Boron removal using Li-Al-OH layered double hydroxide prepared by one-step mechanochemical approach

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Abstract: In this study, Li-Al-OH layered double hydroxide (LDH), which was prepared by solvent-free one-step mechanochemical reaction of LiOH and $Al(OH)_3$, was applied to remove boron from aqueous solution. Dry-grinding for 3 h at a rotational speed of 500 rpm, Li/Al molar 1/2 was the optimum condition to prepare highly crystalline of Li-Al LDH phase with no evident impure phases. Two milling products with Li/Al molar ratio at 1/2 and 2/2 were evaluated for boron adsorption. The results confirmed that Li/Al molar ratio 2/2 sample showed high boron adsorption capacity due to the physical adsorption of Li-Al-OH LDH and chemical synergism of phase gel $Al(OH)_3$. The adsorption isotherms, described by the Langmuir model, indicated maximum monolayer boron uptake capacity 45.45 mg/g, implying competitive adsorption capacity of the material in our experiment.

Keywords: Li-Al-OH LDH, mechanochemical preparation, boron adsorption, physical and chemical synergism, competitive adsorbent

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1 Introduction

Boron naturally exists extensively in earth's hydrosphere and lithosphere [1]. In nature, boron is always found as compounds combining with oxygen and other elements. Boron compounds were widely used in many industries, such as glass, electronics, ceramics, porcelain, cosmetics, semiconductors, leather, pharmaceuticals, insecticides, catalysts, fuel, and cleaning products [2]. The glass industry was the biggest consumer among them, which consumes more than half of the total production of boron compounds [1]. Moreover, boron was also an essential or at least a beneficial micronutrient for plants, human beings and animals [2]. However, it became toxic when the amount of boron was slightly greater than required, and toxicity effects caused by excess boron were more common than boron deficiency in the environment. Since a series of environmental and health issues have been found caused by boron, in 2011, WHO revised the guideline value of boron to 2.4 mg/L in drinking water [1]. However, only a few of countries followed the WHO recommendation, bcause the value of 2.4 mg/L exceeded the tolerate concentration of many crops. Therefore, in most cases lower boron concentrations could be acceptable, consequently, boron removal is a challenging problem. In order to obtain fresh water for drinking and irrigation, electrocoagulation [3], chemical precipitation [4], reverse osmosis [5], adsorption [6] have been used to boron recycling in the solution. Boron removing by adsorption process possesses low cost, adaptability, high separating efficiency advantages [1]. Various sorbents has been utilized in adsorption processes for boron removal, including activated carbon, fly ash, natural minerals, layered double hydroxides (LDHs), biological materials, oxides, mesoporous silica, complexing membranes and selective resins [1]. LDHs have aroused great attention in recent years due to their specific lamellar structure, high surface area, acidic-basic buffering capacity, high ion-exchange capacity, economic and versatile [7]. Frederick et al. [8] reviewed boron

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removal by LDH and confirmed its potential wide use in purification of water in boron removal.

Layered double hydroxides (LDHs) are a group of synthetic anionic clays possessing a general formula as: $[M^{2+}_{1-x}\ M^{3+}_{x}(OH)_2]^{x+}A^{y-}_{x/y}\cdot nH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{y-} represents the interlayer anions [9]. These materials have wide potential applications in various fields, including environmental protection, pharmaceutical preparation, organic synthesis, elastomer compositing, etc [10]. Among the numerous LDHs, Li/Al LDH is the only reported M(I)M(III) LDH which has the formula $[LiAl_2(OH)_6]^{+}A^{y-}_{1/y}\cdot nH_2O$. As such, the layer charge density of Li/Al LDH is the highest of all LDHs. Thus Li/Al LDH is superior to M(II)/M(III) LDHs because of its higher anion-exchange capacity. The uses of Li/Al LDH as adsorbents for the removal of contaminants especially heavy metals from wastewaters have been strongly addressed. Li-Al LDH, have been reported high adsorption efficiency toward Cr(V) because of the highest layer charge density among LDH compounds [11], but there are limited reports on the adsorption potential of Li/Al LDH in boron removal.

Li-Al LDH can be synthesized in aqueous solution operation including co-precipitation, hydrothermal method or urea decomposition-homogeneous precipitation [12]. However, solution operation mentioned above may result in some problems, such as the formation of intermediate phases as impurities and increasing cost of production. Alternative processes to manufacture Li-Al LDH are required with the purpose to realize a much more environment-friendly process without emission of large amounts of wastes. Mechanochemical treatment to synthesize LDHs reported by William et al. [13] is an entire solvent-free approach to synthesis LDHs. It is promising to manufacture LDHs in large scale by mechanochemical approach because of their easy operation, energy-saving, and no waste

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water emission. Mg-Al-OH [13], Mg-Al-NO_3 [14], Ca-Sn [15] LDHs have been manufactured by the solvent-free mechanochemical process. In this work, we reported the fundamental data obtained with Li-Al LDH synthesized via a one-step mechanochemical route. Meanwhile, the synthetic Li-Al LDH was added into boron solution to understand their adsorption performance. Furthermore, to elucidate the reaction mechanism and the adsorption mechanism involved, we performed physics measurements and equilibrium studies on the boron up taking process.

2 Materials and methods

All chemicals including LiOH (Sinopharm Group Co Ltd., Shanghai, Analytical reagent), $Al(OH)_3$ (Sinopharm Group Co Ltd., Shanghai, Analytical reagent), boric acid (Sinopharm Group Co Ltd., Shanghai, Analytical reagent), NaOH (Sinopharm Group Co Ltd., Shanghai, Analytical reagent), azomethine-H hydrate (Alfa Aesar, Thermo Fisher Scientific, Analytical reagent) were used as received, without further purification. All solutions were prepared with deionized water.

2.1 Preparation of LDH

Two-gram mixture of LiOH and $Al(OH)_3$ was milled at alterable Li/Al molar ratio to prepare Li-Al LDH in a planet mill (QM-3SP04, Nanjing NanDa Instrument Plant, China), which has four mill pots (50 cm^3 inner volume each) made of stainless-steel with 7 steel-balls of 17 mm diameter. Mill speed in this work was kept constant at 500 rpm (auto rotational speed). The milling time was set to be 2 h, 3 h, 4 h, 5 h, respectively and the Li/Al molar ratio was determined to be 1/2, 2/2. No washing or other treatment was done with the powder before X-ray diffraction, FTIR analysis, and surface zeta potential test.

2.2 Adsorption experiments

All solutions were prepared and stocked in polyethylene block container. Boric acid was

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used to prepare B solutions for batch adsorption experiments and B quantitative analysis. A certain amount of boric acid was added into 500 ml capped polyethylene bottles and dissolved in 100 ml deionized water, then 0.1 g of LDH sample was added into the B solution, following by shaking for 5 h with water bath (DKZ-2, Yiheng Shanghai, China) at approximately 25 ℃. Finally, the obtained solutions were centrifuged (LXJ, Anke Shanghai, China). The supernatant liquor was analyzed residual boron concentration using azomethine-H hydrates color-developing agent in UV-VIS spectrophotometer (Orion Aquamate 8000, Thermo, America) at 420 nm. The powder in the bottom of the bottles was collected and dried for 2 h at 50 ℃ for X-ray diffraction, FTIR analysis, and surface potential test.

2.3 Physics measurements

Powder X-ray diffraction patterns of the samples were recorded on a Rigaku MAX-RB RU-200B diffractometer using CuKa radiation (λ= 1.5403 Å) at the scanning rate of 15° min^{-1} and step size of 0.02° in the 2θ range of 3°–70°, operating at 20 kV and 50 mA. Fourier transformed infrared (FT-IR) (Nicolet6700, Thermo, America) spectra of the samples were measured using KBr as a diluent over 4000-500 cm^{-1}. Firstly, samples were mixed with KBr in a 1/200 ratio of their mass and then pressed to form a pellet for the measurement by diffuse reflection-Flourier transformed infrared spectroscopy from 400 cm^{-1} to 4000 cm^{-1}. The zeta potential of the powder was analyzed by zeta meter (Malvern, Zetasizer90, UK).

3 Results and discussion

3.1 Adsorption studies of the prepared Li/Al LDH

3.1.1 Effect of milling time on adsorption capacity

Fig. 1 shows the X-ray diffraction patterns for the as-prepared LDH at different milling time. Milling time obvious influences the reaction degree and consequently crystallization of

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raw materials. After dry milling of the mixture sample for 2 h, typical pattern of LDH (JCPDS card 51-0355) was clearly observed with evident existence of gibbsite. When the milling time was increased to 3 h, the sample exhibited a typical layered double hydroxides structure as illustrated by its well-defined XRD pattern, in which the feature peaks included a high-intensity peak (001) at low degree (2θ= 10.26°) followed by two weaker peaks (002 at 2θ= 24.64°, 003 at 2θ= 35.64°). Continuously increasing the milling time leads to a reduction in the integrated intensity of reflections from Li-Al LDH and increases their width (Fig. 1). The decrease in the integrated intensity of the reflections is testimony to amorphization of the components. The d_{001} basal value gave 7.56, 7.59, 7.61 and 7.62 Å at 2, 3, 4 and 5 h milling, respectively. Considering no other anions were involved in the preparation process expect tiny CO_2 from the air, the anions in the interlamination of Li-Al LDH could only be CO_3^{2-} and OH^-. Previous studies gave 7.54–7.56 Å of d_{001} basal value for Li–Al–OH LDH and 7.6 Å for Li–Al–CO_3 LDH [10]. The increase in d_{001} basal value from 7.56 Å to 7.62 Å with the increase in milling time in Fig. 1 suggested the dominant existence of OH^- anions in the LDH synthesized in the first three hours and CO_3^{2-} anions in the LDH synthesized in the third hour later.

Fig.2 shows batch adsorption results of the as-prepared Li-Al LDH products dry–milled for different times with absorbent dosage 1g/L, boron concentration 200mg/L at 25℃ for 5 h. The initial pH value was approximately 8.2 after adding 0.1g LDH sample into the B solution. Borate ion ($B(OH)_4^-$) and H_3O^+ can be formed by the hydrolysis of boric acid (H_3BO_3) [16, 17]. At pH 8.2, the main B species were confirmed to be $B(OH)_3$ and $B(OH)_4^-$ [8]. In all experiments, only the presence of $B(OH)_3$ and $B(OH)_4^-$ in solution were considered.

A well lamellar structure in the LDH materials is essential for good adsorption performances of LDH. After milling for 3 h, almost complete reaction between LiOH and

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$Al(OH)_3$ to form Li-Al LDH was confirmed and the corresponding adsorption capacity of the sample reached 28.21 mg/g. Longer time milling than 3 h weakened the degree of crystallinity and the corresponding adsorption capacity of the sample obviously declined, which indicated 3 hours may be the optimum point.

3.1.2 Effect of molar ratio on adsorption capacity

By keeping 3 h of milling, the effect of molar ratio of Li/Al on the preparation of LDH was investigated by comparing two mixtures with the ratio of 1/2 and 2/2, respectively and the results were presented in Fig. 3. Although LDH phase was observed from both two patterns, only the ratio of Li/Al at 1/2 gave a pure phase without observable impurity phases. In the upper pattern, namely the starting materials $LiOH/Al(OH)_3$ at 2/2, peaks of $LiOH·H_2O$ and $LiAlO_2$ were observed. Starting material LiOH remained in the products as $LiOH·H_2O$ due to its excessive addition. The formation of $LiAlO_2$ in the milled mixtures was due to the solid reaction between $Al(OH)_3$ and LiOH [18].

Fig.4 (a) shows batch adsorption results of the prepared Li-Al LDH products dry-milled at different Li/Al mole ratio. It was discovered that Li/Al mole ratio 2/2 showed higher boron adsorption capacity (33.41 mg/g). After adding 0.1 g sample into 200 mg/L B solution, the initial pH value was 8.2 for 1/2, 9.0 for 1/1. The dissolution of $LiAlO_2$ and unreacted alkaline $LiOH·H_2O$ led to the increase of pH value. We conducted a control experiment to testify the influence of initial pH on boron removal using 5 % NaOH solution as pH modifier. 0.1 g sample (Li/Al molar ratio 1/2, milling time 3 h) was added into 100 ml 200 mg/L B solution and then the pH value of the solution was adjusted to 8.2, 9.0, 10.8, respectively. Fig.4 (b) indicated boron removal declined with an increase of initial pH, which proved the intensification of boron removal by Li/Al 2/2 was not caused by the pH increase.

Li-Al LDH phases and considerable $LiAlO_2$ can be apparent observed in Li/Al 2/2

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sample. $LiAlO_2$ may play a vital role in adsorbing considerable amount of boron acid and thus increase the boron adsorption capacity compared with the Li/Al 1/2 sample. The boron adsorption mechanism of $LiAlO_2$ will be discussed in the 3.2.1 part.

The results suggest that Li/Al 1/2, grinding time 3 h may be the optimized technical parameters to produce highly crystalline of Li-Al LDH phase, while Li/Al 2/2, grinding time 3 h may the optimized technical parameters to produce high adsorption capacity of Li-Al LDH for boron removal.

3.2 Discussion

3.2.1 Reaction mechanism

The theory formula of Li-Al-OH LDH is $LiAl_2(OH)_7 \cdot xH_2O$ [19] which indicates Li/Al=1/2 is suitable for the synthesis of Li-Al-OH. The reaction degree (Eq.1) increases with the adding of milling time can be presented as:

$$LiOH+2Al(OH)_3 \rightarrow LiAl_2(OH)_7 \quad (1)$$

The high value of Li/Al does no help to the formation of LDH structure for chemical reaction between $Al(OH)_3$ and redundant LiOH as shown in Fig.3 (Eq. 2-4).

$$LiOH+Al(OH)_3 \rightarrow LiAlO_2+2H_2O \quad (2)$$

$$\frac{1}{2}LiOH+Al(OH)_3 \rightarrow \frac{1}{2}LiAl_2(OH)_7 \quad (3)$$

$$\frac{1}{2}LiOH+\frac{1}{2}H_2O \rightarrow \frac{1}{2}LiOH \cdot H_2O \quad (4)$$

Total reaction progress can be presented as Eq. 5:

$$2LiOH+2Al(OH)_3 \rightarrow LiAlO_2+\frac{1}{2}LiAl_2(OH)_7+\frac{1}{2}LiOH \cdot H_2O+\frac{3}{2}H_2O \quad (5)$$

3.2.2 Adsorption mechanism

Generally, the boron ion can be removed by LDH through two mechanisms: ion-exchange (indicated by the increasing of d_{003} spacing [17]) and surface adsorption (indicated by the

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shifting of zeta potential to negative value [20, 21]). In order to identify the adsorption mechanism, XRD patterns were carried out as shown in Fig. 5. The interlayer space d_{003} was 2.47 Å before adsorption and 2.49 Å after adsorption. Nearly invariable d_{003} indicated that the mechanism of boron uptake for the LDH was not ion-exchange and interlayer -OH made no difference to remove boron. Miyata [22] proved -OH possesses the highest position of the ion selectivity of HT-like compounds which cause none ion-exchange between boron species and -OH. The zeta potential of the materials before and after adsorption shifted to negative direction from -1.85 mV to -11.15 mV in pH 8.75 which coincided well with experimental results from Kentjono et al. [20] implying the adsorption of boron on the external surface of the material by surface complex formation.

Fig. 5 shows the FT-IR patterns of the sample (B) before adsorption and sample (A) after adsorption. Infrared bands positioned 3465 cm^{-1}, 1649 cm^{-1}, 1637 cm^{-1}, 1027 cm^{-1} and 534 cm^{-1} observed in the spectrum of sample (B) were attributed to Li-Al LDH [10]. The bands positioned at 866 cm^{-1} observed from the spectrum of the sample was attributed to lithium hydroxide monohydrate [10]. A doublet at 1437 and 1503 cm^{-1} in (B) may be the CO_3 absorption band [18] confirming CO_2 adsorption from ambient because milling was conducted in the atmosphere and LiOH would easily react with CO_2 [10]. Infrared bands around 788 cm^{-1} and 696 cm^{-1} were attributed to the $LiAlO_2$.

In comparison, the spectrum of the hydroxide after adsorption represents the typical bands of Li-Al LDH sample from the previous reports [10]. The spectrum of sample (A) has a broader absorption band in the -OH stretching region centering at 3471 cm^{-1}. The $LiAlO_2$ in the sample transformed to phase gel $Al(OH)_3$ as shown in Eq.5 and helped to adsorb boron acid. Zhu et al. [23] proved phase gel $Al(OH)_3$ can react with H_3BO_3 as shown in Eq. 6. The absence of any sharp peaks in this region at around 3471 cm^{-1} proved the chemical analyses

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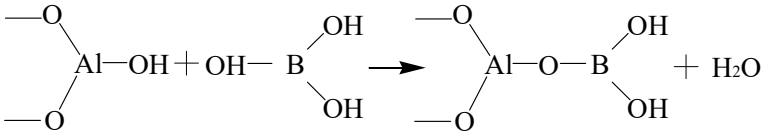
that boron was held directly to the hydroxide surface. The infrared bands around 1016 cm^{-1} and 944 cm^{-1} observed from the spectrum of the sample (A) were attributed to tetrahedral borate [24] and $B(OH)_4^-$ [16], respectively [10], confirming the presence of $B(OH)_4^-$ units on the surface of the sample.

Above all, the boron adsorption mechanisms of Li-Al-OH LDH sample prepared by one-step dry-milling could be surface adsorption of anion boron species on LDH and chemical adsorption of boron acid by gel phase $Al(OH)_3$ came from hydrolysis of $LiAlO_2$. The specific responses were shown in Eq. 6-7.

$$LiAlO_2+2H_2O\rightarrow LiOH+[Al(OH)_3] \quad (6)$$



(7)

0.1g Li/Al 2/2 (grinding time 3 hours) samples were added into 100ml B solutions with various concentration of for 5 h shaking without pH adjustment. The data obtained from the adsorption process was fitted into Langmuir adsorption isotherm shown in Fig.7. The maximum monolayer boron uptake capacity value and Langmuir constant (b) value are 45.45mg/g, 0.01964 L/mg, respectively, with R^2 0.95722. Ferreira et al. [16] reported a maximum boron uptake capacity of 14.0 mg/g for Mg-Al (NO_3) LDH and 3.6 mg/g for Mg–Fe (NO_3) LDH. Jiang et al [17] confirmed maximum adsorption capacity of 1.2–13 and 16.1–17.3 mg/g for uncalcined Mg-Al(NO_3) LDH and Mg-Al(NO_3) LDH calcined at 450 ℃, respectively. Maximum adsorption capacity of boron removal from optoelectronic wastewater using Mg-Al (NO_3) LDH was reported to be 37.9 mg/g [20]. Boron uptake capacity of Li-Al LDH in our experiment was comparable with previous reports.

4 Conclusions

Li-Al-OH LDH was prepared by solvent-free one-step milling and was used to adsorb boron from aqueous solution in this study. The experimental results suggested the following

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conclusions:

1. Three hours of milling at 500 rpm, Li/Al molar ratio 2/2 was the optimum condition to prepare superior B adsorption capacity of Li-Al-OH LDH. Adsorption isotherms suggest maximum monolayer boron uptake capacity can reach 45.45 mg/g which is competitive to other LDH boron adsorbents.
2. XRD patterns of the sample before and after adsorption shows little increasing of d_{003} spacing indicating the ion-exchange between boron species and OH^- does limited help to remove boron. FT-IR patterns of the sample after adsorption confirmed the vibration of anion boron species. Zeta potential shifting to negative direction illustrated boron adsorption on the surface of the material.
3. Phase gel $Al(OH)_3$ came from hydrolysis of $LiAlO_2$ may do considerable contributions to boron removal by chemical absorption.

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Reference

[1] Guan Z, Lv J, Bai P, Guo X. Boron removal from aqueous solutions by adsorption — A review. Desalination. 2016;383:29-37.

[2] Hilal N, Kim GJ, Somerfield C. Boron removal from saline water: A comprehensive review. Desalination. 2011;273:23-35.

[3] Ezechi EH, Isa MH, Kutty SRM, Yaqub A. Boron removal from produced water using electrocoagulation. Process Safety and Environmental Protection. 2014;92:509-14.

[4] Lin J-Y, Shih Y-J, Chen P-Y, Huang Y-H. Precipitation recovery of boron from aqueous solution by chemical oxo-precipitation at room temperature. Applied Energy.

2016;164:1052-8.

[5] Hsui C-Y. The optimal allocating pumping rate of a multi-well system for a brackish water desalination plant. Desalination. 2008;221:215-24.

[6] Sun L, Huang J, Liu H, Zhang Y, Ye X, Zhang H, Wu A, Wu Z. Adsorption of boron by CA@KH-550@EPH@NMDG (CKEN) with biomass carbonaceous aerogels as substrate. J Hazard Mater. 2018;358:10-9. Epub 2018/06/30.

[7] Wang SL, Hseu RJ, Chang RR, Chiang PN, Chen JH, Tzou YM. Adsorption and thermal desorption of Cr(VI) on Li/Al layered double hydroxide. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2006;277:8-14.

[8] Theiss FL, Ayoko GA, Frost RL. Removal of boron species by layered double hydroxides: a review. J Colloid Interface Sci. 2013;402:114-21. Epub 2013/05/03.

[9] Zhong L, He X, Qu J, Li X, Lei Z, Zhang Q, Liu X. Precursor preparation for Ca-Al layered double hydroxide to remove hexavalent chromium coexisting with calcium and magnesium chlorides. Journal of Solid State Chemistry. 2017;245:200-6.

[10] Qu J, He X, Wang B, Zhong L, Wan L, Li X, Song S, Zhang Q. Synthesis of Li–Al layered double hydroxides via a mechanochemical route. Appl Clay Sci. 2016;120:24-7.

[11] Wang S-L, Lin C-H, Yan Y-Y, Wang MK. Synthesis of Li/Al LDH using aluminum and LiOH. Applied Clay Science. 2013;72:191-5.

[12] Qu J, Zhang Q, Li X, He X, Song S. Mechanochemical approaches to synthesize layered double hydroxides: a review. Applied Clay Science. 2016;119:185-92.

[13] Tongamp W, Zhang Q, Saito F. Preparation of meixnerite (Mg–Al–OH) type layered double hydroxide by a mechanochemical route. Journal of Materials Science. 2007;42:9210-5.

[14] Tongamp W, Zhang Q, Saito F. Mechanochemical route for synthesizing nitrate form of layered double hydroxide. Powder Technology. 2008;185:43-8.

[15] Ferencz Z, Szabados M, Ádok-Sipiczki M, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I. Mechanochemically assisted synthesis of pristine Ca(II)Sn(IV)-layered double hydroxides and their amino acid intercalated nanocomposites. Journal of Materials Science. 2014;49:8478-86.

[16] Ferreira OP, de Moraes SG, Duran N, Cornejo L, Alves OL. Evaluation of boron removal from water by hydrotalcite-like compounds. Chemosphere. 2006;62:80-8. Epub 2005/06/07.

[17] Jiang J-Q, Xu Y, Quill K, Simon J, Shettle K. Laboratory Study of Boron Removal by Mg/Al Double-Layered Hydroxides. Industrial & Engineering Chemistry Research. 2007;46:4577-83.

[18] Kharlamova OA, Mitrofanova RP, Isupov VP. Mechanochemical synthesis of

 doi:10.20944/preprints201811.0477.v1

fine-particle γ-$LiAlO_2$. Inorganic Materials. 2007;43:645-50.

[19] Britto S, Kamath PV. Polytypism in the lithium-aluminum layered double hydroxides: the $[LiAl_2(OH)_6]+$ layer as a structural synthon. Inorg Chem. 2011;50:5619-27. Epub 2011/05/25.

[20] Kentjono L, Liu JC, Chang WC, Irawan C. Removal of boron and iodine from optoelectronic wastewater using Mg–Al (NO_3) layered double hydroxide. Desalination. 2010;262:280-3.

[21] Rojas Delgado R, Arandigoyen Vidaurre M, De Pauli CP, Ulibarri MA, Avena MJ. Surface-charging behavior of Zn-Cr layered double hydroxide. J Colloid Interface Sci. 2004;280:431-41. Epub 2004/11/10.

[22] Miyata SJC, Minerals C. Anion-Exchange Properties of Hydrotalcite-Like Compounds. 1983;31:305-11.

[23] Zhu D, Cheng D, Geng M, Liu W. Analysis to structural regimes of boron–containing adsorption complex on the surface of aluminum hydroxide. Journal of Huazhong Agricultural. 1998;17:40-4.

[24] Ay AN, Zümreoglu-Karan B, Temel A. Boron removal by hydrotalcite-like, carbonate-free Mg–Al–NO_3-LDH and a rationale on the mechanism. Microporous and Mesoporous Materials. 2007;98:1-5.

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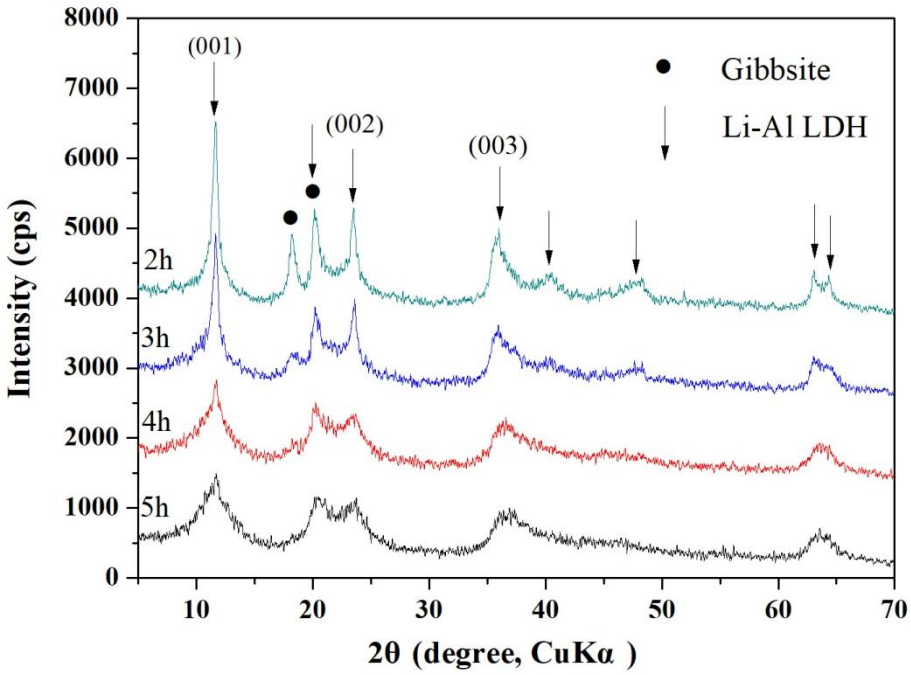

Fig. 1 XRD patterns of Li-Al LDH sample prepared at different milling times.

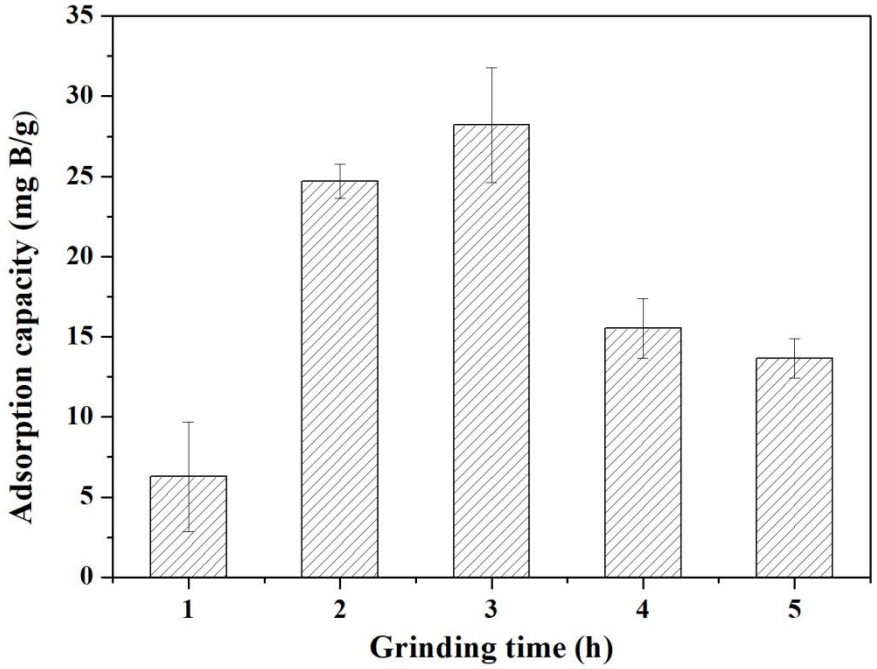

Fig. 2 Boron adsorption by prepared LDHs as a function of milling times without pH adjustment.

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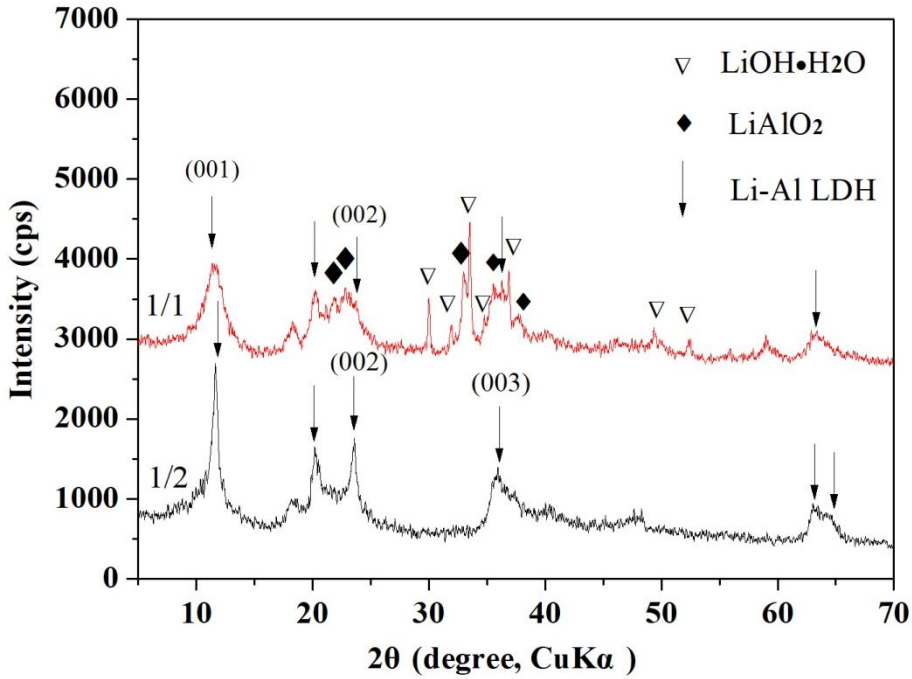

Fig. 3 XRD patterns of prepared Li-Al-OH LDHs by milling different molar ratios of LiOH and $Al(OH)_3$.

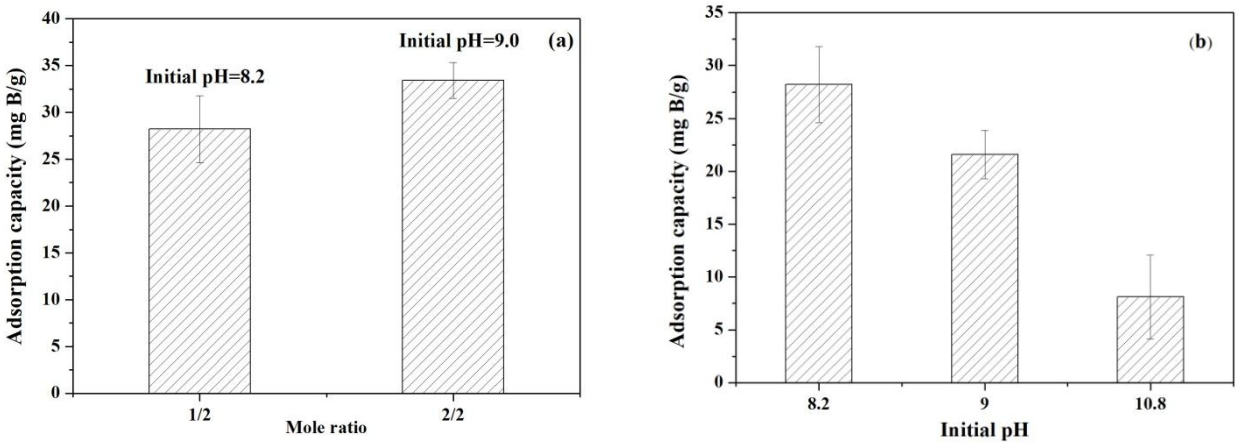

Fig. 4 (a) Boron adsorption under different conditions: (a) boron adsorption by prepared LDHs as a function of Li/Al molar ratio without pH adjustment; (b)boron adsorption as a function of initial pH adjusted by NaOH solution.

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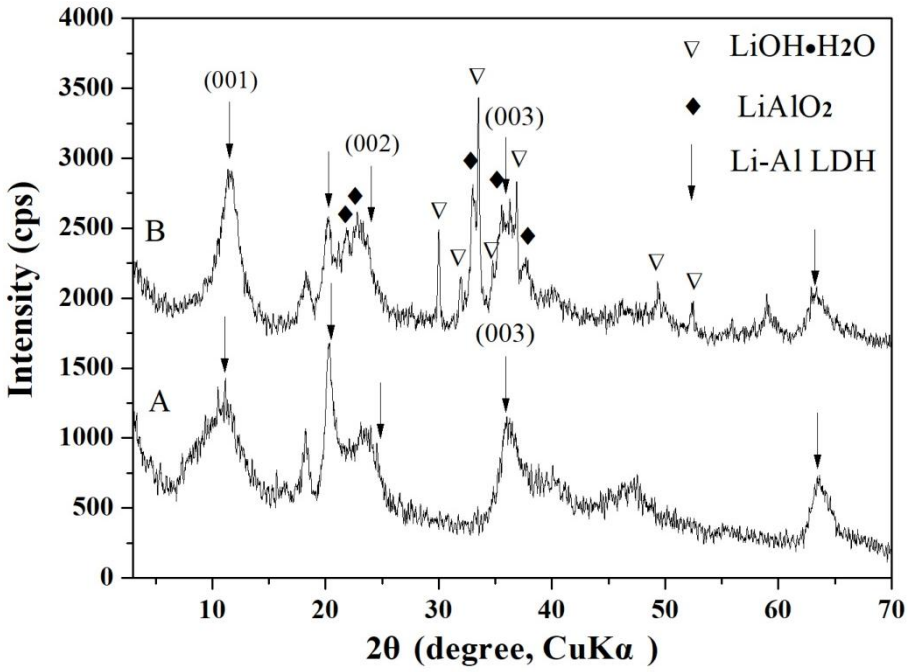

Fig. 5 XRD patterns of Li-Al-OH LDH studied before adsorption (B) and after adsorption (A).

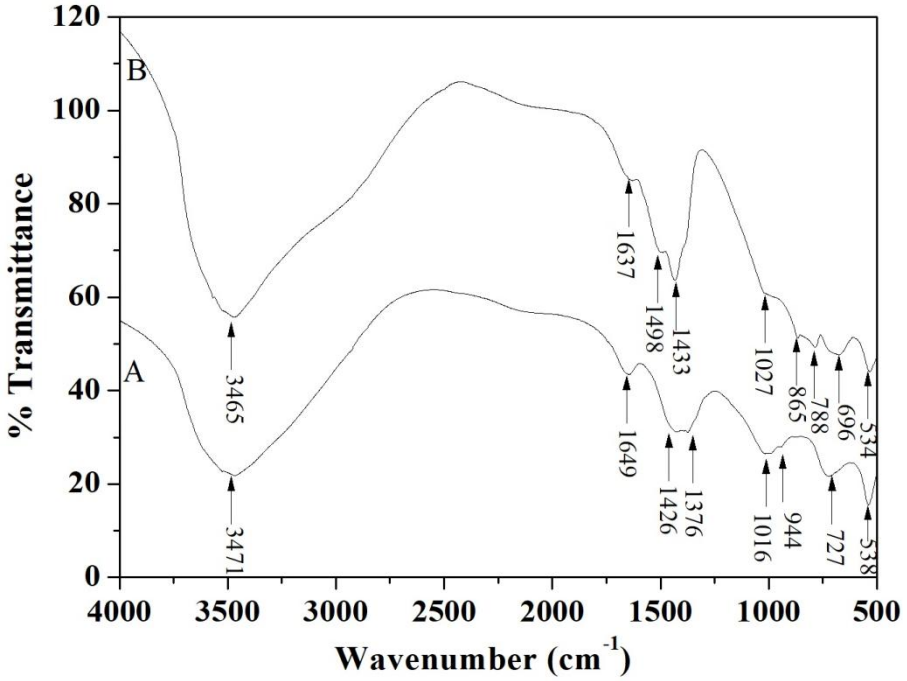

Fig. 6 FT-IR patterns of Li-Al-OH LDH studied before adsorption (B) and after adsorption (A).

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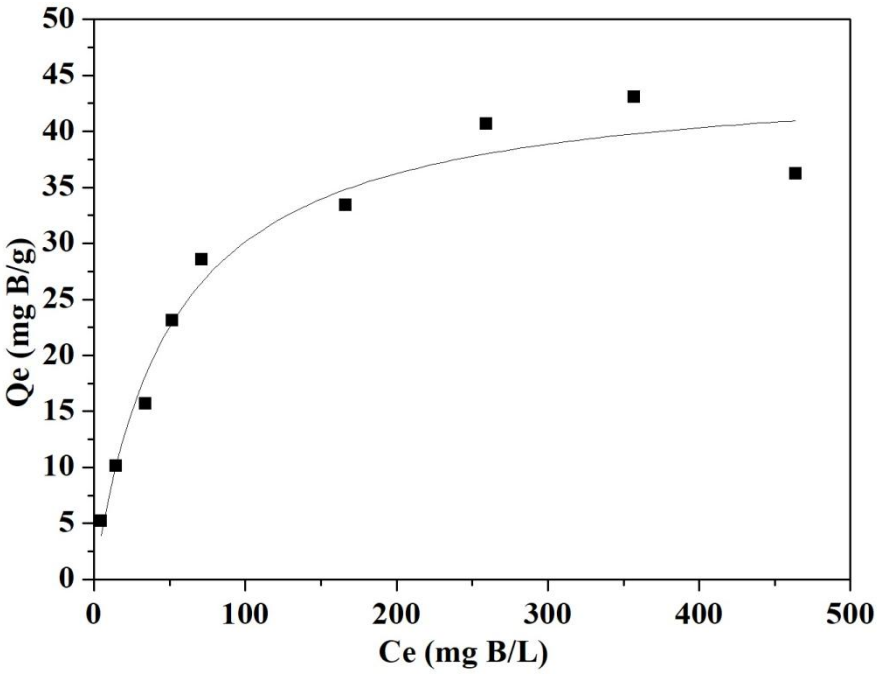

Fig. 7 Adsorption Langmuir isotherm on Li-Al-OH LDH.