

Removal of borate by layered double hydroxides prepared through microwave-hydrothermal method



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ARTICLE INFO

Keywords:
LDHs
Borate
Sorption
Mechanism

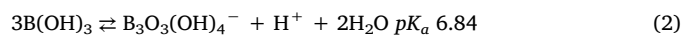
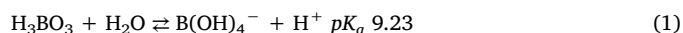
ABSTRACT

Layered double hydroxide (LDH) is considered effective in borate removal from water solutions. In this work, LDHs were prepared by microwave-hydrothermal method, characterized by X-Ray diffraction (XRD) and transmission electron microscopy (TEM), and applied for borate removal from a water solution. The results suggested that the LDHs prepared by microwave-hydrothermal method had the smallest particles size compared with other LDHs synthesized by urea and traditional hydrothermal method. Due to size reduction, the LDHs prepared by microwave-hydrothermal method had a higher borate sorption capacity. Based on the results of the XRD pattern and ^{11}B -NMR, the sorption mechanism of M-LDH is discussed in the paper. Ion-exchange was the predominant mechanism of borate removal, but surface sorption likely accompanied this process. In addition, the data obtained for the sorption of the three types of LDHs fitted well with the pseudo-second-order kinetic model and Langmuir sorption isotherm with a high correlation coefficient. The sorption amount of borate by M-LDH was 2.16 mmol/g, which is higher than that absorbed by U-LDH and H-LDH. Furthermore, the co-existing anion, especially carbonate, plays a role in hindering the sorption.

1. Introduction

Boron is one of the most important modern industrial materials, and its compounds are widely used for the manufacturing of a range of products, such as glass, semiconductors, and pharmaceuticals [1]. Although boron is an essential element for plant growth, at elevated levels it can become toxic [2,3]. There are some specific symptoms of boron toxicity in plants, including edge and tip necrosis, yellowing spots on the leaves, suppression of root cell division, dwarfing, followed by reduced photosynthesis levels, lower yields, and even death of plants [4]. In addition, excessive exposure to boron can also be detrimental to animals and humans [5]. Therefore, almost all countries have strict guidelines on the levels of boron content in drinking water. Moreover, with the gradually increasing concentration of boron in the environment, the establishment of methods for the removal of the compounds of this element has become exceedingly important [3,6].

Boric acid has excellent water solubility but its structure and nature change under different environmental conditions [7]:



Due to this extreme solubility, small size of uncharged molecules,

and variability, the removal of boron from contaminated wastewater is extremely difficult [2]. Nevertheless, different methods have been developed for the removal of boron from solutions, such as coagulation, reverse osmosis, and sorption. Among these methods, the sorption process is especially useful due to its advantages over the other methods in terms of generating lower amounts of waste for disposal and lower costs [8]. Therefore, the application of adsorbents has been widely studied as a core technology for boron sorption and removal. A large number of adsorbents, including red mud [9], boron-specific resin [10,11], and layered double hydroxides (LDHs) [12–14] have been studied. The cost of adsorbents is an important factor that determines their economic viability and, consequently, their uptake by industry. Thus, the capacity of low-cost adsorbents for removal of boron from aqueous solutions has been extensively investigated in recent years [15].

Layered double hydroxide (LDH) is commonly categorized as an anionic clay mineral. Its general formula is $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{X+} (\text{A}^{n-})_{x/n} \cdot n\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, X is $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, and A is the interlayer anion of valence n [16,17]. A wide variety of M^{2+} , M^{3+} , X, and A^{n-} belong to a large class of isostructural materials with various physical and chemical properties. Each type of LDH has specific properties that are essential to the effective removal of different toxic contaminants, such as chloride

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ion [18], heavy metal ions [19], borate [20], polycyclic aromatic hydrocarbons [21], and so on. Therefore, LDHs have potential applications in the removal of toxic substances.

Up to now, various approaches for LDHs preparation have been employed. Among them, the simplest and common method is co-precipitation [22]. In this method, the divalent and trivalent metallic ions are used as precursors. After pH adjustment, their mixture is stirred constantly for a short time to obtain crystallized particles. However, in this technique, nucleation and particle growth overlap, and therefore differences in crystallinity over time and large crystallite size distributions are difficult to avoid [23]. To obtain well-crystallized and uniformly distributed particles, post-treatments, such as hydrothermal treatment have been widely applied to enhance the dissolution of hydroxide precipitate and the subsequent crystal growth. However, achieving high crystallinity levels requires long periods of time (up to several days in some cases) [24], and the long post-treatment time sharply decreases the surface area, which may influence the sorption performance. Another common approach for LDH preparation, the urea method, was developed by [25]. In this technique, urea releases ammonia and carbonate, and a pH value within the approximate range of 7–9 is reached. This process can be easily controlled, which makes it attractive. In addition, the precipitates of metal ions and other compounds prepared by this procedure consist of platelet-like primary particles with homogeneous sizes and well-defined hexagonal shapes [25]. Although well particles have been obtained by the urea method, they were found to possess a large particle size and small surface area values [24].

Microwaves (MWs) can be used as a source of heating in the above-cited synthesis procedures to narrow the size distribution, enhance the surface area, and reduce the synthesis time [26]. In contrast to the traditional methods, microwave heating is a new type of heating, characterized by an extremely rapid increase in the temperature, selectivity, and higher thermal efficiency. One of the most widely used of microwaves in the synthesis of materials is microwave hydrothermal. Since Komarneni et al. [27] prepared the LDHs by microwaves hydrothermal, many researchers have found that the application of microwave heating in the synthesis process can not only reduce the synthesis time, but also increase the surface area and change the textural properties [28,29]. These advantages are important for its application in environmental remediation.

Therefore, in this work, we prepared LDHs using the microwave-hydrothermal method and used the obtained LDHs for borate sorption. We evaluated their capacities and compared them with those of LDHs synthesized by traditional methods, such as the urea hydrothermal method and co-precipitation. In addition, the sorption mechanism of LDHs has also been discussed.

2. Materials and methods

2.1. Chemicals

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), boric acid (H_3BO_3), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium chloride (NaCl) in special grade were used as received without purification.

2.2. Methods

2.2.1. Synthesis of LDHs by the microwave-hydrothermal method

$\text{Al}(\text{NO}_3)_3$ (1.87 g) and $\text{Mg}(\text{NO}_3)_2$ (2.56 g) were added into 50 mL of water solution, followed by stirring until the solution became clear and transparent. Next, pH of the solution was adjusted to 10 ± 0.2 with 1 mol/L NaOH. Then, the solution was stirred continuously for 30 min, transferred into a teflon vessel, and placed in a microwave digestion system (ETHOS A, Milestone, Italy), the temperature in which was increased to 120 °C at 10 °C/min increments. Further, this temperature

was maintained for 3 h, and then the product was allowed to cool to room temperature. The cooled seriflux was processed through solid-liquid separation by centrifugation in a supercentrifuge (SRX201, TOMY, Japan) at 10,000 rpm for 10 min. The device was cleaned several times with ultrapure water. Then, the solid residues were dried for 12 h in a vacuum freeze dryer (FD-5N, EYELA, Japan), and designated as M-LDH.

2.2.2. Synthesis of LDHs by the hydrothermal method

$\text{Al}(\text{NO}_3)_3$ (1.87 g) and $\text{Mg}(\text{NO}_3)_2$ (2.56 g) were added into 50 mL of a solution containing 1.75 g NaNO_3 . After their complete dissolution, the pH value of the solution was adjusted by the addition of 1 mol/L NaOH. Then, the solution was stirred continuously for 30 min, transferred into a teflon vessel which was kept in an oven at a constant temperature of 120 °C for 48 h. Further, the products were washed with ultrapure water. Finally, the solid residues were dried for 12 h in a vacuum freeze dryer, and referred to as H-LDH.

2.2.3. Synthesis of LDHs by the urea method

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.09 g), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.29 g), and urea (4.90 g) were dissolved in a beaker to form a clear solution with a total volume of 50 mL. The solution was then transferred into a teflon vessel, which was placed in an oven at 100 °C for 48 h. After that, the slurry was separated by centrifugation at 10,000 rpm for 10 min, and the products were rinsed with deionized water and air-dried overnight. The resulting sample obtained through this method was named U-LDH.

2.2.4. Characterization

The XRD patterns of LDHs were determined using an X-ray diffractometer (D8 Advance, Bruker, Germany) with a $\text{Cu K}\alpha$ radiation. The accelerating voltage and applied current were 30 kV and 20 mA, respectively. The size and morphology of the synthesized nanoparticles were observed with a transmission electron microscope (JEM-2100, JEOL, Japan). After dispersion with an ultrasonicator, several droplets of a mixture of the nanoparticles and ethanol were deposited on a carbon-coated Cu grid. Solid-state ^{11}B NMR spectra for sorption residues were recorded using ECA 800 (JEOL, Japan) with Delta NMR software version 4.3. 2D NMR spectroscopy of ^{11}B was acquired.

2.2.5. Sorption

To evaluate borate adsorption, samples of 40 mL of a simulation solution containing a concentration of 2.5 mM boric acid and 0.100 g of M-LDH, H-LDH, and U-LDH, respectively, were placed in an oscillator at room temperature (25 ± 2 °C) and a rotation speed of 200 rpm. The pH value was adjusted to 7 by 1 M NaOH. At each setting time, the solution was collected and filtered through a 0.20- μm membrane filter. To determine boron concentration, the filtered solution was diluted and analyzed through ICP-AES (Perkin Elmer 8500, Yokohama, Japan). The solid residuals after boron sorption were supplied for XRD and ^{11}B NMR. To explore the effects of competitive anions on the sorption of borate by M-LDH, 0.100 g sorbent was added into 40 mL of 2.5 mM boron solution containing 50 mM of a competing anion (either CO_3^{2-} or Cl^-), and the mixtures were shaken for 48 h. Finally, the supernatant was removed and filtered through a 0.2- μm membrane before determination of B content by ICP-AES.

3. Result and discussion

3.1. Characterization

The diffraction peaks in the XRD pattern of around 11° and 22° of the three samples suggested that LDHs have been successfully prepared by the different methods used (Fig. 1). It is noteworthy that the materials obtained through the urea method (U-LDH) had a higher degree of crystallinity than the LDHs prepared by of hydrothermal (H-LDH) and microwave-hydrothermal (M-LDH) methods. And materials

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