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Removal mechanism of polymeric borate by calcined layered double hydroxides containing different divalent metals

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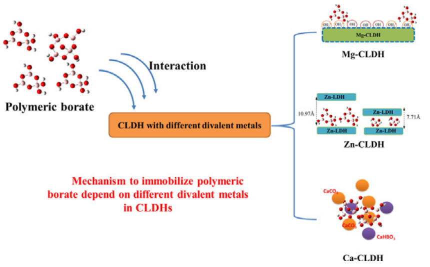
HIGHLIGHTS

- Removal mechanism of polymeric borate by different CLDHs has been discussed.
- Regeneration was inhibited and borate could not be immobilized effectively by Mg-CLDH.
- Intercalation of polymeric borate is main removal mechanism of boron by Zn-CLDH.
- Formation of ettringite and $CaCO_3$ was the main reasons for boron removal by Ca-CLDH.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal mechanism of polymeric borate by calcined layered double hydroxides is not clear. In this work, layered double hydroxides containing different divalent metals were synthesized and calcined to produce calcined layered double hydroxides (Zn-, Mg-, and Ca-CLDH). Then, Zn-, Mg-, and Ca-CLDH were applied to remove polymeric borate. Zn-CLDH showed better performance for the removal of borate than Ca-CLDH, and hardly any borate was removed by Mg-CLDH. Based on the characterization results, the detailed removal process of polymeric borate by different calcined layered double hydroxides is discussed. Because there is little H_3BO_3 that can act as a trigger, and ligand promoted dissolution of the complex H_3BO_3 and MgO is prevented. Therefore, Mg-CLDH could not transform to the layered structure to immobilize the borate. For the Zn-CLDH, Zn-CLDH transformed into Zn-LDH, and polymeric borate was absorbed into the interlayer of layered double hydroxides, which is the dominant mechanism of borate removal by Zn-CLDH. Reconstruction of the Ca-LDH from the Ca-CLDH was more rapid than the other calcined layered double hydroxides. However, formation of borate-containing ettringite was the main removal mechanism in the first stage. With increasing reaction time, the reaction between CO_3^{2-} and Ca^{2+} released from ettringite, and the regeneration of Ca-LDH to form $CaCO_3$ were the main reasons for borate removal in the second stage.

1. Introduction

Boron is widely distributed in the aqua sphere and lithosphere of the earth [1]. Because of its unique properties, it is extensively used in the manufacture of semiconductors, glass wools, and flame retardants [2]. Although boron is an essential micronutrient that is important for the growth and development of animals and plants,

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excess intake of boron has adverse effects on organisms. Based on the analysis of the toxicokinetics of boron, the World Health Organization proposed a guideline of 2.4 mg boron/L drinking water in 2011 [3]. Therefore, the development of effective methods for the removal of boron species from water will undoubtedly have many applications [4].

Because sorption is considered to be one of the most effective methods for borate removal [5], as a core component of the sorption process, sorbents with low cost have been rapidly developed in recent years, such as active carbon [6], red mud [7], dolomite [8], and mineral materials [9]. Among these materials, layered double hydroxides (LDHs), a type of highly efficient and practical anion adsorbent, have been widely applied to anion removal [10]. They have high sorption efficiency for the sorption of borate, especially calcined LDHs (CLDHs) [11,12]. Many publication have been proved that the sorption density of borate by CLDHs was higher that of LDHs [2,12]. Differing from the uncalcined product, CLDHs are considered to be bimetallic oxides after calcination at around 500 °C [10,13]. According to Hibino and Tsunashima [14] and Millanged et al. [13], the difference between CLDHs and the unique stratified structure of LDHs is that CLDHs are a type of solid solution that is formed by the dissolution of trivalent metals into the lattices of divalent metallic oxides. This type of structure is capable of hydrating in aqueous solution to regenerate electropositive metallic hydroxide layers that can capture anions, thereby removing anions from solution [15]. In 2013, Theiss et al. [4] suggested that this process of structural regeneration and capture of anions is the primary mechanism for the high-efficiency absorption of borate in CLDHs. However, in 2014, Isaacs-Paez et al. [16] suggested that this process of high-efficiency absorption of borate in CLDHs is not a simple process of electrostatic sorption after structural regeneration, and another reactive mechanism exists between CLDHs and borate in the process of structural regeneration. Based on the sorption mechanisms in the reports of Demetriou et al. [17] and Sasaki et al.[18], we discovered that the reactions between Zn-Al-CLDH, Mg-Al-CLDH, and Ca-Al-CLDH with borate were actually a complicated process that involves the interactions among CLDHs, newly generated LDHs, borate, and OH$^-$ [19]. However, the above finding is primarily based on a low concentration of boron. When the concentration of boron is <25 mM, only the monomers of H_3BO_3 and $B(OH)_4{}^-$ exist. When the concentration of boron is >25 mM, borate exists in the form of polymers [1,20]:

$$3B(OH)_3 \leftrightarrows B_3O_3(OH)_4{}^- + H^- + 2H_2O \tag{1}$$

$$2B(OH)_3 + 2B(OH)_4{}^- \leftrightarrows B_4O_5(OH)_4{}^{2-} + 5H_2O \tag{2}$$

Although the boron concentration in natural water is considerable less than 25 mM, in the boron-containing waste water discharged during manufacturing processes, the concentration of borate is higher than this value [21]. Therefore, it is necessary to investigate the sorption mechanism between CLDHs and polymeric borate. Considering that CLDHs can be decomposed by different divalent metals, and given that CLDHs formed by different divalent metals have different properties [22,23], sorption of polymeric borate must have a different sorption mechanism to monomeric borate. In this study, the sorption of polymeric borate in CLDHs containing different divalent metals is investigated, and the interaction mechanisms between polymeric borate and the different types of CLDHs are proposed and then discussed.

2. Experimental methods

2.1. Chemicals

Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), urea (CON_2H_4), boric acid (H_3BO_3), and sodium hydroxide (NaOH) were of special grade and used as received from Wako (Osaka, Japan) without purification.

2.2. Preparation of LDHs with different divalent metals

To synthesize LDHs with the divalent metals Zn and Mg (Zn-LDH and Mg-LDH), $Al(NO_3)_3{\cdot}9H_2O$ (3.09 g), M^{2+} salt ($Mg(NO_3)_2{\cdot}6H_2O$, 4.29 g; $Zn(NO_3)_2{\cdot}6H_2O$, 4.98 g) and urea (4.90 g) were dissolved in ultrapure water in a beaker to form a clear solution with a total volume of 50 mL. The solution was then transferred to a Teflon vessel, which was placed in an oven at 100 °C for 36 h. The resulting slurry was then separated by centrifugation at 10,000 rpm for 10 min. The products were rinsed with deionized water, and then freeze–dried overnight. In this method, hydrolysis of urea was included two steps, the formation of ammonium cyanate (NH_4CHO), with subsequent fast hydrolysis of cyanate to ammonium carbonate:

$$CO(NH_2)_2 \rightarrow NH_4CNO \tag{3}$$

$$NH_4CNO + 2H_2O \rightarrow 2NH_4{}^+ + CO_3{}^{2-} \tag{4}$$

The hydrolysis reactions of ammonium ions to give ammonia and carbonate to give hydrogen carbonate result in a pH of about 9 (Carbonate is also used as an anion in the formation of LDHs) [1]. This pH is stabilized and is suitable for precipitating a large number of metal hydroxides. Therefore, different type of LDHs with well crystallized and hexagonally shaped.

Because Ca-LDH could not be synthesized by the urea method, the microwave-assisted method was used. A solution containing $Ca(NO_3)_2{\cdot}4H_2O$ (3.78 g) and $Al(NO_3)_3{\cdot}9H_2O$ (3.09 g) in molar ratio 2:1 was added to 50 mL of 0.5 mol/L $NaNO_3$ solution, and the pH was adjusted to 12 with 2 mol/L NaOH. The resulting slurry was transferred to a Teflon vessel and placed in a Milestone Ethos Plus microwave oven (Sorisole, Italy). The temperature was increased to 150 °C within 10 min, maintained at this temperature for 3 h, and then naturally cooled to room temperature. The cooled slurry was subjected to solid–liquid separation by super-centrifugation at 10,000 rpm for 10 min and then washed several times with ultrapure water. The solid residues were then dried overnight in a vacuum freeze–drier. Before the sorption experiments, all of the LDHs were calcined at 500 °C for 3 h.

2.3. Sorption experiments

Sorption experiments were performed with the calcined products in 30 mmol/L H_3BO_3. The initial pH was adjusted to 7.00 using 1 mol/L NaOH. For the sorption experiments, 0.100 g of the calcined products were added to 40 mL borate solutions, followed by shaking at 15,650 g and room temperature using a shaking incubator TB-16R (Takasaki Kagaku, Kawaguchi, Japan). At certain time intervals, the supernatants were filtered (0.20 μm) to determine the total concentrations of B, Ca, Zn, Mg, and Al by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 8300, PerkinElmer, MA, USA).

2.4. Characterization

The crystalline phases of the various LDHs were determined using an X-ray diffractometer (Ultima IV, Rigaku, Tokyo, Japan) with Cu Kα radiation. The accelerating voltage and applied current were 40 kV and 40 mA, respectively, with a scanning speed of 2 min^{-1} and a scanning step of 0.02. Brunauer–Emmett–Teller (BET) surface area measurements were performed using an MX-6 surface analyzer (Bel Japan Inc., Toyonaka, Japan) at three points by the nitrogen adsorption method. The morphologies of the solid products before