Research article

# Use of Mg–Al oxide for boron removal from an aqueous solution in rotation: Kinetics and equilibrium studies

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## A R T I C L E  I N F O

## A B S T R A C T

Mg–Al oxide prepared through the thermal treatment of $CO_3^{2-}$ intercalated Mg–Al layered double hydroxides ($CO_3 \cdot$Mg–Al LDH) was found to remove boron (B) from an aqueous solution. B was removed by the rehydration of Mg–Al oxide accompanied by combination with $B(OH)_4^-$. When using twice the stoichiometric quantity of Mg–Al oxide for Mg/Al = 4, the residual concentration of B dropped from 100 to 2.8 mg/L in 480 min, and for Mg/Al = 2, it decreased from 100 to 2.5 mg/L in 240 min. In both cases, the residual concentration of B was highlighted to be lower than the current Japanese effluent standards (10 mg/L). The removal of B can be explained by way of pseudo-first-order reaction kinetics. The apparent activation energy of 63.5 kJ mol$^{-1}$, calculated from the Arrhenius plot indicating that a chemical reaction dominates the removal of B by Mg–Al oxide (Mg/Al = 2). The adsorption of B acts upon a Langmuir-type phenomena. The maximum adsorption ($q_m$) and equilibrium adsorption constants ($K_L$) were 7.4 mmol g$^{-1}$ and $1.9 \times 10^3$, respectively, for Mg–Al oxide (Mg/Al = 2). $B(OH)_4^-$ in $B(OH)_4 \cdot$Mg–Al LDH produced by the removal of B was observed to undergo anion exchange with $CO_3^{2-}$ in solution. Following regeneration, the Mg–Al oxide maintained the ability to remove B from an aqueous solution. This study has clarified the possibility of recycling Mg–Al oxide for B removal.

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## 1. Introduction

Boron (B) is an essential micronutrient for human beings; however, it sometimes pollutes drinking water sources, leading to various environmental and health problems (Wang et al., 2014). Borate in wastewater is difficult to treat as it does not generate insoluble compounds with heavy metal ions or alkaline earth metals. However, when aluminum salts and calcium hydroxide are added to borate-containing wastewater, the borate concentration in the treated water decreases to a lesser quantity rather than maximum permissible Japanese effluent standard (10 mg/L). This decrease occurs because of borate adsorption by the produced calcium aluminate. In Japan, this method is widely used for wastewater treatment; however, the method results in vast amounts of sludge generation caused by the addition of large amounts of aluminum salts and calcium hydroxide. Therefore, the development of a new treatment method for borate-containing wastewater is required. Wang et al. have well reviewed the removal technology of B dissolved in aqueous solutions (Wang et al., 2014). It includes adsorption process using chelating resin and inorganic materials; membrane process using ion-exchange membranes, reverse osmosis, and electrocoagulation; and hybrid process using polymer-enhanced ultrafiltration and adsorption-membrane filtration. In case of inorganic materials, e.g., fly ash and calcined magnesite have the capacity to take up B in an aqueous solution. However, these materials are reported to be nonrecyclable. In this study, for aqueous $H_3BO_3$, a new treatment method is proposed for removing B using Mg–Al oxide through the production of Mg–Al layered double hydroxides (Mg–Al LDHs), as presented in Fig. 1.

The formula of Mg–Al LDH are typically denoted as $[Mg^{2+}_{1-x}Al^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, the significance of x is the molar ratio of $Al^{3+}/(Mg^{2+} + Al^{3+})$ ($0.20 \leq x \leq 0.33$), $A^{n-}$ is anion, for example $CO_3^{2-}$ or $Cl^-$ (Cavani et al., 1991; Ingram and Taylor, 1967; Allmann, 1968; Mills et al., 2012). By calcination at 450°–800 °C, the $CO_3^{2-}$ intercalated Mg–Al LDH ($CO_3 \cdot$Mg–Al LDH) can be converted to Mg–Al oxide, expressed as eq 1:

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + x/2CO_2 + H_2O \qquad (1)$$
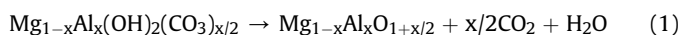
The Mg–Al oxide is able to incorporate water molecules

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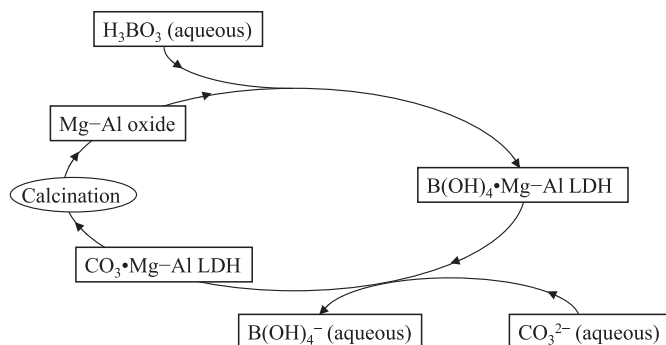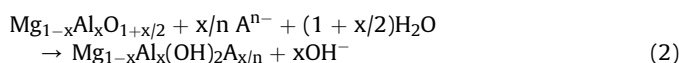  *E-mail address:* kameda@env.che.tohoku.ac.jp (T. Kameda).

**Fig. 1.** Scheme for the proposed treatment method of aqueous $H_3BO_3$ by Mg−Al oxide.

(rehydration) and anions, resulting in the reconstruction of the structure of LDH:

$$Mg_{1-x}Al_xO_{1+x/2} + x/n\ A^{n-} + (1 + x/2)H_2O$$
$$\rightarrow Mg_{1-x}Al_x(OH)_2A_{x/n} + xOH^- \qquad (2)$$

Recently, LDH and Mg−Al oxide have been examined to remove humic acid, various types of oxyanions, arsenic, phosphate, benzopurpurine 4B, acid phosphatase, acid red G dye, acid green 68:1, thiosulfate, iodide, $ClO_4^-$, and chromium(VI) from an aqueous solution (Gasser et al., 2008; Goh et al., 2008, 2009; Goh and Lim, 2010; Hosni and Srasra, 2010; Setti et al., 2010; Zhu et al., 2010; Wu et al., 2011; Tong et al., 2012; Santos et al., 2013; Geng et al., 2013; Wu et al., 2013; Iglesias et al., 2014; Lin et al., 2014; Song and Wu, 2014). Mg−Al oxide can also be used for the treatment of B in order to produce Mg−Al LDH intercalated with $B(OH)_4^-$ ($B(OH)_4 \cdot Mg$−Al LDH). $B(OH)_4 \cdot Mg$−Al LDH is treated with $CO_3^{2-}$ in an aqueous solution, allowing anion exchange between $B(OH)_4^-$ in Mg−Al LDH and $CO_3^{2-}$ to regenerate $CO_3 \cdot Mg$−Al LDH. $CO_3 \cdot Mg$−Al LDH is calcined to regenerate Mg−Al oxide, which can be reused for the remediation of aqueous $H_3BO_3$. Mg−Al oxide has previously been shown to remove B from an aqueous solution (Yoshioka et al., 2007; Paez et al., 2014); however, these studies have not considered the treatment of the complex after B removal. In the current study, we used Mg−Al oxide to remove B from aqueous solution, also examined the effect of the Mg/Al molar ratio, amount of Mg−Al oxide and temperature. In addition, kinetics and equilibrium studies were performed, and the adsorption behavior was considered. Furthermore, the effect of coexistent $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ on the removal of B was examined. The B desorption from the produced $B(OH)_4 \cdot Mg$−Al LDH was also investigated using $Na_2CO_3$ solution, and the reproduced $CO_3 \cdot Mg$−Al LDH was calcined to regenerate Mg−Al oxide, which was further examined for its uptake of B in an aqueous solution.

## 2. Experimental

Only reagent grade chemicals were used without any additional purification.

### 2.1. Preparation of Mg−Al oxide

Mg−Al oxide was obtained through the thermal treatment of Mg−Al LDH intercalated with $CO_3^{2-}$ ($CO_3 \cdot Mg$−Al LDH). The coprecipitation reaction for $CO_3 \cdot Mg$−Al LDH can be explained by eq3. In the present study, x values of 0.20 and 0.33 were used. The stoichiometric coefficients of 0.20 and 0.33 for $CO_3^{2-}$ were

calculated in function to neutralize the brucite-like octahedral layers positive charge when Mg was replaced by Al at Mg/Al molar ratio either 4 or 2.

$$(1 - x)Mg^{2+} + xAl^{3+} + x/2CO_3^{2-} + 2OH^-$$
$$\rightarrow Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \qquad (3)$$
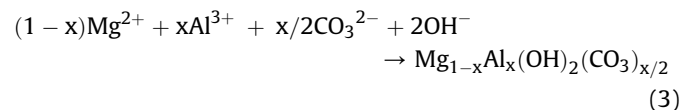
The preparation of $CO_3 \cdot Mg$−Al LDH was followed as added Mg−Al solution dropwise to $Na_2CO_3$ solution and maintained pH 10.5 throughout the reaction. The Mg−Al nitrate solutions comprised with 0.40 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.10 M $Al(NO_3)_3 \cdot 9H_2O$ or 0.33 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.17 M $Al(NO_3)_3 \cdot 9H_2O$ was added to deionized water to obtain Mg/Al molar ratio 4 and 2 respectively. The Mg−Al nitrate solution (500 mL) was added dropwise to 0.1 M $Na_2CO_3$ solution (500 mL), the reaction condition was maintained 30 °C temperature and 15 mL min⁻¹ addition rate with agitate mildly. A pH of 10.5 was retained by adding appropriate amounts of 1.25 M NaOH solution. The successive suspension were kept for settling down for 1 h at 30 °C temperature and filtered followed by washing with deionized water repeatedly. The resultant precipitate was proceeded to drying for 40 h at 40 °C under reduced pressure (133 Pa) The obtained products were confirmed to be $CO_3 \cdot Mg$−Al LDH, as presented in Fig. S1. The obtained $CO_3 \cdot Mg$−Al LDH was calcined to get Mg−Al oxide at 500 °C for 2 h, as expressed by eq4.

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + (x/2)CO_2 + H_2O \qquad (4)$$
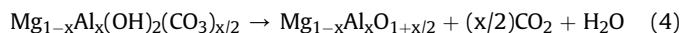
The Mg−Al oxides prepared via thermal treatment of $CO_3 \cdot Mg$−Al LDHs with an initial Mg/Al molar ratio of 4 and 2 are hereafter called Mg−Al oxide (Mg/Al = 4) and Mg−Al oxide (Mg/Al = 2), respectively. Fig. S2 presents the XRD patterns for (a) Mg−Al oxide (Mg/Al = 4) and (b) Mg−Al oxide (Mg/Al = 2). In both cases, the products were confirmed to be Mg−Al oxide. Table 1 exhibits the elemental compositions of various Mg−Al oxides. A proximate value of the experimental Mg/Al molar ratio with the initial, indicating $CO_3 \cdot Mg$−Al LDH preparation and Mg−Al oxide formation according to Eqs. (3) and (4).

### 2.2. Removal procedure of boron from an aqueous solution

$H_3BO_3$ was dissolved in deionized water to prepare $H_3BO_3$ solution. The Mg−Al oxides were added to the 500 mL of 100 mg/L $H_3BO_3$ solutions. The successive suspensions were stirred at 10°C−60 °C for 840 min with continuous bubbling of $N_2$ during the procedure. pH was monitored throughout the experiment. Samples of the suspension were collected at specific time periods and instantly filtered passing through a membrane filter (0.45 μm). The residual B, dissolved $Mg^{2+}$ and $Al^{3+}$ was estimated from the filtrates. The quantity of the Mg−Al oxide required for borate removal was 1−2 times the stoichiometric quantities shown in eq5 and is indicated using the notation eq1−eq2.

$$Mg_{1-x}Al_xO_{1+x/2} + xB(OH)_4^- + (1 + x/2)H_2O$$
$$\rightarrow Mg_{1-x}Al_x(OH)_2(B(OH)_4)_x + xOH^- \qquad (5)$$
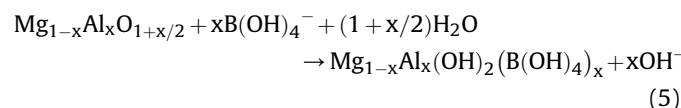
The adsorption isotherm study of B with Mg−Al oxide was conducted, therefore, a mixed 20 mL 0.01−0.06 M $H_3BO_3$ solution and 0.1 g Mg−Al oxide was shaken at 30 °C for a week using 50 mL screw-top tubes.

To examine the effect of coexistent anions on B removal, NaCl, $NaNO_3$, or $Na_2SO_4$ was added to the $H_3BO_3$ solution. The amount of