Removal of Boron from Water by Mg-Al-Ce Hydrotalcite Adsorption

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Abstract: Boron is an important micronutrient for plants, animals and human. A magnesium aluminum cerium hydrotalcite (Mg-Al-Ce-HT) was successfully prepared by co-precipitation method for boron removal. XRD, FT-IR, SEM, EDS, and XPS analyses were employed to confirm the structure and characteristic. The adsorption efficiency of Mg-Al-Ce-HT was studied as a function of initial pH, the amount of adsorbent, the concentration of initial boric acid and contact time. pH of the solution appears to have little effect on boron sorption at pH less than 8.0. When the pH exceeds 8.0, the adsorption capacity decreases. The optimum amount of adsorbent is 200 mg and the maximum adsorption capacity reaches 32.52 mg g⁻¹. Boron removal will reach the equilibrium within 160 min. The adsorption isotherm shows the adsorption is a spontaneous and endothermic process. And the data i well fitted with Langmuir model, indicating that the adsorption is a monolayer adsorption.

Key words: boron removal; hydrotalcite; adsorption

Boron is an important micronutrient for plants, animals and human in the world. However, high concentrations of boron are also harmful to animals and plants. Excessive boron not only reduces fruit yield, leading to premature and large leaf damage, but also leads to dysfunction of the cardiovascular, nervous, digestive and sexual systems of humans and animals. In the earth’s crust, the average abundance of boron is 10 × 10⁻⁶. Boron is often found in seawater, groundwater and industrial wastewater. The concentration of boron in seawater is between 4 and 5 mg L⁻¹, but in some active volcanoes and groundwater with geothermal activity, the concentration of boron will reach 119 mg L⁻¹. The amount of boron in industrial wastewater is usually at a high level, and it is very likely that these wastewaters will be discharged into rivers or seawater. In 2011, the World Health Organization limited the maximum concentration of boron in drinking water to below 2.4 mg·L⁻¹, and many countries set higher standards for boron. Therefore, it is important to find an effective boron removal method. At present, the methods for removing boron from water mainly include adsorption, ion exchange, electrocoagulation, chemical coagulation, reverse osmosis, and membrane separation. Among these various techniques for the adsorption of boron, the fixed bed method based on solid adsorbent has been proven to be superior because of its operational simplicity and high adsorption efficiency. At present, common adsorbents for adsorbing boron include boron selective resin, fly ash, industrial waste, natural materials, oxides and hydroxides, hydrotalcite and metal organic frameworks. Among them, hydrotalcite (hydrotalcite) is an economical and simple adsorbent to remove boron.

In this work, Mg-Al-Ce-HT was prepared by the coprecipitation method. And the effects of initial pH, adsorbent content, initial boric acid concentration, experimental temperature and contact time on the adsorption performance were studied through a series of experiments.

1 Experimental section

1.1 Sample preparation

All reagents were of chemical reagent grade and used without further purification. The Mg-Al-Ce hydrotalcite were synthesized by the co-precipitation method. Mg(NO₃)₂·6H₂O (25 mmol), Al(NO₃)₃·9H₂O (1 mmol) and Ce(NO₃)₃·6H₂O (4 mmol) were dissolved in 40 mL deionized water (Solution I). NaOH (3.47 g) and Na₂CO₃ (0.35 g) were dissolved in 40 mL deionized water (Solution II). Solution I was added into solution II with stable stirring and placed at room temperature for 6 h. The precipitate was sepa-
rated by centrifugation and washed several times with deionized water until the pH of the supernatant nearly 8.0. The sediment was dried in vacuum at 60 °C for 12 h. The dried product was calcined at 400 °C for 4 h.

1.2 Boron adsorption

In boron adsorption studies, amount of Mg-Al-Ce-HT was added into 50 mL aqueous solution of 100 mg L⁻¹ H₃BO₃. The mixture was placed in a conical flask and shaken up in the temperature controlled shaker for 12 h at 25 °C. The adsorbent was filtered off and the boron concentration of the residual solution was tested by ICP-OES. In order to explore the impact of different factors in the experiments, the amount of adsorbent, initial pH, initial concentration of boric acid and contact time was set as variable quantity in different batch experiments. For an adsorption and thermodynamics study, Mg-Al-Ce-HT was added into a series of boric acid aqueous solutions at different temperatures (308 K, 313 K, and 323 K). The adsorbent was dispersed into these boron solutions with dosage of 200 mg. The mixtures were placed in 50 mL conical flask and shaken up in the temperature controlled shaker for 12 h. The adsorbents were filtered off when the adsorption process finished, and the boron concentration was analyzed by ICP-OES.

1.3 Data analysis

The boron adsorption experiments used batch experiments method. The effects of adsorbent content, initial pH, initial concentration, adsorption isotherms contact time were investigated, respectively. According to the experiments data of the boric acid concentration after adsorption, the adsorption percentages (∊) and adsorption capacity (Cₛ) were calculated by the following equations:

\[ ∊ = \frac{C₀ - Cₛ}{C₀} \times 100\% \]  (1)

\[ Cₛ = \frac{(C₀ - Cₛ)V}{m} \]  (2)

Where \(C₀\) (mg L⁻¹) is initial concentration of boric acid; \(Cₛ\) (mg L⁻¹) is equilibrium concentration of boric acid; \(m\) (g) is mass of the adsorbent; \(V\) (mL) is volume of the solution.

2 Results and discussion

2.1 Characterization

Figure 1 showed the TG-DSC curve for the Mg-Al-Ce-HT precursor. According to the curve, the Mg-Al-Ce had a broad endothermic peak and the calcination temperature around 300°C to 400°C with a corresponding mass loss in the TG curve. Meanwhile, the DSC curve in 350°C shows a broad exothermic peak, which corresponds to dehydration of Mg-Al-Ce-HT, forming the final hydrotalcite structure. As the bound water in Mg-Al-Ce-HT is broken, the material’s structure has changed and formed the hydrotalcite structure. When the temperature rising above 400°C, the structure tends to be stabilized with no more changed. Therefore, 400°C is considered as the optimum calcination temperature for Mg-Al-Ce-HT and the materials are used for all the subsequent experiments.

![Fig. 1 TG-DSC curves of Mg-Al-Ce-HT precursor](image)

In order to contrast the difference of materials in different adsorption process and confirm the structure of the adsorbent, the XRD test was conducted for the materials, which were before calcination (Mg-Al-Ce-HT precursor), the materials used in adsorption (Mg-Al-Ce-HT) and the materials after adsorption (adsorbed Mg-Al-Ce-HT). The XRD diffraction patterns of Mg-Al-Ce-HT precursor (a), Mg-Al-Ce-HT adsorbent (b) and adsorbed Mg-Al-Ce-HT material (c) were shown in Fig.2. From Fig.2, crystal plane (003), (006), (009), (018), (110), (113) are indexed in (a) and (b) curves, which are same as the literature[20]. The material is proved to have the hydrotalcite structure. Due to Mg-Al-Ce-HT precursor is the unheat-treated materials, the free water and nitrate radical decrease the diffraction peak intensity. When the materials are calcined, the free water and nitrate radical are removed and the intensity of the diffraction is strengthened. From Fig.2(b), characteristic diffraction peaks of some metal oxide
are displayed. At $2\theta = 28.68^\circ$ and $47.68^\circ$ (JCPDS 02-1306), the peaks of cerium oxide are displayed, the peaks of aluminum oxide and magnesium oxide are shown at $2\theta = 33.20^\circ$, $56.50^\circ$ (JCPDS 29-0063) and $2\theta = 38.14^\circ$, $62.08^\circ$ (JCPDS 65-0467), respectively. As shown in Fig.2 (b), a part of the materials is changed to metal oxide because of the calcination. After the adsorption (c), the materials structure is recovered to the structure before calcination because of the memory effect of hydrotalcite, the crystal plane peaks are similar to the Fig.2(a).

![Fig.2 XRD patterns of the Mg-Al-Ce precursor (a), Mg-Al-Ce-HT before adsorption (b), and Mg-Al-Ce-HT after adsorption(c)](image)

FT-IR spectra of the Mg-Al-Ce-HT precursor (a), Mg-Al-Ce-HT material (b), and adsorbed Mg-Al-Ce-HT material (c) are shown in Fig.3. As can be seen from Fig.3, the structures of these material are stable. At the range of 3400-3650 cm$^{-1}$ broad band, all the curves have characteristic absorption bands, which are due to the stretching mode of structural O-H groups in the metal hydroxide layer. At 1636.78 cm$^{-1}$, the hydroxyl groups O-H bending vibrations are clearly displayed. For the curves (a) and (c), there is a sharp peak at 3699.76 cm$^{-1}$, which can be attributed to O-H vibrate peak in the residual water. The bands in curve (b) at 1384.64 cm$^{-1}$ and 1456.47 cm$^{-1}$ are attributed to CO$_3^{2-}$ in the material. The metal-oxygen-metal stretching vibration is displayed at 1048.12 cm$^{-1}$. Because of the weak interaction during the adsorption, the peak of boron is not shown in the spectra.

![Fig.3 FT-IR spectra of Mg-Al-Ce-HT precursor (a), Mg-Al-Ce-HT materials (b), the adsorbed materials (c)](image)

Scanning Electron Microscope (SEM) images of Mg-Al-Ce-HT are shown in Fig.4 (a). As shown in the images, the Mg-Al-Ce-HT is composed of the flaky shape with irregular size (10-100 μm). And the samples have no crystalline structure.

![Fig.4 SEM images of Mg-Al-Ce-HT (a) and Mg-Al-Ce-HT (b) and corresponding EDS mappings of O (c), Mg (d), Al (e), Ce (f)](image)

Energy Dispersive Spectroscopy (EDS) analyses of the Mg-Al-Ce-HT are shown in Fig.4. Figure 4(b) shows the original image of Mg-Al-Ce-HT, and Fig.4 (c-f) show that the atoms of O, Mg, Al, and Ce are well-distributed in the materials. The ratio of these elements’ abundance is 27.20%:1.17%:3.51%, which is accorded with the synthesized proportion. In this material, there are a lot of oxygen atoms, it displays...
that the material exist in metal oxide or hydrate. Combined with the results of FT-IR, it is proved that the oxygen in the materials existed in the form of hydroxyl groups. The hydroxyl has an important role in boron removal.

In order to confirm the possible mechanism of boron removal in Mg-Al-Ce-HT, XPS spectra of Mg-Al-Ce samples are shown in Scheme 1 (b). As can be seen from the spectra, there exist the peaks for Mg2p, Al2p, Ce3d, C1s and O1s in the adsorbent. And the spectra show that the materials structure are nearly unchanged in adsorption process. The boron peak in the material after adsorption appears at 198 eV, showing that the boron is adsorbed in the materials successfully.

The strong peaks of Mg2p, Al2p, and Ce3d in Mg-Al-Ce-HT before and after adsorption are displayed in Fig.5. The peaks of Mg2p, Al2p, Ce3d are appeared in 48.7, 73.4 and 881.3 eV, respectively. It represents that the structure of Mg-Al-Ce-HT are nearly unchanged in adsorption process, and the results is in good agreement with XRD and FT-IR analyses.

![Fig.5 XPS spectra of Mg2p, Al2p, Ce3d, C1s and O1s in Mg-Al-Ce-HT before and after adsorption](image-url)
The spectra of C1s, O1s in Mg-Al-Ce-HT before and after adsorption are shown in Fig.5. The strong peaks at 283.8 eV and 284.7 eV are corresponded to the C 1s spectrum and the carbon atoms of carbonate CO$_3^{2-}$ on the surface. The strong peaks at 528.5 eV is corresponded to the metal oxide (M-O), and the band energies of 529.7 eV and 531.2 eV present hydroxyl group bonded to metal (M-OH) and oxygen of water (H$_2$O). Contrasting the peaks in Mg-Al-Ce-HT before and after adsorption, the CO$_3^{2-}$ is disappear and the amount of metal oxide is increased. It can be indicated that the -OH on the adsorbent surface participated in the boric acid adsorption.

With the hydration creating, at the pH of solution above 8.0, the -OH is massive produced and dispersed in the solutions, and the H$_3$BO$_3$ (B(OH)$_3$) will gradually change to B(OH)$_4^-$ in solutions$^{[21]}$. Because B(OH)$_4^-$ and OH$^-$ are negatively charged, the B(OH)$_4^-$ excludes with OH$^-$, the OH$^-$ in materials are not easy to capture the boron, so the adsorption process is slowly until adsorption equilibrium.

In short words, the driving forces of adsorption reaction are mainly depended on the reaction of the boric acid reacts with the hydroxyl produced by hydration of metal ions. When the metal ions hydrate in water, the hydroxyl is released on the surface of metals, the boric acid will react with the hydroxyl and adsorb on the metals. With the hydration reaction, the dissociative hydroxyl in solutions is gradually increased, the boric acid will react with the dissociative hydroxyl straightly, and inhibit the adsorption of boric acid in materials.

2.2 Effect of initial pH and mechanism of adsorption

The initial pH of boric acid will affect the adsorption behavior considerably. In order to investigate the effect of initial pH on boron removal, the experiments were carried out. The experiments condition was the same as the adsorption experiment, with the initial pH set at the range of 3.0-12.0. The equilibrium amounts of boron adsorbed onto the Mg-Al-Ce-HT were plotted in Fig.6 (a). Figure 6(a) shows that the values of Cs for Mg-Al-Ce-HT are around 21 mg g$^{-1}$ and almost constant in the pH range of 3.0-8.0. At pH above 8.0, Cs is decreased by the pH increasing. When the pH rises to 12.0, the Cs of the adsorbent is dropped into 2 mg g$^{-1}$. At the boron concentration below 216.68 mg L$^{-1}$, it often exists in B(OH)$_3$ or B(OH)$_4$$^{[22]}$. The B(OH)$_3$ would convert to B(OH)$_4^-$ in alkaline condition.
ZHANG, et al.: Removal of boron from water by Mg-Al-Ce hydrotalcite adsorption

2.3 Effect of the amounts of adsorbent content

In order to investigate the effect of adsorbent content, series of experiments were conducted. The experiments condition was the same as the adsorption experiment, with the adsorbent dosage set from 50 mg to 350 mg. The effect of adsorbent contents is shown as Fig.7. The curve shows that the adsorption capacity is decreased with the adsorbent content increasing, and the adsorption percentages are increased at the same condition. At the low adsorbent content, there are a small amount of effective adsorption sites in the system, which will cause the adsorption percentages at the low level and the adsorbent capacity at the high level. With the increase of adsorbent content, the effective adsorption sits gradually increases, leading to the adsorption capacity decreases from 35 to 15 mg g\(^{-1}\) and the adsorption percentage increase from 30% to 90%. At the 200.00 mg of the adsorbent capacity, the system reaches adsorption equilibrium. Therefore, 200.00 mg is considered as the optimum adsorbent content for boric acid and used for all the subsequent experiments.

2.4 Effect of the initial concentration of boric acid
In order to investigate the effect of initial concentration of boric acid on boron removal, the experiments were carried out. The effect of initial boric acid concentrations were investigated varying from 20 to 200 mg L\(^{-1}\) at 298.0 K. Figure 8(a) shows that the amounts of boron adsorbed on Mg-Al-Ce-HT are significantly affected by the initial feed concentrations of boron. We can observe the adsorbent content is increasing with the initial concentration increasing, and reach adsorption equilibrium at 140.00 mg L\(^{-1}\), and the curve keeps balance with the increase of the initial boric acid concentration. The reason of the phenomenon is as follows: As the initial concentration of boric acid at low concentration, the effect adsorption site is excess in the system; With the increase of the boric acid concentration, the fraction of concentration and adsorption site are increased, and the adsorption efficiency is also increased; When the adsorbent reaches adsorb saturation, the efficiency is not further changed.

The maximum adsorption capacity was confirmed by Langmuir model fitting. The result of Langmuir model fitting is displayed in Fig.8 (b). According to the fitting curve, the maximum adsorption capacity is 32.52 mg g\(^{-1}\). The correlation coefficient of the fitting curve is 0.9271, and the result is within the permitted range of errors.

2.5 Effect of contact time and sorption kinetics

Effect of the contact time between adsorbent and boric acid solutions was explored. The experiments curve was shown in Fig.9. In the first 100 min, the adsorption capacity is increased quickly with the increase of the contact time. Then, the adsorption efficiency becomes weak gradually. When the contact time comes to 160 min, the adsorption generally reaches the equilibrium, and the adsorption capacity is increasing slowly. The reason is ascribed to the ratio of adsorbent and the concentration of boric acid. At the beginning of the adsorption, there are a lot of boric acid in the solution, and the adsorbent is also massive in the system. Therefore, the adsorption process is fast at the beginning. With the adsorption proceeding, the adsorption capacity gradually reached saturation, and the speed of the adsorption is getting gradually slowly. When the adsorption reaches the adsorption equilibrium, the adsorption capacity is unchanged with the increase of the contact time.

The data of the contact time is fitted by pseudo-first-order and pseudo-second-order adsorption kinetics model. The equations of these models are described as follows:

\[
\ln(q_e - q_t) = \ln q_e - k_1t 
\]

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} 
\]

The results showed the pseudo-second-order correlation coefficient \((R^2=0.9133)\) is higher than the pseudo-first-order correlation coefficient \((R^2=0.7548)\). The pseudo-second-order kinetics model is fitted for the
adsorption better.

2.6 Effect of the experimental temperature and adsorption isotherms

The thermodynamic parameters of boron adsorption on Mg-Al-Ce-HT were calculated. The Gibbs free energy change ($\Delta G$, kJ mol$^{-1}$), enthalpy ($\Delta H$, kJ mol$^{-1}$) and entropy change ($\Delta S$, kJ mol$^{-1}$K$^{-1}$) were calculated as following equations:

$$\Delta G = -RT \ln K_c$$

(5)

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

(6)

$$K_c = \frac{Q_e}{c_e}$$

(7)

Where $R$ is the universal gas constant, which value is 8.314 kJ mol$^{-1}$; $T$ is the Kelvin temperature in experiment process; $K_c$ is the distribution coefficient by Henry model. The $\Delta G$, $\Delta H$ and $\Delta S$ can be reached by the Van’s hoff plot $\ln K_c$ against 1/$T$ (Fig.10). And the data of the $\Delta G$, $\Delta H$, $\Delta S$ and the fitting R-square are shown in Table 1. Due to $\Delta G$ is negative, the adsorption process of the boron removal is spontaneous on Mg-Al-Ce-HT. While the $\Delta H$ in thermodynamic parameters is positive, and the boron adsorption capacity is increasing with the temperature increasing, the adsorption is an endothermic process. AS $\Delta H$ and $\Delta S$ are positive, the $\Delta H$ is unfavorable for spontaneous adsorption, but the $\Delta S$ is favorable for spontaneous adsorption. Therefore, the driving force of boron removal on Mg-Al-Ce-HT is controlled by an entropy effect rather than an enthalpy change.

3 Conclusion

In Conclusion, the Mg-Al-Ce-HT with high performance for boric acid adsorption was successfully prepared. Effect of initial pH, initial concentration of boric acid, experimental temperature and contact time on boron removal were investigated. At the initial pH exceeds 8.0, the adsorption capacity will be stabilized at max value. With the amount of adsorbent content increasing, the adsorption capacity decreases and the adsorption percentages increases, and 200.00 mg is considered to be the optimum adsorbent content. The initial concentration of boric acid is another factor for boron removal. As the initial concentration of boric acid increasing, the adsorption capacity is increased, and till the initial concentration up to a certain extent, the adsorption capacity is settled out and stabilized at a value. The best initial concentration of boric acid is 100.00 mg g$^{-1}$, and the adsorption reaches the adsorption equilibrium within 160 min. The result shows that the pseudo-second-order adsorption kinetics model fits for the adsorption process better.

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Mg-Al-Ce 水滑石吸附去除水中的硼

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摘 要：用共沉淀法成功制备了镁铝铈水滑石（Mg-Al-Ce-HT），通过 XRD, FT-IR, SEM, EDS 和 XPS 等分析手段对材料进行了表征。通过静态吸附实验研究了 Mg-Al-Ce-HT 的吸附效率与初始 pH, 吸附剂剂量, 初始硼酸浓度和接触时间的关系。当 pH 小于 8.0 时, 溶液 pH 对硼吸附几乎没有影响; 当 pH 超过 8.0 时, Mg-Al-Ce-HT 对硼的吸附容量降低。吸附剂的最佳用量为 200 mg, 最大吸附容量为 32.52 mg g⁻¹, 对硼的吸附去除在 160 min 内达到平衡。吸附等温模拟表明吸附过程是一个自发的吸热过程，数据用 Langmuir 模型拟合更好，表明吸附是单层吸附。

关 键 字：除硼；水滑石；吸附动力学；吸附效率

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