One-step synthesis of layered double hydroxide-intercalated gluconate for removal of borate

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A B S T R A C T

The sorption of borate by ion exchange using a traditional layered double hydroxide (LDH) is affected by external conditions such as coexisting anions. Hydrotalcite intercalated with d-gluconate (G–LDH) was synthesized through a one-step microwave-assisted treatment and characterized by XRD, TEM, FTIR, TG/DTA and two-dimensional ^{11}B NMR. Several factors that influence sorption of borate were investigated: gluconate content in the LDH, G–LDH dosage, coexisting anions, initial pH of borate solution and sorption temperature. The synthesized adsorbent exhibited a greater borate sorption rate than the traditional hydrotalcite (NO_3–LDH) or a boron-specific resin. The maximum sorption capacity was 1.27 mmol/g (obtained by fitting to the Langmuir model). The G–LDH sorption density increased with increasing initial borate concentration and adsorbent dosage. In the presence of 50 mM sulfate, sorption of borate by NO_3–LDH significantly decreased and no obvious sorption could be observed, whereas the sorption of borate by G–LDH was maintained at $\sim$0.57 mmol/g. ^{11}B NMR indicated that the sorption mechanism of borate by G–LDH is mainly through bischelate and monodentate types of complexation with borate. This mechanism is similar to that of CRB05, and fundamentally different from that of NO_3–LDH.

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1. Introduction

Boron and its compounds have a wide variety of applications, such as in the chemical industry, electronics and medicine [1–3]. However, excess boron is harmful to organisms [4]. Numerous studies indicate that chronic boron exposure causes cutaneous disorders [3], retards growth [5], and adversely affects the male reproductive systems of rats and mice [6–8]. Wastewaters and residues discharged from industrial boron production generally contain boron, which affects the environment and squanders boron resources. The elimination of boric pollutants from water and the improved use of boron resources could have significant implications.

Numerous methods for removing boron from water and wastewater have been explored, such as reverse osmosis [9–13], precipitation–coagulation [14], electrodialysis [15], membrane filtration [16,17] and sorption processes (including ion exchange) [12,13,18]. Among these methods, sorption generates minimal waste and is more cost effective. Consequently, adsorbents have been studied extensively for boron sorption [19–21]. Hydroxyl-containing boron-selective adsorbents, such as boron-specific resins, are considered to be one of the most promising materials for

boron removal [16]. However, the high production costs of these resins limit their use [22]. Other common adsorbents, such as oxides [23], layered double hydroxides (LDHs) [21] and activated carbon [24], although less expensive, are ineffective, because of the variability of borate under different aqueous conditions and low adsorbent selectivity [18]. Therefore, a modification of common adsorbents with hydroxyl groups to develop a sorbent with lower cost, higher efficiency and better selectivity would be useful for boron removal.

As highly efficient and practical anion absorbents, LDHs have been applied widely in the catalytic degradation and sorption of environmental pollutants, with great potential in many applications [25]. Ferreira et al. and Jiang et al. used LDHs to remove borate from solution [12,26]. These studies, based on the synthesis of LDH intercalated with nitrate, achieved boron removal by taking advantage of the stronger adhesion between borate and the host layer compared with the adhesion between the nitrate and metal layer, resulting in ion exchange of borate with nitrate in the LDH interlayer. Although this method effectively removes borate, different anions in aqueous environments, especially divalent anions, significantly influence borate sorption by LDH [27]. The attractive force within the interlayer is far greater than that between the monovalent anions [28]. Therefore, LDH is ineffective in immobilizing borate in complicated practical water systems. The main improvement needed to develop technology for boron removal

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by LDH is to increase the selectivity of sorption and the sorption rate of boron by LDH. Considering the simple synthesis, low cost and environmental friendliness of LDH, the insertion of a polyhydroxylic organic group into the LDH ion layer could make the LDH for boron sorption less susceptible to interference from other anions, and increase its sorption rate.

In a previous report, LDH was intercalated with gluconate, which contains polyhydroxylic groups, and the ability of the sorbent to form complexes with borate was evaluated for removal of borate [29]. However, the synthesis method was complicated, requiring multiple steps, and the mechanism of sorption has not yet been clearly elucidated. So, in the present work, an easy and efficient method to intercalate the gluconate into the LDH was developed. The resultant new material was characterized using several techniques and applied to removal of borate, to evaluate its efficiency. The sorption mechanism was carefully examined based on XRD and ^{11}B NMR characterization of solid residues after sorption of borate.

2. Experimental method

2.1. Chemicals

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), sodium gluconate ($C_6H_{11}NaO_7$), boric acid (H_3BO_3), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) were special grade, and used as-received from WAKO (Osaka, Japan). A boron-specific chelating resin (Diaion® CRB 05) was purchased from Mitsubishi Chemical Co. (Tokyo, Japan).

2.2. Preparation of hydrotalcite with gluconate radical intercalation

1.87 g $Al(NO_3)_3$ and 2.56 g $Mg(NO_3)_2$ were added to 50 mL of water containing 1.09, 2.18, 4.36 or 6.5 g sodium gluconate to form molar ratios of [gluconate]/[Mg^{2+}] = 0.5, 1, 1.5 or 2. Once the solution became transparent with stirring, its pH was adjusted to 10 ± 0.2 with 1 mol/L NaOH. The solution was stirred continuously for 30 min, transferred to a Teflon vessel, placed in a microwave digestion system (ETHOS A, Milestone, Italy) and its temperature increased to 120 °C in 10 °C/min increments. The temperature was maintained for 180 min and the solution then allowed to cool to room temperature. The cooled reaction mixture was processed through solid–liquid separation on a supercentrifuge at 10,000 rpm for 10 min and cleaned several times with ultrapure water. The solid residues were dried for 12 h in a vacuum freeze drier and designated as G–LDH-0.5, G–LDH-1, G–LDH-1.5 or G–LDH-2, where the numbers represent the molar ratios of [gluconate]/[Mg^{2+}] used in preparation.

Hydrotalcite intercalated with nitrate (NO$_3$–LDH) was prepared by a similar method, but without sodium gluconate, to compare the borate sorption efficiency with that of the G–LDH series.

2.3. Characterization

The crystalline phases of various G–LDHs were determined using an X-ray diffractometer (XRD, Ultima IV, Rigaku, Japan) with Cu Kα radiation. A D/teX Ultra detector and no reflection sample holder were applied. The accelerating voltage and current were 40 kV and 40 mA, with a scanning speed of 2°/min and scanning step of 0.02°. Simultaneous thermogravimetric and differential thermal analyses (TG–DTA 2000SA, Bruker, Japan) were performed atmospherically from room temperature to 800 °C at a heating rate of 10 °C/min. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FTIR spectrometer (FT/IR-670 Plus, Japan). Transmission electron microscopy (TEM) images were obtained using a TECNAI-20 (Philips, Netherlands) transmission electron microscope.

Solid-state ^{11}B NMR spectra for sorption residues were collected using an ECA 800 (JEOL, Japan). Two dimensional ^{11}B NMR spectra were acquired. Multi-quantum magic angle spinning (MQ-MAS) was employed to acquire the ^{11}B NMR spectra at a field strength of 18.79 T, acquisition time of 5.12 ms and F2 and F1 resolutions of 195.31 and 2.00 kHz, respectively.

The solid-state ^{13}C MAS NMR spectra of sodium gluconate and G–LDH, before and after borate sorption, were also recorded using an ECA 400 (JEOL, Japan); the cross-polarization (CP) contact time was 5 ms and 10,000 scans were taken. Chemical shifts were referenced externally to tetramethylsilane (TMS; δ = 0 ppm) using the methyl signal of hexamethylbenzene (δ = 17.36 ppm) as a secondary standard.

To investigate the metallic, organic carbon and nitrate contents of the G–LDH series and NO$_3$–LDH, LDH samples prepared under different conditions were dissolved in 0.01 mol/L HCl. Solutions were diluted to determine the Mg and Al concentrations using an inductively coupled plasma emission spectrometer (ICP-AES, VISTA-MPX, Seiko Instruments, Japan). A total organic carbon analyzer (TOC-V CHS, Shimadzu, Japan) was used to determine the organic carbon and total nitrogen contents in solution.

2.4. Sorption experiments

A total of 40 mL of simulated solution containing a known concentration of boric acid was prepared at pH 7.0. Because borate at neutral pH is predominantly in a molecular form, it is not removed by many water treatments, such as reverse osmosis, at pH < 9.2. To test the sorption of boron on new materials, the initial pH of the solution should be <9.2. However, LDHs always dissolve to some extent under acidic conditions, thus influencing their properties. Therefore, the solution pH for testing the sorption behavior of these new LDHs should be neutral or weakly alkaline. Thirdly, several researchers have reported that boron-specific resins containing N-methylglucamine showed good performance for boron removal at neutral pH [30,31]. The gluconate in our LDHs has a similar structure to that of glucamine, and acts in a similar way to remove boron. So, we chose an initial pH of 7.0 for the boron solutions in this study. Then, 0.100 g of G–LDH, NO$_3$–LDH or CRB 05 were added into these simulated solutions. The temperature was kept at 25 ± 2 °C and the solutions were stirred at 200 rpm in an oscillator. After each time interval, aqueous solution was taken out and filtered through a 0.20-µm membrane filter. The total reaction time for experiments to measure the rate of sorption was 30 min, while the time for the sorption isotherm experiments was 24 h. The filtered solutions were diluted and then subjected to ICP-AES to determine boron concentrations. The solid residues after sorption of borate were freeze-dried and supplied for X-ray diffraction, FTIR, ^{11}B NMR and ^{13}C NMR. The influence of pH on sorption of borate was also determined through a similar process to that described above, but the initial pH was adjusted to be either 4.0, 7.0, 9.0 or 11.0 using 1 M NaOH and 1 M HCl.

To explore the effects of competitive anions on the sorption of boron by G–LDH-1.5, 0.100 g sorbent was added to 40 mL of 2.5 mmol/L boron solution containing 50 mmol/L competing anions (SO_4^{2-} or Cl^-) and the mixtures were shaken for 24 h. After this time, the supernatant was taken out and filtered through a 0.2 µm membrane before determination of B content by ICP-AES.

The effect of temperature on the sorption was examined as follows. Firstly, 40 mL of 2.5 mmol/L borate solution, initial pH 7.0, was placed in a constant temperature oscillator for 1 h, with the temperature increased to the required value. After that, 0.100 g G–LDH-1.5 was added to the solution. At each time interval, the