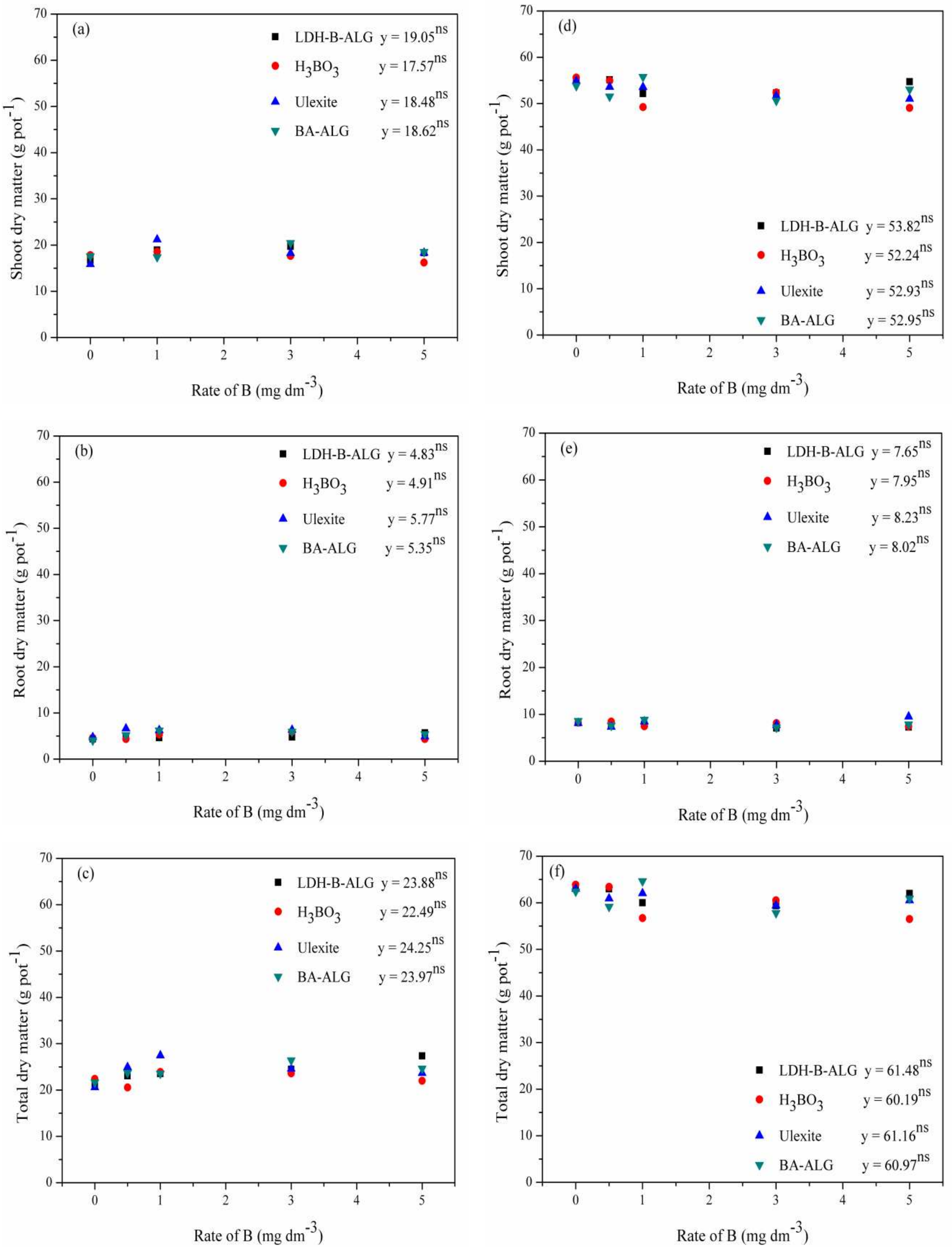

Fig. S1: Shoot, root and total dry matter as a function of the applied B (H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG) in first (a, b, and c) and second (d, e, and f) cultivation. ns = not significant.

Cumulative Release and Leaching of Boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3 and BA-ALG:

The B release test was performed and adapted from the ''*in vitro*'' release method, described by Bin Hussein and coworkers.[1] A factorial 6 x 2 was established with six collection times (0, 0.5, 1, 2, 4, and 6 hours), and two B sources (LDH-B-ALG and Mg_2Al-B-LDH). The experiment was conducted in a randomized complete block design with four replicates. The water used in the boron release test was H_2O deionized-Milli-Q system. Using an Erlenmeyer's flask with 250 mL of capacity, 45 mg L^{-1} of total B from the B sources and 100 mL of the water were added. At pre-established times (0, 0.5, 1, 2, 4, and 6 hours), a slight agitation was performed to homogenize the solution and aliquots of 5 mL were withdrawn. Immediately afterwards, 5 mL of the water was added in order to keep the volume constant. The analyses of B concentration were performed according to the method described by López and coworkers.[2]

The leaching in soil columns was performed the same as described in section "2.2 Boron leaching in soil columns" of this manuscript, except for the boron sources (LDH-B-ALG and Mg_2Al-B-LDH) and incubation time (1, 5, 10, 15, 20, 25, and 30 days).

The B release and leaching tests were replicated comparing H_3BO_3 and BA-ALG sources. The collection and incubation times was the same previously described.

The cumulative release and leaching of B from LDH-B-ALG and Mg_2Al-B-LDH are shown in Fig. S2a. In the first collection, the total B released from LDH-B-ALG and Mg_2Al-B-LDH were equivalent to 0.6% and 0.7%, respectively of the total B. After 6 hours of LDH-B-ALG and Mg_2Al-B-LDH application, 54.7% and 100% of the B were released, respectively. LDH-B-ALG presented a cumulative B release significantly lower at 2, 4, and 6 hours of collection than Mg_2Al-B-LDH source. For H_3BO_3 and BA-ALG sources (Fig S2c), the B release from BA-ALG was significantly lower at 0.5, 1, and 2 hours compared to H_3BO_3. The total B released (100%) from H_3BO_3 and BA-ALG were at 2 and 4 hours of collection, respectively.

Regarding B leaching, as expected, the leachate had more quantity of B when Mg_2Al-B-LDH was applied (Fig. S2b). For the first leaching collection time, 1.7% and 5.2% of the total B applied were leached from the LDH-B-ALG and Mg_2Al-B-LDH sources, respectively. At 30 days, after the LDH-B-ALG and Mg_2Al-B-LDH application, 67% and 88% of B was leached, respectively. The B leaching from LDH-B-ALG was significantly lower at 10, 15, 20, 25, and 30 days of incubation compared to Mg_2Al-B-LDH. These results showed a higher B leaching profile from Mg_2Al-B-LDH compared to LDH-B-ALG. The slow leaching profile was also confirmed for BA-ALG, in which in all incubation times the B leached was lower compared to H_3BO_3 (Fig. S2d).

The results presented by LDH-B-ALG in the release and leaching of B study, suggested a lower release and leaching profile by LDH-B-ALG compared to Mg_2Al-B-LDH, showing an advantage in producing LDH-B-ALG beads compared to the Mg_2Al-B-LDH in powder form.

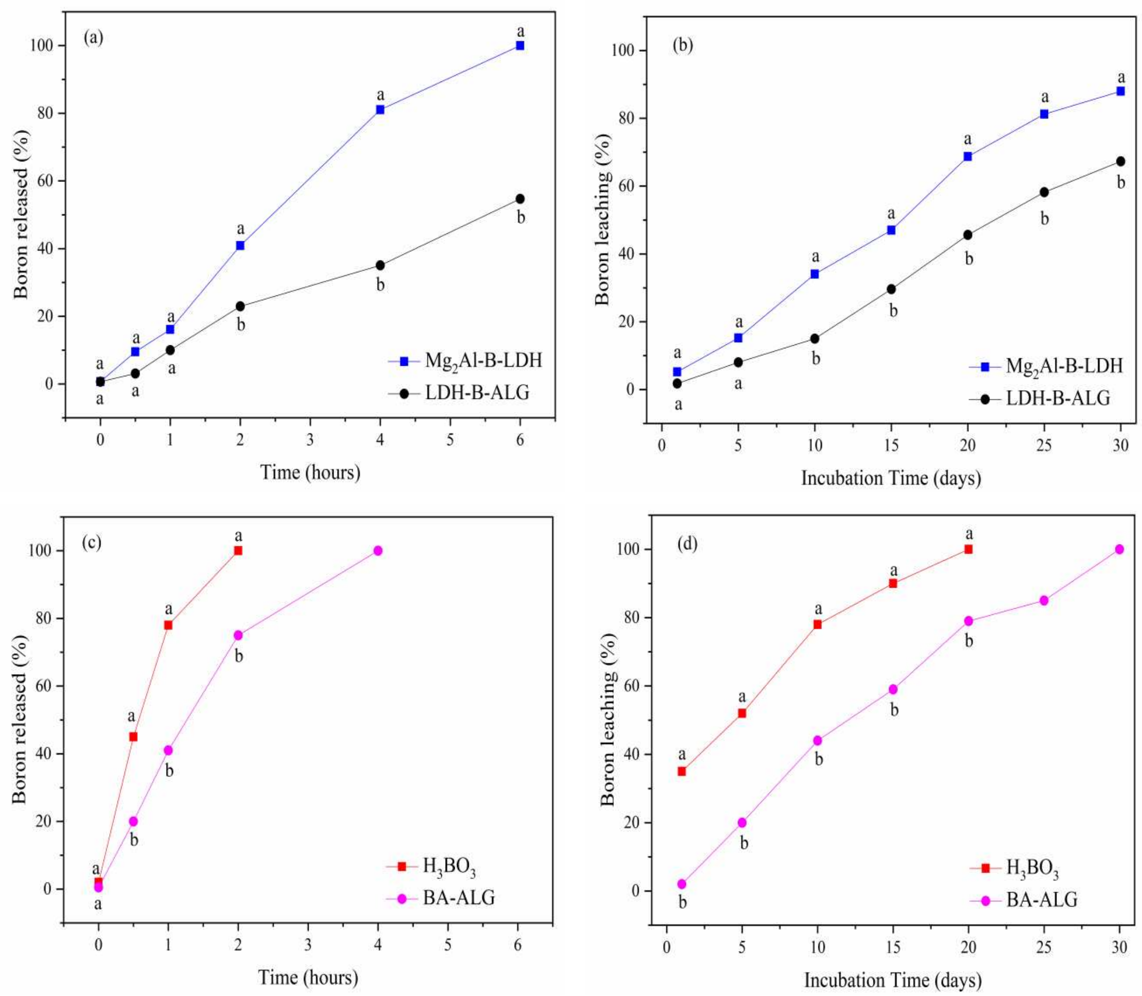

Fig. S2: Cumulative release (a and c) and leaching (b and d) of boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3, and BA-ALG. Values followed by the same lowercase letter within each time (hours) and incubation time (days), indicate that the mean of release and leaching of B, are not significantly different at $p<0.05$ according to Tukey test between B fertilizer sources.

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GENERAL CONCLUSIONS

The pristine Mg_2Al-B-LDH was successfully synthesized and characterized by XRD, ATR-FTIR, and SEM. The B availability in the clayey and sand soil after the application of Mg_2Al-BLDH was lower than that for H_3BO_3 for most incubation times as a result of the slower release of B from LDH compared to the soluble source of B. Mg_2Al-B-LDH and H_3BO_3 sources were solubilized similarly in the clayey and sandy soils and released B equally to the plants in the first cultivation of sunflower. In annual crops with immediate nutrient requirement, the results presented confirm that the B releasing from Mg_2Al-B-LDH did not impair the development of plants. Thus, results from a single cultivation in clayey and sandy soils confirmed that Mg_2Al-B-LDH can be used as an alternative source of B for plants, providing enough B release that match plant requirements. The second cultivation of sunflower in sandy soil (81% of sand) without replenish of B, showed a toxic effect on the plants when H_3BO_3 was used. For Mg_2Al-B-LDH, the release profile of B was slow and continuous, even for doses above the recommendation such as 5 mg dm^{-3} of B. These results suggested that Mg_2Al-B-LDH can be safely used as a source of B to supply this micronutrient to the plants in sandy soils for an extended period of time compared to conventional soluble sources. In the B leaching experiment in sandy soil columns, the slower and gradual release profile of Mg_2Al-B-LDH significantly decrease the amount of B leached compared to H_3BO_3. In regions with predominance of sandy soils with a high precipitation rates and nutrient leaching is a concern, the results of this study highlight the use of Mg_2Al-B-LDH as a promising slow release B fertilizer.

LDH-B-ALG microspheres was successfully synthesized and characterized by XRD, ATR-FTIR, and SEM. The chemical characterization for LDH-B-ALG showed that Mg_2Al-B-LDH (powder form) was successfully incorporated into the alginate polymer. The slow release of B from LDH-B-ALG, compared with all the sources applied in the B release and leaching tests, suggests a potential increase in the B accumulation in the root zone and fertilizer use efficiency from LDH-B-ALG. Additionally, LDH-B-ALG application when compared to BA-ALG, H_3BO_3, and Ulexite, provided B to plants with superior efficiency in soil of pH 7.5. LDH-B-ALG was solubilized similarly in the soil compared to the other B sources in greenhouse experiments without leaching and increasing rates of B. However, in greenhouse experiments with sandy soil subject to leaching, the lower leaching profile from LDH-

B-ALG application resulted in a higher shoot and total B uptake from total cultivation of sunflower and cotton. These results suggested that LDH-B-ALG can improve the B accumulation in top soil and B uptake by plants. In our case of interest, for sandy soils with low organic matter and prone to B leaching, LDH-B-ALG can successfully be used as B slow release fertilizer for plants.

In conclusion, the LDH-B-ALG application under controlled conditions was the most promising B source to be used in soils prone to B leaching. This study lays a robust platform for future field studies on the validation of these slow-release materials in agricultural settings. The alginate beads containing LDHs and fertilizers will serve as foundation for future studies focusing on macronutrients and micronutrients, that it is important to sustainability of agriculture and food security.