

# Adsorption of Boron from a Simulated Soil Solution Using Zn–Al and Mn-Doped Zn–Al Layered Double Hydroxides

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**Abstract**—Three types of layered double hydroxides (LDHs) including Zn–Al and Mn-doped Zn–Al LDHs with Mn 2 and 10 mol % respect to Zn content (Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively) were prepared. The effect of various parameters such as time, boron concentration, pH, temperature, ionic strength and competing anions were investigated to compare the efficacy of synthesized LDHs for boron adsorption in a simulated soil solution. The results suggest that the adsorption capacity of B is enhanced by incorporation of Mn in the Zn–Al LDH. The highest adsorption was observed for Zn–Mn<sub>2</sub>–Al probably due to its higher specific surface area as well as due to the ion exchange mechanism in combination with surface adsorption. The kinetics of boron adsorption on the LDHs followed a pseudo-second order model. The isotherm data of Zn–Al was matched with Langmuir model while the sorption data for Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were described by both Langmuir and Freundlich models. Although boron adsorption slightly increased with increasing pH from 5 to 9, it decreases at pH > 9 because of the competition of OH<sup>−</sup> groups and change in LDH surface charge at pH > p*H*<sub>ZPC</sub>. The negative values of Δ*H*<sub>r</sub><sup>0</sup> showed that adsorption of boron was exothermic in nature. The presence of competing anions interfere boron adsorption. Moreover, an increase of electrolyte concentration led to a decrease of boron adsorbed on the LDHs. It seems that Zn–Mn<sub>2</sub>–Al could be used as an effective sorbent for boron adsorption in soil solution, as it indicated the highest affinity to boron even at high pH and ionic strength conditions.

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## 1. INTRODUCTION

Although boron (B) is an essential element for all living organisms, the concentration range within which B is changed from a nutrient to a pollutant is rather narrow [1]. Toxic B levels are, most likely, to occur in dry areas, particularly in soils irrigated with the B-rich irrigation water [2]. Therefore, a removal of B from soil solutions containing high concentration of this element is necessary to reduce its adverse effects (e.g. cutaneous disorders and retarded growth) [3] on living creatures.

Among various separation technologies applied for the removal of B from water and wastewater (e.g. chemical coagulation [4], using of composite materials [5], reverse osmosis [6], etc.), adsorption process has been extensively investigated due to its effectiveness and simplicity [7].

Up to now, many adsorbents have been exploited for the adsorption of B from aqueous solutions, such as, fly ash [8], magnesium-aluminum oxide [9] and modified clays [10]. However, in the past few decades, layer double hydroxides (LDHs) have been considered as one of the most effective adsorbents for inorganic

anions such as borate in aqueous solutions [11–15] because of high anion exchange property and surface area [16]. The formula of LDHs is generally described as  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A^{n-})_{x/n} \cdot m(\text{H}_2\text{O})$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations, respectively,  $A^{n-}$  is an interlayer anion with the charge of  $n$  and  $m$  is the number of interlayer water molecules [16]. Although LDH materials are commonly prepared by combining divalent and trivalent metals in the equal ratio, more metals can be introduced in the brucite layer to achieve a large variety of composition [17]. Some studies have reported that the adsorption capacity enhanced by application of ternary LDHs. For example, Bharali and Deka [18] revealed that the presence of Cu greatly increased the adsorption capacity of the Mg–Cu–Al LDH for removal of organic dye contaminants compared with Mg–Al LDH. Nonetheless, almost no detailed study has been performed to examine the adsorption behavior of B on ternary LDHs in aqueous system. Therefore, the objective of this study is to compare the adsorption of B capacity of binary LDH (Zn–Al LDH) and ternary LDH (Zn–Mn–Al LDH) in the simulated soil solu-

**Table 1.** XRD parameters and specific surface areas of synthesized LDHs

Samples	$d_{003}$ , Å	$d_{110}$ , Å	Lattice parameters		BET specific surface area, m <sup>2</sup> g <sup>-1</sup>
			$a$ , Å	$c$ , Å	
Zn–Al	8.968	1.539	3.078	26.904	10.1
Zn–Mn <sub>1</sub> –Al	8.918	1.539	3.078	26.754	11.3
Zn–Mn <sub>2</sub> –Al	8.858	1.537	3.074	26.574	21.2

tion and to investigate the factors including time, initial B concentration, temperature, pH, ionic strength and competing anions influencing the adsorption of boron.

## 2. MATERIALS AND METHODS

All the chemicals used were of analytical grade and obtained from Merck manufacture. A modified urea hydrolysis method [19] was employed to synthesize nitrate form of Zn–Al and Mn-substituted Zn–Al LDHs with Zn(+Mn)/Al molar ratio of 2. Herein the contents of Mn with respect to Zn corresponded to 2% and 10% molar ratio. Accordingly, the synthesized materials denoted as Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al for the samples without Mn, with 2 and 10 mol % Mn with respect to Zn content. For the synthesis of studied LDHs, appropriate amounts of Zn (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Al (NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O and Mn(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O were dissolved in NH<sub>4</sub>NO<sub>3</sub> of 1 M to obtain 0.5 M aqueous solution (the addition of NH<sub>4</sub>NO<sub>3</sub> causes an increase of nitrate/urea molar ratio and the decrease of pH leading to the formation of pure nitrate containing LDHs). Then, urea (1.65 M) was added and the transparent mixture was maintained at 90°C under stirring. After 24 h, white solids were collected by filtration (Whatman 42 filter paper), washed with deionized water and subsequently dried at 70°C for 18 h.

The synthesized LDHs were analyzed for their total concentration of metal ions using an inductively coupled plasma optical emission spectrometry (ICP-OES) (ARCOS FHE12) after digestion in 1 : 1 HCl : H<sub>2</sub>O [20]. X-ray diffraction (XRD) patterns were obtained on a Unisantix XMD 300 diffractometer using monochromatic CuK<sub>α</sub> radiation operated at 45 kV and 0.8 mA. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet AVATAR 370 scanner at 400–4000 cm<sup>-1</sup>. The BET specific surface area of the LDHs was measured by N<sub>2</sub> adsorption isotherm using an automatic surface analyzer (Belsorp mini II), see Table 1.

The zero-point charge (pH<sub>ZPC</sub>) of prepared LDHs was determined using the method suggested by Fiol and Villaescusa [21]. The experiment was performed by adding 0.1 g of synthesized LDHs to 20 mL KNO<sub>3</sub> solution (0.03 M) with pH previously set by 0.1 M

HNO<sub>3</sub> and 0.1 M KOH solutions (shaking time = 24 h, initial pH 4–12). The pH<sub>ZPC</sub> was identified as the initial pH with minimum ΔpH, a difference between resulting and initial pH.

Anion exchange capacity (AEC) of LDHs was obtained by Wada and Okamura [22] method. At first, LDHs were saturated by 1 M NH<sub>4</sub>Cl solution buffered at pH 7, then washing steps were conducted with 0.1 M NH<sub>4</sub>Cl for five times and, finally, chloride ions were displaced by five additions of nitrate ions using 1 M KNO<sub>3</sub>. Chloride concentrations in the extracts were measured by titration with silver nitrate [23].

To determine the adsorption kinetics of B on the LDHs, the batch experiments were applied. Briefly, 0.1 g of synthesized LDHs were mixed with 20 mL of aqueous solution containing a concentration of 2.5 mM H<sub>3</sub>BO<sub>3</sub> in KNO<sub>3</sub> electrolyte solution (0.03 M ionic strength) at pH 7. After shaking for contact time ranging from 5 to 240 min, the suspensions were filtered and concentration of boron in supernatants measured by Azomethine-H method [24]. Data of time-dependent adsorption of B were plotted against pseudo-first order and pseudo-second order models. The mathematical forms and parameters of these models are shown in Table 2.

The adsorption isotherms were studied using an initial concentration range of 0.25 to 10 mM of H<sub>3</sub>BO<sub>3</sub> at pH 7 (solid-to-solution ratio of 5 g L<sup>-1</sup>, I = 0.03 M KNO<sub>3</sub> and shaking time = 240 min). The isotherm data of LDHs were fitted using the models summarized in Table 3. The influence of temperature on the adsorption of B by LDHs was investigated at initial concentration of 2.5 mM of H<sub>3</sub>BO<sub>3</sub> and different temperatures of 288 to 318 K (solid-to-solution ratio of 5 g L<sup>-1</sup>, I = 0.03 M KNO<sub>3</sub>, pH 7 and shaking time = 240 min). The pH dependence of the adsorption of B by LDHs was evaluated using 2.5 mM H<sub>3</sub>BO<sub>3</sub> at pH 5–10 (solid-to-solution ratio of 5 g L<sup>-1</sup>, I = 0.03 M KNO<sub>3</sub> and shaking time = 240 min).

In order to study the effect of competing anions on the adsorption of B by synthesized LDHs other experiment was set up in the presence of phosphate, sulfate, chloride and bicarbonate as commonly competitive anions in soil solutions. 0.1 g of synthesized LDHs were mixed with 20 mL of all 5 anions at a concentration of 2.5 mM of each anion (pH 7 and shaking time

**Table 2.** Kinetic constants for the adsorption of B onto the LDHs

Model	Equation	Zn–Al			Zn–Mn <sub>1</sub> –Al			Zn–Mn <sub>2</sub> –Al		
		constant	R <sup>2</sup>	RMSE	constant	R <sup>2</sup>	RMSE	constant	R <sup>2</sup>	RMSE
Pseudo-first order	$q_t = q_e(1 - \exp(-k_1t))$	$q_e = 0.153$ $k_1 = 0.202$	0.950	0.010	$q_e = 0.245$ $k_1 = 0.185$	0.935	0.014	$q_e = 0.308$ $k_1 = 0.189$	0.963	0.012
Pseudo-second order	$q_t = q_e^2 k_2 t / (1 + q_e k_2 t)^{-1}$	$q_e = 0.206$ $k_2 = 0.761$	0.963	0.006	$q_e = 0.292$ $k_2 = 0.634$	0.988	0.006	$q_e = 0.376$ $k_2 = 0.548$	0.993	0.006

$q_t$  and  $q_e$  (both mmol g<sup>-1</sup>) are B adsorbed at time  $t$  (min) and at equilibrium time, respectively;  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mmol<sup>-1</sup> min<sup>-1</sup>) are adsorption rate constant for pseudo-first order and pseudo-second order, respectively.

= 240 min). The amounts of phosphate and sulfate were determined by ascorbic acid [25] and turbidimetric [26] methods, respectively. Bicarbonate was calculated from the difference between the amount of nitrate exchanged and sum of adsorbed phosphate, sulfate, boron and chloride [27]. The adsorption of B under different ionic strengths from 0 to 0.1 M KNO<sub>3</sub> was studied at initial concentration of 2.5 mM of H<sub>3</sub>BO<sub>3</sub> (solid-to-solution ratio of 5 g L<sup>-1</sup>, pH 7 and shaking time = 240 min).

All experiments in the present study were repeated twice. The pH adjustments were performed by adding 0.5 M KOH and 0.5 M HNO<sub>3</sub>, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Physicochemical and Structural Characterization of Materials

Elemental analysis revealed that the Zn(+Mn)/Al molar ratios of Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were 1.82 (±0.03), 1.70 (±0.02) and 1.66 (±0.04), respectively, which were smaller than the molar ratio of 2 in a starting solution. This result could be attributed to a synthetic method of the LDHs. In fact, a decrease of the pH of the resulting solution in this method has two different effects. On the one hand, it causes the formation of pure nitrate containing LDHs. On the other hand, it leads to a slowing the formation of LDH resulting in small M<sup>2+</sup>/M<sup>3+</sup> ratios. Inayat et al. [19] and Hatami et al. [28] have been reported the same results for preparation of Zn–Al LDH by this method. Moreover, the values of M<sup>2+</sup>/M<sup>3+</sup> molar ratios decreased by increasing molar content of Mn in relation to Zn. This observation was in agreement with the finding of Morales-Mendoza et al. [29] for a synthesis of Mn-doped Zn–Al LDHs. They stated that the decrease of molar ratios is an indication that the desired content was not achieved using ternary LDH. Based on these results, the empirical formulas can be expressed as Zn<sub>0.64</sub>Al<sub>0.36</sub>(OH)<sub>2</sub>(X)<sub>0.36</sub>1.23H<sub>2</sub>O, (Zn + Mn)<sub>0.63</sub>Al<sub>0.37</sub>(OH)<sub>2</sub>(X)<sub>0.37</sub>1.32H<sub>2</sub>O and (Zn + Mn)<sub>0.62</sub>Al<sub>0.38</sub>(OH)<sub>2</sub>(X)<sub>0.38</sub>1.01H<sub>2</sub>O for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively.

The values of BET specific surface area for all studied LDHs were summarized in Table 1. The highest specific surface area (21.2 m<sup>2</sup> g<sup>-1</sup>) was found for Zn–Mn<sub>2</sub>–Al.

The XRD pattern of Zn–Al exhibited (Fig. 1a) sharp and symmetric peaks at low 2θ (003 and 006) and broad and asymmetric reflections at higher 2θ of 015 and 018, which are characteristic ones for the layered structure. The XRD pattern of Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were similar to Zn–Al indicating that these LDHs also possess a basic LDHs structure. However, the ternary LDHs, particularly Zn–Mn<sub>2</sub>–Al, showed broader and weaker reflections compared with that of Zn–Al, suggesting lower crystallinity of these LDHs [30]. It was probably due to the difference in the ionic radii of Zn<sup>2+</sup> (0.74 Å, [31]) and Mn<sup>2+</sup> (0.67 Å, [31]). Lattice parameters ( $a = 2d_{110}$  and  $c = 3d_{003}$  [32]) of synthesized LDHs were summarized in Table 1. The values of lattice parameters were in agreement with those of Zn–Al LDH with nitrate as the interlayer anion reported elsewhere [33, 28]. Furthermore, both lattice parameters slightly decreased with increasing amount of Mn<sup>2+</sup> (Table 1) which could be assumed as an evidence of the isomorphic substitution in LDHs framework [29, 31, 34]. Therefore, it seems that the substitution of Mn in ternary LDHs led to reduction of both lattice parameters and crystallinity in these LDHs.

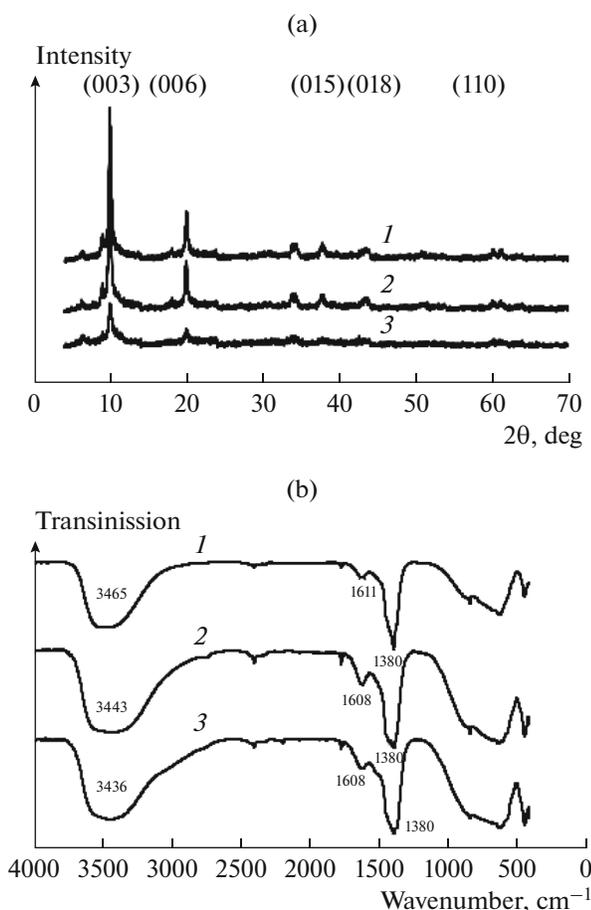
The FT-IR spectra of the samples were typical for LDH compounds, as featured by two bands around 3460 and 1611 cm<sup>-1</sup> which were assigned to the O–H stretching vibrations and H–O–H bending vibration of the interlayer water molecule, respectively (Fig. 1b) [11, 35]. Furthermore, a strong band at 1380 cm<sup>-1</sup> was attributed to the N–O stretching vibration indicating the presence of nitrate ions intercalated in the interlayer space of the LDHs [36–38].

The pH<sub>ZPC</sub> of Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were 9.04 (±0.20), 8.95 (±0.15) and 8.90 (±0.20), respectively. It seems that the incorporation of Mn did not significantly change the pH<sub>ZPC</sub> of LDHs. Yang et al. [39] and Yan et al. [40] reported the values of

Table 3. Isotherm constants for the adsorption of B onto the LDHs

Model	Equation	Zn–Al			Zn–Mn <sub>1</sub> –Al			Zn–Mn <sub>2</sub> –Al		
		constant	R <sup>2</sup>	RMSE	constant	R <sup>2</sup>	RMSE	constant	R <sup>2</sup>	RMSE
Freundlich	$q_e = k_F C_e^{1/n}$	$k_F = 0.178$ $1/n = 0.369$	0.922	0.041	$k_F = 0.199$ $1/n = 0.363$	0.976	0.025	$k_F = 0.272$ $1/n = 0.347$	0.977	0.032
Langmuir	$q_e = \frac{bk_L C_e}{1 + k_L C_e}$	$b = 0.398$ $k_L = 0.993$	0.998	0.006	$b = 0.472$ $k_L = 1.250$	0.974	0.026	$b = 0.539$ $k_L = 1.627$	0.975	0.034

$q_e$  (mmol g<sup>-1</sup>) is B adsorbed per unit mass of LDH,  $C_e$  (mmol L<sup>-1</sup>) is B equilibrium concentration,  $k_F$  (mmol<sup>(1-1/n)</sup> g<sup>-1</sup> L<sup>1/n</sup>) and  $n$  are Freundlich constants,  $k_L$  (L mmol<sup>-1</sup>) is constant related to binding energy,  $b$  (mmol g<sup>-1</sup>) is maximum adsorption capacity,  $q_m$  (mmol g<sup>-1</sup>) is saturated sorption capacity,  $E$  (kJ mol<sup>-1</sup>) is adsorption energy.



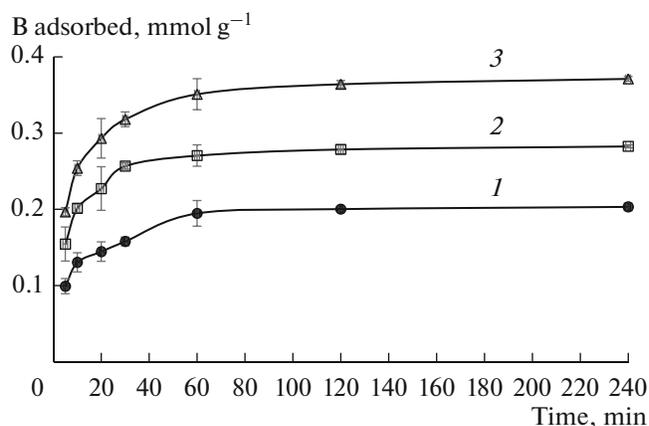
**Fig. 1.** XRD patterns (a) and FT-IR spectra (b) of Zn–Al (1), Zn–Mn<sub>1</sub>–Al (2) and Zn–Mn<sub>2</sub>–Al (3) before the adsorption of boron.

10.26 and 8.69 for the pH<sub>ZPC</sub> of Zn–Al LDHs, respectively.

The amounts of AEC were 2.43 (±0.02), 2.55 (±0.04) and 2.68 (±0.10) mEq g<sup>-1</sup>, for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively. The measured AEC values were less than theoretical AEC values (2.73 (±0.05), 2.81 (±0.03) and 2.97 (±0.07) mEq g<sup>-1</sup> for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively) which were calculated from structural formulas. In most studies, this observation has been assigned to the blocking of anion exchange sites by carbonate anions [41–43]. In other words, carbonate anion acts as an interfering one for achieving the maximum anion exchange capacity. The surface dissolution of small particles of LDHs during the measurement of AEC could be considered as another factor that affects the AEC of LDHs [44].

### 3.2. Kinetics of Boron Adsorption

The effect of contact time on the adsorption of B by synthesized LDHs suggests that adsorption process



**Fig. 2.** Adsorption of boron on the different LDHs as a function of time from solution containing 2.5 mM H<sub>3</sub>BO<sub>3</sub>: Zn–Al (1), Zn–Mn<sub>1</sub>–Al (2) and Zn–Mn<sub>2</sub>–Al (3). Solid-to-solution ratio = 5 g L<sup>-1</sup>, initial pH 7, I = 0.03 M KNO<sub>3</sub>.

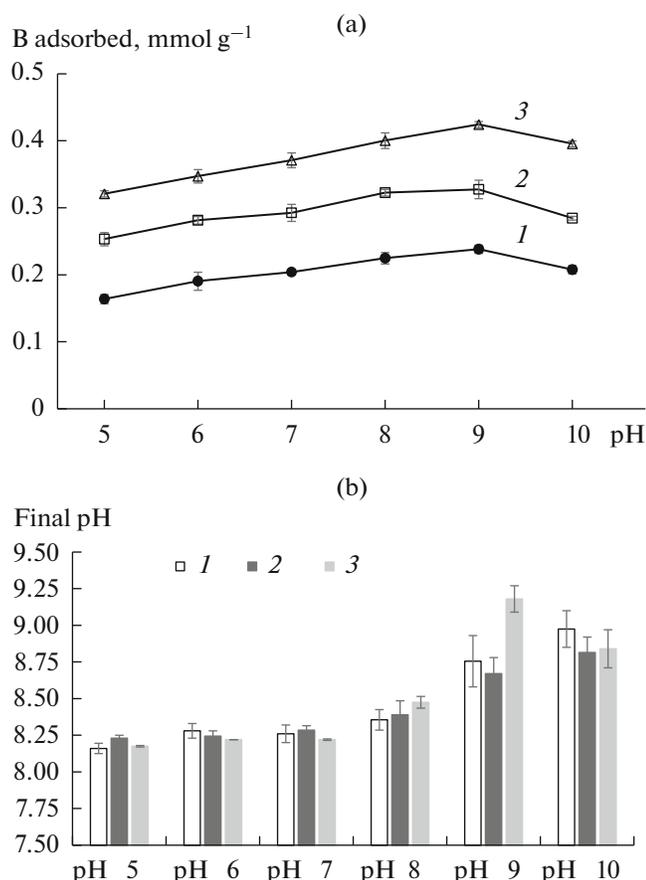
starts sharply and then proceeds rapidly for 120 min when equilibrium was achieved (Fig. 2). This behavior has already been reported for the adsorption of different anionic species on LDH compounds [45–48]. The adsorption capacities for B at equilibrium were 0.20 (±0.02), 0.29 (±0.01) and 0.37 (±0.02) mmol g<sup>-1</sup> for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively. Therefore, it may be concluded that the Mn-doped Zn–Al LDHs, especially Zn–Mn<sub>2</sub>–Al, were able to improve the adsorption capacity compared with that of Zn–Al. A specific surface area of the LDHs accounted for this result because the order of adsorption capacities was in agreement with the BET measurements (Table 1). Furthermore, the adsorption capacity of the LDHs could be influenced by the adsorption mechanisms that will be discussed later.

Although the adsorption processes completed in 120 min, a contact time of 240 min was settled for further experiments to provide adsorption completion.

In order to clarify the adsorption kinetics of B on LDHs, the experimental data were analyzed with non-linear pseudo-first-order and pseudo-second-order equations [49]; the results are presented in Table 2. The determination coefficient (R<sup>2</sup>) and root mean square error (RMSE) for estimating the goodness-of-fit of the models to the kinetics data are listed in Table 2. The values of RMSE [50] were obtained as follows:

$$RMSE = \left[ \frac{\left( \sum (q_t - q_t^*) \right)^2}{(n - p)} \right]^{0.5}, \quad (1)$$

where  $q_t$  and  $q_t^*$  (both in mmol g<sup>-1</sup>) were the observed and simulated amounts of B adsorbed at time  $t$ , respectively;  $n$  was the number of experimental data points and  $p$  was the number of fitted parameters.



**Fig. 3.** Influence of initial pH of the solution containing 2.5 mM  $\text{H}_3\text{BO}_3$  on (a) the adsorption of B by different LDH and (b) the pH of the resulting solution: Zn–Al (1), Zn–Mn<sub>1</sub>–Al (2) and Zn–Mn<sub>2</sub>–Al (3). Solid-to-solution = 5 g L<sup>-1</sup>,  $I = 0.03$  M  $\text{KNO}_3$ , shaking time = 240 min.

The highest  $R^2$  (0.963–0.993) and lowest RMSE (0.006) values were observed for pseudo-second-order model for all LDHs. The calculated values of  $q_e$  for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were 0.206, 0.292 and 0.376 mmol g<sup>-1</sup>, respectively, which are close to the experimental values. These values imply that the adsorption of B on synthesized LDHs follows the pseudo-second-order model. Same type of kinetics was reported in previous studies of the adsorption of B by LDHs compounds [3, 35, 51, 52]. The highest value of the adsorption rate constant for pseudo-second-order ( $k_2$ ) was found for Zn–Al (Table 2), suggesting that Zn–Al sorption equilibrium was reached faster than Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al. Therefore, Zn–Al shows different sorption behavior with respect to other LDHs [51].

### 3.3. Influence of pH on the Adsorption of Boron

Soil solutions have different pH depending on soil-forming factors (parent material, time, topography,

climate and organisms) [53]; therefore, the investigation of the adsorption of B by LDHs at different pH is helpful for assessing the efficiency of these compounds at different pH. The adsorption capacity of prepared LDHs over the pH range of 5–10 is shown in Fig. 3a. According to the results, the highest adsorption of B in studied LDHs was in the pH range of 8–9 while the adsorption amounts decreased above and below these values. Since at pH about 9 the concentration of  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  species are practically the same ( $\text{p}K_a = 9.2$ ) [11], the increase of the adsorption of B in this pH range could be related to increasing of  $\text{B}(\text{OH})_4^-$  concentration in the solution. Although at higher pH values (~9 to 11)  $\text{B}(\text{OH})_4^-$  is a predominant species [11], the amounts of adsorbed B declined at pH > 9 probably because of the competition between  $\text{OH}^-$  and  $\text{B}(\text{OH})_4^-$  anions for the sorption sites on the LDHs as well as because of the electrostatic repulsion between  $\text{B}(\text{OH})_4^-$  and the negatively charged adsorbent at pH >  $\text{pH}_{\text{ZPC}}$  [12]. The same behavior for the adsorption of B on LDHs was reported by Kentjono et al. [12] and Koilraj and Srinivasan [54]. The result of this experiment suggests that the external surface adsorption mechanism could be involved in the adsorption of B by synthesized LDHs due to variations in adsorbed amounts of B at different pH values.

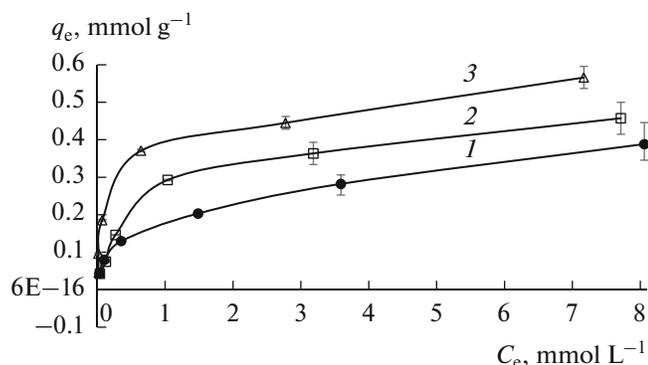
As shown in Fig. 3b, the pH values of the resulting solution of studied LDHs were between 8.16 ( $\pm 0.03$ ) and 9.18 ( $\pm 0.09$ ) suggesting high buffering capacity of LDHs [55]. This result was in agreement with the findings obtained by Ferreira et al. [11], who reported the pH of the resulting solution of 9 for Mg–Al LDH after the adsorption of B in the pH range 4–10.

According to the literature,  $\text{B}(\text{OH})_4^-$  typically exists as predominant species at low concentration (<25 mM) and at higher pH values (~9 to 11) [54]; therefore,  $\text{B}(\text{OH})_4^-$  was probably a predominant species in our study.

### 3.4. Adsorption Isotherms

The adsorption isotherm was carried out to describe the distribution of B between the liquid and adsorbent. The result showed that the adsorption amounts increased with increasing concentration of B from 0.25 to 10 mM and reached 0.39 ( $\pm 0.06$ ), 0.46 ( $\pm 0.04$ ) and 0.57 ( $\pm 0.03$ ) mmol g<sup>-1</sup> for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively (Fig. 4). However, the percentage of adsorbed B decreased with its concentration from 86.7, 84.8, 91% to 19.4, 22.9, 28.3% for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively, probably due to the saturation of the adsorption sites.

The isotherm data were modeled by nonlinear forms of Freundlich and Langmuir equations [56] as

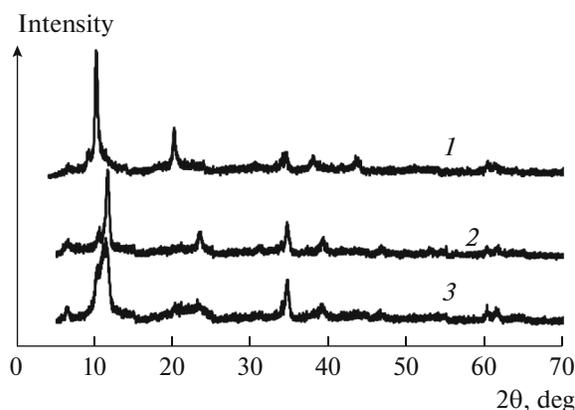


**Fig. 4.** Isotherms of the adsorption of boron by the different LDHs from solution containing 2.5 mM H<sub>3</sub>BO<sub>3</sub>: Zn–Al (1), Zn–Mn<sub>1</sub>–Al (2) and Zn–Mn<sub>2</sub>–Al (3). Solid-to-solution ratio = 5 g L<sup>-1</sup>, initial pH 7, I = 0.03 M KNO<sub>3</sub>, temperature = 25°C, shaking time = 240 min.

shown in Table 3. According to this fitting, the isotherm data for Zn–Al was best fitted by the Langmuir model with higher R<sup>2</sup> value as well as lower RMSE value than by the Freundlich model. Nevertheless, the experimental data for Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were matched well with both Freundlich and Langmuir models. Comparable results were reported by Ferreira et al. [11], Kameda et al. [52] and Gao et al. [3]. Upon Langmuir model, the maximum of adsorption capacity for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al was obtained at 0.398, 0.472 and 0.539 mmol g<sup>-1</sup>, respectively (Table 3). For Freundlich model, the values of 1/n were found between 0 and 1 (0.369, 0.363, and 0.347 for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al, respectively), indicating favorable sorption of B on LDHs [55, 57].

It is well known that the Langmuir model assumes a monolayer surface adsorption behavior; while Freundlich model implies a multilayer adsorption [58]. Hence, the adsorption of B on the outer surface of Zn–Al should be the most important adsorption mechanism in this compound, although the interlayer anion exchange mechanism may also be involved in this case. However, for Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al both mechanisms are probably important. In order to confirm this assumption, the XRD of prepared LDHs after the adsorption of B was studied (Fig. 5).

After the adsorption of B, the XRD pattern of Zn–Al did not show significant difference; while the d<sub>003</sub> values for Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al diminished to 7.68 Å and 7.84 Å, respectively. This result was in agreement with the finding of Kameda et al. [52] for the adsorption of B in Mg–Al–NO<sub>3</sub> LDH with molar ratio of 2. They stated that ion exchange between NO<sub>3</sub><sup>-</sup> and B(OH)<sub>4</sub><sup>-</sup> caused to decrease of d<sub>003</sub> value from 8.9 Å to 7.6 Å. Furthermore, they also indicated that the d<sub>003</sub> value for Mg–Al–Cl LDH did not change



**Fig. 5.** XRD patterns of Zn–Al (1), Zn–Mn<sub>1</sub>–Al (2) and Zn–Mn<sub>2</sub>–Al (3) after the adsorption of boron.

because of small amount of adsorbed B in this compound. Qiu et al. [51] reported the same results for reduction of interlayer spacing after the adsorption of B in Ca–Al LDH. That is, in addition to the value of surface area of materials, the type of adsorption mechanism influences the amount of adsorbed B in the synthesized LDHs. The amounts of the adsorbed B for Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al were higher than those in Zn–Al due to their higher BET specific surface areas and the presence of ion exchange mechanism along with surface adsorption mechanism in these compounds. The lowest adsorption was observed in Zn–Al because of its lowest specific surface area as well as low possibility of ion exchange mechanism to be involved, as evidenced by the absence of changes in the XRD pattern (Fig. 5). The ion exchange mechanism in ternary LDHs could be attributed to their smaller measured Zn(+Mn)/Al molar ratios compared with that in Zn–Al (see Section 3.1). Ay et al. [45] showed that reduction of M<sup>2+</sup>/M<sup>3+</sup> molar ratio led to an increase of the number of positive sites (M<sup>3+</sup>) in the LDHs layers allowing easier exchange of interlayer’s anions with replacing anions.

### 3.5. Influence of Temperature on the Adsorption of B

In a real soil solution system, soil temperature varies daily and seasonally by variations in the air temperature. Therefore, before applying LDHs to the real soils, it is necessary to study the influence of temperature on the adsorption of B by these compounds in the simulated soil solution. The results of this experiment indicated that the percentage of the adsorbed B slightly decreased with temperature increasing from 288 to 318 K suggesting the interactions of adsorbate and adsorbent were exothermic (Table 4). The temperature dependence of the adsorption of B is associated with changes in several thermodynamic parameters such as Gibbs free energy ( $\Delta G_r^0$ ), standard

**Table 4.** Effect of temperature on thermodynamic parameters of the adsorption of boron by LDHs

LDHs	Temperature, K	B adsorbed, %	Thermodynamic parameters		
			$\Delta G_r^\circ$ , kJ mol <sup>-1</sup>	$\Delta H_r^\circ$ , kJ mol <sup>-1</sup>	$\Delta S_r^\circ$ , J mol <sup>-1</sup>
Zn–Al	288	43.6 (±0.1)	–12.071	–11.432	2.289
	298	40.6 (±0.1)	–12.188		
	308	35.6 (±0.8)	–12.045		
	318	33.5 (±0.3)	–12.197		
Zn–Mn <sub>1</sub> –Al	288	61.9 (±1.9)	–13.856	–10.762	10.722
	298	58.6 (±0.4)	–12.979		
	308	54.2 (±1.9)	–13.995		
	318	51.9 (±2.2)	–14.212		
Zn–Mn <sub>2</sub> –Al	288	78.8 (±2.4)	–15.824	–12.673	10.686
	298	74.2 (±0.6)	–15.745		
	308	71.7 (±0.5)	–15.949		
	318	69.0 (±2.2)	–16.124		

enthalpy change ( $\Delta H_r^\circ$ ) and standard entropy change ( $\Delta S_r^\circ$ ) of adsorption. The Gibbs free energy ( $\Delta G_r^\circ$ ) was determined using the following equation [47]:

$$\Delta G_r^\circ = -RT \ln K_d, \quad (2)$$

where  $R$ ,  $T$  and  $K_d$  are universal gas constant, the temperature in Kelvin, and the distribution coefficient, respectively. The  $K_d$  values were estimated as follows [47]:

$$K_d = q_e / C_e, \quad (3)$$

where  $q_e$  and  $C_e$  are the amount of B adsorbed per unit mass of the LDHs and the B concentration per unit volume of solution, respectively.

Van't Hoff equation was used for calculating values of  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  [47]:

$$\ln K_d = -\Delta H_r^\circ / RT + \Delta S_r^\circ / R. \quad (4)$$

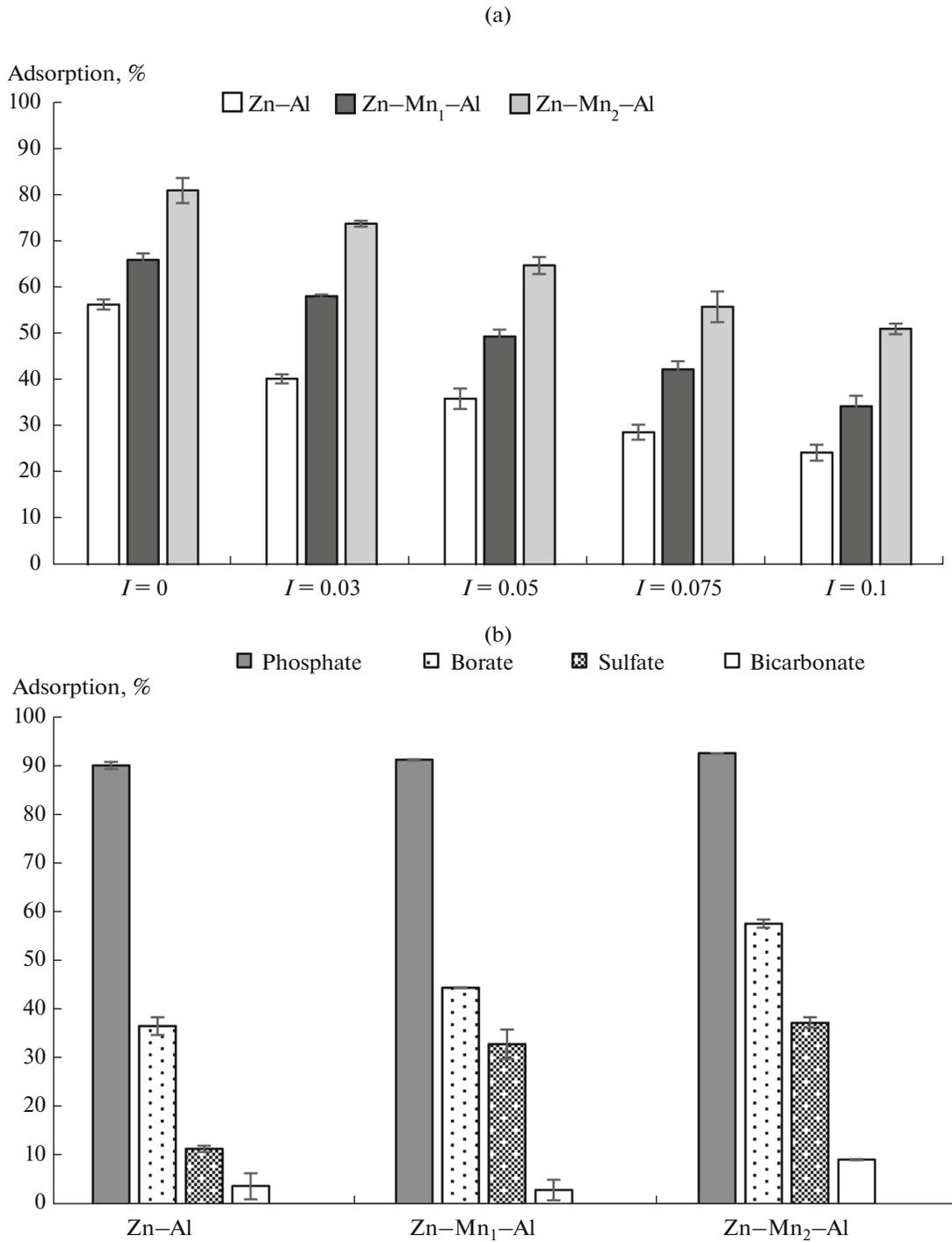
Constants in this equation ( $\Delta H_r^\circ$  and  $\Delta S_r^\circ$ ) were found using  $\ln K_d$  versus  $1/T$  plots. The slope and intercept of the lines were  $\Delta H_r^\circ / R$  and  $\Delta S_r^\circ / R$ , respectively.

All calculated parameters are summarized in Table 4. Negative values of  $\Delta G_r^\circ$  at each temperature indicate the spontaneous nature of the adsorption of B in the LDHs. A reduction in  $\Delta G_r^\circ$  values with increasing temperature suggested more favorable adsorption at higher temperature. Moreover, the higher negative  $\Delta G_r^\circ$  values for the adsorption of B on Zn–Mn<sub>2</sub>–Al suggest that the adsorption in this sample was more energetically favorable than in the other LDHs. The exothermic nature of adsorption was also confirmed

by the negative values of  $\Delta H_r^\circ$ . The obtained values of  $\Delta H_r^\circ$  implied that the adsorption processes on the LDHs were physical in nature, since the typical enthalpy change in physical adsorption process is 5–40 kJ mol<sup>-1</sup> [7]. However, Kentjono et al. [12] suggested that a combination of ion exchange and physical sorption mechanisms is probably involved in the adsorption of B by Mg–Al LDH, because  $\Delta H_r^\circ$  value was very low (13.524 kJ mol<sup>-1</sup>). The positive values of  $\Delta S_r^\circ$  correspond to the increased randomness at the solid/solution interface during the adsorption of B on the LDHs. These findings were in agreement with the results of Kentjono et al. [12] and Koilraj and Srinivasan [54] for the adsorption of B by Mg–Al LDH and Zn–Al LDH, respectively.

### 3.6. Influence of Solution Ionic Strength on the Adsorption of B

Electrolyte concentration of soil solution is considered as one the most important factors that affect the availability of nutrients in soil system. This experiment was carried out to evaluate the adsorption of B by the LDHs as a function of ionic strength of the simulated soil solution. As shown in Fig. 6a, the percentages of the adsorption of B for Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al significantly decreased from 56.7 (±1.1), 66.4 (±1.4) and 81.4 (±2.7) to 24.65 (±1.7), 43.7 (±2.8) and 51.5 (±1.1), respectively, with increasing ionic strength from 0 to 0.1 M KNO<sub>3</sub>. This observation may be attributed to the competition for adsorption sites between B and nitrate in background solution. Among synthesized LDHs, Zn–Mn<sub>2</sub>–Al showed the highest



**Fig. 6.** Effect of ionic strength (a) and competing anions (b) on the adsorption of boron by Zn-Al, Zn-Mn<sub>1</sub>-Al and Zn-Mn<sub>2</sub>-Al. Solid-to-solution ratio = 5 g L<sup>-1</sup>, initial pH 7, shaking time = 240 min.

adsorption capacity at the studied ionic strengths suggesting that this compound may be applicable for the adsorption of B even in saline environment. Hosni and Srasra [59] reported the same behavior for phosphate adsorption by LDH at varied ionic strength (0.001 to 0.1 M).

### 3.7. Influence of Competing Anions on the Adsorption of B

Since other anions can affect the adsorption of B in soil solution, the selectivity of synthesized LDHs towards B was studied in the presence of four anions (phosphate, sulfate, chloride and bicarbonate) at

equivalent concentration of boron (2.5 mM) in the simulated soil solution (Fig. 6b). The results indicate that the percentage of adsorbed anions on Zn–Al, Zn–Mn<sub>1</sub>–Al and Zn–Mn<sub>2</sub>–Al changed in the following order: chloride  $\approx$  0 < bicarbonate < sulfate < borate < phosphate. Hence, the phosphate was the most competitive anion against boron adsorption. This result was in agreement with the findings of Koilraj and Srinivasan [54]. They reported the order of phosphate > carbonate  $\approx$  chromate > hydroxyl > chloride > nitrate for the interference of other anions in uptake of borate by Zn–Al LDH. Furthermore, this behavior of phosphate anion has also been reported by Halajnia et al. [42] and Hatami et al. [28] for the adsorption of nitrate and phosphate by Mg–Al LDH and Zn–Al LDH, respectively. Generally, some factors such as anion charge and charge to radius ratio could influence the selectivity of LDHs in the anion adsorption [54, 60]. In the present study, Zn–Mn<sub>2</sub>–Al was able to adsorb about 60% of total B, although the amounts of B adsorbed onto the LDHs decreased in the presence of other anions (Fig. 6b). This result suggests the appropriate affinity of Zn–Mn<sub>2</sub>–Al for B even in multi-anionic environments. Other studies have also revealed the decrease of the adsorption of B by LDHs in the presence of sulfate, carbonate and chloride [61] and sulfate, bicarbonate, chloride and fluoride [35].

#### 4. CONCLUSIONS

The results of this study indicated that Zn–Mn<sub>2</sub>–Al could be used as an effective adsorbent for the removal of boron from solutions. This result could be related to the higher BET specific surface area and presence of ion exchange mechanism in this compound. The highest adsorption of boron was obtained in the pH range of 8–9 suggesting high performance of the LDH for the adsorption of B in alkaline soils (pH > 7) compared with acidic soils (pH < 7).

Calculated thermodynamic parameters revealed that the adsorption process was exothermic and it increased with decreasing temperature, therefore, it seems that the synthesized LDH can efficiently enhance the removal of boron from the soil solutions during the cold and nongrowing seasons. However, the results of selectivity experiment showed that the presence of competing anions, particularly phosphate, in the soil solution can suppress the adsorption capacity of the LDH. Moreover, our findings emphasized the importance of the electrolyte concentration of solution on the adsorption of boron by the LDH. Although Zn–Mn<sub>2</sub>–Al showed the highest adsorption of boron compared with other compounds in the entire range of ionic strength, the efficiency of the LDH for the adsorption of boron in non-saline soils would be much higher than that in the saline soils.

Despite the promising properties of the studied LDHs for the adsorption of boron, it is necessary to evaluate the amounts of desorbed boron from these compounds after the adsorption processes. Hence, further research on the behavior of LDHs for the boron desorption is necessary.

#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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