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Synthesis of Mg/Al double-layered hydroxides for boron removal

Jie Liu, Xiuli Guo, Junsheng Yuan*

Engineering Research Center of Seawater Utilization Technology, Ministry of Education, Hebei University of Technology, Tianjin, China
Tel. +86 22 6020 4598; Fax: +86 22 6020 4274; email: jsyuan@hebut.edu.cn

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ABSTRACT

About 5 mg/L boron are present in seawater. Excessive boron is harmful to living beings so, boron removal is extremely essential in seawater desalination process. Mg/Al double-layered hydroxides (Mg–Al–LDHs) materials, which show excellent boron removal properties, were synthesised by chemical co-precipitation method in this paper. The effects of molar ratio of Mg/Al, concentration of solution, reaction time and temperature, drying time and temperature on boron removal capacity were evaluated. All the experimental conditions had an influence on boron removal capacity by affecting the degree of crystallinity and crystallite size. The concentration of solution has a notable effect on boron adsorption property of LDHs. The products calcined in 450°C had a better boron removal capacity. The best adsorption capacity for boron was 33 mg/g.

Keywords: Boron; Mg/Al double-layered hydroxides; Adsorption; Co-precipitation

1. Introduction

Boron is widely distributed in both the hydrosphere and lithosphere of natural environment in the form of complex compounds combining with oxygen and other elements. Boron and boride are extensively used in chemical, metallurgical, electronics, medicine, national defense and other industrial department, such as flame retardants, detergents, wood preservatives, antifreeze and micronutrient fertilizers and so on [1]. As an essential nutrient, boron plays an important role for human beings, animals and plant growth in the appropriate quantity range. Boron is essential for the development of an embryo for at least vertebrates and relating to immune function of organisms and bone metabolism [2,3]. For plants, boron is a structural component of primary cell walls and helps to form neat structure of the cell wall which provides stability to the cell wall matrix. Boron also is involved in lignifications, membrane transports, enzyme interactions, nucleic acid synthesis, phenol and carbohydrate metabolism, and the transport of sugar, polyol and hydroxy acid [4]. Though boron is essential for living beings in many ways, it becomes toxic when the amount of boron is slightly greater than requirement. So the intakes need to be tightly controlled. The standards or guidelines about boron concentration of drinking water had been established by various environmental regulation organisations [5]. For example, World Health Organisation (WHO) has set 2.4 mg/L of boron as the limit in drinking water. Meanwhile, "for most of the world, the concentration of boron in drinking water is judged to be below 0.5 mg/L".

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*Corresponding author.

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The researches of boron removal from wastewater and seawater are always meaningful tried by a range of technologies including adsorption [6–8], ion exchange [9], electrocoagulation [10], chemical precipitation [11], Donnan dialysis [12] and so on. The methods of boron selective resin, membranes and adsorption membranes filtration were researched and applied widely in recent years. Boron removal capacity was improved by grafting a boric acid chelating group, i.e. N-methyl-D-glucamine in the researches of boron selective resin treatment, also optimal operating parameters, such as pH, temperature and so on, were investigated. The prime of membranes methods were nanofiltration (NF) and reverse osmosis (RO) membranes. The researching emphases were ameliorating membranes characters and exploring optimal pH, operating temperature and operating pressure. Recent years, one of development tendency of boron removal technology was the integration of multiple methods, which can make use of the advantages of different methods. Adsorption membrane filtration (AMF) is getting more and more attention. The AMF process has been identified as a promising boron removal method with high performance and low operation cost [13]. The main advantage of AMF was utilising the high absorptive selectivity of boron selective resins (BSR) and the simple operation of membrane filtration process. All of these techniques have advantages and disadvantages, and the selection of which should be based on the treatment efficiency and operating cost.

Another development trend of boron removal methods is using natural materials and inorganic materials. Among these materials, double-layer hydroxides (LDHs) is receiving more and more attention in recent years because it is environment-friendly, cost-effective, safe and harmless. LDHs or hydrotalcites are types of synthetic anionic clays, and their structure can be represented by the general formula $M(II)_{1-x}M(III)_x(OH)_{2}(A^{n-})_{x/n}\text{-}mH_2O$, in which both divalent (M(II)) and trivalent cations (M(III)) give positively charged sheets. The positive charge is balanced by intercalation of anions (A^{n-}) in the hydrated interlayer regions. The interlayer anion together with the stoichiometric coefficient (x) may be varied over a wide range, giving a range of isostructural materials [14]. LDHs have been used as adsorbent of phosphate in pharmaceutical application, base-catalyst and inorganic anion-exchanger for adsorption of various anions, such as F^-, Cl^-, Br^-, NO_3^- and HPO_4^{2-} [15,16]. The boron absorption properties were also studied [17–20]. Recently, organic and inorganic hybrid materials with new functions based on layered compounds have also been focused the spotlight of attention [21].

Although LDHs as boron removal adsorbent were researched to some extent, the effects of synthetic conditions and adsorption conditions on the boron adsorption capacity had not been investigated systematically. So, Mg–Al–(NO_3)–LDH for boron removal was prepared by chemical co-precipitation method in the present work. The synthetic conditions, including reacting temperature and time, molar concentration, mole ratio and drying condition, were investigated in detail. At the same time, the utilisation of LDHs in seawater desalination process was also investigated.

2. Experimental

2.1. Materials preparation

Al $(NO_3)_3$ and Mg $(NO_3)_2$ were selected as aluminium and magnesium source, and NaOH solution was alkaline source. The different concentrations of boron solution were prepared with boric acid and distilled water. Curcumin used as the analysing reagent of boron concentration with ethanol (95%).

2.2. Sample preparation

The LDHs containing Mg/Al were prepared by co-precipitation method. At first, a mixed solution of Al_2 $(NO_3)_3$ and Mg $(NO_3)_2$ was prepared with Al $(NO_3)_3$ and Mg $(NO_3)_2$ in given concentrations (C_M) and Mg/Al molar ratio. Then the mixed solution was slowly added into NaOH solution under stirring at 40℃. The temperature was elevated to a given value and kept constant. The final products were separated by centrifugation and washed five times by distilled water. Finally, the products were dried, calcined, grinded and kept for testing. All the experimental condition parameters could be adjusted according to experiment requirements.

2.3. Boron removal tests

1.0 g adsorbent was added into 100 ml of 1,000 mg/L boron solution and was stirred 10 h then the supernatant liquor was centrifuged. The boron concentration of the solution was analysed by acid–base titration ($B \geqslant 100$ mg/L) and curcumin spectrophotometry ($B \leqslant 100$ mg/L) [22]. And the adsorption capacity could be calculated by the following equation:

$$Q = (C_0 - C_1)V/m \quad (1)$$

where Q is boron removal capacity, mg/g; C_0 is the boron concentration before adsorption, mg/L; C_1 is the boron concentration after adsorption, mg/L; V is the volume of boron solution, L; and m is the quantity of adsorbent, g.

2.4. Characterisation

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku 2500 PC (Japan) using Cu K_α radiation ($k = 1.5406$ Å) radiation at 40 mA and 40 kV and a scanning rate of 12 min^{-1} at an interval of 0.02°. The particle morphology of LDHs was observed by a high-resolution scanning electron microscope (HITACHI S-4800 SEM) at an accelerating voltage of 3.0 kV. The elemental composition was determined by scanning electron microscope–energy dispersive X-ray spectrometer (SEM–EDS).

3. Results and discussion

3.1. The effects of molar ratio of Mg/Al

The effect of molar ratio of Mg/Al on adsorption capacity was investigated and the results were shown in Fig. 1. The adsorption capacity was nearly constant when the molar ratio of Mg/Al was between one and four, which was a little smaller when molar ratio of Mg/Al was out of the range. When molar ratio of Mg/Al was two, the adsorption capacity was larger compared with others. The affiliated number of –OH by Mg and Al were different due to their charge, so the molar ratio has an effect on the reaction ratio between metal positive and hydroxide ions.

To investigate the effects of molar ratio of Mg/Al on the LDHs crystal structure, the products when the molar ratio of Mg/Al was 2–4 were analyzed by XRD system, and the results were shown in Fig. 2. The characteristic peaks became sharper with the increasing of molar ratio of Mg/Al, which indicated the crystals regularity was increased. The aluminum ion in the octahedral center was affected by the oxygen weak field, the stabilisation of corresponding crystal field and the stabilisation of complexes of aluminum ion with oxygen declined. When the molar ratio of Mg/Al increased, the aluminum content on layer board reduced. Because the structure stability was strengthened, the diffraction peak intensity in XRD spectrum diagram increased and the peak became harp gradually. The regularity of crystals was increased with the molar ratio of Mg/Al increasing from two to four. However, the boron removal capacity had not changed apparently, so it could be concluded that boron removal were not only affected by crystals regularity, but also some other facts.

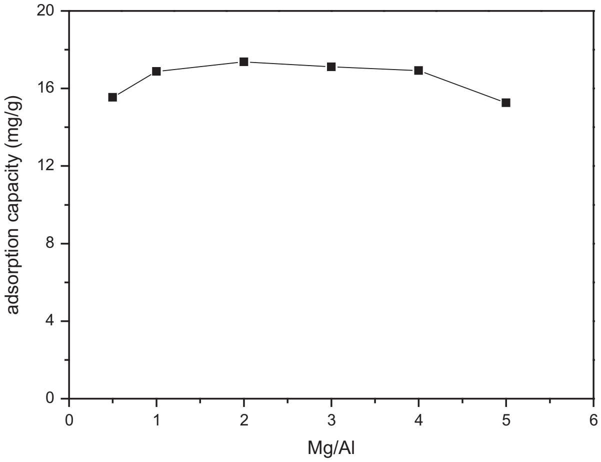


Fig. 1. Effect of molar ratio of Mg and Al for boron removal (C_M: 2 mol/L, reaction time: 3 h, reaction temperature: 90℃, drying time: 24 h, drying temperature: 100℃).

3.2. The effect of concentration of the mixed solution

The effect of the mixed solution concentration of Al $(NO_3)_3$ and Mg $(NO_3)_2$ on adsorption capacity was shown in Fig. 3. The largest boron adsorption capacity was 17.4 mg/g when the concentration of the mixed solution was 2 mol/L, it was indicated that the proportion between the hydroxyl ions and cation (Mg^{2+}, Al^{2+}) had an important influence on boron removal. A non-constant pH method was used in this paper, in which the mixed solution (2 mol/L) was dropped into the sodium hydroxide solution. That is to say, fixed quality OH^- and different quality cation (Mg^{2+}, Al^{3+}) were added in reactions, so the ending the pH of reaction was different when changing the cation concentration. The influence of concentration on boron removal could be regarded as the influence of pH. The pH does not only influence the solubility of solutes and crystal growth rate, but also change the growth of elementary structure, finally decided the

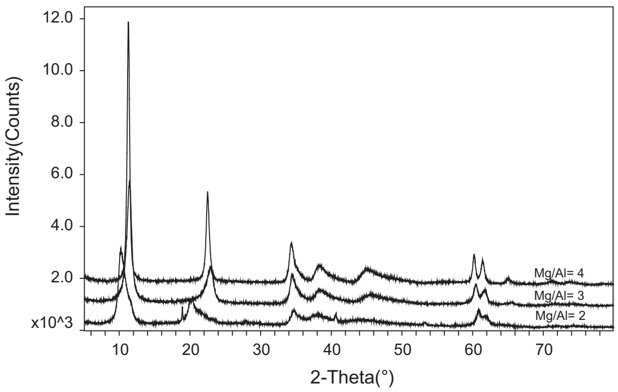


Fig. 2. XRD analysis of different molar ratio products.

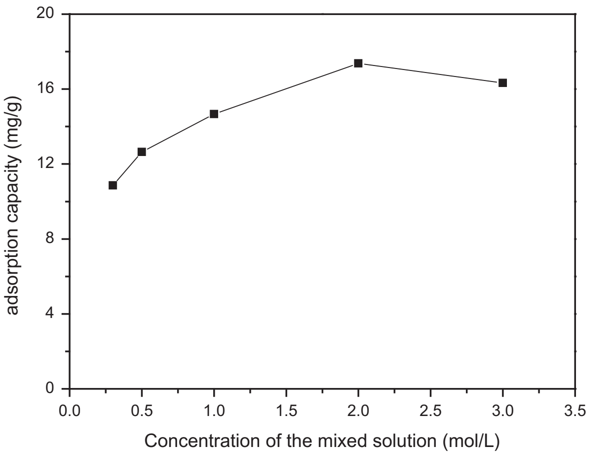


Fig. 3. Effect of concentration for boron removal (Mg/Al: 2, reaction time: 3 h, reaction temperature: 90℃, drying time: 24 h, drying temperature: 100℃).

crystal structure, size and beginning temperature of crystallisation [23]. When pH was 10, the boron removal capacity of products was more satisfactory in some references.

The XRD analysis results were shown in Fig. 4. The peaks became broad and short with the increasing of concentration and when the peak intensity decreased. When the concentration was different in solution, the degree of supersaturation was changed in the reaction process, which has an obvious effect on the regularity of crystal. Growth rate of crystal was faster in the high degree of supersaturation, but flaw of crystal structure was also easy to be formed. In the low degree of supersaturation, growth rate of crystal was relatively slow and crystal structure was integrated. So it was beneficial to the growth of the crystal, and the neat structure and greater size crystals could be obtained. Oppositely, the higher concentrations were helpful for nucleation process. The structure regularity of crystals prepared became worse and particle size was smaller compared to the one in the low concentrations. It was indicated that the adsorption capacity was the highest in this study when the concentration was 2 mol/L so it could be concluded that both of the particle size and regularity of crystals could influence the capacity of boron removal.

3.3. The effect of reaction temperature and time

The effect of reaction temperature on boron removal was shown in Fig. 5. The adsorption capacity increased with temperature from 50℃ to 90℃, whereas it was declined slightly when the temperature

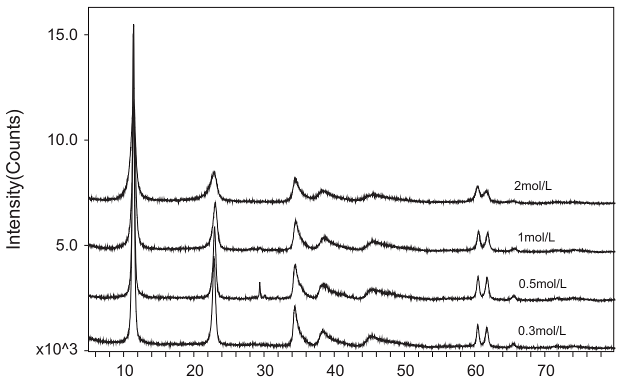


Fig. 4. XRD analysis products of different concentration.

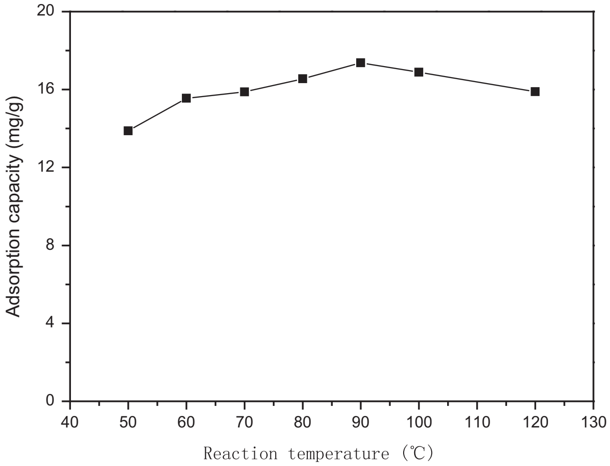


Fig. 5. Effect of reaction temperature for boron removal (C_M: 2 mol/L, Mg/Al: 2, reaction time: 3 h, drying time: 24 h, drying temperature: 100℃).

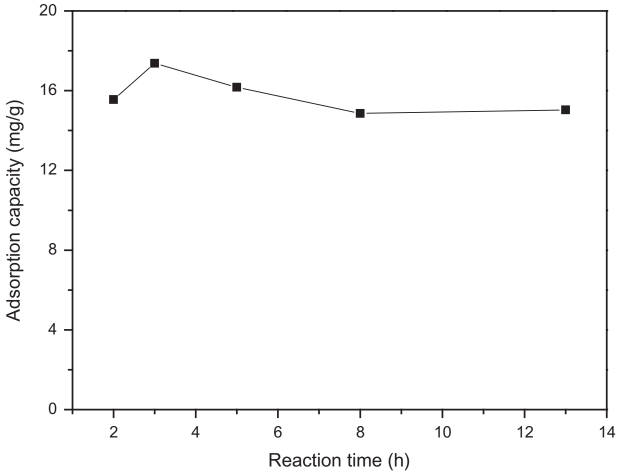


Fig. 6. Effect of reaction time for boron removal (C_M: 2 mol/L, Mg/Al: 2, reaction temperature: 90℃, drying time: 24 h, drying temperature: 100℃).

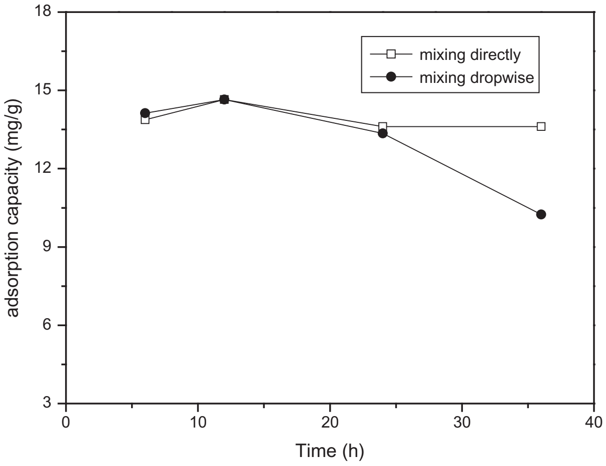
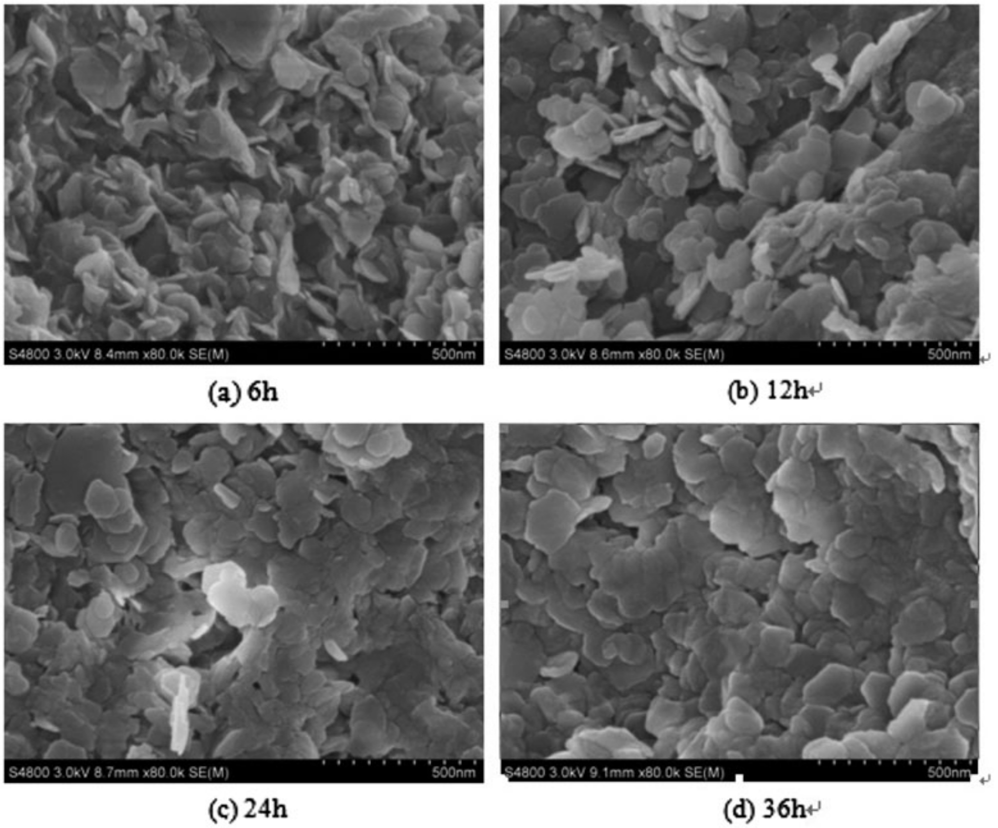


Fig. 7. The effect of different hydrothermal condition.

was higher than 90℃. The influence of reaction time on boron removal was revealed in Fig. 6. The adsorption capacity was the optimal when the reaction time was 3 h in the range of experimental value 2–13 h.

A series of complicated changes of particles would be occurred in the process of reacting precipitation. Small particles dissolved to disappear gradually, large particles grew and mean particle sizes increased finally. The other change was that the amorphous structure transformed into crystalline ones. Reaction temperature and time affected boron removal capacity by influencing particle size and regularity, simultaneously. Prolonging reaction time, the crystal structure of the products became more regular, and the characteristic peaks on the XRD spectrum diagram become sharper. High temperature was beneficial to the crystal growth, but the effect of temperature on crystal regularity of products was ambiguous. According to the experimental results, the reaction temperature 90℃ and the reaction time 3 h was best.

Degree of crystallinity reflects a crystal structure ordering. A good degree of crystallinity is accompanied by an increase of crystallite size in most cases. In general, the higher temperature and the longer time in reaction, the higher degree the crystallinity of products and the bigger the crystallite size. The boron removal capacity of products was related to crystallinity and crystallite size. The selected reaction temperature and time should insure a higher crystallinity and smaller crystallite size, which was helpful to boron removal.



(a) 6h (b) 12h

(c) 24h (d) 36h

Fig .8. SEM photographs of LDH prepared at different reaction time.

A hydrothermal synthesis experiment was carried out to confirm former conclusion. Hydrothermal synthesis method was tested at different reaction time and different mixing patterns. The adsorption capacity of products prepared by hydrothermal synthesis method was shown in Fig. 7. The adsorption quantities reduced with reaction time, and the products prepared by direct mixing had weaker adsorption capacity than products prepared by dropwise mixing.

The best of boron removal capacity was 12 h from the adsorption data in Fig. 7. The sizes of particles prepared by hydrothermal synthesis method were shown in Fig. 8. The particle sizes become bigger and more uniform with time increasing. Degree of crystallinity was high and crystallite size was smaller from SEM photos (Fig. 8(b)) compared with others. Combined with adsorption data and SEM photos, the affecting facts of adsorption capacity were degree of crystallinity and crystallite size.

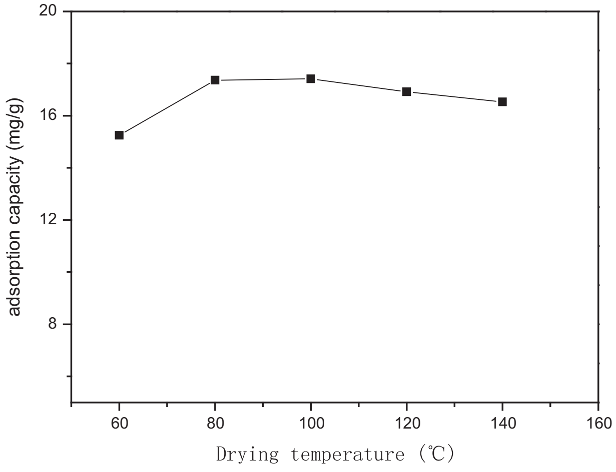


Fig. 9. Effect of drying temperature (C_M: 2 mol/L, Mg/Al: 2, reaction temperature: 90℃, reaction time: 3 h, drying time: 24 h).

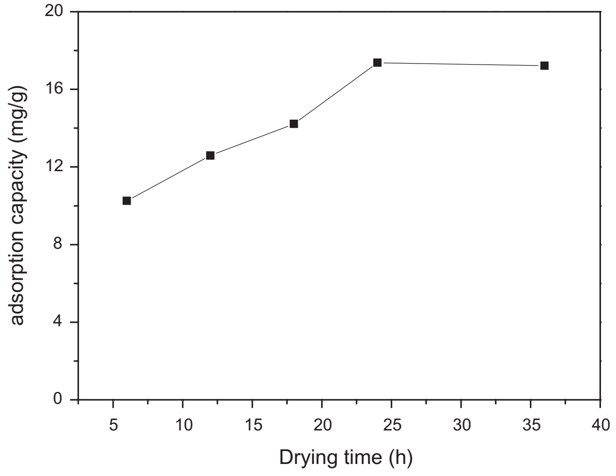


Fig. 10. Effect of drying time (C_M: 2 mol/L, Mg/Al: 2, reaction temperature: 90℃, reaction time: 3 h, drying temperature: 100℃).

3.4. *The effect of drying temperature and time*

The effect of drying temperature and time was demonstrated in Figs. 9 and 10. The adsorption capacity increased with prolonging drying time and rising drying temperature to some extent. The reason could be concluded from the following two aspects.

On one hand, the drying conditions has an obviously influence on the corresponding surface tension of products, which induce to an agglomerate among some particles. Then the related application characters of particle surface would be affected. In the process of boron removal, surface adsorption was the prime principle of removing boron. Once agglomerate phenomenon happened, the particle size would become

Table 1
Effects of calcinations and mixing method

	Calcinations temperature (℃)	Adsorption capacity (mg/g)
Directly mixing	Without calcining	11.53
	350	20.61
	450	17.24
Dropwise mixing	Without calcining	16.72
	350	23.98
	450	21.39

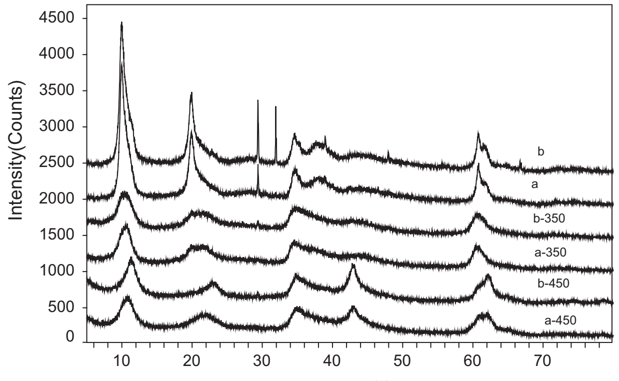


Fig. 11. XRD analysis of calcinations a: directly mixing, without calcining; b: dropwise mixing, without calcining; a-350: directly mixing, calcined under 350℃; b-350: dropwise mixing, calcined under 350℃; a-450: directly mixing, calcined under 450℃; b-350: dropwise mixing, calcined under 450℃).

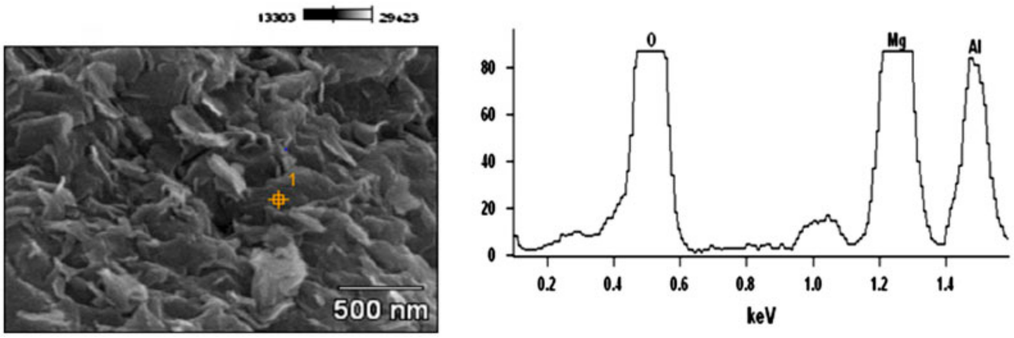


Fig. 12. SEM–EDS images of the products.

big and the specific surface area decreased. All of these reduce the adsorption site between boron and adsorbent, finally boron removal capacity decrease.

On the other hand, the water molecules are easier to be taken off in higher temperature, so there is more space for boron adsorption. However, while the temperature was beyond a certain value aggregation happened, which could reduce specific surface area of particles and be adverse to adsorption for boron, so an optimal drying temperature was required. The drying temperature of 100˚C was considered to be appropriate from the experimental results in this paper. In the same way, water could be removed more completely by prolonging drying time and 24 h is long enough.

3.5. The effect of calcination

Results of different calcinations temperature and mixing method were showed in Table 1. The adsorption capacity of calcined products was superior to the one without calcining, and products prepared by dropwise mixing were better than the one prepared by direct mixing. The XRD results of those products are shown in Fig. 11. There were motley peaks of $NaNO_3$ in the XRD spectrogram of both non-calcination products, and the peaks disappeared by calcination, which showed that $NaNO_3$ had decomposed at high temperature. The peaks of MgO appeared in the XRD spectrogram of 450˚C calcination products. It was produced from the partial decomposition of LDHs when the temperature was higher than 400˚C. The decomposition of products was the reason of decrease of adsorption capacity.

3.6. SEM–EDS analysis of LDHs

The products were analysed by scanning electron microscope-energy dispersive X-ray spectrometer (SEM–EDS). In SEM–EDS analysis, back scattered images by SEM were observed and the elemental compositions were analysed with EDS. An example spectrum was shown in Fig. 12, and the elemental composition data for product in Table 2. The main elements contained in products were O, Mg and Al, the atom ratio of Mg/Al was two. The atom number of O element (73%) was excess the demanded number (63%) of the Mg and Al. It was demonstrated that hydroxide was the major form of oxygen in LDHs. And the oxygen existed in form of bound water between the layers maybe is another one. There were also a small amount of carbon and nitrogen elements existing in form of CO_3^{2-} and NO_3^- in the products, though those elements were not detected because of little content beyond limit of detection. In addition, oxygen element also existed in crystal water.

Table 2
SEM–EDS results for products

Element	Weight (%)	Atom (%)
O	63.37	73.15
Mg	23.55	17.89
Al	13.08	8.96

Table 3
Composition of seawater and desalted water

Ions	Seawater (mg/L)	Desalted water (mg/L)
Cl^-	19,350	210
SO_4^{2-}	2,710	9
HCO_3^-	140	2
B	5	
Na^+	10,770	130
Mg^{2+}	1,290	4
Ca^{2+}	410	1

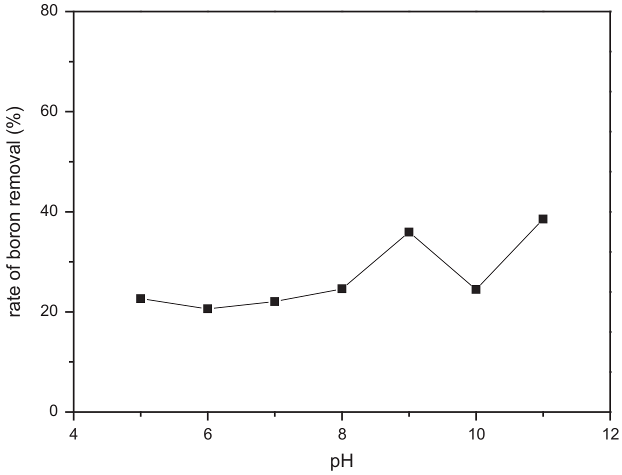


Fig. 13. Boron removal capacity in different pH seawater.

3.7. Boron removal tests of seawater and desalted water

The LDHs were synthesised in selected conditions and were tested for boron removal in seawater under different pH values. The composition of seawater was shown in Table 3 and the results were shown in Fig. 13. The boron removal ratios were increased slightly with the increase of pH value when the pH value was lower than nine. However, the boron removal ratio was not more than 40%. When the pH value was adjusted to more than nine, the flocks of Mg $(OH)_2$ was appeared which had influence on the adsorption of boron, which could also be shown in Fig. 13. A scaling would be induced under high pH value when LDHs was used in seawater desalination process. So the pH value for boron removal should not be higher than nine when it was used as a pretreatment.

From the result in Fig. 13, it was indicated that the salts in water has significant effect on the boron removal which induce to lower removal ratio. There were so many ions in seawater which had interference with the process of boron removal. So using LDHs as the pretreatment of seawater desalination in the removal of boron may be is not a suitable choice. The boron removal test on desalted water was carried out. The composition was shown in Table 3. The results of boron removal of Mg–Al (NO_3) LDHs for desalted water were showed in Table 3.

The boron removal ratio was almost above 90% in the desalted waster (Table 4), and the value was not influenced by the boron concentration. The difference between these two water types was indicated the ion interference was an important factor on the absorption of LDHs. So, in seawater desalination process, LDHs should be used as a post-treatment technology to enhance the boron removal ratio.

Table 4
Rates of boron removal from different boron concentration desalted water

Boron concentration (mg/L)	1.95	4.08	7.1	8.6	9.9
Rates of boron removal (%)	94.36	95.83	95.92	94.07	87.78

4. Conclusions

The Mg–Al (NO_3) LDH for boron removal was prepared by chemical co-precipitation method in this paper. The effect of molar ratio of Mg/Al, the calcined products were superior to non-calcinations, products dropwise mixing were better than products in direct mixing. The appreciate calcination temperature was 350℃. The factors affecting boron removal capacity were crystallinity and crystallite size. All of the investigated preparation conditions affected boron removal capacity through affecting the products crystallinity and crystallite size. The maximum adsorption capacity of the LDHs was 33 mg/g.

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