

Removal Behavior of Hydrocalumite for As(III) and As(V) from Aqueous Solution

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Abstract

Removal behavior of hydrocalumite (HC) for removals of As(III) and As(V) was examined. The mixed solution of 0.6 M CaCl₂ and 0.3 M AlCl₃ or that of 0.6 M Ca(NO₃)₂ and Al(NO₃)₃ was prepared, added into 1 M solution of NaCl, Na₂CO₃, Na₂SO₄ and NaNO₃, and stirred at 50 °C for 6 h with keeping pH 12.5 adjusted by 10 % NaOH to obtain the product including HC. HC can be synthesized using NaCl and NaNO₃ solutions, while calcium carbonate (calcite and vaterite) and ettringite were synthesized using Na₂CO₃ and Na₂SO₄, respectively. HC-NO₃, HC-Cl and ettringite can remove As(V), while only HC-NO₃ can remove As(III). Removal of As(III) using HC is lower than that using hydrotalcite (HT), while that of As(V) using HC is almost same as that using HT. With increasing dosage of HC, removals of both As(III) and As(V) increase.

Keywords: Hydrocalumite, Hydrotalcite, As(III) removal, As(V) removal

1. INTRODUCTION

Arsenic is a highly toxic pollutant that cause severely adverse effects on human health once released into the ecosystem. The long-term consumption of high-arsenic water may cause various diseases, such as skin lesions, peripheral vascular disease, hypertension and even cancers (Yoshida et al. 2004; Hopenhayn 2006). Unfortunately, the occurrence of arsenic in water has become more and more frequent with the blooming impact of modern industry and life activities (Hartley et al. 2013). Hence, the World Health Organization (WHO) has tightened the upper-limit of arsenic in drinking water from 50 to 10 µg/L, and this standard has been adopted by many countries suffering from arsenic contamination (Welch et al. 2000). Arsenic has been found in the ground water obtained from shallow tube wells (120 to 330 cm) of many countries. In India and Bangladesh, where the effects of arsenic poisoning are most devastating, 60 to 90 % of the total arsenic in the ground water is available in the trivalent states (Harvey et al. 2002). The

concentration range of the arsenic in these regions varies from 0.05 to 0.30 mg/L; somewhere it reaches up to even 3.0 mg/L (Mondal et al. 2006).

Different technologies have been developed and applied for arsenic removal (Kumer et al. 2013; Wu et al. 2013). Large-scale treatment facilities often use conventional coagulation with alum or iron salts, followed by filtration (Scott et al. 1995; Scott and Morgan 1995; Hering et al. 1996; Chen et al. 1999). Lime softening and iron removal by aeration-filtration are also common conventional treatment processes that can partially remove arsenic from ground water (Mcneill and Edwards 1997). Adsorption has been proven to be a good removal technique for heavy metals removal from aqueous solutions (Mahatantila et al. 2012; Rio and Martin 2012; Chen et al. 2012).

Among the technologies for arsenic wastewater treatment, adsorption is still one of the most popular choices worldwide (Mohan and Pittman 2007). Thereby, numerous types of materials have been studied in terms of the structure and

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properties, considering their critical role in adsorbing free arsenic from water. Among them, layered double hydroxides (LDHs) have emerged as an attractive adsorbent in recent decades, for their large surface area, excellent thermal stability and high selectivity given by the ion intercalation (Lu et al. 2016). Generally, LDHs are octahedral brucite-like layered materials with a formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} were divalent and trivalent metallic cations, such as Zn^{2+} , Mg^{2+} , Fe^{2+} , Co^{2+} , etc. and Al^{3+} , Cr^{3+} , Fe^{3+} , etc., respectively (Goh et al. 2008). A^{n-} is the interlayer anion, which can neutralize the positive charge originated by the presence of trimetallic cation in the layers and be flexibly substituted according to the property of the adsorbate (Yu et al. 2015). To date, most interlayer anions in LDHs targeting on arsenic removal are inorganic anions, such as Cl^- , NO_3^- , CO_3^{2-} and SO_4^{2-} (Grover et al. 2009; Bagherifan et al. 2014; Jiang et al. 2015).

In this study, hydrocalumite, which is composed of Ca and Al, including Cl^- , NO_3^- , SO_4^{2-} and CO_3^{2-} , was tried to be synthesized to remove As from aqueous solution because hydrocalumite is the cheapest LDHs, and removal behavior of As using hydrocalumite was compared with that using the most popular LDH, hydrotalcite.

2. EXPERIMENTAL

All analytical grade chemicals used in the experiments were purchased from Wako Chemical Co. Ltd., Japan. The stock solutions of As(III) and As(V) were prepared by dissolving $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$, respectively, in distilled water.

2.1 Synthesis

The products for As removal were synthesized from the mixed solution of Ca and Al in Na_2CO_3 , Na_2SO_4 , $NaCl$ and $NaNO_3$ solution for synthesis of hydrocalumite including various anions. In addition, hydrotalcite including NO_3^- ($MgAl-NO_3$) was synthesized to compare the As removal. $M^{2+}/M^{3+} = 2$ (molar ratio) in the mixed solution was adjusted by mixing 0.6 M $CaCl_2$, $Ca(NO_3)_2$, or $Mg(NO_3)_2$ aqueous solution and 0.3 M $AlCl_3$ or $Al(NO_3)_3$ aqueous solution. In the case of the synthesis of the product- CO_3 , $-SO_4$, $-Cl$, the mixed solution of 0.6 M $CaCl_2$ solution (100 mL) and 0.3 M $AlCl_3$ solution (100 mL) was added into 100 mL of 1 M $NaCl$ solution, 1 M Na_2SO_4 solution, or 1 M Na_2CO_3 solution to synthesize the product- Cl , the product- SO_4 , and the product- CO_3 , respectively. In the case of the synthesis of the product- NO_3 and $MgAl-NO_3$, the mixed solution of 0.6 M $Ca(NO_3)_2$ solution (100 mL) or 0.6 M $Mg(NO_3)_2$ solution (100 mL) and 0.3 M $Al(NO_3)_3$ solution (100 mL) was added into 100 mL of 1 M $NaNO_3$ solution to

synthesize the product- NO_3 and $MgAl-NO_3$, respectively. The mixture (300 mL) was stirred at 50 °C for 6 h. During stirring, pH of the solution was maintained at pH 12 or 10.5 ($MgAl-NO_3$) by dropping 10 w/v% $NaOH$ solution. After stirring, precipitates were filtered, washed with distilled water, and then dried at 80 °C to obtain the product.

The products were identified using X-ray diffraction (XRD) (RINT-2500, Rigaku). To determine chemical composition of the products, 0.1 g of the product- NO_3 and the product- Cl , $-SO_4$, $-CO_3$ were perfectly dissolved in 10 mL of 0.1 M HCl solution and 0.1 M HNO_3 solution, respectively. The contents of Ca^{2+} and Al^{3+} were measured by inductively-coupled plasma spectrometers (ICP-AES) (SPS3000, Seiko instruments), and those of Cl^- , NO_3^- and SO_4^{2-} were determined using ion chromatograph (ICS-3000, Dionex).

2.2 As removal

The As removal ability of the products were determined as follows. 0.2 g of the product was added into 40 mL of the solution with 0.1 M As(III) or 0.1 M As(V) in 50 mL of centrifuged tube, and the tube was shaken with reciprocal shaker for 17 h. After shaking, the tube was centrifuged, As concentration in the supernatant was measured using ICP-AES, and the removal of As was calculated using Eq. (1);

$$\text{Removal\%} = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

where C_0 and C_e are initial As concentration and measured As concentration, respectively.

Effect of dosage on As removal using the product- NO_3 ($CaAl-NO_3$) was examined in comparison with that using $MgAl-NO_3$. 0.01 – 0.2 g of the $CaAl-NO_3$ (HC) or $MgAl-NO_3$ (HT) was added into 20 mL of the solution with 0.1 M As(III) or 0.1 M As(V) in 50 mL of centrifuged tube, and the tube was shaken with reciprocal shaker for 17 h. After shaking, the tube was centrifuged, As concentration in the supernatant was measured using ICP-AES, and the removal of As was calculated using Eq. (1).

Effect of reaction time on As removal using $CaAl-NO_3$ was examined in comparison with that using $MgAl-NO_3$. 0.1 g of $CaAl-NO_3$ (HC) or $MgAl-NO_3$ (HT) was added into 100 mL of the solution with 0.1 M As(III) or 0.1 M As(V) in 250 mL of beaker, and the slurry was stirred with magnetic stirrer. During stirring, a part of the slurry (2 mL) was collected at various time, filtrated and As concentration in the filtrate was measured using ICP-AES, and the removal of As was calculated using Eq. (1).

3. RESULTS AND DISCUSSION

The mineralogical phases of the product synthesized in in (a) Na₂CO₃ solution, (b) Na₂SO₄ solution, (c) NaNO₃ solution and (d) NaCl solution are shown in Fig. 1. Hydrocalumite can be synthesized in NaNO₃ and NaCl solution, while ettringite and calcium carbonates, calcite and vaterite are synthesized in Na₂SO₄ solution and Na₂CO₃ solution, respectively. The peak intensities of hydrocalumite in the product synthesized in NaCl is higher than those in NaNO₃.

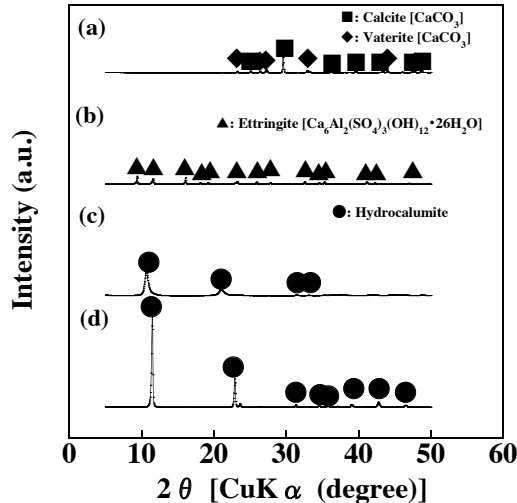


Fig.1 XRD patterns of the product in (a) Na₂CO₃ solution, (b) Na₂SO₄ solution, (c) NaNO₃ solution and (d) NaCl solution

Chemical compositions of the products are shown in Table 1. The Ca/Al molar ratios of the product-NO₃ and product-Cl are 2.24 and 2.26, respectively, which indicate that hydrocalumite with the Ca/Al molar ratio = ca. 2 can be synthesized using the Ca/Al mixed solution with the Ca/Al molar ratio =2. The Ca/Al ratio of the product-SO₄ is 2.95, which is almost same as that of ettringite (3.0). The product-CO₃ has high Ca content due to the calcium carbonate in the product.

Content (mmol/g)	Ca	Al	NO ₃	SO ₄	Cl
Product-NO ₃	7.6	3.4	1.9		
Product-SO ₄	5.9	2.0		1.4	
Product-Cl	7.9	3.5			2.4
Product-CO ₃	10.7	0.03			

As removals of various products are shown in Fig. 2. For As(III) removal, product-NO₃ can remove As(III) and the percentage of As removal is 8 %, while other products can't.

For As(V) removal, The product-NO₃, -SO₄ and -Cl can remove As(V) and the percentages of As(V) removal are 100 %, 100 % and 78 %, respectively, while the product-CO₃ can't, because hydrocalumite and ettringite are known as anion exchanger.

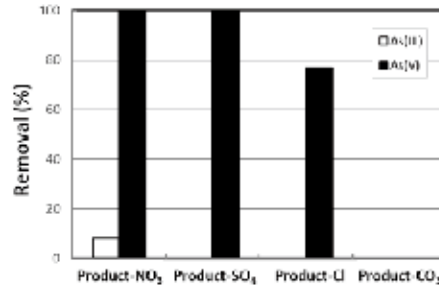


Fig.2 As removals of various products

From these results, the product-NO₃ including hydrocalumite with NO₃ is considered as a good material for As removal from aqueous solution.

Removals of As(III) and As(V) in aqueous solution using CaAl-NO₃ and MgAl-NO₃ are shown in Fig. 3. For CaAl-NO₃ (HC), removals of both As(III) and As(V) are very low at the dosage of 0.5 g/L. With increasing the dosage, the removal of As(III) gradually increases to 20 % at the dosage of 10 g/L, and that of As(V) rapidly increases to 90 % at the dosage of 2.5 g/L and then be almost constant. For MgAl-NO₃ (HT), removal of As(V) is 80 - 90 % at the dosage of 0.5 - 10 g/L. With increasing the dosage, the removal of As(III) gradually increases to 80 % at the dosage of 5 g/L and then be almost constant.

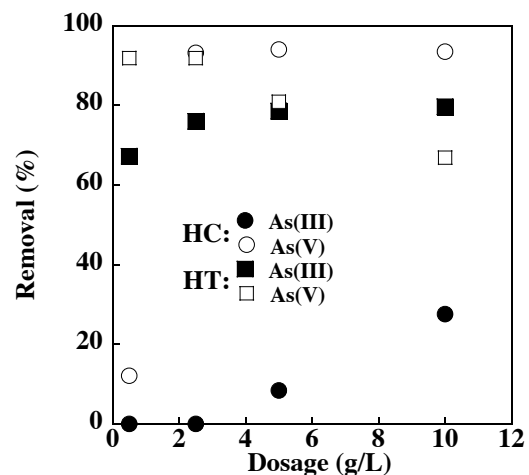


Fig.3 Removals of As(III) and As(V) in aqueous solution using CaAl-NO₃ and MgAl-NO₃

Removals of As(III) and As(V) in aqueous solution during the reaction using CaAl-NO₃ and MgAl-NO₃ are shown in Fig. 4. For CaAl-NO₃ (HC), removal of As(III) gradually increases to 10 % for 60 minutes and then be almost constant, while that of As(V) rapidly increases to 90 % at the initial stage of 5 minutes and then almost constant. For MgAl-NO₃ (HT), removals of both As(III) and As(V) rapidly increases to 80 % and 90 % at the initial stage of 5 minutes, and then almost constant.

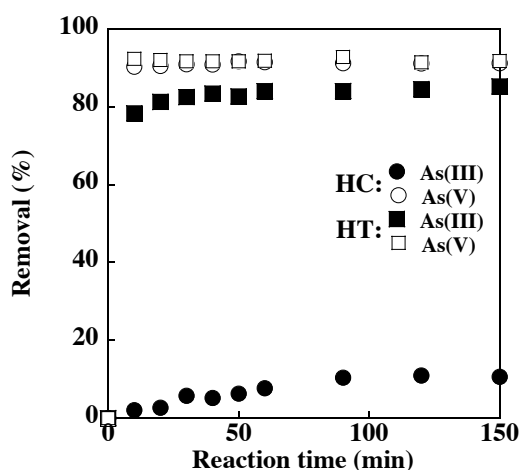


Fig.4 Removals of As(III) and As(V) in aqueous solution during the reaction using CaAl-NO₃ and MgAl-NO₃

From these results, CaAl-NO₃ has almost same removal ability for As(V) as MgAl-NO₃, while CaAl-NO₃ has lower removal ability for As(III) than MgAl-NO₃.

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