Application of Aluminum Dross-Derived Layered Double Hydroxides to Removal of Organic Compounds in Aqueous Solution

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Abstract
Layered double hydroxides (LDHs) with hydrophobic surface by surfactant modification were prepared using aluminum dross as a raw material, to develop a new recycling method of aluminum dross. The physical properties including crystal structure, surface texture and contact angle were investigated for the LDHs modified with dodecyl sulfate ions (DS) as a surfactant. The removal tests of dilute toluene in aqueous solution were demonstrated using the DS- type LDHs (DS-LDHs).

Organic modification of the LDHs synthesized from aluminum dross can be achieved successfully by an anion exchange with DS. The toluene in aqueous solution (initial concentration; 10 and 50 mg/dm$^3$) is removed using the DS-LDHs. It was clarified that the DS-LDHs synthesized from aluminum dross can be used as an excellent adsorbent for dilute organic compounds in aqueous solution.

Key words: Aluminum dross, Layered double hydroxide, Inorganic anion exchanger, Waste water treatment

1. Introduction
Aluminum dross generated in conventional aluminum purification and recycling processes, is one of the industrial by-products to be recycled. The aluminum dross is mainly composed of the mixture of metallic aluminum, and aluminum oxides, chlorides and nitrides. Recently, 5 million tons or more of aluminum dross are annually generated in all the world$^1$. For example, the aluminum dross in Japan is reused as a deoxidizer in a steel-manufacturing process and as an aggregate in cement. However, large amounts of aluminum dross are also disposed of in landfills, because of its toxicity and high flammability or various economical reasons in reusing and recycling. Development of new economical and ecological recycling methods is desired for the aluminum dross.

The authors$^2$-$^6$ have already reported a series of the recycling methods for aluminum dross including the preparation of hydrotalcite-like compounds (double hydroxide composed of Mg and Al, abbreviated as HTs hereafter) using the aluminum dross as a raw material, and its application to an anion exchanger for the removal of toxic anionic substances such as As, B, Cr and Se in aqueous solution. The HTs are classified as a kind of layered double hydroxides (abbreviated as LDHs) composed of metal complex hydroxide: \[ \left[ M^{2+}, M^{3+}(OH)_{2}\right]^{x+}\left[ (A_n^{2-} \right. \left. x/n \cdot mH_2O\right]^{-x} \] (x = 0.2–0.33). The $M^{2+}$ and $M^{3+}$ are divalent and trivalent metal ions, respectively, and $A_n^{2-}$ is exchangeable anionic species. The HTs and LDHs are known as an excellent anion exchanger$^7,8$. In many papers$^7$-$^{15}$, various LDHs can thus be applied for the antacid, removal of harmful anions, carrier support for catalyst, a drug delivery system and so on.

The LDH containing organic anions can be used as a carrier of organic compounds like surfactant, chelating agent and so on$^{9,17}$. For example, various anionic surfactants such as dodecyl sulfate ions, dodecylbenzene sulfonate ions and octane sulfonate ions are easily captured in the LDH structure by an anion exchange reaction.
This kind of surfactant-modified LDHs can remove the dilute organic compounds in aqueous solution. The synthesis of organically modified LDHs from aluminum dross rather than pure reagents for this application may contribute to the effective use of aluminum dross and the potential to lower production cost. It appears that no research has been conducted according to the organically modified LDHs synthesized from aluminum dross. Therefore, this concept is considered to be an interesting and unique method for recycling of aluminum dross.

In this study, the preparation of various LDHs was carried out using the aluminum dross leachates as a starting material. The LDHs were organically modified with dodecyl sulfate ions by an intercalation. The fundamental physical properties were measured for the obtained LDHs. The removal tests of dilute toluene in aqueous solution as a model substance were conducted with the organically modified LDHs.

2. Experimental

Aluminum dross used in this study was generated from used Al alloys such as car bodies, engine components and window frames. The aluminum dross powder was leached with 2.0 mol/dm$^3$ HCl under the condition of 2.5 g:100 cm$^3$ solid-liquid ratio, 5h leaching time and room temperature by mixing with a magnetic stirrer. After the acid leaching operation, the filtrate and residue were separated with a vacuum filtration equipment.

The syntheses of LDH using the leachate of aluminum dross as a starting material were conducted by a co-precipitation method. Various leachates by HCl and a metal reagent of M$^{2+}$Cl$^-$ [M$^{2+}$; Mg$^{2+}$, Ca$^{2+}$ and Zn$^{2+}$] as a divalent cation source were mixed to keep the M$^{2+}$/Al$^{3+}$ ratio of 2.5. In order to synthesize the LDHs containing Cl$^-$ as an exchangeable anion, 200 cm$^3$ of the Mg-Al mixed solution obtained at the same solid-liquid ratio was slowly added to 100 cm$^3$ of 0.64 mol/dm$^3$ NH$_4$Cl solution, while constantly stirring by a magnetic stirrer. Solution pH (LDH synthesis pH) was maintained by adding 30 w/v% NaOH. The LDH synthesis pHs of Mg-Al, Ca-Al and Zn-Al LDHs from the aluminum dross leachate were set at 11, 12 and 8, respectively. The LDH crystallization reaction was allowed for 24 h aging by a magnetic stirrer at room temperature. The resulting precipitate was recovered by a vacuum filtration followed by washing with distilled water and drying at 70°C.

Removal tests were conducted for dilute toluene in aqueous solution with the DS-LDH synthesized from aluminum dross. Dilute toluene solutions (initial concentration; 10 and 50 mg/dm$^3$) of 30 cm$^3$ and the DS-LDH of 0.3 g were contacted for 3 h at room temperature. Wet cake and mother liquor were separated, and then the residual toluene concentrations in the solution were analyzed with a HPLC equipment (GL Science Co., Ltd., GL-7400 HPLC System). For comparison, the removal tests with the reagent grade Mg-Al LDH were carried out for 4 organic compounds (p-dichlorobenzene, trichloroethylene, toluene and benzene, initial concentration; 20 mg/dm$^3$) in aqueous solution, according to the same way mentioned above.
3. Results and Discussion

3.1 Aluminum dross and resulting LDHs used in this study

The raw materials of DS-LDHs, that is, the aluminum dross and the resulting Cl-type LDHs before DS modification were the same samples used in our previous study. Basic information of the aluminum dross leachate and the resulting LDHs reported in the paper was summarized below.

The HCl leaching of aluminum dross was conducted to extract the metal components of LDH such as Mg, Ca and Al into the leachate. Table 1 shows the chemical composition of aluminum dross leachate used in this study. The concentration and content of Al in the HCl leachate are 14.8 g/dm³ and 89.3 mass%, respectively. Other metals in the leachate are identified to be Cu, Ca, Mg, Fe, Si and Zn. The dissolution percentage after the HCl leaching is about 65 mass% to the original aluminum dross.

The XRD patterns of various LDHs synthesized by a co-precipitation method are shown in Figure 1. The LDHs obtained from pure reagent are also indicated. The peak pattern of Mg-Al LDH is identified as a main crystalline material. The formation of Ca-Al and Zn-Al LDHs can be also confirmed, though some unidentified peaks are present due to the presence of by-products. The XRD patterns of dross-derived LDHs are found to be almost the same as those of standard samples synthesized from reagent.

The chemical composition of various LDHs synthesized from aluminum dross is shown in Table 2. All metals in the aluminum dross leachates are confirmed to be perfectly precipitated in the reaction products. A slight amount of acid-soluble metals such as Mg, Ca, Zn and Fe are also contained by a co-precipitation reaction. The impurity components like Fe and Cu may be mere contamination as a form of metal hydroxide. Generally, the intercalated amount of anion may be theoretically equal to the Al³⁺ amount in the LDH, because the anion exchange sites in the LDH are based on the Al³⁺ parts in double hydroxide layer. This means that the Al³⁺ amount should be in accord with the anion exchange capacity of LDHs.

### Table 1 Chemical composition of aluminum dross leachate

|       | Al       | Cu | Ca | Mg | Fe | Si | Zn | Mn | Ti |
|-------|----------|----|----|----|----|----|----|----|----|
| Concentration [mg/dm³] | 14800 | 569 | 346 | 329 | 231 | 150 | 97  | 40  | 14 |
| Content [mass%]      | 89.3    | 3.4 | 2.1 | 2.0 | 1.4 | 0.9 | 0.6 | 0.2 | 0.1 |

![Fig. 1 XRD patterns of various LDHs synthesized by a co-precipitation method](image)
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Table 2  Chemical composition of various LDHs synthesized from aluminum dross

| LDH   | Chemical composition [mmol/g] |
|-------|------------------------------|
|       | Mg  | Ca  | Zn  | Al  | Ti  | Fe  | Cu  | Si  |
| Mg-Al | 8.44| 0.02| 0.01| 3.64| —   | 0.03| 0.06| 0.04|
| Ca-Al | 0.09| 6.80| 0.01| 3.53| —   | 0.03| 0.06| 0.03|
| Zn-Al | 0.02| —   | 6.85| 2.48| —   | 0.02| 0.04| 0.03|

It is considered from the Al\(^{3+}\) amount in LDHs that the anion exchange capacities of the Mg-Al, Ca-Al and Zn-Al type LDHs are estimated to be about 3.4 mmol/g, 3.6 mmol/g and 2.5 mmol/g, respectively.

3.2 Physical property of organically modified aluminum dross LDH

Organic modification for hydrophobic surface was carried out by contacting DS\(^-\) in aqueous solution. Figure 2 shows the XRD patterns of various DS\(^-\) LDHs obtained by an ion exchange reaction. According to our previous researches on the DS\(^-\) LDH synthesized from reagent\(^{16,17}\), it is found that the first peaks at around 20 = 3.5° in Fig. 2(a)–(c) are caused by the intercalation of DS\(^-\) into LDH interlayer. The d-spacing of these peaks is also considered to be almost the same as the interlayer distance of reaction product, and this varies corresponding to the size of exchangeable anion. As an example, the value of d-spacing (2.80 nm) in Fig. 2(a) may be reasonable in considering the sum of ion length of DS\(^-\) (about 2.13 nm) and thickness of magnesium hydroxide layer (0.48 nm)\(^{16,17}\), suggesting that the DS\(^-\) is oriented vertically to the direction of LDH basal seat.

The SEM photograph of Mg-Al, Ca-Al and Zn-Al LDHs modified with DS\(^-\) is shown in Figure 3. The secondary particles of reaction product are formed by coagulation of fine particles, though the shape itself of fine particles is a little different among 3 kinds of LDH. The particle size of reaction products is confirmed to be approximately 30 micrometers by a SEM observation.

The contact angle of pelletized DS\(^-\) LDH to water was measured to evaluate hydrophobic property on the LDH surface. Figure 4 illustrates the contact angle of DS\(^-\) LDH pellet to water. It is found that the contact angles of Mg-Al, Ca-Al and Zn-Al LDHs modified with DS\(^-\) are about 87°, 85° and 91°, respectively, and their values are similar among them. With reference to the reagent grade LDH\(^{16,17}\), the contact angles of various surfactant-modified LDHs with dodecyl sulfate ions, dodecylbenzene sulfonate ions and octane sulfonate ions exist in the range from 85° to 110°, whereas the original NO\(_3^-\) type Mg-Al LDH before surfactant modification shows about 30°. Therefore, the order of contact angle in Figure 4 reveals that the LDH surface becomes adequately hydrophobic by the modification treatment.

It is considered from a series of results in Figures 3–5 that the DS\(^-\) LDH synthesized from aluminum dross may be used as a removal agent for dilute organic compounds in aqueous solution.

3.3 Removal tests of dilute toluene with DS\(^-\) LDH synthesized from aluminum dross

The surfactant-modified LDH can be applied to an adsorbent for dilute organic compound in aqueous solution. At first, the removal tests using the reagent grade LDH modified with DS\(^-\) were conducted for model substance of organic compounds. As typical examples, Figure 5 shows the effect of DS\(^-\) adsorption amount on the removal of 4 organic compounds including p-dichlorobenzene, toluene, trichloroethylene and benzene. The re-
Removals of all organic compounds are remarkably increasing with an increase in the DS$^-$ adsorption amount, respectively. The removals of p-dichlorobenzene, trichloroethylene and benzene are slightly decreasing over 2 mmol/g of adsorption amount, whereas that of toluene remains almost constant at about 75%. It appears that the best removal ability for the 4 organic compounds, in other word, the most hydrophobic surface can be obtained at the 1.6 mmol/g of DS$^-$ adsorption amount. The order of removal among them is as follows; p-dichlorobenzene $>$ toluene $>$ trichloroethylene $>$ benzene. It is also found that this order corresponds to the degree of solubility in water, that is, p-dichlorobenzene (0.008 g/100 cm$^3$) $<$ toluene (0.045 g/100 g) $<$ trichloroethylene (0.11 g/100 g) $<$ benzene (0.18 g/100 g), implying that the removal ability is mainly caused by the affinity of organic compound to water.

It has been clarified from our previous stud-

| Sample        | Contact angle [°] |
|---------------|-------------------|
| Mg-Al LDH     | 87°               |
| Ca-Al LDH     | 85                |
| Zn-Al LDH     | 91                |

Fig. 3 SEM photograph of Mg-Al, Ca-Al and Zn-Al LDHs modified with DS$^-$

Fig. 4 Contact angle of DS$^-$ LDH to water

Fig. 5 Effect of DS$^-$ adsorption amount on removal of organic compounds (Initial concentration; 20 mg/dm$^3$)
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ies\textsuperscript{16,17} that almost largest contact angle of the reagent grade LDH can be obtained at around the 1.6 mmol/g adsorption amount, and at the same time the DS\textsuperscript– in LDH below the 1.6 mmol/g adsorption amount is not released again in further removal operation. When the DS adsorption amount is more increased, the hydrophobic particle surface modified with DS\textsuperscript– by anion exchange reaction can capture a slight amount of DS\textsuperscript– in solution by not anion exchange but hydrophobic interaction\textsuperscript{16,17}. As a result, it implies that the hydrophilic group of DS\textsuperscript– adsorbed on the particle surface orients toward outside in this situation, resulting in a little decline of contact angle or removal ability of organic compound.

On the other hand, the molecules of various organic compounds in aqueous solution are considered to be adsorbed mainly on the surface of LDH particles, especially in the case of dilute solutions like 20 ppm. The regeneration treatment of LDH after adsorption may be difficult in the practical use, due to the disintegration of LDH structure with the repeated solid-liquid contact operation.

Removal tests of dilute toluene in aqueous solution were conducted with the DS\textsuperscript– LDH synthesized from aluminum dross. The adsorption removal of toluene is shown in Figures 6 and 7. The DS\textsuperscript–-intercalated amount in all LDHs is the same (1.6 mmol/g) in these experiments. The removal of toluene using the Mg-Al LDH in Figure 6 is the highest (64%) of all, while the percentage is a little lower than that from the reagent LDH (73%). No difference in toluene removal is found between the initial concentrations, as shown in Figures 6 and 7. The order of toluene removal is as follows; Mg-Al LDH > Zn-Al LDH > Ca-Al LDH. Though the reason why this order appears is not clarified yet in contrast to the similar contact angles (Figure 4), it is considered that this is mainly caused by the deference in structural stability of LDH, in contacting with toluene-containing solution. Concretely, the disintegration of the LDH structure or the release of DS\textsuperscript– from LDH interlayer may take place in the toluene removal operation.

It is concluded that the LDHs obtained from aluminium dross can be used as an excellent adsorbent based on their anion exchange ability for dilute organic compounds like toluene in aqueous solution. The possibility to apply this kind of modified LDH to a waste water treatment is found by a series of research results.

4. Conclusions

The preparation of 3 kinds of LDH (Mg-Al, Ca-Al and Zn-Al LDHs) was conducted using aluminum dross as a raw material. The LDHs were organically modified by an intercalation. The physical properties including crystal structure, surface texture and contact angle were investigated for the LDHs modified with dodecyl sulfate ions. The removal tests for toluene in aqueous solution were demonstrated with the DS\textsuperscript– LDHs synthesized from aluminum dross.

Organic modification of the LDHs synthesized from aluminum dross can be achieved successfully by applying an anion exchange operation with DS\textsuperscript–. The DS\textsuperscript– LDHs with hydrophobic surface show higher contact angles over 85°. The dilute toluene in aqueous solution (initial concentration; 10 and 50 mg/dm\textsuperscript{3}) is removed with the DS\textsuperscript– LDHs. It is clarified from a series of experimental results that the DS\textsuperscript– LDHs synthesized from aluminum dross can be used as an excellent adsorbent for dilute organic compounds in aqueous solution.
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