Original Paper

Removal of Harmful Anions in Aqueous Solution
with Various Layered Double HydroxidesNorihiro MURAYAMA^{1,2*}, Daisuke SAKAMOTO¹, Junji SHIBATA¹
and Marjorie VALIX²¹Department of Chemical, Energy and Environmental Engineering, Kansai University, Japan²School of Chemical and Biomolecular Engineering, The University of Sydney, Australia

Abstract

Four types of layered double hydroxides (LDHs) were synthesized by a co-precipitation method. The ability of various LDHs to remove anionic species including As(III), As(V), B, Cr(VI) and Se(IV) was investigated. Removal tests were performed primarily by a batch operation. The Cr(VI) removal was conducted by both batch and column studies. For the column removal tests, LDH pellets were prepared using a granulator and 5% poly-vinyl alcohol solution as binder.

Among the LDHs tested, Mg-Al-NO₃⁻ LDH showed the optimal removal of anionic species, and it demonstrated excellent removal of As(V), Se(IV) and Cr(VI) particularly at the low anionic concentrations. The order of anionic removal by the LDHs is as follows; Mg-Al-NO₃⁻ LDH > Mg-Al-Cl⁻ LDH >> Mg-Al-SO₄²⁻ LDH > Mg-Al-CO₃²⁻ LDH. The selective uptake of anion had the following order; As(V) > Se(IV) > Cr(VI) > As(III) > B. This study has demonstrated the uptake of harmful anions is influenced by the two specific factors, (1) the originally intercalated anions in the LDH, and (2) valency of anionic target species in aqueous solution. Column study also demonstrated that about 350 times Cr(VI) in solution per unit volume of LDH pellet can be removed, though this resulted in minor change in pH of the solution and greater NO₃⁻ elution. This study has revealed the ability of LDH to remove harmful anionic species and its practical application in wastewater treatment.

Key words: Layered double hydroxide, Anion exchanger, Harmful anion, Water purification

1. Introduction

Layered double hydroxide (LDH), also referred to as anionic clay, consists of metal complex hydroxide structure; $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} \cdot [(A^{n-})_{x/n} \cdot mH_2O]^{x-}$ ($x = 0.2-0.33$). Here, M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, and A^{n-} is the anionic species providing the inorganic anion exchanger functionality^{1,2}. For example, the Mg/Al type LDHs and Ca/Al type LDHs belong to hydroxalcalite and hydroxalcalumite mineral family, respectively. The positive charges at the M^{3+} sites in the metal hydroxide structure provide the anion exchange sites. This anion exchange property of LDH is attributed to capture anionic species by its intercalation within the interlayer structure¹⁻⁴.

Numerous papers have related the application of various LDHs including removal of harmful anions, carrier support for catalyst, a drug delivery system and so on⁵⁻¹². Our works have reported the preparation of LDHs synthesized from reagent and industrial by-products including aluminum dross, dust and steelmaking slag with anionic species including As, B, Cr, Se, P, organic carboxylates and anionic surfactants and their application in wastewater treatment¹³⁻²³. However, the systematic kinetics and equilibrium adsorption testing required for the design of a removal unit and the quantitative evaluation of the selectivity of LDHs prepared have not been adequate. In addition testing of the LDHs in continuous operation in a column absorber is quite limited.

In this study, various Mg/Al type LDHs with Cl⁻, NO₃⁻, CO₃²⁻ and SO₄²⁻ as an exchangeable anion were synthesized by a co-precipitation

Accepted 25 October, 2012

*e-mail: murayama@kansai-u.ac.jp

Table 1 Synthesis condition of various LDHs

	LDH	Mg source	Al source	Anion source	Synthesis pH
(a)	Mg-Al-NO ₃ ⁻	Mg(NO ₃) ₂	Al(NO ₃) ₃	NH ₄ NO ₃	11
(b)	Mg-Al-Cl ⁻	MgCl ₂	AlCl ₃	NH ₄ Cl	11
(c)	Mg-Al-SO ₄ ²⁻	MgSO ₄	Al ₂ (SO ₄) ₃	(NH ₄) ₂ SO ₄	10
(d)	Mg-Al-CO ₃ ²⁻	MgCl ₂	AlCl ₃	Na ₂ CO ₃	11

method. The removal property of these LDHs for harmful anionic species including As(III), As(V), B, Cr(VI) and Se(IV) was investigated. The removal of Cr(VI) was researched by batch and column operations. In the column tests, LDH pellets prepared using a granulator were used.

2. Experimental

2.1 Synthesis of LDH by co-precipitation method

Four types of Mg/Al type LDHs with NO₃⁻, Cl⁻, SO₄²⁻ and CO₃²⁻ as an exchangeable anion were prepared by a co-precipitation method. In this study the naming convention used is exemplified by the following example, Mg/Al type LDH containing NO₃⁻ was referred to as "Mg-Al-NO₃⁻ LDH". The synthesis conditions of various LDHs are summarized in Table 1. The LDH samples used are also the same as those used in our previous study¹⁹. That is, the co-precipitation method is similar to that mentioned in our paper¹⁹, and this involved the addition of two metal salts to a solution containing the anionic guest species followed by appropriate pH adjustment. For example in the synthesis of Mg-Al-NO₃⁻ LDH, 500 cm³ of 0.5 mol/dm³ Mg(NO₃)₂ + 0.2 mol/dm³ Al(NO₃)₃ were dropped into 250 cm³ of 0.64 mol/dm³ NH₄NO₃ solution of whilst vigorous stirred with a magnetic stirrer. The solution pH was also adjusted at the same time to 11.0 with 30 w/v% NaOH. In this test the ratio of Mg²⁺/Al³⁺ was set to be 2.5. The precipitate was aged whilst stirred for 24 h, then filtered, washed with distilled water and dried at 343 K. Similar method was adopted in preparing Mg-Al-Cl⁻ LDH, Mg-Al-SO₄²⁻ LDH and Mg-Al-CO₃²⁻ LDH using NH₄Cl, (NH₄)₂SO₄ and Na₂CO₃ as the guest anion species, respectively (see Table 1). Syntheses of each LDH were confirmed by an X-ray diffraction (Rigaku Co. Ltd., RINT-TTRIII). The resulting surface morphology was examined by a scanning electron microscopy (KEYENCE Co. Ltd., VE-9800).

2.2 Anion removal with various LDHs

Removal tests using the Mg-Al-NO₃⁻ LDH, Mg-Al-Cl⁻ LDH, Mg-Al-SO₄²⁻ LDH and Mg-Al-CO₃²⁻ LDH were carried out using primarily batch

operation to remove As(III), As(V), B, Cr(VI) and Se(IV) as target materials. Removal of Cr(VI) were also conducted in column tests. The solutions containing the above toxic materials were prepared by dissolving As₂O₃ with dilute NaOH solution or by dissolving H₃AsO₄, H₃BO₃, K₂CrO₄ and H₂SeO₃ with distilled water. The initial pHs of As(III), As(V), B, Cr(VI) and Se(IV) solutions were about 11.0, 2.5, 6.0, 4.3 and 2.8, respectively.

Batch removal tests were carried out by contacting 0.3 g of LDHs with 30 cm³ of single component target material solution at various concentrations. The solution was agitated continuously with a vertical shaker (TAITEC Co. Ltd., SR-2DW). After 1h the solution was filtered immediately and the concentration of the remaining target material was analyzed by inductively-coupled plasma spectrometers (Shimadzu Co. Ltd., ICPS-7000 Ver. 2 and ICPS-7510) using a standard procedure.

2.3 Preparation method of pelletized LDH (LDH pellet)

The dried Mg-Al-NO₃⁻ LDH powder was pelletized using a pan type granulator (Toyo Seisakusho Co. Ltd., DPZ-01) with 5 wt% polyvinyl alcohol (Kuraray Co. Ltd., Kuraray POVAL 217, abbreviated as PVA) solution as binder. The process involved placing the dried LDH powder into a rotating pan granulator and spraying the powder with the 5 wt% PVA solution to achieve a weight ratio of LDH: PVA solution of 100 g: 30 g. The pelletized product was dried at 343 K for 24 h. The dried pellets were sieved using 1.40 mm and 0.85 mm sieves, and then the product fraction of 0.85–1.40 mm were recovered as LDH sample (abbreviated as LDH pellet) to use for the removal tests. The apparent density of the LDH pellet measured by a specific gravity meter (Mettler Toledo Co. Ltd., SGM-6) was 1.85 g/cm³. Characteristics of the LDH pellet are shown in Table 2.

2.4 Cr(VI) removal with LDH pellet by batch and column operations

Removal of Cr(VI) with the LDH pellet were carried out by both batch and column tests. The procedures for batch removal test are similar to that described in section 2.2. Column test was

conducted using glass column, 565 mm height and 10 mm internal diameter. Ten grams of the pellets were packed in the column to achieve a height of 150 mm and volume of 11.8 cm³. The 100 mg/dm³ Cr(VI) solution was continuously metered into the column in a downward stream at the rate of SV4 (0.79 cm³/min). The effluent from the bottom part of column was collected by a fraction collector (Toyo Seisakusyo Co. Ltd., CHF122SC). The concentrations of Cr(VI) and NO³⁻ remaining in the effluent were determined by the inductively-coupled plasma spectrometers and by an ion chromatography (Nihon Dionex Co. Ltd., DX-500), respectively.

3. Results and Discussion

3.1 Anion removal with various LDHs

Figure 1 shows the XRD patterns of various LDHs synthesized by a co-precipitation method. The Mg-Al type LDH peak pattern was identified as the main crystalline material for all reaction products. The diffraction angle of the first peaks at around $2\theta = 11^\circ$ in Fig. 1(a)–(d) varied and this is attributed to the different exchangeable guest an-

Fig. 1 XRD patterns of various LDH products

ions in the LDH. These peaks are derived from the (006) plane of LDH structure, that is, the inter-layer distance of reaction product. These are also found to shift corresponding to the size of exchangeable anion^{13,19}. Though it is not shown in these figures, the anion exchange capacity of Mg-Al-NO₃⁻ LDH may be estimated to be about 3.6 meq/g from the amount of Al in the LDH which is considered to be almost equal to the amount of anion exchange site. The exchange capacities of the other LDHs, Mg-Al-Cl⁻ LDH, Mg-Al-SO₄²⁻ LDH and Mg-Al-CO₃²⁻ LDH are considered to be about 3.5 meq/g, 3.1 meq/g and 3.5 meq/g, respectively¹⁹.

The removal of various target anions with Mg-Al-NO₃⁻ LDH is illustrated in Figure 2. For comparison, the experimental data of As(III) and As(V) are quoted from our previous paper¹⁹. The equilibrium pHs after removal operation exist in the pH range between 7.2 to 10.6 by the pH buffer action of LDH^{15,18}. From this pH range, the dominant anionic species of As(III), As(V), B, Cr(VI) and Se(IV) are thought to be the forms such as AsO₂⁻, H₂AsO₄⁻, HAsO₄²⁻, HSeO₃⁻, B(OH)₄⁻, CrO₄²⁻ and SeO₃²⁻. As shown in Figure 2, the removal of As(III), As(V) and Se(VI) increased with an increase in equilibrium concentration. On the other hand, in case of Cr(VI) and B, their removals increased drastically with increasing equilibrium concentration in the region below 30 mg/dm³, but no further increase in removal was observed at the concentration above 30 mg/dm³. The selectivity for anion exchange has the following order; As(V) > Se(IV) > Cr(VI) > As(III) > B. It is considered that this order is attributed to the difference in the valency of anionic species, in other

Fig. 2 Removal of various harmful anions with Mg-Al-NO₃⁻ LDH

Fig. 3 Removal of various harmful anions with Mg-Al-Cl⁻ LDH

Fig. 5 Removal of various harmful anions with Mg-Al-CO₃²⁻ LDH

Fig. 4 Removal of various harmful anions with Mg-Al-SO₄²⁻ LDH

words, the anionic species with larger valency was favorably removed by LDH.

The removal properties of Mg-Al-Cl⁻ LDH, Mg-Al-SO₄²⁻ LDH and Mg-Al-CO₃²⁻ LDH are shown in Figures 3, 4 and 5, respectively. Here, the As(III) and As(V) are also cited data¹⁹. Among the target anions, As(V) was taken up selectively by all the LDHs. Whereas the removal of As(III) and B were found to be very low. The removal behavior of Se(IV) and Cr(VI) varied with the type of LDH with the following order; Mg-Al-NO₃⁻ LDH > Mg-Al-Cl⁻ LDH >> Mg-Al-SO₄²⁻ LDH > Mg-Al-CO₃²⁻ LDH. The results show the divalent anions like SO₄²⁻ or CO₃²⁻ are stable in the LDH structure, and these do not participate well in the anion exchange reaction, unlike the monovalent anions like NO₃⁻ or Cl⁻^{1,2,13}. This is attributed to the stronger Coulomb's attractive force

between divalent anions and positively charged exchange site in the LDH, and also the weaker force in the case of monovalent anions. It appears the difference in the removal of target anionic species is influenced by the type of LDH and the valency of anionic species in aqueous solution. The results in Figures 2, 3, 4 and 5 demonstrated the Mg-Al-NO₃⁻ LDH the best removal for the anionic species among four LDHs prepared in this study.

In general, the selectivity of an ion exchanger may be enhanced with the dilution of solution. The removal property of LDH for dilute solution within the ppm order is important from the viewpoint of the practical waste water treatment for the harmful anionic species. The removal behavior of Mg-Al-NO₃⁻ LDH which showed the best performance was investigated in detail, using dilute solutions below 100 mg/dm³. Figure 6 shows the ion exchange isotherms of harmful materials with the Mg-Al-NO₃⁻ LDH in low concentration region. The shape of isotherms for As(V), Se(IV) and Cr(VI) near Y axis showed a very sharp incline demonstrating the excellent performance of Mg-Al-NO₃⁻ LDH in the removal of anionic species from dilute solutions. The Cr(VI) removed was about 60 mg/g, which corresponds to about 2.3 meq/g as a standard of CrO₄²⁻. Therefore, 64% to the exchange capacity (3.6 meq/g) is estimated to be occupied with CrO₄²⁻. Whereas the removal of As(III) and B is thought to be difficult as shown in Figure 6. The order of anion exchange in dilute solutions is similar to that shown in Figure 2, that is, As(V) > Se(IV) > Cr(VI) > As(III) > B.

Fig. 6 Ion exchange isotherms of dilution solutions of harmful anions on Mg-Al-NO₃⁻ LDH

Table 2 Preparation parameters and characterization of LDH pellets

Binder	5 wt% PVA solution
Mixing ratio	100 g of LDH: 30 g of PVA solution
Particle size distribution	0.85–1.40 [mm]
Apparent pellet density	1.85 [g/cm ³]

* Molecular weight of PVA: 221,000

3.2 Cr(VI) removal with LDH pellet by batch and column operations

Dried powder of the Mg-Al-NO₃⁻ LDH was pelletized under the condition shown in Table 2 by using the pan type granulator. Photograph 1 illustrates the SEM of the original LDH powder and pelletized product (LDH pellet). These photographs show that the LDH powder are characterized by block-like structure with smooth surface. The particle size distribution of the LDH is relatively wide from submicron to 50 or more micrometers. The LDH pellets have an elliptical shape with smooth surface, and fine particles of the LDH powder are found to be well agglomerated.

The rate of Cr(VI) removal by the Mg-Al-NO₃⁻ LDH pellets is shown in Figure 7. The removal of Cr(VI) increased with a contact time but remained constant after 45 min. At equilibrium, the Cr(VI) removed was about 9.5 mg/g-LDH pellet. A slight increase in solution pH was observed due to the pH buffer action of LDH during the column test. This implies that the partial dissolution of metal hydroxide from the LDH structure may have taken place with its contact with weakly acidic Cr(VI) solution, that is, due to the potential instability of the LDH.

Figure 8 compares the removal of Cr(VI) be-

(a) Powder

(b) Pellet

Photo. 1 SEM of (a) powdered and (b) pelletized Mg-Al-NO₃⁻ LDH

Fig. 7 Rate of Cr(VI) removal with Mg-Al-NO₃⁻ LDH pellet (Initial conc.: 100 mg/dm³, Solid-liquid ratio: 0.3 g:30 cm³)

tween powder and pelletized Mg-Al-NO₃⁻ LDHs. The Cr(VI) removal by the LDH pellet increased remarkably at concentration below 10 mg/dm³ equilibrium concentration, and increased more gradually at the higher concentration. Although

Fig. 8 Comparison of Cr(VI) removal between powder and pellet of Mg-Al-NO₃⁻ LDH

Fig. 9 Breakthrough curve for Cr(VI) removal on Mg-Al-NO₃⁻ LDH pellet (Initial conc.: 100 mg/dm³, Space velocity: 4, Bed volume: 11.8 cm³(=10 g))

the shapes of Cr(VI) removal curves exhibited by the LDH powder and LDH pellet are essentially similar, the amount removed by the pellets are about 20 mg/g lower than that of the LDH powder. It is considered that this phenomenon may be caused by the differences in surface area or efficiency of solid-liquid contact between LDH powder and LDH pellet. The advantage, however of the pellets is the ease of the solid-liquid separation and its applicability in continuous operation.

Figure 9 illustrates the breakthrough curve of Cr(VI) with the Mg-Al-NO₃⁻ LDH pellet. No Cr(VI) elution is found until about 4,000 cm³ of effluent volume by the strong affinity of the LDH to Cr(VI). The breakthrough point was set to be the 0.5 mg/dm³ of Cr(VI) concentration which occurred with the 4,080 cm³ of effluent volume. This means that it is possible to treat about 350 times the Cr(VI) solution to the LDH pellet volume (11.8 cm³). At the 6140 cm³ of effluent volume,

the Cr(VI) concentration approached about 100 mg/dm³ of initial concentration. In the region up to the breakthrough point, the total amount of Cr(VI) removed was estimated to be 0.93 meq/g-LDH pellet.

On the other hand, NO₃⁻ is released from the LDH, as a result of anion exchange reaction between anionic species of Cr(VI) in solution. The NO₃⁻ concentration gradually decreased with metering of effluent volume into the column becoming zero, when the effective anion exchange site in the LDH pellet was saturated under this condition and the outlet Cr(VI) concentration reached its initial concentration (100 mg/dm³) again. The total amount of NO₃⁻ released until the breakthrough point was calculated to be about 2.0 meq/g-LDH pellet. The reason for the greater elution quantity of NO₃⁻ relative to Cr(VI) is not clarified yet, but it is considered that this is mainly caused by the elution of NO₃⁻ from anion exchange sites with the partial disintegration of LDH structure, that is to say, with partial dissolution of hydroxide parts in the LDH referred to earlier.

4. Conclusion

The removal properties of various LDHs, Mg-Al-NO₃⁻ LDH, Mg-Al-Cl⁻ LDH, Mg-Al-SO₄²⁻ LDH and Mg-Al-CO₃²⁻ LDH synthesized by a coprecipitation for anionic species including As(III), As(V), B, Cr(VI) and Se(IV) were examined in this study. Removal tests were conducted by batch and column methods.

The Mg-Al-NO₃⁻ LDH showed the best anionic removal among the four LDHs prepared in this study. The order of removal performance is as follows; Mg-Al-NO₃⁻ LDH > Mg-Al-Cl⁻ LDH >> Mg-Al-SO₄²⁻ LDH > Mg-Al-CO₃²⁻ LDH. This order suggests the stability of the divalent anions like SO₄²⁻ or CO₃²⁻ on the LDH structure and thus their poor exchange properties. The Mg-Al-NO₃⁻ LDH demonstrated an excellent ability to remove dilute concentrations of As(V), Se(IV) and Cr(VI) with the following order; As(V) > Se(IV) > Cr(VI) > As(III) > B. The use of LDH pellets were shown to effectively treat about 350 times of the Cr(VI) solution to the LDH pellet volume in a column test. Although the pellets showed a lower Cr(VI) uptake amount of about 20 mg/g compared with the powdered LDH, the pellets application in column operations is a key advantage for the practical application of this adsorbent. The LDH also demonstrated some minor instability when contacted with the weak acidic effluent solutions. These are exhibited by the greater elution of NO₃⁻ ions rela-

tive to Cr(VI) and change in pH resulting from the partial dissolution of the hydroxide component of the LDH. This study has revealed the ability of LDH in the practical removal of harmful anionic species from wastewater.

Acknowledgements

This research was partially supported by Kansai University's Overseas Research Program for the year of 2011 and the MEXT, Supported Program for the Strategic Research Foundation at Private Universities, 2012–2016.

References

1. E. Narita: Nendo Kagaku, **46**, pp. 207–218 (2007)
2. S. Miyata: Clays and Clay Minerals, **31**, pp. 305–311 (1983)
3. K. Okada, K. Mimura, S. Nogi: Nendo Kagaku, **34**, pp. 40–47 (1994)
4. S. Velu, A. Ramani, V. Ramaswamy, B.M. Chanda, S. Sivasanker: Studies in Surface Science and Catalysis, **118**, pp. 941–950 (1998)
5. Y. Ono and E. Suzuki: Shokubai, **34**, pp. 509–514 (1992)
6. T. Yamagishi, Y. Oyanagi, E. Narita: Nihon Kagakukaishi, **4**, pp. 335–341 (1993)
7. F. Malherbe, C. Forano, J. Besse: Journal of Materials Science Letters, **18**, pp. 1217–1219 (1999)
8. H. Hirahara, S. Aizawa, H. Sato, S. Takahashi, Y. Umetsu, E. Narita: Nendo Kagaku, **45**, pp. 6–13 (2005)
9. Y. Chuang, Y. Tzou, M. Wang, C. Liu, P. Chiang: Industrial & Engineering Chemistry Research, **47**, pp. 3813–3819 (2008)
10. S. Vreysen and A. Maes: Applied Clay Science, **38**, pp. 237–249 (2008)
11. L. Gaini, M. Lakraimi, E. Sebbar, A. Meghea, M. Bakasse: Journal of Hazardous Materials, **161**, pp. 627–632 (2009)
12. T. Kameda, H. Takeuchi, T. Yoshioka: Materials Research Bulletin, **44**, pp. 840–845 (2009)
13. N. Murayama, H. Yamamoto, J. Shibata: Kankyo Shigen Kogaku, **51**, pp. 92–98 (2004)
14. J. Shibata, N. Murayama, M. Tanabe, H. Yamamoto: Kagaku Kogaku Ronbunshu, **31**, pp. 74–79 (2005)
15. N. Murayama, M. Tanabe, R. Shibata, H. Yamamoto, J. Shibata: Kagaku Kogaku Ronbunshu, **31**, pp. 285–290 (2005)
16. N. Murayama, J. Shibata, K. Sakai, S. Nakajima, H. Yamamoto: Kankyo Shigen Kogaku, **53**, pp. 6–11 (2006)
17. J. Shibata, N. Murayama, H. Yamamoto: Japanese Patent Disclosure, H06-151744 (2006)
18. J. Shibata, N. Murayama, S. Nakajima: Kagaku Kogaku Ronbunshu, **33**, pp. 273–277 (2007)
19. J. Shibata, N. Murayama, D. Sakamoto, M. Okada: Kagaku Kogaku Ronbunshu, **35**, pp. 60–65 (2009)
20. N. Murayama, H. Ushiro, S. Hattori, T. Miyoshi, J. Shibata: Kagaku Kogaku Ronbunshu, **37**, pp. 526–531 (2011)
21. N. Murayama, I. Maekawa, H. Ushiro, J. Shibata, E. Udagawa: Kagaku Kogaku Ronbunshu, **38**, pp. 176–182 (2012)
22. N. Murayama, I. Maekawa, H. Ushiro, Y. Moyoshi, J. Shibata, M. Valix: International Journal of Mineral Processing, **110–111**, pp. 46–52 (2012)
23. N. Murayama, R. Hara, T. Miyoshi, J. Shibata, E. Udagawa: Kagaku Kogaku Ronbunshu, **38**, pp. 234–241 (2012)