



Research paper

Sorption of borate onto layered double hydroxides assembled on filter paper through in situ hydrothermal crystallization

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ABSTRACT

Boric acid is known to be difficult to immobilize because it has a pK_a of 9.23, which means it is present in a molecular form in most aqueous environments and can be changed in the structure and nature with the change of the environmental conditions. Layered double hydroxides (LDHs) are potential sorbents for borate. However, the drawbacks of using LDHs for borate removal are that they are affected by the presence of other anions and are difficult to separate from water. In the present work, novel composites of Mg–Al type of LDH, synthesized onto filter papers and then intercalated with gluconate (F-LDH-G) were prepared. LDH with interlayer of carbonate form was first immobilized onto the surface of filter paper (F-LDH-CO₃) by in situ hydrothermal crystallization, and then ion-exchanged sequentially with chloride (F-LDH-Cl) followed by gluconate. The influence of the molar ratio of gluconate/LDH and reaction time on F-LDH-G synthesis was explored. Products were characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and nuclear magnetic resonance as well as measurements of borate sorption. The optimal molar ratio of gluconate/LDH and reaction time for preparing F-LDH-G from F-LDH-Cl were 40 and 24 h (F-LDH-G-40–24 h), respectively. F-LDH-G-40–24 h had higher sorption density and greater stability than both the original filter paper and the filter papers containing other LDHs, even in the presence of other anions. ¹¹B NMR and XRD results indicate that the principal mechanism for borate immobilization on F-LDH-G-40–24 h is complexation of gluconate with borate in both bischelat and monodentate forms. The novel composite is boron-specific and facilitates solid/liquid separation.

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1. Introduction

Boron is a ubiquitous element in rocks, soil and water and is an essential element for life on earth (Nishihama et al., 2012; Wolska and Bryjak, 2013). However, it is a potential hazard and excessive uptake of boron may cause adverse effects in organisms (Hilal et al., 2011). When irrigated with water containing excess boron, crops may wither, experience accelerated decay and ultimately die (Nadav, 1999). Weir and Fisher (1972) and Roe et al. (1972) reported that chronic exposure to boron may cause cutaneous disorders and retarded growth in rats. Although boron toxicity in humans has not been reported, the maximum permissible concentration of boron in industrial discharge and drinking water is regulated in most countries, according to the World Health Organization (Hilal et al., 2011).

There is no easy or simple method for boron removal from natural and wastewater (Xu and Jiang, 2007), because boric acid has a pK_a of 9.23, and thus is usually in molecular form. Acceptable methods for boron removal include physical and chemical processes, such as reverse osmosis (Hyung and Kim, 2006; Rodríguez Pastor et al., 2001), electro-dialysis (Oren et al., 2006) and boron-specific resins (Badruk et al.,

1999). However, methods such as the use of a boron-specific resin (which are the most feasible boron sorbents with high selectivity) are relatively costly.

LDHs are hydrotalcite-like compounds, similar in structure to the naturally occurring hydrotalcite mineral. They are a family of anionic-exchangeable clays with a large variety of compositions and physico-chemical properties (Cadars et al., 2011) and are used in a wide variety of applications; for example, as catalysts (Antonyraj and Kannan, 2011; Xu et al., 2012), in sensors (Chen et al., 2013; Yuan et al., 2013) and as anion scavengers (Seida and Nakano, 2002; Zhao et al., 2011). Despite the fact that the existence of hydrotalcites in the natural environment is rather limited, these materials can be synthesized easily and modified under laboratory conditions (Wan et al., 2012). LDHs have been shown to be efficient for boron removal (Ay et al., 2007; Kentjono et al., 2010), where the principal mechanism for boron removal from water by LDHs is via intercalation by anion exchange. However, in practice, solutions may contain a variety of anions that may affect borate sorption efficiency and interfere with boron adsorption. Interference from divalent anions is particularly problematic (Goh and Lim, 2010), since their attraction to the interlayer is stronger than that of monovalent anions (Miyata, 1983). This is one of the key problems that limit the application of LDHs in water treatment. Another drawback of LDHs is that they are more difficult (compared with adsorbents of larger particle size) to

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separate from water after treatment. The small size of LDH particles means that precipitation and separation may take longer; in turn, more steps may be required for the treatment process, which limit its industrial application. To overcome these limitations and ensure that LDHs can be used for borate removal, separated from solution and also be used as fillers in fixed bed reactors for continuous treatment, it is critical to prevent interference from other anions and immobilize LDHs on an inexpensive porous carrier.

In this study, LDHs were fabricated on the surface of common filter papers using an in situ homogeneous precipitation accomplished by urea hydrolysis (Costantino et al., 1998). Gluconate and chloride were then intercalated into the LDH interlayer to enhance sorption of borate. The resulting composite filters were characterized physicochemically and their sorption efficiency, adsorption mechanism and factors affecting boron removal were investigated.

2. Experimental method

2.1. Chemicals

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium gluconate ($\text{C}_6\text{H}_{11}\text{NaO}_7$), boric acid (H_3BO_3), urea ($\text{CH}_4\text{N}_2\text{O}$), sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) were used as received without purification (all special grade from WAKO Industrial Chemicals, Osaka, Japan). The main component of the filter paper (M-085, Toyo Advantec, Japan) used was cotton cellulose. The diameter and thickness of the filter paper were 47 and 0.8 mm, respectively.

2.2. Synthesis of materials

2.2.1. Preparation of filter paper modified by LDH with carbonate interlayer

1.71 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.65 mmol), 1.25 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.35 mmol) and 5.60 g urea (93.2 mmol) were completely dissolved in water to form a clear solution with a total volume of 50 mL. Filter paper was placed into the solution before being transferred into a Teflon vessel in a conventional oven at 95 °C for 48 h. The paper was removed from the vessel, rinsed thoroughly with deionized water and dried at 60 °C overnight. The filter paper prepared in this step was termed F-LDH- CO_3 .

2.2.2. Preparation of filter paper modified by LDH intercalated with chloride

A piece of F-LDH- CO_3 was placed in a plastic bottle, to which 50 mL of an aqueous solution containing 2.5 mmol/L HCl and 25 wt.% NaCl was added. The plastic bottle was sealed and placed in a thermostatted chamber at 25 °C. The vessel was agitated at a constant rate for 24 h. The filter paper was washed several times with deionized water and freeze-dried overnight. The resulting product was termed F-LDH-Cl.

2.2.3. Preparation of filter paper modified by LDH intercalated with gluconate

Chloride was ion-exchanged with gluconate in the F-LDH-Cl interlayer. First, sodium gluconate solutions of different concentrations were prepared by adding 0.13, 0.53, 1.06, 2.12 or 2.65 g to water in 50-mL plastic bottles (molar ratio of gluconate/LDH: 5, 20, 40, 80 or 100, respectively). F-LDH-Cl was placed into a bottle and shaken for different reaction times (12, 24 and 48 h) before being removed, washed and freeze-dried overnight. Samples synthesized in this step were termed F-LDH-G-5–24 h, F-LDH-G-20–24 h, F-LDH-G-40–24 h, F-LDH-G-80–24 h, F-LDH-G-100–24 h, F-LDH-G-40–12 h, and F-LDH-G-40–48 h; the first and second numbers represent the molar ratio of gluconate/LDH during the preparation process and the reaction time, respectively. The overall F-LDH-G synthesis process is shown in Fig. 1.

2.3. Characterization

The crystalline sorbent phases were confirmed by X-ray diffraction (XRD, Ultima IV, Rigaku, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation. The accelerating voltage and applied current were 40 kV and 40 mA, respectively, with a scanning speed of 2°/min and scanning step of 0.02°. Fourier transform infrared (FTIR) spectra were collected on a JASCO FTIR spectrometer (FT/IR-670 Plus, Hachioji, Japan) using Attenuation Total Reflection methods. Filter paper morphology was observed using scanning electron microscopy (SEM) VE-9800 (KEYENCE, Osaka, Japan) at an accelerating voltage of 20 kV.

^{13}C NMR spectra were collected on a JEOL-ECA 400 (Akishima, Japan). The resonance frequencies and field strength were 150.91 MHz and 14.09 T, respectively. Chemical shifts were referenced externally to tetramethylsilane at δ 0 ppm using the methyl signal of hexamethylbenzene at δ 17.36 ppm as a secondary standard. Solid-state ^{11}B NMR spectra for sorption residues were collected on a JOEL ECA 800 (Akishima, Japan) with 4-mm high-speed spinning probes in a single pulse method. At a field strength of 18.8 T, the resonance frequency was 256.6 MHz for ^{11}B . Typical acquisition parameters were spinning speed 15 kHz, pulse length 2.5 s and recycle delay 10 s (^{11}B).

To determine the metal content, 0.05 g of filter paper, F-LDH- CO_3 , F-LDH-Cl or F-LDH-G-40–24 h was added to a solution containing 7 mL of 60% HNO_3 and 0.5 mL of 30% H_2O_2 . This solution was transferred into a Teflon vessel, placed in a microwave digestion system (ETHOS A, Milestone, Italy) and its temperature increased to 230 °C in 30 min. This temperature was maintained for 20 min before allowing the samples to cool to room temperature. All filter paper was then dissolved and the resultant solutions diluted for determination of Mg and Al by inductively coupled plasma atomic emission spectrometry (ICP-AES, VISTA-MPX, Seiko Instruments, Tokyo, Japan).

2.4. Sorption experiments

2.4.1. Time effect on sorption of boron by different materials

Filter paper, F-LDH- CO_3 , F-LDH-Cl or F-LDH-G-40–24 h (0.5 g) was added to 40 mL of a 2.5 mmol/L H_3BO_3 solution in 50-mL bottles. The initial pH of this solution was adjusted to 7.0. At pH < 9.2, the predominant species of borate is a molecular form (H_3BO_3), which can barely be removed by some water treatment technologies, such as reverse osmosis. Therefore, to test the sorption of boron by the new materials, the initial pH of solution must be less than 9.2. However, LDHs are dissolved by acids; therefore, the solution pH should be neutral or weakly alkaline. Several researchers have reported that boron-specific resins containing n-methyl glucamine groups possess good performance for boron removal near neutral pH (Nishihama et al., 2012; Qi et al., 2002). The gluconate in our LDHs has a similar structure to glucamine, and is expected to function in the same way for boron removal. Therefore, the initial pH of the boron solution was set to 7.0. Then, the bottles were shaken on a shaker for 20 min before 1 mL of liquor was removed with a syringe and filtered through a membrane filter (pore size 0.2 μm) for ICP-AES analysis.

2.4.2. Sorption densities of different materials

The sorption densities of the filter paper and F-LDH- CO_3 , F-LDH-Cl and F-LDH-G-40–24 h were determined. Solutions of H_3BO_3 (0–60 mmol/L) were prepared and their initial pH was adjusted to 7.0. A filter paper was added to 40 mL of borate solution, followed by shaking at 100 rpm at 25 °C. After 24 h, supernatants were filtered (0.2 μm) for determination of total B concentration by ICP-AES.

2.4.3. Effect of competing anions

To explore the effects of competitive anions on the sorption of boron by F-LDH-G-40–24 h, 0.5 g sorbent was added to 40 mL of 2.5 mM boron solutions containing 50 mM competing anions (SO_4^{2-} or Cl^-) and the mixtures were shaken for 24 h. After this time, the supernatant

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