Synthesis and Characterization of LDHs (Layered Double Hydroxides) Intercalated with EDTA (Ethylenediaminetetracetic Acid) or EDDS (N, N'-1, 2-Ethanediybis-1-Aspartic Acid)

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Abstract: The hydrotalcite-like compound $[\text{Zn}_2\text{Al}(\text{OH})_6] \text{NO}_3 \cdot n\text{H}_2\text{O}$ and $[\text{Mg}_2\text{Al}(\text{OH})_6] \text{NO}_3 \cdot n\text{H}_2\text{O}$ (shorted as ZnAl-NO_3 and MgAl-NO_3) was intercalated with the chelating agent EDTA (Ethylenediaminetetraacetic Acid) and EDDS (N, N'-1, 2-Ethanediybis-1-Aspartic Acid) by anion exchange. The materials synthesized in this work were characterized by chemical analysis, FT-IR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy) and XRD (Powder X-ray Diffraction) to confirm their properties. In order to discuss the adsorption capacity of LDHs (Layered Double Hydroxides), the adsorption experiment was investigated under the optimum condition (10 mg, 25 °C and 100 $\mu\text{g} \cdot \text{L}^{-1}$). The amount of metallic ions adsorbed by LDHs intercalated with EDTA and precursor LDHs were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and AAS (Atomic Absorption Spectrometry). The intercalation of EDTA leads to improve the adsorption capacity of LDHs. LDHs intercalated with chelating agents have generally high affinity for removing metallic ions, and they can be efficient adsorbents for metallic ions.

Key words: Layered Double Hydroxide, chelating agents, metallic ions, adsorption.

1. Introduction

LDHs (Layered Double Hydroxides) or anionic clays is lamellar ionic compound containing a positively charged layer and exchangeable anions in the interlayer. They consist of brucite-like layers, and are represented by the general formula $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2] (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where cationic M^{II} and M^{III} are divalent and trivalent metals and occupy the octahedral holes in the brucite-like layer. A^{n-} is the interlayer exchangeable anions, which is located in the hydrate layered galleries, and x is the layer charge density $x = [\text{M}^{\text{II}}]/([\text{M}^{\text{II}}] + [\text{M}^{\text{III}}])$ [1-3].

In this compound, the positive charge excess is produced by isomorphic substitution of divalent for trivalent cations and compensated by the introduction of anions (usually together with water) in the interlayer space [4, 5]. Since the interlayer anions are easily exchangeable, various types of anions can be intercalated in its structure. This property makes LDHs suitable for many applications including pollutant remediation sorbents, antacids, catalysts and anionic exchangers [2, 3, 6].

Intercalation of anionic ligands is also an efficient way to incorporate different metal cations to LDHs, and there are some reports about the adsorption of anions such as phosphate anions. The capacity of LDHs as adsorbents of pollutant has been extensively reported both for inorganic [7] and organic [8, 9] anions. LDHs also can be intercalated with different

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polydentate ligands as scavengers of these solids to metal cations and lanthanides [10-12].

EDTA (Ethylenediaminetetracetic Acid) is a chelating agent widely used in industry and agriculture. It forms strong complexes with the ratio 1:1 between heavy metal ions and ligand. EDDS (N, N'-1, 2-Ethanediybis-1-Aspartic Acid) is also a chelating agent, which may offer a biodegradable alternative to EDTA, and is currently used on a large scale in numerous applications [13, 14].

Considering the structure of LDHs and the properties of chelating agents, LDHs modified with chelating agents has been studied as the potential adsorbents of heavy metals from the aqueous solution. The potential adsorbents for these compounds may be due to the stability of the chelates formed by ligands and metals [15-17].

The aim of this work is at first to synthesize and characterize LDHs intercalated with EDTA or EDDS, and then to investigate the efficiency of the materials as adsorbent for metallic ions from aqueous solution for more practical use.

The following five kinds of compounds synthesized in authors' present work are ZnAl-NO₃ (L1), ZnAl-EDTA (L2), MgAl-NO₃ (L3), MgAl-EDTA (L4) and MgAl-EDDS (L5). To confirm the effect of intercalation with EDTA, the adsorption of metallic ions onto L1 and L2 are also compared.

2. Experiment

2.1 Materials and Reagents

Chemical reagents including Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O, Na₂H₂EDTA·2H₂O, NaOH and Cd(II) Cu(II), Pb(II) standard solution were purchased from Kanto Chemical Co., Inc.; EDDS (35%) was purchased from Sigma Co. Ltd.; and all reagents used were of analytical grade. CO₂ free water (> 18.2 MΩ) which was treated as an ultrapure water system (RFU 424TA, Advantech Aquarius) was employed throughout the work.

2.2 Synthesis of the Adsorbents

The synthesis of LDHs intercalated with EDTA or EDDS includes two steps: (1) the preparation of the precursor L1 or L3, and (2) the anion-exchange reaction of this compound with chelating agents [18]. All the synthesis was purged with N₂ to avoid CO₂ uptake from atmosphere.

2.2.1 Synthesis of Precursor L1 and L3

L1 was prepared by dropping addition of a 100 mL aqueous solution of 0.02 mol·L⁻¹ Zn(NO₃)₂·6H₂O and 0.01 mol·L⁻¹ Al(NO₃)₃·9H₂O to a 100 mL NaOH solution. Then, the solutions were agitated at 70 °C for 8h, separated by centrifugation and washed until neutral. L3 was also synthesized by using Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O as the similar method [19, 20].

2.2.2 Synthesis of L2, L4 and L5

L2 was synthesized as follows. Under a N₂ atmosphere, 0.015 mol of EDTA was added to the 150 mL of suspended solution of L1. Then, the mixing solutions were agitated at 70 °C for 8 h, separated by centrifugation, washed until neutral and then dried at 60 °C overnight [10, 16]. L4 and L5 were synthesized by L3 as the similar method for L2.

2.3 Characterization of These Adsorbents

Elemental chemical analyses of C, H and N in LDHs were carried out using an elemental analyzer instrument (JMC10, J-SCIENCE LAB CO., Ltd.). Infrared spectra were obtained using the KBr disc method, with wavenumbers from 400 to 4,000 cm⁻¹ on a FT-IR (Spectrum One, Perkin Elmer Inc.). XRD (X-ray Powder Diffraction) of LDHs samples were carried out on a RINT2500HR-PC (RIGAKU Corporation) using Cu Kα radiation in the scanning range of 2-80°. The surface morphology of LDHs was surveyed using scanning electron microscopy (SEM; JCM-6000, JEOL). The element distribution and the component analysis were also analyzed by Electron probe micro analyzer (EPMA; 1600, Shimadzu Corporation).

2.4 Adsorption Experiments

The adsorption experiments of Cd(II), Cu(II), Pb(II) using L1, L2 were carried out. A certain amount of L1 or L2 were contacted with 30 mL of an aqueous solution containing known initial metallic ions of 100 $\mu\text{g}\cdot\text{L}^{-1}$ (Cd(II)) and 200 $\text{mg}\cdot\text{L}^{-1}$ (Cu(II), Pb(II)). Adsorption experiments were conducted under the condition of contact time from 0 min to 8 h at 25 °C. The experiment using metallic ions solution without the adsorbent was also performed to estimate the potential loss of metallic ions by process such as precipitation.

Following each sorption experiment, the suspension containing the adsorbent and solution including metallic ions were filtered through a 0.45 μm membrane filter (Mixed Cellulose Ester 47 mm, Advantec MFS, Inc.) to remove ion that have been adsorbed into the adsorbent. Then, the concentration in the filtrate was determined by inductively coupled plasma atomic emission spectrophotometer (ICP-AES; SPS 1500, Seiko Instrument Inc.) and atomic absorption spectrometry (AAS; Z5000, Hitachi Corporation).

The metallic ions uptake by each adsorbent was calculated using the Eq. (1):

$$Q = \frac{(C_0 - C_e)}{W} \cdot V \quad [\mu\text{g}\cdot\text{g}^{-1}] \quad (1)$$

where Q is the adsorption capacities at equilibrium ($\mu\text{g}\cdot\text{g}^{-1}$), C_0 and C_e are the initial and equilibrium concentrations of metallic ions in a batch system respectively [$\mu\text{g}\cdot\text{g}^{-1}$], V is the volume of the solution (L), and W is the weight of each adsorbent (g) [19, 20].

3. Results and Discussion

3.1 Synthesis and Characterization of LDHs

The chemical analysis of LDHs samples is shown in Table 1. The molar ratio of $M^{\text{II}} / M^{\text{III}}$ in L1 or L3 is nearly 2 which is well fitted to the expected formula. However, L2, L4 or L5 has lower $M^{\text{II}} / M^{\text{III}}$ ratio than L1 or L3. The presence of polydentate ligand

(Zn-EDTA or Al-EDTA complex) can result in this decrease of the ratio. Moreover, the decrease suggests that octahedron in hydroxyl layer has a partial dissolution ($\text{p}K_{\text{sp}}$ ($\text{Zn}(\text{OH})_2$) = 13.7, $\text{p}K_{\text{sp}}$ ($\text{Al}(\text{OH})_3$) = 32.7, $\text{p}K_{\text{sp}}$ ($\text{Mg}(\text{OH})_2$) = 12.7) during the anion exchange reaction which is performed at pH 5-6 [10, 16, 21]. The C/N of L2 is 4.35, while that of EDTA ligand is 5; and the little gap between them may be mainly due to the registration of nitrate ions in the interlayer. The more nitrate ions are included in LDHs, the lower C/N value is [22].

The FT-IR spectra of L1 and L2 are shown in Fig. 1, and that of L3, L4, L5 are shown in Fig. 2. Typical M-OH (M: metallic ions) vibration modes due to the hydroxide layer between 400 and 1,000 cm^{-1} [23] are found in both Figs. 1(a) and (b).

The very sharp peak at 1,385 cm^{-1} in Fig. 1(a) is attributed to the NO_3^- stretching vibration. The NO_3^- stretching vibration at 1,385 cm^{-1} is not observed from Fig. 1(b). It may be due to the group which is hidden by the band at 1,394 cm^{-1} [22, 24]. The absorption bands at 1,600 and 1,394 cm^{-1} are characteristics of the symmetrical and asymmetrical vibration of COO^- groups. The position of these bands is similar to the spectrum of LDHs which is reported by Park et al. [25, 26]. It is found that EDTA has been intercalated into the interlayer successfully, although a certain amount of $-\text{NO}_3^-$ may still retain in the compound judging from the results of chemical analysis. The wide band at around 3,450 cm^{-1} may be attributed to the H-bondings stretching vibrations of $-\text{OH}$ groups and water molecules. The band at 1,623 cm^{-1} of L1 and L3 are assigned to water bending vibration [2, 22].

XRD patterns of L1 and L2 are shown in Fig. 3, and those of L3, L4 and L5 are shown in Fig. 4. They are typical XRD patterns of LDHs. The strong diffraction peaks at low angle, assigned to basal planes (003), (006), (009), were sharp and symmetric compared to the peaks at high angle, which are characteristics of clay mineral having a layered structure [25-27]. From the XRD pattern, the basal spacing (d) values of

Table 1 Chemical analysis of LDHs synthesized in this work.

	Atomic ratios			Proposed formula
	M ^{II} /M ^{III}	C/H	H/N	
L1	2.10	0.00	5.72	[Zn ₂ Al(OH) ₆] ₂ NO ₃
L2	0.97	0.41	10.6	[Zn ₂ Al(OH) ₆] ₂ [C ₁₀ H ₁₄ N ₂ O ₈]
L3	2.23	0.01	8.79	[Mg ₂ Al(OH) ₆] ₂ NO ₃
L4	1.19	0.36	18.2	[Mg ₂ Al(OH) ₆] ₂ [C ₁₀ H ₁₄ N ₂ O ₈]
L5	1.49	0.31	26.3	[Mg ₂ Al(OH) ₆] ₂ [C ₁₀ H ₁₃ N ₂ NaO ₈]

Fig. 1 FT-IR spectrum of sample (a) L1, (b) L2.

Fig. 2 FT-IR spectrum of sample (a) L3, (b) L4, (c) L5.

Fig. 3 XRD of sample (A) L1, (B) L2.

Fig. 4 XRD of sample (a) L3, (b) L4, (c) L5.

Table 2 Basal spacing of L2, L3, L4 and L5.

	L1	L2	L3	L4
Basal spacing (nm)	0.89	1.47	0.91	1.42
Gallery height (nm)	0.41	0.99	0.43	0.94

sample were calculated by using Bragg equation and the angle of peak (003).

Then the gallery height was obtained by subtraction from the basal spacing to the layer width (0.48 nm) [26]. The basal spacing and the gallery height of L1, L2, L3 and L4 are shown in Table 2. It indicates that the intercalation of EDTA into NO_3 -LDHs gives rise to an increase of basal spacing.

This basal spacing could identify the existence of EDTA, because it is close to the dimensions of EDTA complexes ($0.9 \text{ nm}^{-1} \cdot \text{nm}$) founded by single crystal XRD of M-EDTA (M: metallic ions) compound [11, 16, 26, 28].

SEM images of all composite synthesized in this work are shown in Fig. 5. These adsorbents have clear plate-like morphology, which is typical for LDHs [29]. Element distribution analyzed of L1, L2, L3 and L4 by EPMA is shown in Fig. 6. After the ion exchange, the element distribution of N decreased obviously (by comparing red parts in these pictures), and this decrease is observed in both ZnAl-LDHs (a, b) and MgAl-LDHs (c, d). Furthermore, it is found that the moles of divalent metals are at least equal to or greater than that of the trivalent metals [10, 30], which is consistent with the results of chemical analysis.

3.2 Adsorption Experiments

In order to confirm the effect of the intercalation with chelate agents on the adsorption capacity of metals, the adsorption experiments of some metallic elements onto L1 and L2 are compared. The adsorption of Cd(II), Cu(II) and Pb(II) onto these LDHs under the optimum condition are shown in Fig. 7, Fig. 8 and Fig. 9, respectively.

Both LDHs were found to take up Cd(II), Cu(II) and Pb(II) from aqueous solutions, and the uptake was found to increase with time. The adsorption capacity of both LDHs for Cd(II), Cu(II) and Pb(II) increased rapidly during the initial stages, and thereafter it

increased gradually. It is generally found that the time which needed to reach equilibrium of L2 was shorter than that of L1. From the adsorption experiment, the improvement of adsorption capacity by intercalation was observed. On the other hand, the adsorption capacity of Cu(II) and Pb(II) at equilibrium was higher than that of Cd(II). It is considered that LDHs remove heavy metal by two mechanisms: chemical precipitation and chelation [20]. In the first case, the hydroxyl anions compete with chelating agents for the precipitation of metal hydroxides at higher pH, and divalent ions are usually selectively dissolved. In the second case, the adsorption affinity is generally determined by the stability constant of the corresponding complex [11, 31, 32].

Fig. 5 SEM image of (a) L1, (b) L2, (c) L3, (d) L4, (e) L5.

Fig. 6 Element distribution of (a) L1, (b) L2, (c) L3, (d) L4 by EPMA.

Fig. 7 Adsorption of Cd(II) onto L1 and L2.

Fig. 8 Adsorption of Cu(II) onto L1 and L2.

Fig. 9 Adsorption of Pb(II) onto L1 and L2.

4. Conclusion

In present study, precursor LDHs containing nitrate ions are synthesized by coprecipitation, and then intercalated with EDTA or EDDS through an anion exchange reaction. Five kinds of synthesized samples are characterized by some instruments. The result from FT-IR etc. suggests that the intercalation into layered double hydroxide is performed successfully. The decrease of M^{II} / M^{III} molar ratio suggests that hydroxyl layer has a partial dissolution during the reaction process.

In the case of the adsorption of Cd(II) onto L1 and L2, Zn(II) released in aqueous solution may affect the removal percentage (maximum 66.7%, not shown) by

competing with Cd(II). It may be attributable to the similar stability constants between chelated zinc and chelated cadmium. However, more detailed research about the stability of adsorbent will be needed in future.

The uptake process of metallic ions onto LDHs includes chelation with chelating agents and precipitation. This complex mechanism enables LDHs intercalated with chelating agents to have high affinity for removing metallic ions. Considering the results of this work, LDHs synthesized in this work can be efficient adsorbents for metal ions.

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