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Research paper

## Removal mechanism of arsenate by bimetallic and trimetallic hydrocalumites depending on arsenate concentration

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## ABSTRACT

We investigated the influence of initial arsenate concentration ( $C_0$ ) in the 5th order of magnitude on removal of arsenate by hydrocalumite (bimetallic layered double hydroxide, LDH) and Mg-doped hydrocalumite (trimetallic LDH) from aqueous solution. These hydrocalumites were prepared by the microwave-assisted hydrothermal treatment. There is a trend that the larger adsorption density of arsenate ( $Q_e$ ) values is observed with bimetallic LDH under low  $C_0$  values and with trimetallic LDH under high  $C_0$  values. The transitional  $C_0$  values ranged at 2.10–2.96 mM. Comprehensively understanding characterization results for the solid residues after adsorption of arsenate by X-ray diffraction,  $^{27}\text{Al}$ -nuclear magnetic resonance, and scanning electron microscopy–energy dispersive X-ray, the mechanism to remove arsenate was dependent on arsenate concentrations. At low arsenate concentration, partial intercalation and dissolution–reprecipitation (DR) happened together. With increasing  $C_0$ , full intercalation and DR happened to bring out one phase of arsenate-bearing hydrocalumite. Under the very high  $C_0$ , DR mechanism happened at the edge sites of LDH sheets, leading that the newly formed massive precipitates block the further intercalation with nitrate. As a result, two phases of LDH were observed. The greater  $Q_e$  with bimetallic LDH in low concentration comes from high crystallinity to enhance partial ion-exchange, and greater  $Q_e$  with trimetallic LDH in high concentration is derived from more fragile properties to enhance DR mechanism.

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### 1. Introduction

Arsenic is a highly toxic pollutant. The presence of elevated concentrations of arsenic is regarded as one of the most serious environmental problems, especially in developing and underdeveloped countries (Bhumbla and Keefer, 1994; Plant et al., 2004). Long-term and excess uptake of arsenic contaminated drinking water causes many human health hazards, such as cancers, skin lesions, and nerve tissue injuries (Bates et al., 1992; Morales et al., 2000). The World Health Organization and many countries have the strict guideline of  $<10 \mu\text{g/L}$  arsenic in drinking water (WHO, 2006). Therefore, inexpensive and appropriate technologies for arsenate removal need to be developed. Many methods have been developed to remove excessive arsenic from water using techniques such as coagulation, electro-coagulation, precipitation, ion exchange, reverse osmosis and adsorption (Mohan and Pittman, 2007).

Because of their high anion-exchange capacity and thermal stability, layered double hydroxides (LDHs) are currently receiving considerable

attention for a wide variety of applications in environmental remediation (Goh et al., 2008). The chemical composition of LDH can be defined as  $[\text{M(II)}_1 - \text{xM(III)}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot n\text{H}_2\text{O}$ , in which M(II) and M(III) are divalent and trivalent metallic cations located in the host layers,  $\text{A}^{n-}$  is the interlayer anion,  $m$  is the number of interlayer water molecules, and  $x$  is the molar ratio of M(III)/(M(II) + M(III)) (Evans and Slade, 2006). LDH has different properties depending on the combination of divalent and trivalent cations and their molar ratio (Guo et al., 2005; Koilraj and Kannan, 2010; Guo et al., 2012; Lv et al., 2012; Zhou et al., 2015). There are several reports that trimetallic LDH influenced the uptake of anionic species. Zhou et al. explained that MgCaFe-LDH lowered adsorption capacity of selenite and chromate compared with MgFe-LDH due to collapse of trimetallic LDH after dissolution of  $\text{Ca}^{2+}$  (Zhou et al., 2015). Meanwhile Koilraj and Kannan observed that ZnAlZr-LDH enhanced adsorption capacity of phosphate than ZnAl-LDH, and exchange precipitation of  $\text{Zn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  happened after dissolution of  $\text{Zn}^{2+}$  from ZnAlZr-LDH (Koilraj and Kannan, 2010). These findings apparently seem to be inconsistent, however, both phenomena is based on chemically fragile characteristics of host layers in trimetallic LDH. Further investigation is necessary in details in a wide range of target anion concentrations.

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To date, tremendous researches have been conducted for hydroxal-cite (MgAl-LDH) (Toraishi et al., 2002; Lazaridis et al., 2002; Doušová et al., 2003; Yang et al., 2005; Bhaumik et al., 2005; Das et al., 2006; Kiso et al., 2005; Peng et al., 2005; Yang et al., 2006; Violante et al., 2009; Goh et al., 2009; Grover et al., 2010; Caporale et al., 2011), while there have been only a few reports about hydroxal-cite (CaAl-LDH) (Grover et al., 2010; Choi et al., 2012; Guo and Tian, 2013). Hydroxal-cite is easily prepared and commonly found in cement (Liu et al., 2011), and contains more regularly arranged anions, cations, and interlayer water molecules than hydroxal-cite (Vieille et al., 2003). The crystallinity of LDH depends on involved metals, and also affects the adsorption characteristics of anionic species. It has been reported that adsorption density of arsenate was larger on hydroxal-cite than hydroxal-cite with the same molar ratio of M(II)/M(III), since the adsorption mechanism with hydroxal-cite involved arsenic exchange as well as partial dissolution and recrystallization (Grover et al., 2010).

In contrast to hydroxal-cite, the removal mechanism of contaminants by hydroxal-cite is through ion-exchange and dissolution-reprecipitation (DR) (Liu et al., 2011). In this process, oxyanion uptake by hydroxal-cite should involve the disruption of the electrostatic interactions and hydrogen bonds between the hydroxide layers and the outgoing anions, followed by the reformation of these bonds with the incoming anions (Radha et al., 2005). This means that the structural stability of hydroxal-cite in the solution is closely related to the mechanism and efficiency of anion removal. Similar to hydroxal-cite, green rust is unstable and can be easily transformed into magnetite and Fe(OH)<sub>2</sub>, even under anoxic conditions (Radha et al., 2005). However, the stability of green rust is improved when the concentration of multivalent oxyanions (PO<sub>4</sub><sup>3-</sup> and AsO<sub>4</sub><sup>3-</sup>) reaches a certain level. The phosphate and arsenate ions adsorbed on the lateral faces may act as a barrier to inhibit the release of interlayer anions (Benali et al., 2001; Bocher et al., 2004; Mitsunobu et al., 2008; Goh and Lim, 2010). If arsenate functions to stabilize the structure of hydroxal-cite, the process of arsenate adsorption onto hydroxal-cite related to the removal mechanism is an interesting issue.

In addition, pollutant removal by LDH has mainly focused on the bimetallic LDH, and there are few reports about pollutant removal by trimetallic LDH, such as Mg-doped hydroxal-cite (trimetallic LDH). Differently from the hydroxal-cite, Ca<sup>2+</sup> is coordinated with six OH groups and the water molecules in the interlayer are also directly coordinated to Ca atoms. Because of this, each interlayer water molecule occupies a certain ordered position to create a well-defined anionic interlayer. More regularly arranged anions, cations, and interlayer water molecules are observed in Ca-Al-LDH compared with Mg-Al-LDH (Pfeiffer et al., 2011; Mora et al., 2011). In addition, the solubility product (*K*<sub>sp</sub>) for hydroxal-cite is 10<sup>-27.10</sup> (Liu et al., 2011) while *K*<sub>sp</sub> for hydroxal-cite is 10<sup>-52.12</sup> (Ravel and Newville, 2005). It is evident that the solubility of hydroxal-cite is lower than that of hydroxal-cite. Therefore, the adsorption mechanism of arsenate to bimetallic LDH may change after Mg is doped into the metallic layers. However, there is a lack of detailed discussion and study on immobilization of anionic species by trimetallic LDH.

In this study, we investigated adsorption of arsenate on bimetallic and trimetallic LDHs in a wide range of arsenate concentrations with 5th orders of magnitude. Using multiple characterization methods, the detailed removal mechanism of arsenate by bimetallic and trimetallic LDHs and the influence of Mg in the metallic layers are discussed.

## 2. Methods

### 2.1. Preparation of LDH

Microwave-assisted hydrothermal methods were used for the synthesis of bimetallic and trimetallic LDHs. For bimetallic LDH, a solution containing specific amounts of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (2.36 g) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1.86 g) adjusted to the molar ratio Ca:Al = 2:1 was

added to 50 mL of 0.50 M NaNO<sub>3</sub>. The pH was adjusted to 12.0 by 2 M NaOH maintained for 2 h. All of the chemical reagents were in special grade, purchased from WAKO chemicals (Osaka, Japan) and used without purification. The resulting slurry was transferred into a Teflon vessel to supply for microwave irradiation with a Milestone Ethos Plus microwave (Soriso, Italy). The temperature was increased to 150 °C within 10 min and then maintained for 3 h. The cooled seriflux was treated by solid-liquid separation by super-centrifugation at 10,000 rpm for 10 min, and washed several times with ultrapure water. The resulting product was freeze-dried and called as bimetallic LDH. Trimetallic LDH was prepared in the same manner to bimetallic LDH. The only difference was that the mixed solution contained Mg<sup>2+</sup> ions with the molar ratio of Ca:Mg:Al = 1.6:0.4:1.0.

### 2.2. Characterization

The crystalline phases within the various bimetallic and trimetallic LDHs were characterized using an X-ray diffractometer (Ultima IV, Rigaku, Akishima, 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 and a scanning step of 0.02°. Brunner-Emmett-Teller (BET) specific surface area measurements were performed using a BELSORP-MR6 surface analyzer (BEL JAPAN Inc., Toyonaka, Japan) with the nitrogen adsorption method. The samples were preheated at 150 °C for 3 h for degassing. The morphologies and the elemental compositions of the products were observed using a VE-9800 scanning electron microscope (Keyence, Osaka, Japan) equipped with an energy dispersive X-ray (EDX) spectrometer at 20 kV accelerating voltage. Elemental analysis was conducted at least 5 particles per one sample and at least 6 points for one particle by SEM-EDX. <sup>27</sup>Al-NMR spectra were collected on a JNM-ECA 800 spectrometer (JEOL, Akishima, Japan) with Delta NMR software version 4.3 using 3.2 nm MQMAS probes and a single pulse method. The resonance frequency for <sup>27</sup>Al was 208.5 MHz at a field strength of 18.8 T. Typical acquisition parameters were spinning speed 250 kHz, pulse length 2.14 μs, and relaxation delay 1 s.

Extended X-ray absorption fine structure (EXAFS) spectra of the Ca K-edge were collected on BL06 at the Kyushu Synchrotron Light Research Center (SAGA-LS, Tosu, Japan). The spectra of the samples were collected using an ionization chamber in transmission mode. The photon energy was scanned in the range of 3.7–5.6 keV for the Ca K-edge. The samples were mixed with boron nitride (BN) and pressed into pellets. All of the spectra were averaged and normalized using IFFEFIT software version 1.2.11 (Ravel and Newville, 2005).

The Ca, Mg, and Al contents in the products were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin Elmer 8500, Yokohama, Japan) after acid decomposition with 6.5 M HNO<sub>3</sub>. The C, H, and N contents were determined by CHN analysis using Yanaco CHN Corder MT-6 Elemental Analyzer (Tokyo, Japan).

### 2.3. Batch adsorption tests

For the adsorption experiments, 0.100 g of product was added to 40 mL of 0.002–10.2 mM KH<sub>2</sub>AsO<sub>4</sub> as the initial concentration (*C*<sub>0</sub>). The mixture was shaken at 100 rpm with an 8 cm stroke in a shaker (TB-16R, Takasaki Kagaku, Kawaguchi, Japan) at room temperature. At intervals, the supernatants were taken and filtered (0.20 μm) and the total Ca, Mg, and Al concentrations were determined by ICP-AES. Concentrations of As lower than 0.02 mM were determined by hydride generation-atomic absorption spectrometry (HG-AAS, Solaar AA series, Thermo Scientific, Yokohama, Japan). The solid residues after adsorption were collected for characterization.

## 3. Results and discussion

Based on the elemental determination using CHN analysis and ICP-AES, the possible chemical formula of bimetallic and trimetallic LDHs

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