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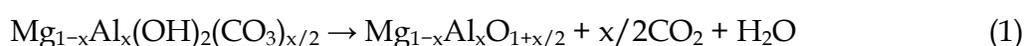


Hybrid Inorganic–organic Composites of Layered Double Hydroxides Intercalated with Organic Acid Anions for the Uptake of Hazardous Substances from Aqueous Solution

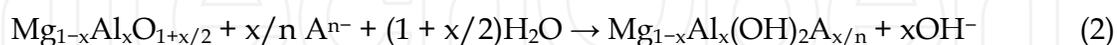
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1. Introduction

Layered double hydroxide (LDH) is an inorganic compound with a layered structure and exhibits anion–exchange properties. Its basic chemical composition is $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, where x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio and A^{n-} indicates an anion with a valency of n (Ingram and Taylor, 1967; Allmann, 1968; Taylor, 1973). Its crystal structure consists of positively charged brucite-like octahedral hydroxide layers containing M^{3+} at M^{2+} sites, which are electrically neutralized by the interlayer anions, and water molecules in the hydration shell of the intercalated anions occupying the remaining interlayer space. Among various types of LDHs composed of different compositions of M^{2+} and M^{3+} , Mg–Al LDH has been used practically as an antacid and a flame retardant (Cavani et al., 1991). Mg–Al LDH intercalated with CO_3^{2-} ($CO_3 \cdot$ Mg–Al LDH) can be transformed into Mg–Al oxide by calcination at 450–800 °C according to the following reaction:



Mg–Al oxide can rehydrate and combine with anions to reconstruct the LDH structure in the following manner:



LDH can intercalate various anions. Recently, modification of LDH with organic anions has received considerable attention, as summarized in a review by Newman and Jones (1998), with possible applications in catalysis, photochemistry, and electrochemistry.

We carried out a series of studies to develop hybrid inorganic–organic composite materials by intercalation of organic anions having functional groups in their structures into the interlayer of LDH. Due to the action of the functional groups of the organic anions, the composite materials are expected to selectively take up and collect both inorganic and organic contaminants present at low concentrations in aqueous solutions.

The aims and concerns presented in this chapter are the preparation of organically modified LDH by intercalation of organic anions into the interlayer of LDH and the uptake of heavy metal ions and nonionic organic compounds by the organically modified LDH.

2. Uptake of heavy metal ions by organically modified LDH

Due to slow reactivity and inefficiency, the application of chelate resins in the treatment of wastewater with a high concentration of heavy metal ions is difficult. Generally, a two-step process is considered acceptable for wastewater treatment. First, the heavy metal ions are removed from the wastewater by a chemical precipitation technique, and then the remaining heavy metal ions are treated using chelate resins. A one-step method capable of achieving highly effective wastewater treatment is desired. A one-step method is thought to be possible by applying a scavenger that can function as chelate resins and can rapidly remove heavy metal ions from wastewater, decreasing the heavy metal ion concentration to the level of the effluent standards in Japan. The aim of the present study was to develop an organic-inorganic composite material to scavenge heavy metal ions from wastewaters. Chelate resin contains functional groups such as aminocarboxylate and polyamine that form chelate bonds with heavy metal ions. Therefore, we developed a scavenger by incorporating an organic acid anion having functional groups in its structure into the inorganic compound. Aminocarboxylates such as an ethylenediaminetetraacetate (EDTA) anion were examined as functional groups. Then, LDH was examined as the inorganic compound.

Several studies have examined the use of LDH and calcined LDH for the preservation of aqueous environments. LDH and calcined LDH can take up oxometalates such as $\text{Cr}_2\text{O}_7^{2-}$, SeO_3^{2-} , SeO_4^{2-} , AsO_3^{3-} , AsO_4^{3-} , TcO_4^- , and ReO_4^- from aqueous solution (Dousova et al., 2003; Gillman, 2006; Goswamee et al., 1998; Kang et al., 1996; Lazaridis and Asouhidou, 2003; Rhee et al., 1997; Tsuji et al., 1999; Wang et al., 2009; Yang et al., 2005; You et al., 2001a; You et al., 2001b). Goh et al. (2008) reviewed the application of LDH for removal of oxometalates. LDH, when acting as a hydroxide, has also acted as a precipitation reagent for heavy metal ions such as Cu^{2+} , Pb^{2+} , and Zn^{2+} in wastewater via hydroxide formation (Fujii et al., 1992). However, heavy metal cations cannot be intercalated in the interlayer of LDH. In order to take up heavy metal cations using inorganic materials from aqueous solution, cationic clay such as montmorillonite is typically used due to its cation-exchange properties. On the other hand, EDTA anions can be intercalated in the interlayer of LDH (Narita et al., 1995). Similarly, stable anionic chelates formed between heavy metal ions and aminocarboxylates such as EDTA can be also intercalated in the interlayer of LDH. For example, the intercalations of $\text{Ni}(\text{EDTA})^{2-}$, $\text{Co}(\text{EDTA})^{2-}$, $\text{Cu}(\text{EDTA})^{2-}$, $\text{Zn}(\text{EDTA})^{2-}$, and $\text{Cd}(\text{EDTA})^{2-}$ have been examined (Sato et al., 1990; Narita et al., 1995; Tsyganok et al., 2001a; Tsyganok et al., 2001b; Lukashin et al., 2003; Tsyganok and Sayari, 2006). Accordingly, we have developed a scavenger by intercalating an EDTA anion in the interlayer of LDH and applied the scavenger to decrease the concentrations of heavy metal ions in aqueous solutions for the first time. In order for the scavenger to take up heavy metal ions from an aqueous solution, the EDTA anion should function as a chelating agent in the interlayer of LDH. In the following section, we discuss our work along with related studies.

2.1 LDH intercalated with EDTA

The EDTA•Mg-Al LDH, which had an EDTA anion intercalated in the interlayer of Mg-Al LDH, was synthesized by adding a solution of $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ to a solution of NaOH and EDTA-2Na (disodium dihydrogen EDTA dihydrate) according to the coprecipitation reaction expressed by Eq. (3) and by mixing at 30 °C for 1 h (Kameda et al., 2005a).



Since the EDTA•Mg–Al LDH was prepared in the pH range where EDTA anions exist stably as tetravalent anions by setting the NaOH concentration in the EDTA solution to 1.2 times the stoichiometric quantity defined by Eq. (3), the EDTA•Mg–Al LDH was considered to be a Mg–Al LDH having EDTA⁴⁻ in the interlayer.

EDTA•Mg–Al LDH was added to 1.0 mM MCl₂ (M = Cu, Cd) solution or a 1:1 mixed chloride solution of Cu²⁺ and Cd²⁺, and then the resultant suspension was kept standing at 20 °C under mild agitation for 60 min (Kameda et al., 2005a). The solution pH was adjusted to 5.0 by addition of 0.1 M hydrochloric acid, and Cu²⁺ and Cd²⁺ did not precipitate as their hydroxides. In this case, the molar ratios of EDTA⁴⁻ in the EDTA•Mg–Al LDH added to M²⁺ in the MCl₂ solution were set at 1.0–2.0 (EDTA⁴⁻ /M²⁺ = 1.0–2.0). For the Cu–Cd mixed chloride solution, the EDTA⁴⁻/(Cu²⁺ + Cd²⁺) molar ratio was set at 0.5. The capacity of CO₃•Mg–Al LDH, the interlayer of which was not chemically modified, was also examined to estimate the function of EDTA⁴⁻ in the interlayer of EDTA•Mg–Al LDH. Figure 1 shows the variation in the concentration of Cu²⁺ with time during the stirring of EDTA•Mg–Al LDH or CO₃•Mg–Al LDH in the CuCl₂ solution. In this case, the molar ratio of EDTA⁴⁻ in the EDTA•Mg–Al LDH added to Cu²⁺ in the CuCl₂ solution was set at 1.0 (EDTA⁴⁻/Cu²⁺ = 1.0). The amount of CO₃•Mg–Al LDH added was equal to that of EDTA•Mg–Al LDH.

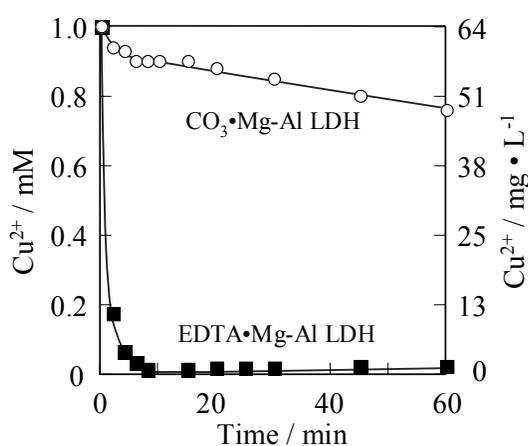


Fig. 1. Variation in the concentration of Cu²⁺ with time during the stirring of EDTA•Mg–Al LDH or CO₃•Mg–Al LDH in the CuCl₂ solution.

For EDTA•Mg–Al LDH, the concentration of Cu²⁺ decreased very rapidly to 0.02 mM (1 mg/L) in 10 min. The uptake of Cu²⁺ was 20 mg-Cu²⁺/g-EDTA•Mg–Al LDH. On the other hand, for CO₃•Mg–Al LDH, the concentration decreased in a substantially slower manner, to 0.9 mM (57 mg/L) in 10 min (2 mg-Cu²⁺/g-CO₃•Mg–Al LDH). This difference in the uptake of Cu²⁺ was attributed to the function of EDTA⁴⁻ in the interlayer of EDTA•Mg–Al LDH. In particular, the Cu(EDTA)²⁻ complex is thought to form in the interlayer of EDTA•Mg–Al LDH. Along with formation of the chelate complexes, Cl⁻ is presumed to intercalate in the interlayer of EDTA•Mg–Al LDH to compensate for the change in negative charge resulting from the change in anionic species from EDTA⁴⁻ to Cu(EDTA)²⁻ in the interlayer. On the other hand, a slight decrease in the concentration of Cu²⁺ was observed for CO₃•Mg–Al LDH (Fig. 1). In this experiment, 0.1 M HCl was added to the solution to maintain the pH at 5.0. Due to the decrease in the local pH by the addition of HCl, Mg²⁺ and Al³⁺ dissolved from CO₃•Mg–Al LDH. Mg²⁺ was observed to be dissolved from the

$\text{CO}_3 \cdot \text{Mg-Al}$ LDH. On the contrary, the concentration of Al^{3+} in the solution was less than 1% at any time. Therefore, the slight removal of Cu^{2+} by $\text{CO}_3 \cdot \text{Mg-Al}$ LDH may be attributable to the coprecipitation of Cu^{2+} with the dissolved Al^{3+} to form Cu-Al LDH. Mg^{2+} dissolved from $\text{EDTA} \cdot \text{Mg-Al}$ LDH as well as $\text{CO}_3 \cdot \text{Mg-Al}$ LDH, while Al^{3+} was detected to a substantially lower concentration than Mg^{2+} in the solution. Consequently, the uptake of Cu^{2+} by $\text{EDTA} \cdot \text{Mg-Al}$ LDH was attributed to both the formation of chelate complexes with EDTA^{4-} in the interlayer and coprecipitation with the dissolved Al^{3+} . Note that $\text{EDTA} \cdot \text{Mg-Al}$ LDH removed Cu^{2+} from an aqueous solution with an initial concentration of 64 mg/L to less than the effluent standards in Japan (3 mg/L) in a short span of 10 min. For $\text{EDTA} \cdot \text{Mg-Al}$ LDH, the concentration of Cd^{2+} decreased with time, and the concentration decreased quickly with increasing $\text{EDTA}^{4-}/\text{Cd}^{2+}$ molar ratio. The concentration decreased to 0.02 mM (2 mg/L) in 10 min at an $\text{EDTA}^{4-}/\text{Cd}^{2+}$ molar ratio of 2.0 (17 mg- $\text{Cd}^{2+}/\text{g-EDTA} \cdot \text{Mg-Al}$ LDH). However, for $\text{CO}_3 \cdot \text{Mg-Al}$ LDH, the decrease in the concentration was extremely slow, and the concentration was still 0.93 mM (104 mg/L) after 10 min (1 mg- $\text{Cd}^{2+}/\text{g-CO}_3 \cdot \text{Mg-Al}$ LDH). The differences in the removal of Cd^{2+} were also attributed to the function of EDTA^{4-} in the interlayer of $\text{EDTA} \cdot \text{Mg-Al}$ LDH. Note that the concentration of Cd^{2+} decreased rapidly from 112 mg/L to less than 1 mg/L at an $\text{EDTA}^{4-}/\text{Cd}^{2+}$ molar ratio of 2.0 in 15 min. For the Cu-Cd mixed chloride solution, the concentration of Cu^{2+} decreased with time more rapidly than that of Cd^{2+} , confirming the preferential uptake of Cu^{2+} over Cd^{2+} from the mixed solution by $\text{EDTA} \cdot \text{Mg-Al}$ LDH. This preferential uptake was probably due to the difference between the stabilities of $\text{Cu}(\text{EDTA})^{2-}$ and $\text{Cd}(\text{EDTA})^{2-}$. The chelate formation constants for $\text{Cu}(\text{EDTA})^{2-}$ and $\text{Cd}(\text{EDTA})^{2-}$ are reported to be 18.8 and 16.5; i.e., $\text{Cu}(\text{EDTA})^{2-}$ is more stable than $\text{Cd}(\text{EDTA})^{2-}$. Thus, it is believed that EDTA^{4-} in the interlayer formed the chelate complex with Cu^{2+} preferentially over Cd^{2+} in the mixed solution. From these results, it can be deduced that EDTA^{4-} maintains its chelating function even when intercalated in the interlayer of Mg-Al LDH.

Perez et al. (2006) examined the uptake of Cu^{2+} , Cd^{2+} , and Pb^{2+} on Zn-Al LDH intercalated with EDTA. $\text{EDTA} \cdot \text{Zn-Al}$ LDH was obtained from $\text{NO}_3 \cdot \text{Zn-Al}$ LDH using the anion exchange method. The uptake of Cu^{2+} , Cd^{2+} , and Pb^{2+} from the aqueous solutions was due to chelation between EDTA and metal cations. The shape of the adsorption isotherms suggests specific interaction and high host-guest affinity. At pH 5.5 and an initial concentration of 10 mM, the amounts adsorbed were 1117, 375, and 871 $\mu\text{mol/g}$ for Cu^{2+} , Cd^{2+} , and Pb^{2+} , respectively. Kulyukhin et al. (2008) examined the adsorption of Sr radionuclides from the aqueous phase on $\text{EDTA} \cdot \text{Mg-Al}$ LDH. The adsorption was apparently associated with the complexation of Sr^{2+} with $[\text{H}_2(\text{EDTA})]^{2-}$ incorporated in the $\text{EDTA} \cdot \text{Mg-Al}$ LDH. Rojas et al. (2009) examined EDTA-modified Zn-Al LDH as a Cu^{2+} scavenger based on removal kinetics and sorbent stability. They noted that the exchange process between $\text{NO}_3 \cdot \text{Zn-Al}$ LDH and $[\text{H}_2(\text{EDTA})]^{2-}$ anions takes place with partial erosion of the layers, causing the intercalation of $[\text{Zn}(\text{EDTA})]^{2-}$ anions instead of the ligand. They insisted that the uptake of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ by $[\text{Zn}(\text{EDTA})]^{2-}$ intercalated in sorbent-LDH results from an exchange reaction between chelated zinc cations in the interlayer and copper cations in solution. Gasser and Aly (2009) examined the kinetic and adsorption mechanisms of Cu^{2+} and Pb^{2+} using $\text{EDTA} \cdot \text{Mg-Fe}$ LDH. Cu^{2+} and Pb^{2+} were adsorbed by $\text{EDTA} \cdot \text{Mg-Fe}$ LDH due to chelation with EDTA from the LDH interlayer. The adsorption of Cu^{2+} was higher than that of Pb^{2+} ; this was attributed to the stability constant of $[\text{Cu}(\text{EDTA})]^{2-}$, which

is higher than that of $[\text{Pb}(\text{EDTA})]^{2-}$. The shape of the adsorption isotherm suggests specific interaction and high affinity. The kinetics of the adsorption of Cu^{2+} onto $\text{EDTA} \cdot \text{Mg-Fe}$ LDH follows first-order reversible kinetics, and the values of the first-order rate constants increased with increasing temperature. The chemisorption step may be the rate-limiting step of adsorption from solution.

In our previous research (Kameda et al., 2005a), the pH of the solution during uptake of Cu^{2+} and Cd^{2+} by $\text{EDTA} \cdot \text{Mg-Al}$ LDH was adjusted to 5.0 by the addition of 0.1 mol/L acid; this pH value was maintained to prevent precipitation of the hydroxides of Cu^{2+} and Cd^{2+} . However, this method resulted in the dissolution of Mg^{2+} from $\text{EDTA} \cdot \text{Mg-Al}$ LDH because of the increasing acidity as Mg^{2+} precipitated as $\text{Mg}(\text{OH})_2$ at $\text{pH} > 10$. Therefore, Cu^{2+} was selected as the divalent metal ion of the LDH host layer because the hydrolysis product of Cu^{2+} ($\text{pK}_{\text{sp}} = 17.3$) is less soluble than that of Mg^{2+} ($\text{pK}_{\text{sp}} = 11.2$). Recently, we prepared Cu-Al LDH intercalated with EDTA ($\text{EDTA} \cdot \text{Cu-Al}$ LDH) by suspending Cu-Al oxide, obtained by calcination of $\text{CO}_3 \cdot \text{Cu-Al}$ LDH, in EDTA solution (Kameda et al., 2011). The reconstruction of Cu-Al oxide to Cu-Al LDH was promoted with increasing temperature and time. The reaction at a pH of ~ 8 suggests that $[\text{H}(\text{EDTA})]^{3-}$ was intercalated in the interlayer of Cu-Al LDH. $\text{EDTA} \cdot \text{Cu-Al}$ LDH was found to take up rare metal ions such as Sc^{3+} and La^{3+} in an aqueous solution at a pH of ~ 6 – 6.5 . The uptake of Sc^{3+} was caused not only by the chelating function of $[\text{H}(\text{EDTA})]^{3-}$ in the interlayer but also by the chemical behavior of Cu-Al LDH itself. On the other hand, the uptake of La^{3+} was caused only by the chelating function of $[\text{H}(\text{EDTA})]^{3-}$ in the interlayer. $[\text{H}(\text{EDTA})]^{3-}$ in the interlayer of $\text{EDTA} \cdot \text{Cu-Al}$ LDH formed a chelate complex with Sc^{3+} more preferentially than with La^{3+} .

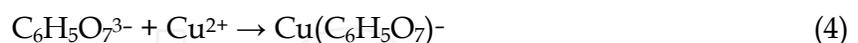
2.2 LDH intercalated with carboxylates

We examined organic acids for leaching heavy metals from fly ash generated by gasification and melting furnace treatments for municipal solid wastes (Saito et al., 2007). Organic acids such as citric, malic, and tartaric acids were found to be effective for leaching heavy metals due to the formation of chelate complexes between the metals and acids on the surface of the fly ash. Since citric, malic, and tartaric acids have the capacity for heavy metal extraction, Mg-Al LDHs intercalated with citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), malate ($\text{C}_4\text{H}_4\text{O}_5^{2-}$), and tartrate ($\text{C}_4\text{H}_4\text{O}_6^{2-}$) anions can be expected to take up heavy metal ions from aqueous solution into the interlayers. Citric, malic, and tartaric acids exist abundantly in nature, and, therefore, the corresponding organic acid anion-intercalated Mg-Al LDHs are more appropriate for commercial-scale applications than $\text{EDTA} \cdot \text{Mg-Al}$ LDH.

Meyn et al. (1990) used the anion exchange method to prepare Mg-Al LDH composite materials with intercalated $\text{C}_6\text{H}_5\text{O}_7^{3-}$ and $\text{C}_4\text{H}_4\text{O}_6^{2-}$, whereas Zhang et al. (2004) prepared Mg-Al LDH intercalated with $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{C}_4\text{H}_4\text{O}_5^{2-}$, and $\text{C}_4\text{H}_4\text{O}_6^{2-}$ through a unique method involving the dissolution of $\text{CO}_3 \cdot \text{Mg-Al}$ LDH to form the corresponding carboxylic acid followed by precipitation in basic solution. Tronto et al. (2001, 2004) used coprecipitation to form Mg-Al LDH intercalated with $\text{C}_6\text{H}_5\text{O}_7^{3-}$.

We prepared Mg-Al LDHs intercalated with $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{C}_4\text{H}_4\text{O}_5^{2-}$, and $\text{C}_4\text{H}_4\text{O}_6^{2-}$ by coprecipitation via dropwise addition of a Mg-Al nitrate solution to citrate, malate, and tartrate solutions, respectively, at a constant pH of 10.5 and investigated the effects of the organic anion concentrations on the formation of the composites (Kameda et al., 2009a). For Mg-Al LDH intercalated with citrate ($\text{citrate} \cdot \text{Mg-Al}$ LDH), low solution concentrations of $\text{C}_6\text{H}_5\text{O}_7^{3-}$ resulted in intercalation of $\text{C}_6\text{H}_5\text{O}_7^{3-}$ into the interlayer at a 26° angle relative to the

brucite-like layers of Mg–Al LDH. At higher $C_6H_5O_7^{3-}$ concentrations, both $Mg(C_6H_5O_7)^-$ and $C_6H_5O_7^{3-}$ were intercalated into the interlayer with an irregular orientation, and $C_6H_5O_7^{3-}$ adsorbed to the surface of the Mg–Al LDH. For Mg–Al LDHs intercalated with malate and tartrate (malate•Mg–Al LDH and tartrate•Mg–Al LDH), the intercalated $C_4H_4O_5^{2-}$ and $C_4H_4O_6^{2-}$ were also oriented at an angle of 26° relative to the brucite-like layers of the Mg–Al LDH, regardless of solution concentration. The amount of intercalated $C_4H_4O_5^{2-}$ for malate•Mg–Al LDH was governed solely by the electric charge balance in Mg–Al LDH and was not affected by increased solution concentration. However, increasing the solution concentration of $C_4H_4O_6^{2-}$ during the formation of tartrate•Mg–Al LDH resulted in both interlayer intercalation and adsorption of $C_4H_4O_6^{2-}$ to the surface of the composite. These Mg–Al LDHs were found to take up Cu^{2+} and Cd^{2+} rapidly from an aqueous solution at a constant pH of 5.0 (Kameda et al., 2008a). This capacity was mainly attributed to the formation of citrate–metal, malate–metal, and tartrate–metal complexes in the interlayers of the Mg–Al LDHs. The uptake of Cu^{2+} increased in the order malate•Mg–Al LDH < tartrate•Mg–Al LDH < citrate•Mg–Al LDH. The uptake of Cd^{2+} increased in the order malate•Mg–Al LDH < tartrate•Mg–Al LDH = citrate•Mg–Al LDH. These differences in Cu^{2+} and Cd^{2+} uptake were attributable to differences in the stabilities of the citrate–metal, malate–metal, and tartrate–metal complexes. These results indicate that $C_6H_5O_7^{3-}$, $C_4H_4O_5^{2-}$, and $C_4H_4O_6^{2-}$ were adequately active as chelating agents in the interlayers of Mg–Al LDHs. We also examined the kinetics of the uptake of Cu^{2+} and Cd^{2+} by citrate•Mg–Al LDH, malate•Mg–Al LDH, and tartrate•Mg–Al LDH (Kameda et al., 2010a). The Mg–Al LDHs were added to 500 mL of 1.0 mmol/L $Cu(NO_3)_2$ or $Cd(NO_3)_2$ solution. The molar ratio of citrate, malate, or tartrate in Mg–Al LDH to Cu^{2+} or Cd^{2+} in the nitrate solution was set to 1.0. The resultant suspension was left to stand at 10, 20, and 30 °C for 60 min with stirring at a constant pH of 5.0. The concentrations of Cu^{2+} and Cd^{2+} decreased with time and increasing temperature. The accelerated rate of Cu^{2+} and Cd^{2+} uptake by the Mg–Al LDHs at high temperatures implies that the uptake reactions were governed by chemical reactions rather than mass transfer. The reactions were examined kinetically based on the chemical equation. The uptake of Cu^{2+} by citrate•Mg–Al LDH was attributed to the 1:1 chelation between Cu^{2+} and citrate as follows:



This reaction gives the following rate equation:

$$d[Cu(C_6H_5O_7)^-]/dt = k[C_6H_5O_7^{3-}][Cu^{2+}] \quad (5)$$

where t is the reaction time, and k is the apparent rate constant. Because

$$d[Cu(C_6H_5O_7)^-]/dt = d[Cu^{2+}]/dt \text{ and } [C_6H_5O_7^{3-}]/[Cu^{2+}] = 1, -d[Cu^{2+}]/dt = k[Cu^{2+}]^2 \quad (6)$$

The integration of Eq. (6) gives

$$1/[Cu^{2+}] = kt + 1 \quad (7)$$

Assuming that x is the degree of Cu^{2+} uptake, $[Cu^{2+}]$ can be expressed as $1 - x$ because the initial Cu^{2+} concentration was 1.0 mmol/L. Equation 7 can be converted to Eq. (8):

$$1/(1 - x) = kt + 1 \quad (8)$$

The uptake rate of Cu^{2+} by citrate•Mg–Al LDH was determined from Eq. (8), and the plot of $1/(1-x)$ versus t is shown in Fig. 2.

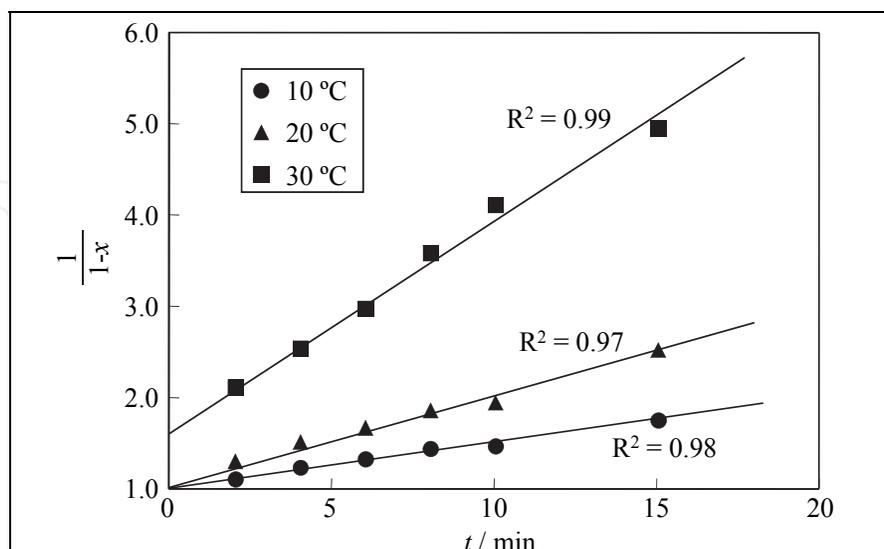


Fig. 2. Plot of $1/(1-x)$ vs. t for uptake of Cu^{2+} by citrate•Mg–Al LDH.

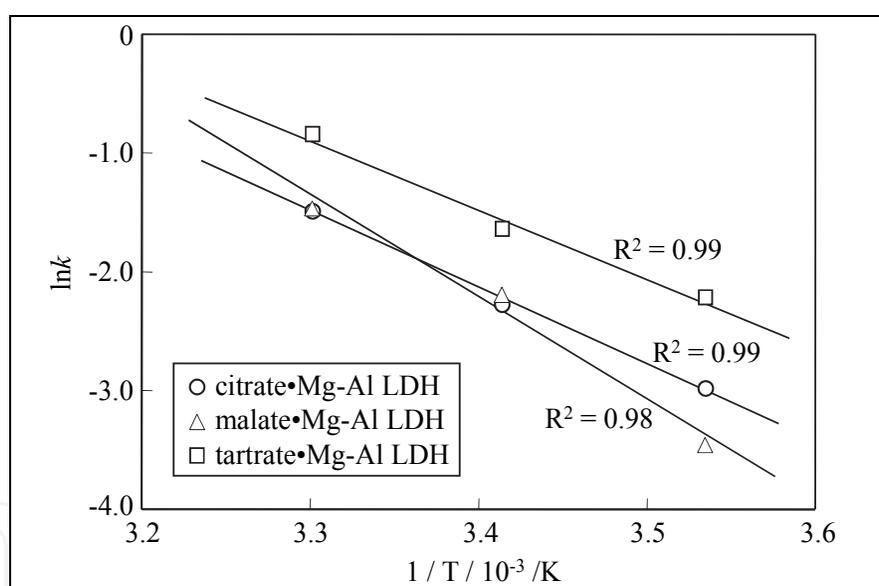
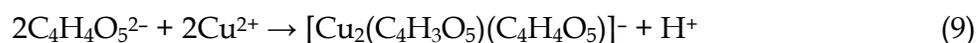


Fig. 3. Arrhenius plot of the apparent rate constant for uptake of Cu^{2+} by Mg–Al LDHs.

Good linearity was obtained at each temperature, indicating that the reaction rate could be expressed by Eq. (5). At 30 °C, the value of the intercept was not 1.0, suggesting that the precipitation rate of Cu–Al LDH, which formed between a few Cu^{2+} cations and dissolved Al^{3+} , was very fast. The apparent rate constants at 10, 20, and 30 °C were 5.1×10^{-2} , 1.0×10^{-1} , and 2.3×10^{-1} , respectively. Thus, the apparent rate constant increased with increasing temperature. An Arrhenius plot of k , determined from the slopes of the straight lines in Fig. 2, is shown in Fig. 3; this plot yields an apparent activation energy of 53.1 $\text{kJ}\cdot\text{mol}^{-1}$. This value confirms that the uptake of Cu^{2+} by citrate•Mg–Al LDH proceeded under chemical reaction control because the apparent activation energy for the chemical reaction was larger than 30 $\text{kJ}\cdot\text{mol}^{-1}$. The uptake of Cu^{2+} by this LDH occurred via chelation between Cu^{2+} and

citrate. The uptake of Cu^{2+} by malate•Mg–Al LDH was attributed to the 2:2 chelation between Cu^{2+} and malate and is expressed as



This reaction gives the following rate equation:

$$d[[\text{Cu}_2(\text{C}_4\text{H}_3\text{O}_5)(\text{C}_4\text{H}_4\text{O}_5)]^-]/dt = k[\text{C}_4\text{H}_4\text{O}_5^{2-}]^2[\text{Cu}^{2+}]^2 \quad (10)$$

where t is the reaction time, and k is the apparent rate constant. Because

$$d[[\text{Cu}_2(\text{C}_4\text{H}_3\text{O}_5)(\text{C}_4\text{H}_4\text{O}_5)]^-]/dt = -(1/2) \cdot d[\text{Cu}^{2+}]/dt \text{ and } [\text{C}_4\text{H}_4\text{O}_5^{2-}]/[\text{Cu}^{2+}] = 1, \\ -(1/2) \cdot d[\text{Cu}^{2+}]/dt = k[\text{Cu}^{2+}]^4 \quad (11)$$

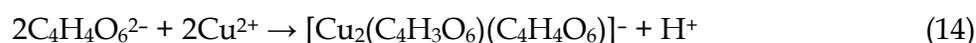
Integration of Eq. (11) gives

$$(1/6) \cdot [\text{Cu}^{2+}]^{-3} = kt + 1/6 \quad (12)$$

Equation 12 can be converted to Eq. (13):

$$(1/6) \cdot (1 - x)^{-3} = kt + 1/6 \quad (13)$$

The uptake rate of Cu^{2+} by malate•Mg–Al LDH was determined from Eq. (13). The plot of $(1/6) \cdot (1 - x)^{-3}$ versus t showed good linearity at each temperature, indicating that the reaction rate could be expressed by Eq. (10). At 30 °C, the value of the intercept was not 1/6. This was due to the very fast precipitation rate of Cu–Al LDH. The apparent rate constants at 10, 20, and 30 °C were 3.1×10^{-2} , 1.1×10^{-1} , and 2.3×10^{-1} , respectively. The apparent rate constant increased with increasing temperature. An Arrhenius plot of k , determined from the slopes of the straight lines, is also shown in Fig. 3. The apparent activation energy in this case was $71.2 \text{ kJ}\cdot\text{mol}^{-1}$, confirming that the uptake of Cu^{2+} by malate•Mg–Al LDH proceeded under chemical reaction control. Furthermore, the uptake of Cu^{2+} by this LDH occurred via chelation between Cu^{2+} and malate. The uptake of Cu^{2+} by tartrate•Mg–Al LDH was attributed to the 2:2 chelation between Cu^{2+} and tartrate, and is expressed as



This reaction gives the following rate equation:

$$d[[\text{Cu}_2(\text{C}_4\text{H}_3\text{O}_6)(\text{C}_4\text{H}_4\text{O}_6)]^-]/dt = k[\text{C}_4\text{H}_4\text{O}_6^{2-}]^2[\text{Cu}^{2+}]^2 \quad (15)$$

Because Eq. (15) is similar to Eq. (10), it can be converted to Eq. (13). The uptake rate of Cu^{2+} by tartrate•Mg–Al LDH was determined from Eq. (13). The reaction rate in this case could be expressed by Eq. (15) because the plot of $(1/6) \cdot (1 - x)^{-3}$ versus t gave good linearity at each temperature. The apparent rate constants at 10, 20, and 30 °C were 1.1×10^{-1} , 1.9×10^{-1} , and 4.3×10^{-1} , respectively. An Arrhenius plot of k , determined from the slopes of the straight lines, is also shown in Fig. 3; in this case, the apparent activation energy is $48.9 \text{ kJ}\cdot\text{mol}^{-1}$. Thus, it was confirmed that the uptake of Cu^{2+} by tartrate•Mg–Al LDH proceeded under chemical reaction control. Furthermore, the uptake of Cu^{2+} by this LDH occurred via chelation between Cu^{2+} and tartrate. Similarly, the uptake of Cd^{2+} by three types of Mg–Al LDHs was also examined kinetically based on the chemical equation. For citrate•Mg–Al LDH, the apparent rate constants at 10, 20, and 30 °C were 5.9×10^{-3} , 1.0×10^{-2} , and 2.7×10^{-2} ,

respectively; thus, it is clear that the rate constant increased with increasing temperature. The apparent activation energy was calculated to be $53.6 \text{ kJ}\cdot\text{mol}^{-1}$. This value confirms that the uptake of Cd^{2+} by citrate•Mg–Al LDH proceeded under chemical reaction control. The uptake of Cd^{2+} by this LDH occurred via 1:1 chelation between Cd^{2+} and citrate. For malate•Mg–Al LDH, the apparent rate constants at 10, 20, and 30 °C were 1.3×10^{-2} , 2.3×10^{-2} , and 5.5×10^{-2} , respectively. The apparent activation energy was calculated to be $50.8 \text{ kJ}\cdot\text{mol}^{-1}$, confirming that the uptake of Cd^{2+} by malate•Mg–Al LDH proceeded under chemical reaction control. Furthermore, the uptake of Cd^{2+} by this LDH occurred via 1:2 chelation between Cd^{2+} and malate. For tartrate•Mg–Al LDH, the apparent rate constants at 10, 20, and 30 °C were 5.8×10^{-3} , 2.0×10^{-2} , and 1.2×10^{-1} , respectively. An Arrhenius plot of k provides an apparent activation energy of $106.5 \text{ kJ}\cdot\text{mol}^{-1}$. This value confirms that the uptake of Cd^{2+} by tartrate•Mg–Al LDH proceeded under chemical reaction control. Furthermore, the uptake of Cd^{2+} by tartrate•Mg–Al LDH occurred via 1:2 chelation between Cd^{2+} and tartrate. To summarize, the reaction simply proceeded via chelation at a certain rate, which was different for each combination.

The citrate-modified Mg–Al LDH was suggested to have citrate anions not only intercalated in the interlayer but also adsorbed on the surface (Kameda et al., 2008a, 2009a). Because Mg–Al LDH has the basic structure of $\text{Mg}(\text{OH})_2$, organic acid anions such as citrate are likely to be adsorbed on the surface of $\text{Mg}(\text{OH})_2$. The organic acid anion-adsorbed $\text{Mg}(\text{OH})_2$ is also expected to take up heavy metal ions from aqueous solution. Furthermore, by coprecipitation as well as Mg–Al LDHs intercalated with organic anions, new layered magnesium hydroxides modified with organic acid anions may be produced. Narita et al. and Tagaya et al. have previously reported the formation of layered zinc hydroxides modified with aliphatic carboxylates, aromatic carboxylates, anionic surfactants, and organic oxychlorides (Tagaya et al., 1996; Takahashi et al., 1997; Ogata et al., 1998; Ogata et al., 2000). Hence, layered magnesium hydroxides modified with organic acid anions are also expected to take up heavy metal ions from aqueous solutions. $\text{Mg}(\text{NO}_3)_2$ solution was added dropwise to citrate, malate, and tartrate solutions at 30 °C under mild agitation (Kameda et al., 2009b). Solution pH was adjusted to 10.5 by addition of NaOH solution. After addition of $\text{Mg}(\text{NO}_3)_2$ solution, the resultant suspensions were incubated at 30 °C for 1 h. For malate and tartrate, new layered magnesium hydroxides in which brucite layers were bridged by $\text{C}_4\text{H}_4\text{O}_5^{2-}$ and $\text{C}_4\text{H}_4\text{O}_6^{2-}$ were prepared. The $\text{C}_4\text{H}_4\text{O}_5^{2-}$ and $\text{C}_4\text{H}_4\text{O}_6^{2-}$ may also have been absorbed on the surfaces of the hydroxides. For citrate, $\text{Mg}(\text{OH})_2$ with absorbed $\text{C}_6\text{H}_5\text{O}_7^{3-}$ was produced. These materials were found to take up Cu^{2+} rapidly from an aqueous solution at a constant pH of 5.0. The Cu^{2+} uptake was attributed to the formation of chelate complexes of Cu^{2+} with $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{C}_4\text{H}_4\text{O}_5^{2-}$, and $\text{C}_4\text{H}_4\text{O}_6^{2-}$.

Nakayama et al. (2007) examined mercaptocarboxylic acid as a chelating agent. Mercaptocarboxylic acids were intercalated into Mg–Al LDH accompanied by oxidation of mercapto groups to form disulfide. The intercalation compound selectively adsorbed Hg^{2+} and Ag^+ , whereas there was almost no adsorption of Pb^{2+} and Cu^{2+} . Quantitative adsorption of Hg^{2+} was observed for mercaptosuccinic acid and 3,3'-dithiodipropionic acid intercalated by LDH. The adsorption sites were verified to be disulfide bonds. The selective adsorption of heavy metal ions was due to the effect of a confined field in the interlayer of LDH. Pavlovic et al. (2009) investigated the adsorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} by LDHs intercalated with the chelating agents diethylenetriaminepentaacetate (dtpa) and meso-2,3-dimercaptosuccinate (dmsa). $\text{NO}_3\cdot\text{Zn}$ –Al LDH was intercalated with the chelating agents dtpa and dmsa by anion exchange, and the adsorption of these metal ions occurred mainly

through chelation by interlayer ligands. The adsorption isotherms indicated a high host-guest affinity. The presence of dmsa in the Zn-Al LDH interlayer increased the affinity for the metal ions relative to dtpa•Zn-Al LDH. Although Cu^{2+} , Cd^{2+} , and Pb^{2+} were mainly adsorbed by chelation, a certain amount may have been precipitated due to the higher surface alkalinity of the LDH. PbCO_3 was also detected. Precipitation of amorphous metal and isomorphous substitution of Zn^{2+} by another metal ion in the brucite-like layer might also have been involved in the adsorption processes. Liang et al. (2010) also examined the sorption of Pb^{2+} by LDH intercalated with dtpa. Mg-Al LDH intercalated with dtpa was prepared by coprecipitation. The maximum adsorption of Pb^{2+} was about 170 and 40 mg/g for dtpa•Mg-Al LDH and Cl•Mg-Al LDH, respectively. Langmuir isotherms described the sorption data well, and a pseudo-second-order kinetic model fit the sorption kinetic processes better for both the LDHs. The mechanism of Pb^{2+} adsorption on dtpa•Mg-Al LDH can be explained by Pb-dtpa chelation, while that for Cl•Mg-Al LDH was primarily surface-induced precipitation.

3. Uptake of nonionic organic compounds by organically modified LDH

Recently, LDH and its oxide have been investigated as scavengers to treat wastewater containing anionic organic contaminants. The materials are known to function as effective anion adsorbents in the uptake of phenols, terephthalate, anionic surfactants, ionizable pesticides and herbicides, humic and fulvic acid, anionic dyes, and colored organics from aqueous solutions (Ulibarri et al., 1995; Hermosin et al., 1996; Pavlovic et al., 1997; Barriga et al., 2002; Crepaldi et al., 2002; You et al., 2002a; Orthman et al., 2003; Pavlovic et al., 2005; Li et al., 2005; Cardoso and Valim, 2006; Vreysen and Maes, 2008; Chao et al., 2009; Gaini et al., 2009; Valente et al., 2009; Setti et al., 2010; Sun et al., 2010). Based on the ability of LDH to intercalate various types of anions in interlayers, organic-inorganic composite materials could be produced by intercalation of organic anions having functional groups in their structure into the interlayers of LDH. LDHs modified with organic anions are expected to take up nonionic organic compounds from aqueous solution depending on the functional groups in the structure of the intercalated organic anions. For example, Mg-Al LDH intercalated with dodecylsulfate (DS) could adsorb hydrophobic pesticides such as linuron, atrazine, acephate, and diazinon from aqueous solution (Villa et al., 1999). This is due to the modification of the interlayer surface of the LDH from hydrophilic to hydrophobic. Modification of Mg-Al LDHs with DS and dodecylbenzenesulfonate resulted in very high adsorption of the uncharged pesticide triadimefon (Celis et al., 2000). The high adsorption of triadimefon was due to the paraffin-like sorbents. Dissolution of the hydroxide structure of the LDHs at low pH (< 4) limited their use as sorbents in acidic conditions. For interlayer adsorption of triadimefon in LDHs, X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) studies indicated weak interactions between the pesticide molecules and the sorbents, in agreement with the high reversibility observed in the adsorption-desorption isotherms. You et al. (2002b) examined the surfactant-enhanced adsorption of organic compounds by Mg-Al LDHs. Organo-Mg-Al LDHs were prepared by incorporating anionic surfactants, octylsulfate, DS, 4-octylbenzenesulfonate, and dodecylbenzenesulfonate, into Mg-Al LDH via ion exchange. The anionic surfactants were intercalated into Mg-Al LDH with the surfactants oriented perpendicular in the interlayer. The octylsulfate formed bimolecular films, and other surfactants resulted in monolayer structures. Intercalation of

surfactants into Mg–Al LDH decreased the surface area, whereas surfactants dramatically enhanced the LDH affinity for 1,2,4-trichlorobenzene and 1,1,1-trichloroethane in aqueous solutions. Adsorption potential depended on the type of surfactant as well as the configuration of surfactant molecules within Mg–Al LDH interlayers. The adsorption characteristics indicated that the retention of organic compounds by organo-Mg–Al LDHs was due to a partitioning mechanism. Zhao and Nagy (2004) investigated DS•Mg–Al LDHs with a Mg/Al molar ratio of 2–5 for trapping chlorinated organic pollutants in water. Adsorption of trichloroethylene and tetrachloroethylene by DS•Mg–Al LDH did not follow a simple trend with increasing organic content but rather varied with probable DS configuration and LDH composition. DS•Mg–Al LDH with a Mg/Al molar ratio of 3 had the highest affinity for both hydrophobic organic compounds in water because it has the optimal charge density for forming an effective partition medium with the LDH interlayer. DS•Mg–Al LDH with a Mg/Al molar ratio of 2 had the lowest sorption affinity, although it contained the highest amount of DS, and adsorption is thought to occur on edge/external surface area. Wang et al. (2005) examined the surface modification of Mg–Al LDH and incorporation of hydrophobic organic compounds. Surface properties of Mg–Al LDHs intercalated with DS and dodecylbenzenesulfonate were modified from hydrophilic to hydrophobic. Both Mg–Al LDHs adsorbed the nonionic hydrophobic organic pesticide, chlorpyrifos, which was successfully retained in the hydrophobic region of both Mg–Al LDHs. Chuang et al. (2008) examined the removal of 2-chlorophenol from aqueous solution by $\text{NO}_3\cdot\text{Mg}\text{--Al}$ LDH and DS•Mg–Al LDH. The dissociation of 2-chlorophenol was 8.56. A high concentration of 2-chlorophenol was adsorbed by the hydrophilic–hydrophilic physical interaction of $\text{NO}_3\cdot\text{Mg}\text{--Al}$ LDH when the pH was >8.56 ; however, the hydrophobic–hydrophobic partition interaction of DS•Mg–Al LDH was more important when the pH was <8.56 . The efficiencies of both LDHs with respect to the enhancement of 2-chlorophenol adsorption are strongly dependent on pH, speciation, ionic strength, and metal dissolution. As mentioned above, organo LDH has the potential to take up nonionic organic contaminants from an aqueous solution. We studied the preparation of organo-Mg–Al LDH and its uptake of bisphenol A. Furthermore, we studied the selective uptake of nonionic organic contaminants from aqueous solution. These studies are discussed in the following sections.

3.1 Nonselective uptake of aromatic compounds

Recently, the contamination of effluents and water in our environment with hazardous organic materials has become more serious, and a great deal of effort has been made to develop water-cleaning technology and materials usable for this purpose. It is generally known that toxic organic contaminants, including PCB (polychlorinated biphenyls), dioxin, fran, and other so-called endocrine disruptors and organic halides have low solubility in water. For effective elimination of toxic organic materials from aqueous environments, the development of an adsorbent or absorbent for these materials at fairly low concentrations is an urgent requisite. Some types of oils are candidates for the role of scavengers. Sufficiently frequent contact of the contaminants with these oils will require an energy-intensive process and dispersion of oil droplets of adequately small size coupled with oil–water phase separation. To overcome these challenges, the primary objective of this series of studies was to investigate the use of solid particles modified with organic materials that perform the

function of picking up the target organic contaminant. Solids of this type are expected to enable handling of the solid particles housing the oily and viscous organic materials and even the water-soluble materials in their structure. The first attempt was the formation of LDH particles holding an organic substance with the desired function in their interlayers. When anionic organic acid species are intercalated into the interlayers of LDH, they remain functional; the chemically modified LDH can be an effective scavenger for organic contaminants in aqueous effluents.

We prepared DS•Mg–Al LDH with a Mg/Al molar ratio of 3 by adding a solution of $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ to an aqueous solution of DS at a constant pH of 10.0 (Kameda et al., 2005b). The intercalation of DS^- into Mg–Al LDH was controlled primarily by the charge balance between the positive electric charge of Al-bearing brucite-like octahedral layers and the anion in the interlayer. The capacity of DS•Mg–Al LDHs and $\text{CO}_3\cdot\text{Mg}$ –Al LDH to take up bisphenol A from an aqueous solution was examined by suspending 100-mg samples in 20 mL of 100 mg/L bisphenol A solution under shaking at 20 °C for 10~360 min. For DS•Mg–Al LDHs with a DS/Al molar ratio of 1.0, the concentration of bisphenol A decreased very rapidly to 15 mg/L within 30 min. For DS•Mg–Al LDH with a DS/Al molar ratio of 0.5, the concentration of bisphenol A decreased to 50 mg/L within 30 min. However, for $\text{CO}_3\cdot\text{Mg}$ –Al LDH with no DS content, only a slight decrease in the concentration of bisphenol A was observed. These results indicate that DS^- in the interlayer gives rise to the uptake of bisphenol A from the aqueous solution into the chemically modified Mg–Al LDH, probably caused by the hydrophobic interactions between the DS^- and bisphenol A. The organic material DS maintained adequate functionality in the interlayer of DS•Mg–Al LDH and can be handled as a fine powder with hydrophobic properties. In the XRD patterns of DS•Mg–Al LDH before and after the uptake of bisphenol A, no detectable change was observed. This implies that the basal spacing of DS•Mg–Al LDH was not affected by the uptake of bisphenol A, i.e., bisphenol A did not cause the interlayer to expand by being incorporated into the space between the intercalated DS^- and $\text{Mg}(\text{OH})_2$ -type host lattice. Bisphenol A is thought to be incorporated into the openings between the alkyl groups of DS^- in the interlayer of DS•Mg–Al LDH; this space is approximately 22 Å. It is generally accepted that the large interlayer space, occupied by organic anions, accommodates organic compounds of long molecular lengths, such as bisphenol A. The extraction of bisphenol A taken-up by DS•Mg–Al LDH with a DS/Al molar ratio of 1.0 has been attempted using ethanol. In the extraction with deionized water free of ethanol, the concentration of bisphenol A was 16.8 mg/L, corresponding to extraction of less than 5% of the bisphenol A uptaken by DS•Mg–Al LDH; extraction of bisphenol A with water was minimal. The concentration of bisphenol A in the extraction media increased sharply with increasing ethanol concentration and was as high as 320 mg/L for 99.5% ethanol solution. This observed value is equivalent to approximately 90% of the bisphenol A taken-up by DS•Mg–Al LDH. The bisphenol A taken-up by DS•Mg–Al LDH was easily extracted with ethanol. This extraction was attributed to the hydrophobic interactions between ethyl groups of ethanol and methyl groups of bisphenol A as well as hydrogen bonds formed by hydroxyl groups of the two compounds. The DS^- intercalated in the interlayer of DS•Mg–Al LDH was not dissolved by ethanol solution. To confirm the stable intercalation of DS^- in the interlayer after extraction, the uptake capacity of ethanol-treated DS•Mg–Al LDH for bisphenol A in an aqueous solution was compared with that of fresh DS•Mg–Al LDH. In

the presence of a suspension of ethanol-treated DS•Mg–Al LDH, the concentration of bisphenol A decreased from 100 mg/L to 11.9 mg/L, similar to that for fresh DS•Mg–Al LDH (10.9 mg/L). This result proves that DS•Mg–Al LDH was regenerated by the extraction of bisphenol A with ethanol, i.e., the intercalated DS⁻ remained in the interlayer. DS⁻ was rigidly fixed in the interlayer, in contact with ethanol as well as bisphenol A solution. To summarize, it was confirmed that DS•Mg–Al LDH retains its activity during repeated cycles of uptake and extraction of bisphenol A. The DS⁻ in the solid particles was in a stable arrangement in the solid phase while simultaneously reacting rapidly with bisphenol A outside the particles.

We examined the preparation and characterization of Mg–Al LDHs intercalated with 2-naphthalene sulphonate (2-NS⁻) and 2,6-naphthalene disulphonate (2,6-NDS²⁻) (Kameda et al., 2006). 2-NS•Mg–Al LDH and 2,6-NDS•Mg–Al LDH, with 2-NS⁻ or 2,6-NDS²⁻ intercalated in the interlayer of Mg–Al LDH, were prepared by dropwise addition of a mixed aqueous solution of Mg(NO₃)₂ and Al(NO₃)₃ at a Mg/Al molar ratio of 3.0 to an aqueous ethanol solution of 2-NS-Na or to an aqueous solution of 2,6-NDS-Na₂ at a constant pH of 10.0 and left standing at 30 °C for 1 h. The intercalated 2-NS⁻ and 2,6-NDS²⁻ maintained their intrinsic molecular structure in the interlayer of Mg–Al LDH. XRD analysis confirmed that 2-NS•Mg–Al LDH had two basal spacings of approximately 19 and 9 Å. It is likely that 2-NS⁻ was intercalated in the interlayer of Mg–Al LDH in two orientations. It is believed that the naphthalene ring of 2-NS⁻ was oriented parallel and perpendicular to the brucite (Mg(OH)₂)-like layers of Mg–Al LDH. The 2-NS/Al molar ratio in the 2-NS•Mg–Al LDH increased with increasing 2-NS/Al molar ratio in solution, and the interlayer of Mg–Al LDH was intercalated with 2-NS⁻ to near full capacity for neutralization of the positive charge of the host lattice at a 2-NS/Al molar ratio of 2.0 in solution. The XRD patterns of 2,6-NDS•Mg–Al LDH exhibited very weak, broad peaks corresponding to the basal spacings at 2θ ranging from 6–11°, suggesting an irregular arrangement of 2,6-NDS²⁻ in the Mg–Al LDH interlayers. This was attributed to the limited mobility of the 2,6-NDS²⁻ resulting from the pin-up of the anions at the two –SO₃⁻ groups on either side of the interlayer. In contrast to 2-NS⁻, the intercalation with 2,6-NDS²⁻ was approximately 80% of the value expected due to the charge balance on the Mg–Al LDH. The disordered configuration of 2,6-NDS²⁻ in the interlayer of Mg–Al LDH was presumed to restrict the intercalation.

We also investigated the properties of 2-NS•Mg–Al LDH and 2,6-NDS•Mg–Al LDH as scavengers for organic contaminants having aromatic rings in their molecular structures (Kameda et al., 2007). The ability of 2-NS•Mg–Al LDH and 2,6-NDS•Mg–Al LDH to take up bisphenol A from aqueous solution was examined by suspending 0.1 g of the samples in 20 mL of 100 mg/L bisphenol A solution while shaking at 20 °C for 10–360 min. Figure 4 shows the variation in the concentration of bisphenol A with time for 2-NS•Mg–Al LDHs and for CO₃•Mg–Al LDH as a reference material.

For 2-NS•Mg–Al LDHs, the concentration of residual bisphenol A decreased very rapidly from 100 mg/L to 10 mg/L or less in the first 30 min and then decreased fairly slowly. In particular, at a 2-NS/Al of 0.43, the lowest molar ratio, the concentration decreased to less than 3 mg/L within 30 min. In contrast, for CO₃•Mg–Al LDH without chemical modification of the interlayer, only a slight decrease in the bisphenol A concentration was observed. These results demonstrate that the adsorption of bisphenol A on the LDH particles plays a minor role and that the intercalated organic entity may be largely responsible for the uptake of bisphenol A from aqueous solution. The uptake of bisphenol A from aqueous solution was attributed to the association of the naphthalene rings of the 2-

NS⁻ with the benzene rings of the incorporated bisphenol A. 2,6-NDS•Mg–Al LDH also had the potential to take up bisphenol A from aqueous solution. The intrinsic functions of the naphthalene ring of 2,6-NDS²⁻ were unchanged in the interlayer and positively affected the uptake of bisphenol A due to the association between the aromatic rings. Mg–Al LDH with lower contents of 2-NS⁻ or 2,6-NDS²⁻ in the interlayer had larger potential to take up bisphenol A from aqueous solution than that with more intercalated organic acid. The former is thought to have larger spaces to accommodate more bisphenol A in the interlayer than the latter, which had limited space due to the higher content of the intercalated entity. It is expected that practical water-cleaning processes should be able to continuously treat wastewater contaminated with hazardous organic compounds at an acceptable flow rate. This can be achieved by passing wastewater through a column containing adsorbents. In our study, the test solutions containing bisphenol A and ethanol were alternately passed through a DS•Mg–Al LDH particle column (length = 48 mm, inner diameter = 4.6 mm) to examine the cycles of uptake of bisphenol A and elution of uptaken bisphenol A by ethanol (Kameda et al., 2009c). The test solution containing bisphenol A, ethanol, or deionized water was passed through the column at a rate of 1.5 mL/min at 80 psi using a gradient pump according to the designed pattern of flow. The column packed with fine particles of the adsorbent produced a high pressure drop, and a high operation pressure was applied to maintain the desired flow rates. The volume of the column was 0.8 mL, and the space velocity was calculated to be 112.5 h⁻¹ under the conditions used in this study. The column was filled with 0.5 g of DS•Mg–Al LDH particles and maintained at 20 °C using a water bath. Metal filters with pore diameters of 2.0 and 0.5 μm were placed at the top and bottom of the column to hold the particles. Residual bisphenol A in the effluent from the column was continuously monitored at a wavelength of 280 nm using a photomultiplier detector. First, deionized water was passed through the column for 10 min to clean the column and to monitor the system. Then, bisphenol A solution was fed to the column. Figure 5 presents the variation in the absorbance (λ = 280 nm) observed using the photomultiplier detector for a flow of 100 mg/L bisphenol A solution without the column and that for the effluent from the column containing DS•Mg–Al LDH particles.

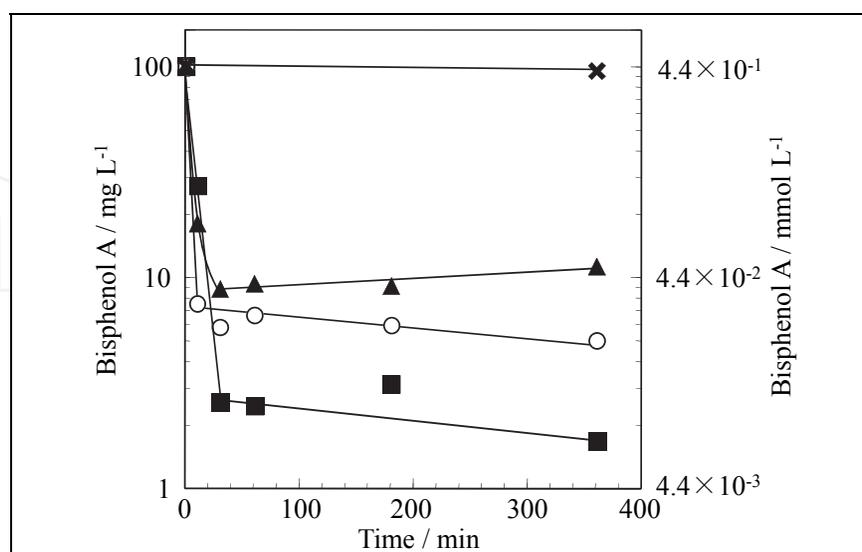


Fig. 4. Variation in the concentration of bisphenol A with time for suspensions of 2-NS•Mg–Al LDHs and CO₃•Mg–Al LDH in bisphenol A solution. 2-NS•Mg–Al LDH: the 2-NS/Al molar ratio was 0.43 (■), 0.82 (○), and 0.96 (▲) CO₃•Mg–Al LDH: (×)

In the absence of the column (Fig. 5(a)), no absorbance was detected during the first 10 min of deionized water flow. The line corresponding to the first 10 min in Fig. 5(a) is hereafter referred to as the baseline. Immediately after the flow of bisphenol A solution, the absorbance quickly increased to a value corresponding to the concentration of bisphenol A and remained constant. This proves that the bisphenol A in aqueous solution was continuously monitored with high sensitivity by the detector. When deionized water was passed through the column containing DS•Mg–Al LDH particles (Fig. 5(b)) for 10 min, the absorbance rapidly increased and immediately decreased to the baseline. The rapid increase in the absorbance may be attributable to the dissociation of molecular sodium dodecylsulfate (SDS) dissolved in the intercalated DS⁻ medium in DS•Mg–Al LDH due to hydrophobic interactions. As a result, the DS•Mg–Al LDH particles in the column required an initial washing with water to remove SDS from the LDH. After the first 10 min (Fig. 5(b)), when bisphenol A was passed through the column, the measured absorbance remained on the baseline for 200 min, i.e., the concentration of bisphenol A in the effluent was less than the detection limit of the detector used in this study (0.1 mg/L). This elimination of bisphenol A was observed for the effluent with a volume 356 times that of the column. This suggests that bisphenol A was taken up by the DS•Mg–Al LDH particles during its flow through the column. However, the absorbance gradually increased after 200 min, indicating the presence of bisphenol A in the effluent. This reflects the gradual decrease in the accommodation space for bisphenol A in the interlayers of DS•Mg–Al LDH with time, approaching a break-through point, 260 min, at which the concentration reached 10 mg/L. The column has the potential to be used for the treatment of bisphenol A solution for 260 min under the conditions used in this study. Due to the flow of bisphenol A solution through the column, the pH of the effluent increased immediately from an initial value of 5.2 to near 7.0 and then remained in the range of 6.0–8.0. The Mg²⁺ concentrations were very low at each stage. These results are acceptable according to the water quality standard in Japan (5 < pH < 9; Mg²⁺ is not listed there). From the XRD analysis, it can be deduced that the configuration of the intercalated DS⁻ in DS•Mg–Al LDH was not affected by the flow of bisphenol A solution.

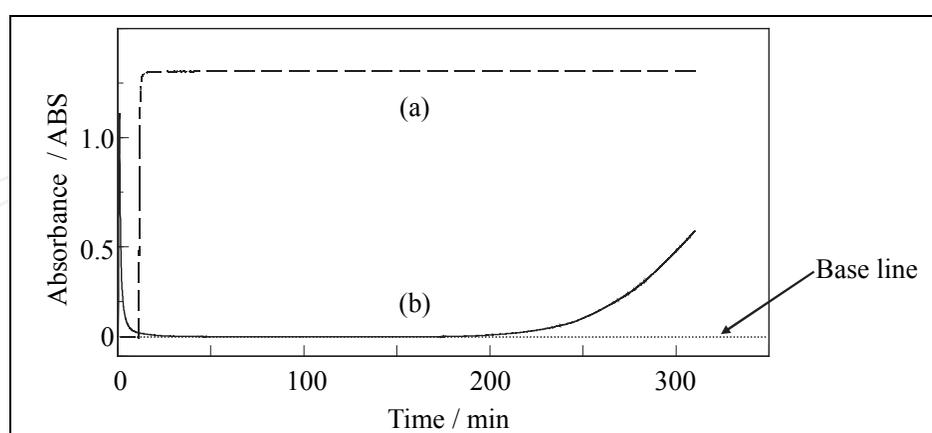


Fig. 5. Variation in absorbance ($\lambda = 280$ nm) observed using a photomultiplier detector for (a) flow of 100 mg/L bisphenol A solution without a column and (b) effluent from a column containing DS•Mg–Al LDH particles.

Furthermore, bisphenol A solution and ethanol were alternately passed through a column containing DS•Mg–Al LDH particles to investigate the possibility of continuous treatment, consisting of repeated cycles of bisphenol A uptake from the aqueous solution and ethanol

elution of the uptaken bisphenol A. The designed pattern of the alternate flow of bisphenol A solution and ethanol is presented in Fig. 6 (A). This figure represents a flow series of deionized water for 0–10 min, 100 mg/L bisphenol A solution for 10–40 min, deionized water for 40–45 min, and ethanol solution for 45–60 min to elute bisphenol A from the DS-layer. In the ethanol elution stage, the ethanol concentration increased to 50 vol% at 10 vol%/min during the first 5 min and remained constant at 50 vol% for the following 5 min.

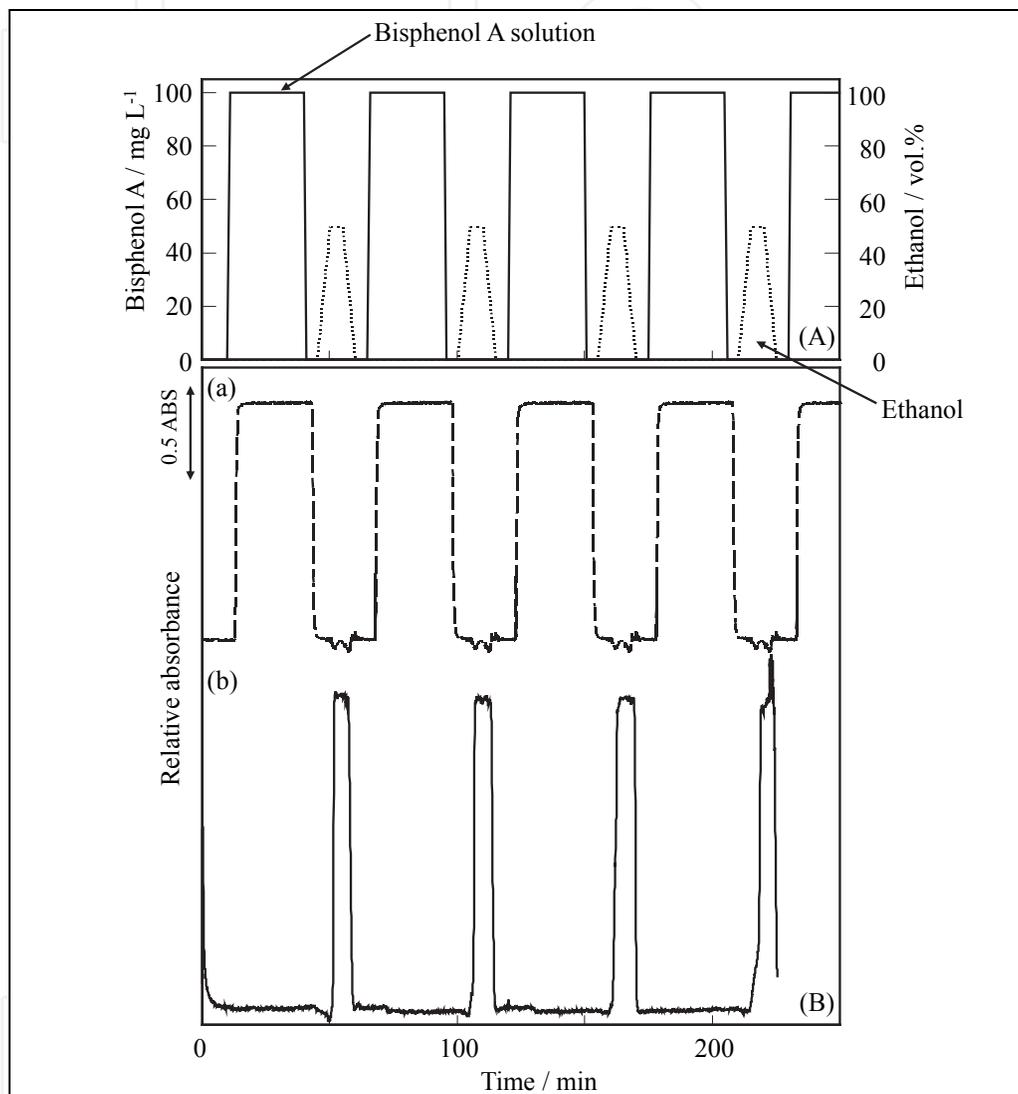


Fig. 6. (A) Designed pattern for alternate flow of bisphenol A solution and ethanol with a flow rate of 1.5 mL/min. (B) Variation in the absorbance ($\lambda = 280$ nm) of the effluent obtained by alternate flow of bisphenol A solution and ethanol (a) without a column and (b) through a column containing DS•Mg–Al LDH particles.

Then, for the last 5 min, the concentration decreased to 0 vol% at a constant rate of 10 vol%/min. After the flow of deionized water for 60–65 min, 100 mg/L bisphenol A solution was passed through the column again, and this cycle was repeated. Figure 6 (B) presents the variation in the absorbance ($\lambda = 280$ nm) for the effluent from the column by the alternate flow of bisphenol A and ethanol solutions and the corresponding curve for the system without the column. For the system without the column (Fig. 6 (B)(a)), a constant absorbance

was obtained for the flow of bisphenol A solution, while no absorbance was detected for the flow of deionized water and ethanol. The variation in the absorbance corresponds well to the flow conditions presented in Fig. 6 (A). For the system with a column containing DS•Mg–Al LDH particles (Fig. 6 (B)(b)), no absorbance was detected during the flow of bisphenol A solution through the column, indicating that bisphenol A was almost completely eliminated by the DS•Mg–Al LDH particles. In contrast, the absorbance increased with the flow of ethanol solution, confirming that bisphenol A taken-up by the DS•Mg–Al LDH particles was eluted by ethanol. The maximum concentration of bisphenol A in ethanol was 130 mg/L, which was higher than the concentration (100 mg/L) of bisphenol A solution, indicating that the bisphenol A was concentrated to 130% under the conditions in this study. These results show that bisphenol A could be continuously eliminated by DS•Mg–Al LDH, which can be regenerated through ethanol elution. This suggests that the uptake of bisphenol A from the aqueous phase and its elution from the DS⁻ layer in the LDH are qualitative and fairly quick processes. The absorbance measurement was performed over 224 min of flow, as presented in Fig. 6 (B)(b), and ceased due to the increase in pressure inside the column. This may be attributable to the swelling of the DS•Mg–Al LDH particles caused by the incorporation of ethanol in the interlayers of the LDH. To summarize, the DS•Mg–Al LDH particles packed in a column were found to continuously take up bisphenol A from the aqueous solution. Furthermore, they were regenerated by elution of the uptaken bisphenol A by ethanol. The column containing DS•Mg–Al LDH particles is expected to be applicable for the treatment of wastewater containing organic substances. According to the results of this study, the composite materials coupling LDH with organic anions are expected to be effective absorbents for organic as well as inorganic contaminants in aqueous solution. By such a technique, water-soluble or intrinsically liquid materials can be applied to water-cleaning processes based on column-style operations.

3.2 Selective uptake of aromatic compounds

In environmental systems, hazardous organic contaminants can coexist with natural organic materials in wastewater effluents. If Mg–Al LDHs intercalated with organic anions selectively take up target organic materials from wastewater streams, they may be useful as effective scavengers for water treatment. To take up target organic materials selectively, the electronic state of the intercalated aromatic anions can be manipulated by the addition of electron-donating or -withdrawing substituents, thereby activating or deactivating the aromatic rings, respectively. Activated and deactivated systems interact strongly, generating a π - π stacked geometry (Gung and Amicangelo, 2006). Mg–Al LDHs intercalated with aromatic anions are thus expected to selectively take up hazardous aromatic compounds from wastewater due to the strong electrostatic attraction between the aromatic rings of Mg–Al LDHs and those of the hazardous aromatics.

We investigated the selective uptake of six aromatic compounds with different functional groups from aqueous solutions by Mg–Al LDH intercalated with 2,7-naphthalene disulfonate (2,7-NDS²⁻) (Kameda et al., 2009d, 2009e). The six examined compounds were 1,3-dinitrobenzene (DNB), nitrobenzene (NB), benzaldehyde (BA), anisole (AS), *N,N*-dimethylaniline (DMA), and 1,2-dimethoxybenzene (DMB). 2,7-NDS•Mg–Al LDH (Mg/Al = 2.9; 2,7-NDS/Al = 0.31) was added to 20 mL of a single solution consisting of each aromatic compound at a concentration of 0.5 mM, and it was shaken at 20 °C for 120 min. In

this case, the amount of 2,7-NDS•Mg–Al LDH added was such that the molar ratio of intercalated 2,7-NDS²⁻ to each compound was 50. To demonstrate the effect of the interlayer anions on the uptake of aromatics, DS•Mg–Al LDH (Mg/Al = 3.2; DS/Al = 0.98) and CO₃•Mg–Al LDH were also used as reference materials. When DS•Mg–Al LDH was added to the single solution, the molar ratio of intercalated DS⁻ to each compound was 50. The amount of CO₃•Mg–Al LDH was 0.5 g. Table 1 shows the uptake of each aromatic compound from the single solution by 2,7-NDS•Mg–Al LDH, DS•Mg–Al LDH, and CO₃•Mg–Al LDH.

Mg–Al LDH	Uptake (%)					
	DNB	NB	BA	AS	DMA	DMB
2,7-NDS ²⁻	84.7	56.5	46.4	28.3	20.4	14.2
DS ⁻	56.0	61.9	41.5	66.9	75.0	62.8
CO ₃ ²⁻	0	5.7	5.1	10.5	13.3	0

Table 1. Uptake of each aromatic compound from a single solution by 2,7-NDS•Mg–Al LDHs, DS•Mg–Al LDH, and CO₃•Mg–Al LDH.

The uptake of each aromatic compound by 2,7-NDS•Mg–Al LDHs and DS•Mg–Al LDH was greater than that by CO₃•Mg–Al LDH. In the case of CO₃•Mg–Al LDH, in which no chemical modification of the interlayer occurred, the uptake was attributed to the adsorption of the aromatic compounds on the surface of the CO₃•Mg–Al LDH particles. The high uptake by 2,7-NDS•Mg–Al LDHs and DS•Mg–Al LDH was attributed to the interaction between the aromatic compounds and the 2,7-NDS²⁻ and DS⁻ intercalated in the interlayer of Mg–Al LDH, respectively. In the case of DS•Mg–Al LDH, the maximum and minimum uptakes were 75.0% for DMA and 41.5% for BA, and the dependence of the uptake on the type of aromatic compound was low. This nonselective uptake was likely due to a hydrophobic interaction between the alkyl groups of DS⁻ intercalated in the interlayer and the benzene ring of the compound in the aqueous solution. For 2,7-NDS•Mg–Al LDH, the uptake decreased in the following order: DNB > NB > BA > AS > DMA > DMB. The maximum and minimum uptakes were 84.7% for DNB and 14.2% for DMB, and the dependence of the uptake on the type of aromatic compound was high. This selective uptake was attributed to π - π stacking interactions between the benzene ring of the compound and the naphthalene ring of 2,7-NDS²⁻ intercalated in the interlayer spaces of Mg–Al LDH. The uptake is thought to depend on the electronic state of the aromatic compound, which, in turn, depends on the functional group. The electronic states of the benzene rings of DNB, NB, and BA are compared as follows. All these compounds contain electron-withdrawing groups, namely, -NO₂ and -CHO groups. The strength of -NO₂ is greater than that of -CHO. DNB has two NO₂ groups, and, therefore, the benzene ring of DNB has the lowest electron density among the aromatics. Additionally, the benzene ring of NB has a lower electron density than that of BA. Next, the electronic states of the benzene rings of AS, DMA, and DMB are compared. These compounds are grouped for comparison because they all contain electron-donating groups, namely, -OCH₃ and -N(CH₃)₂ groups. DMB has two -OCH₃ groups, and, thus, the benzene ring of DMB has the largest electron density among these aromatics. The strength of the -N(CH₃)₂ group is greater than that of the -OCH₃ group. This suggests that the benzene ring of DMA has a larger density of electrons than that of AS. In other words, the density of electrons in the benzene ring in the

aromatics is expected to decrease in the following order: DMB > DMA > AS > BA > NB > DNB. The electronic state of the naphthalene ring of 2,7-NDS²⁻ intercalated into the interlayer of 2,7-NDS•Mg–Al LDH can be described as follows. 2,7-NDS²⁻ has two -SO₃⁻ groups in its structure that are weak electron-withdrawing groups. The naphthalene ring is richer in electrons than the benzene ring is, and, thus, the naphthalene ring of 2,7-NDS²⁻ probably has a larger density of electrons due to the weak electron-withdrawing ability of the two -SO₃⁻ groups. The high uptake of aromatic compounds in the decreasing order of DNB > NB > BA > AS > DMA > DMB by 2,7-NDS•Mg–Al LDH was caused by π - π stacking interactions between the electron-rich naphthalene ring of 2,7-NDS²⁻ intercalated into the interlayer of 2,7-NDS•Mg–Al LDH and the benzene ring of the aromatics, which has lower electron density, in the decreasing order of DMB > DMA > AS > BA > NB > DNB. That is, the electron-poor benzene ring of aromatics showed strong interactions with the electron-rich naphthalene ring of intercalated 2,7-NDS²⁻, and these interactions resulted in the large uptake of aromatics by 2,7-NDS•Mg–Al LDH. Table 2 shows the uptake of multiple aromatic compounds from mixed solutions I and II by 2,7-NDS•Mg–Al LDH. In this case, the mixed solution I contained 0.5 mM DNB, BA, and DMB. The mixed solution II contained 0.5 mM DNB, NB, BA, AS, and DMB.

	Uptake (%)				
	DNB	NB	BA	AS	DMB
Mixed solution I	82.8	—	30.2	—	3.7
Mixed solution II	79.3	47.5	32.2	12.0	6.6

Table 2. Uptake of multiple aromatic compounds from mixed solutions I and II by 2,7-NDS•Mg–Al LDH.

Even for the mixtures, uptake was high; uptake decreased in the order DNB > (NB) > BA > (AS) > DMB. This order matched that of the uptake from the single solution (Table 1). 2,7-NDS•Mg–Al LDH was found to selectively take up aromatic compounds with electron-poor benzene rings from the mixtures in aqueous solution.

NTS•Mg–Al LDH and ANDS•Mg–Al LDH, which respectively contained 1,3,6-naphthalenetrisulfonate (NTS³⁻) and 3-amino-2,7-naphthalenedisulfonate (ANDS²⁻) intercalated in the interlayer spaces, were also prepared by a coprecipitation technique (Kameda et al., 2010b). The naphthalene core of NTS³⁻ was likely oriented parallel to the brucite-like host layers of Mg–Al LDH, lying at the midpoint of the interlayer space. The naphthalene core of ANDS²⁻ was oriented parallel to the brucite-like layers, at the midpoint of the interlayer space, when ANDS•Mg–Al LDH was prepared from a solution with a low concentration of ANDS²⁻. When a solution with a high concentration of ANDS²⁻ was used in the preparation, the naphthalene core of ANDS²⁻ was thought to be oriented in an irregular fashion with respect to the brucite-like layers. NTS•Mg–Al LDH and ANDS•Mg–Al LDH were both capable of absorbing large quantities of aromatics from aqueous solution in the decreasing order of DNB > NB > BA > DMA > AS > DMB. The difference in absorption was attributed to differences in the extent of π - π stacking interactions occurring between the benzene rings of the aromatics and the naphthalene core of the intercalated NTS³⁻ and ANDS²⁻. The uptake of aromatics in these cases probably occurred via insertion of the benzene rings of the aromatics between the naphthalene cores of the intercalated NTS³⁻ and ANDS²⁻ and the brucite-like layers.

We also examined the effect of intercalated aromatic sulfonates on uptake of aromatic compounds from aqueous solutions by modified Mg–Al LDH (Kameda et al., 2010c). We utilized Mg–Al LDHs modified by intercalation with three aromatic sulfonates: 2,7-NDS²⁻, benzenesulfonate (BS⁻), and benzenedisulfonate (BDS²⁻). BS•Mg–Al LDH and BDS•Mg–Al LDH, which respectively contained BS⁻ and BDS²⁻ intercalated in the interlayer space, were prepared by a coprecipitation technique (Kameda et al., 2008b). The intercalated BS⁻ and BDS²⁻ maintained their intrinsic molecular structures within the Mg–Al LDH interlayers. At low intercalation levels, the benzene ring of BS⁻ in BS•Mg–Al LDH was inclined at 30° relative to the plane of the brucite-like layers of Mg–Al LDH. With increasing BS⁻ content, the benzene ring adopted an additional configuration perpendicular to the Mg–Al LDH layers. In BDS-intercalated Mg–Al LDH, the benzene ring of BDS²⁻ was tilted at 26° relative to the plane of the Mg–Al LDH layers. Intercalation levels of BDS²⁻ were smaller than those of BS⁻ despite the greater charge density of BDS²⁻, which was likely attributable to a greater degree of electrostatic repulsion between intercalated anions. The uptake of DNB was notably high and in the order 2,7-NDS•Mg–Al LDH > BS•Mg–Al LDH > BDS•Mg–Al LDH. This was definitively attributed to the π – π stacking interactions between the electron-poor benzene ring of DNB and the electron-rich aromatic rings of the intercalated aromatic sulfonates, which have electron density in the order 2,7-NDS²⁻ > BS⁻ > BDS²⁻. To summarize, the electron-rich aromatic rings of intercalated aromatic sulfonates undergo stronger π – π stacking interactions with the electron-poor benzene ring of DNB. The uptake of AS by 2,7-NDS•Mg–Al LDH and BS•Mg–Al LDH was considerably lower than that of DNB by the same LDHs. The more electron-rich benzene ring of AS was thought to undergo weak π – π stacking interactions with the electron-rich aromatic rings of intercalated 2,7-NDS²⁻ and BS⁻. Finally, we examined the effect of the interlayer spacing of Mg–Al LDH on the ability to take up a nonionic organic material (Kameda et al., 2009f). Mg–Al LDHs, intercalated with 1-propanesulfonate (PS⁻), 1-hexanesulfonate (HS⁻), and 1-dodecanesulfonate (DDS⁻), were prepared by coprecipitation, yielding PS•Mg–Al LDH, HS•Mg–Al LDH, and DDS•Mg–Al LDH, respectively. The increase in the alkyl chain lengths of the Mg–Al LDHs (PS⁻ < HS⁻ < DDS⁻) resulted in the perpendicular orientation of the organic acid anions in the interlayer of Mg–Al LDH, which in turn resulted in more organic acid anions being accommodated in the interlayer space. An organic acid anion with a long molecular length was more easily intercalated in the interlayer of Mg–Al LDH than one with a short molecular length. This was attributed to the hydrophobic interaction between the alkyl chains, affecting the intercalation of the organic acid anions. The uptake of *N,N*-dimethylaniline (DMA) by Mg–Al LDHs increased in the order PS•Mg–Al LDH < HS•Mg–Al LDH < DDS•Mg–Al LDH. The uptake was attributed to the hydrophobic interactions between DMA and the intercalated PS⁻, HS⁻, and DDS⁻. Thus, Mg–Al LDH, which has many large interlayer spacings when intercalated with organic acid anions, can take up a large number of DMA molecules from an aqueous solution.

4. Conclusion

This chapter summarizes the preparation of organically modified LDH by intercalation of organic anions into the interlayer of LDH and the uptake of heavy metal ions and nonionic organic compounds by the organically modified LDH. In particular, we developed hybrid inorganic–organic composite materials capable of selective uptake of heavy metal ions and nonionic organic compounds from aqueous solution. It is significant that we developed a

relatively simple method for the preparation of the composite materials. Moreover, it must be emphasized that the utilization of a water-soluble reagent was possible by the incorporation of the reagent into an inorganic compound. The composite materials could remove heavy metal ions and bisphenol A from aqueous solutions with high concentrations to very low concentrations in a short time. These materials are expected to be applied for actual wastewater treatment.

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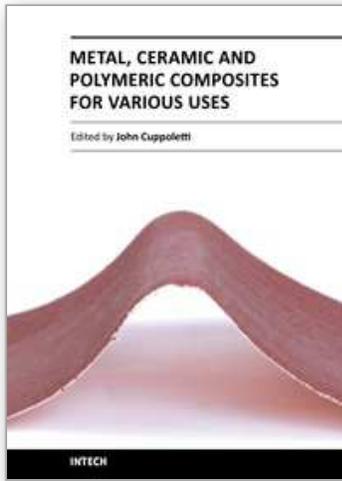
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