1436 Bull. Chem. Soc. Jpn. Vol. 82, No. 11, 1436–1440 (2009)

Preparation of Mg–Al Layered Double Hydroxide Intercalated with 2,7-Naphthalene Disulfonate and Its Selective Uptake of Aromatic Compounds from Aqueous Solutions

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Mg–Al layered double hydroxide intercalated with 2,7-naphthalene disulfonate ion (2,7-NDS•Mg–Al LDH) was prepared by coprecipitation and was found to selectively take up aromatic compounds from aqueous solutions. The amount of material absorbed by 2,7-NDS•Mg–Al LDH depends on the electron-donating or -withdrawing properties of the functional groups on the molecules to be absorbed. The absorption mechanism is dependent on π–π stacking interactions between the aromatic ring of the molecules to be absorbed and the naphthalene moiety of 2,7-NDS^{2-}.

Mg–Al layered double hydroxides (Mg–Al LDHs) are anion-exchange compounds represented by the general formula $[\mathrm{Mg}^{2+}{}_{1-x}\mathrm{Al}^{3+}{}_{x}(\mathrm{OH})_2](\mathrm{A}^{n-})_{x/n}\cdot m\mathrm{H_2O}$, where x is the Al/(Mg + Al) molar ratio and A^{n-} is an anion, with a charge balance of n.[1] Recently, Mg–Al LDHs have attracted considerable attention for waste-water treatment applications, that is for the removal of contaminants from waste water.[2] When intercalated with organic anions, Mg–Al LDHs have been shown to absorb hazardous organic substances from aqueous solutions. For example, Mg–Al LDHs intercalated with anionic surfactants and aromatic anions are able to take up pesticides and chlorinated organic pollutants from aqueous solution.[3] We have found that Mg–Al LDHs intercalated with dodecyl sulfate ions (DS$^-$), 2-naphthalene sulfonate ions (2-NS$^-$), and 2,6-naphthalene disulfonate ions (2,6-NDS^{2-}) absorb bisphenol A from an aqueous solution.[4] The absorption is attributable to hydrophobic interactions between bisphenol A and the intercalated organic anions. In waste-water effluents, hazardous organic contaminants coexist with natural organic materials. By choosing an appropriate intercalant, Mg–Al LDHs may be used to selectively absorb specific organic materials from the waste-water stream. To realize such selective uptake, 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.[5] Activated and deactivated systems are highly reactive, and reactions involving these systems generally yield products with a π–π stacking geometry.[5] Mg–Al LDHs intercalated with aromatic anions would thus be expected to selectively absorb hazardous aromatics from waste water due to the strong electrostatic attraction between the aromatic rings of Mg–Al LDHs and those of the hazardous aromatics. In this study, we prepared Mg–Al LDH intercalated with 2,7-naphthalene disulfonate ion (2,7-NDS^{2-}), as shown in Figure 1. The intercalated materials were shown to selectively take up six aromatic compounds with different functional groups from aqueous solutions.[6] The six examined compounds were 1,3-dinitrobenzene (DNB), nitrobenzene (NB), benzaldehyde (BA), anisole (AS), *N*,*N*-dimethylaniline (DMA), and 1,2-dimethoxybenzene (DMB), shown in Figure 2.

Experimental

All chemicals were of chemical reagent grade (Kanto Chemical, Ltd., Tokyo, Japan; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and were used without further purification.

Preparation. 2,7-NDS•Mg–Al LDH (theoretical formula: $\mathrm{Mg_{0.75}Al_{0.25}(OH)_2(C_{10}H_6(SO_3)_2)_{0.125}}$) was prepared by dropwise addition of Mg–Al solution to a 2,7-NDS^{2-} solution at a constant pH of 10.5. The coprecipitation reaction can be expressed by eq 1. The stoichiometric coefficient of 0.125 for 2,7-NDS^{2-} ($\mathrm{C_{10}H_6(SO_3)_2{}^{2-}}$) is calculated based on the neutralization of the positive electric charge of the Al-bearing, brucite-like octahedral layers due to the replacement of Mg with Al at a Mg/Al molar ratio of 3.0:

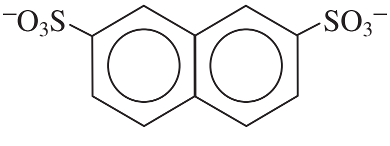

Figure 1. Chemical structure of 2,7-NDS^{2-}.

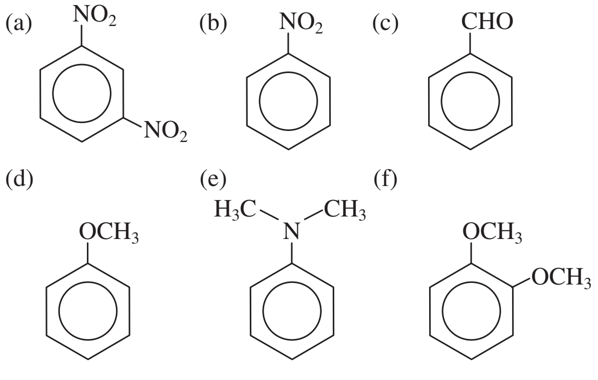

Figure 2. Chemical structures of (a) DNB, (b) NB, (c) BA, (d) AS, (e) DMA, and (f) DMB.

Published on the web November 10, 2009; doi:10.1246/bcsj.82.1436

Table 1. The Chemical Compositions of 2,7-NDS•Mg–Al LDHs, Prepared from Solutions of $R_{2,7\text{-NDS}} = 0.5$–3.0

Entry	$R_{2,7\text{-NDS}}$[a)]	2,7-NDS/Al molar ratio in solution	Chemical composition/wt%			Molar ratio	
			Mg	Al	2,7-NDS	Mg/Al	2,7-NDS/Al
a	0.5	0.25	24.4	8.8	11.5	3.1	0.12
b	1.0	0.5	22.8	8.6	19.3	2.9	0.21
c	2.0	1.0	19.5	7.6	25.0	2.9	0.31
d	3.0	1.5	24.7	9.4	24.5	2.9	0.25

a) $R_{2,7\text{-NDS}}$ represents the ratio of the actual amount of 2,7-NDS^{2-} in solution to the stoichiometric quantity defined by eq 1.

$$0.75\text{Mg}^{2+} + 0.25\text{Al}^{3+} + 0.125\text{C}_{10}\text{H}_6(\text{SO}_3)_2{}^{2-} + 2\text{OH}^- \rightarrow \text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{C}_{10}\text{H}_6(\text{SO}_3)_2)_{0.125} \quad (1)$$

The Mg–Al solution consisted of 0.375 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.125 M $Al(NO_3)_3 \cdot 9H_2O$ in deionized water. The 2,7-NDS^{2-} solution was prepared in deionized water at 0.5–3.0 times the stoichiometric quantities defined in eq 1. Mg–Al solution (250 mL) was added dropwise under mild agitation to 250 mL of the 2,7-NDS^{2-} solution at 10 mL min^{-1} at 30 °C. The solution pH was adjusted to 10.5 by the addition of 0.1 M NaOH solution. The resulting suspensions were allowed to settle at 30 °C for 1 h. 2,7-NDS•Mg–Al LDH particles were recovered by filtering the suspensions, followed by repeated washing with deionized water, and were dried under reduced pressure (133 Pa) for 40 h. Nitrogen (N_2) was bubbled into the solution throughout the operation to minimize the effects of dissolved CO_2.

Uptake of Aromatic Compound from Aqueous Solution. The six aromatic compounds examined are shown in Figure 2. The single test solution consisted of 0.5 mM aromatic compound. Mixed solution I contained 0.5 mM DNB, BA, and DMB. Mixed solution II contained 0.5 mM DNB, NB, BA, AS, and DMB. In a 50-mL Erlenmeyer flask, 2,7-NDS•Mg–Al LDH was added to 20 mL of a single solution or mixed solution I or II. The amount of the 2,7-NDS•Mg–Al LDH added was such that the molar ratio of intercalated 2,7-NDS^{2-} to each compound was 10–100. The flask was shaken at 20 °C for 10–120 min. The resulting suspension was filtered, and the filtrate was analyzed for the aromatic compounds. To demonstrate the effect of the interlayer anions on the uptake of aromatics, DS$^-$-intercalated Mg–Al LDH (DS•Mg–Al LDH)[4] and $CO_3{}^{2-}$-intercalated Mg–Al LDH (CO_3•Mg–Al LDH) were also used as reference materials. The DS•Mg–Al LDH contained 11.7 wt% of Mg, 4.0 wt% of Al, and 39.0 wt% of DS. The calculated Mg/Al and DS/Al molar ratios were 3.2 and 0.98, respectively. The basal spacing of the DS•Mg–Al LDH was 27.5 Å. When DS•Mg–Al LDH was added to the aqueous solutions, the molar ratio of intercalated DS$^-$ to each compound was 50. The amount of CO_3•Mg–Al LDH was 0.5 g.

Characterization Methods. X-ray diffraction (XRD) data for 2,7-NDS•Mg–Al LDHs and the Mg–Al LDHs loaded with the aromatic compounds were acquired using a diffractometer (RINT 2200; Rigaku, Tokyo, Japan) with Cu Kα radiation at 40 kV and 20 mA (scanning rate of 2° min^{-1}). The Mg and Al contents of the materials were determined by dissolution in 1 M HNO_3 followed by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis. The amount of 2,7-NDS^{2-} in the dissolved solutions was determined by high-pressure liquid chromatography (HPLC). For the adsorption experiments, the residual concentrations of the aromatic compounds in the filtrates were determined by HPLC. The quantity of aromatic compound taken up by 2,7-NDS•Mg–Al LDH was calculated by the subtraction of the quantity (in moles) of the aromatic compound in the filtrate from that in the initial solution. The degree of uptake was defined as the ratio of mole percentage of the aromatic compound in the 2,7-NDS•Mg–Al LDH to that in the initial solution.

Results and Discussion

Preparation. Table 1 shows the chemical compositions of 2,7-NDS•Mg–Al LDHs prepared from solutions of $R_{2,7\text{-NDS}}$ with various values. In this case, $R_{2,7\text{-NDS}}$ represents the ratio of the actual amount of 2,7-NDS^{2-} in solution to the stoichiometric quantity defined by eq 1. For all samples, the Mg/Al molar ratios were approximately 3, which was expected, given the preparation procedure above. The 2,7-NDS/Al molar ratios however, were less than the theoretical values. The theoretical formula in eq 1 predicts a value of 0.5. We can reasonably assume that the actual contents of 2,7-NDS^{2-} in the sample were governed by the electric charge balance in Mg–Al LDH, suggesting the intercalation of 2,7-NDS^{2-} in the interlayer space. $CO_3{}^{2-}$, derived from the dissolution of CO_2 into the preparation solution, may be also intercalated in the interlayer of Mg–Al LDH to neutralize the remaining positive charge.

Figure 3 shows the XRD patterns for CO_3•Mg–Al LDH, and 2,7-NDS•Mg–Al LDHs prepared from solutions with $R_{2,7\text{-NDS}}$ values ranging from 0.5 to 3.0. The XRD peaks observed for CO_3•Mg–Al LDH are ascribed to hydrotalcite (JCPDS card 22-700), a hydroxycarbonate of magnesium and aluminum ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$), which occurs naturally and has the structure of a layered double hydroxide. The XRD peaks of LDH are generally indexed on the basis of a hexagonal unit cell, the basal spacing of which is equivalent to $1/n$-th of the c parameter, where n is the number of the repeat layers in the unit cell.[7] The basal spacing is composed of Al-bearing, brucite-like octahedral layers with interlayer spacing, which is affected by the size and orientation of the intercalated anion. For CO_3•Mg–Al LDH (Figure 3a), the observed basal spacing, d_{003}, was 7.9 Å and was composed of a LDH host layer approximately 4.8 Å thick, with an interlayer spacing of 3.1 Å. The XRD patterns of 2,7-NDS•Mg–Al LDHs (Figures 3b–3e) were similar to those of CO_3•Mg–Al LDH (Figure 3a), although the peaks were broader than those for CO_3•Mg–Al LDH. This suggests that the 2,7-NDS•Mg–Al LDHs have the same basic structure as Mg–Al LDH. In Figures 3b–3e, the d_{003} peak of CO_3•Mg–Al LDH shifted from 11.3° to around 10° (2θ), suggesting basal spacing expansion. From the result shown in Table 1, this was most likely caused by the intercalation of 2,7-NDS^{2-}, which is larger than $CO_3{}^{2-}$, into the interlayer space of Mg–Al LDH. The XRD patterns in Figures 3b and 3c for 2,7-

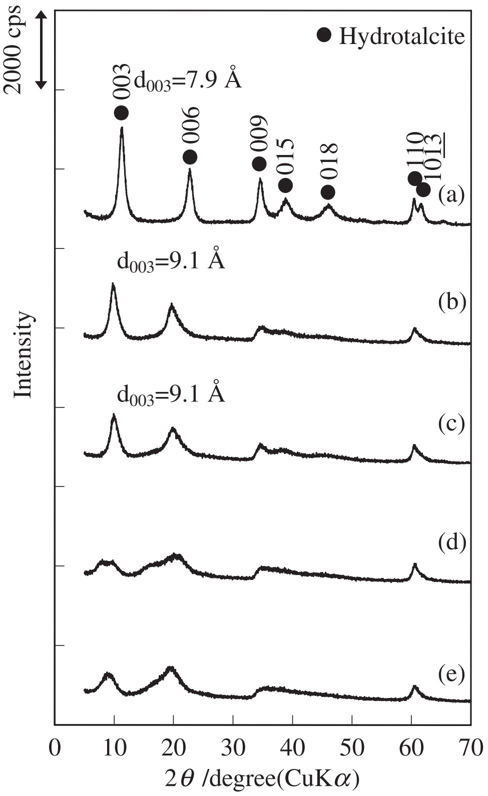

Figure 3. XRD patterns for (a) CO_3•Mg–Al LDH, and 2,7-NDS•Mg–Al LDHs prepared from solutions of $R_{2,7\text{-NDS}} =$ (b) 0.5, (c) 1.0, (d) 2.0, and (e) 3.0.

Table 2. Uptake of Each Aromatic Compound from a Single Solution by 2,7-NDS•Mg–Al LDHs, Prepared with Various $R_{2,7\text{-NDS}}$ Values[a)]

Entry	$R_{2,7\text{-NDS}}$	Uptake/%					
		DNB	NB	BA	AS	DMA	DMB
a	0.5	76.9	52.1	20.0	11.2	14.2	2.1
b	1.0	84.9	58.4	27.8	20.2	23.8	5.1
c	2.0	84.7	56.5	46.4	28.3	20.4	14.2

a) The molar ratio of intercalated 2,7-NDS^{2-} to each compound: 50. Time: 120 min.

Table 3. Uptake of Each Aromatic Compound from a Single Solution by DS•Mg–Al LDH and CO_3•Mg–Al LDH[a)]

Interlayer anion	Uptake/%					
	DNB	NB	BA	AS	DMA	DMB
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

a) The molar ratio of intercalated DS^- to each compound: 50. The amount of CO_3•Mg–Al LDH was 0.5 g. Time: 120 min.

NDS•Mg–Al LDHs of $R_{2,7\text{-NDS}} = 0.5$ and 1.0 show that 2,7-NDS^{2-} was intercalated in a simple configuration, with a basal spacing of 9.0 and 9.1 Å and an interlayer spacing of 4.2 and 4.3 Å, respectively. The molecular structure of 2,7-NDS^{2-} contains a planar-structured naphthalene ring, and the molecular size in the direction perpendicular to the planar structure is determined by the size of the –$SO_3{}^-$ group. By considering the bond length value of S–O to be 1.5 Å, the covalent radius of O to be 0.7 Å, and bonding angle of O–S–O to be 110°, the molecular size in this direction was estimated to be approximately 4 Å. This is very close to the interlayer spacing of 4 Å for the 2,7-NDS•Mg–Al LDHs. The naphthalene ring of 2,7-NDS^{2-} is presumed to be oriented parallel to the brucite-like host layers of 2,7-NDS•Mg–Al LDH. For the XRD patterns in Figures 3d and 3e for 2,7-NDS•Mg–Al LDHs of $R_{2,7\text{-NDS}} = 2.0$ and 3.0, the widely spreading and weakened d_{003} peaks suggest that an irregular arrangement of 2,7-NDS^{2-} in the LDH interlayers leads to stacking of the host layers with irregularly varying basal spacing. This leads to consideration that the two –$SO_3{}^-$ groups in 2,7-NDS^{2-} interact electrostatically with the positive charge of the brucite-like host layer, and the extremities of the individual anions are pinned up to either side of the interlayers. The mobility is limited, not contributing to the well-ordered configuration of 2,7-NDS^{2-} in the interlayers. In the early stages of 2,7-NDS•Mg–Al LDH preparation by the dropwise addition of Mg–Al solution to 2,7-NDS^{2-} solution of $R_{2,7\text{-NDS}} = 2.0$ and 3.0, the Mg–Al LDH lattice developed in the presence of excess amounts of 2,7-NDS^{2-} at a pH of 10.5. This leads to an increase in 2,7-NDS^{2-} content in the interlayer of Mg–Al LDH, resulting in the irregular orientation of 2,7-NDS^{2-} to more effectively accommodate 2,7-NDS^{2-} in the interlayer space. Furthermore, the data in Table 1 shows that the maximum level of intercalation for 2,7-NDS^{2-} is approximately 60% of the expected values for 2,7-NDS•Mg–Al LDH. The low intercalation may be attributable to a greater degree of electrostatic repulsion between intercalated 2,7-NDS^{2-}. 2,7-NDS^{2-}, which is already present in the interlayer space, is presumed to prevent further intercalation of 2,7-NDS^{2-} from solution due to the repulsion of the naphthalene rings. Owing to these reasons, 2,7-NDS^{2-} is assumed to orient in an irregular manner in the interlayer of Mg–Al LDH with the increase of $R_{2,7\text{-NDS}}$ in solution.

Uptake of Aromatic Compound from Aqueous Solution. Tables 2 and 3 show the uptake of each aromatic compound from the single solution by 2,7-NDS•Mg–Al LDHs prepared with various $R_{2,7\text{-NDS}}$ values, DS•Mg–Al LDH, and CO_3•Mg–Al LDH. The uptake of each aromatic compound by 2,7-NDS•Mg–Al LDHs and DS•Mg–Al LDH was larger than that by CO_3•Mg–Al LDH. In the case of CO_3•Mg–Al LDH, in which no chemical modification of the interlayer occurs, the uptake is attributed to the adsorption of the aromatic compounds on the surface of the CO_3•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-NDS^{2-} 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 non-selective uptake is 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.[4] Taking $R_{2,7\text{-NDS}} = 2.0$ (Table 2, Entry c) as an example, with 2,7-NDS•Mg–Al LDHs, 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-NDS^{2-} intercalated in the interlayer spaces of Mg–Al LDH. The uptake is considered 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 –NO_2 and –CHO groups. The strength of NO_2 is greater than that of CHO. DNB has two NO_2 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 does BA. Next, the electronic states of the benzene rings of AS, DMA, and DMB are compared. These compounds are grouped for comparison because all contain electron-donating groups, namely, –OCH_3 and –$N(CH_3)_2$ groups. DMB has two –OCH_3 groups, and thus, the benzene ring of DMB has the largest electron density among these aromatics. The strength of the –$N(CH_3)_2$ group is greater than that of the –OCH_3 group. This suggests that the benzene ring of DMA has a larger density of electrons than does 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-NDS^{2-} intercalated into the interlayer of 2,7-NDS•Mg–Al LDH can be described as follows. 2,7-NDS^{2-} has two –SO_3^- 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-NDS^{2-} probably has a larger density of electrons due to the weak electron-withdrawing ability of the two –SO_3^- groups. The high uptake of aromatic compounds in the decreasing order DNB > NB > BA > AS > DMA > DMB with 2,7-NDS•Mg–Al LDH ($R_{2,7\text{-NDS}} = 2.0$) is caused by π–π stacking interactions between the electron-rich naphthalene ring of 2,7-NDS^{2-} 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 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-NDS^{2-}, and these interactions resulted in the large uptake of aromatics by 2,7-NDS•Mg–Al LDH. Also, Table 2, Entries a and b show that uptake of AS by 2,7-NDS•Mg–Al LDHs prepared with $R_{2,7\text{-NDS}} = 0.5$ and 1.0 was almost the same as that of DMA, in contrast to the case with $R_{2,7\text{-NDS}} = 2.0$. The difference between the strength of –$N(CH_3)_2$ and –OCH_3 groups had less effect on the uptake of AS and DMA by the Mg–Al LDHs.

Figure 4 shows the XRD patterns for 2,7-NDS•Mg–Al LDH ($R_{2,7\text{-NDS}} = 2.0$) loaded with aromatic compounds. Compared with the XRD patterns for original 2,7-NDS•Mg–Al LDH (Figure 3d), no detectable shifts of the diffraction peaks at 2θ around 10°, corresponding to the basal spacing, were observed. This indicates that the uptake of aromatic compound did not cause a detectable change in the interlayer space of 2,7-NDS•Mg–Al LDH. Thus, the uptake of aromatic compound by 2,7-NDS•Mg–Al LDH is probably caused by the incorporation of the aromatic compound into the openings between irregular oriented-naphthalene rings of the 2,7-NDS^{2-} intercalated in the interlayer. Table 2 shows that the uptake of each aromatic compound increased with the increase of $R_{2,7\text{-NDS}}$ from 0.5 to 1.0, i.e., of the 2,7-NDS^{2-} content in 2,7-NDS•Mg–Al LDH. This is attributed to the increase of the intercalated 2,7-NDS^{2-}, leading to increase of reactivity in the interlayer. The same reason is applicable for the increase of the uptake of BA, AS, and DMB with the increase of $R_{2,7\text{-NDS}}$ from 1.0 to 2.0. However, the uptake of DNB and NB was almost the same even when $R_{2,7\text{-NDS}}$ increased from 1.0 to 2.0. This suggests that the electron-rich naphthalene ring of the 2,7-NDS^{2-} intercalated in 2,7-NDS•Mg–Al LDH generated sufficient π–π stacking interactions with the electron-poor benzene ring of aromatics, such as DNB and NB, despite the increased intercalated 2,7-NDS^{2-}.

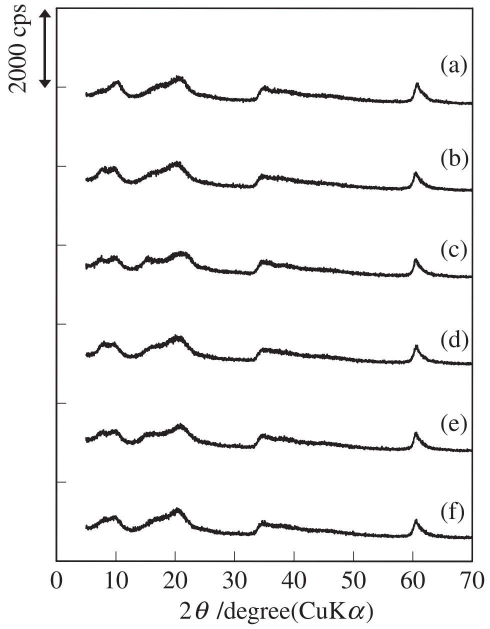

Figure 4. XRD patterns for 2,7-NDS•Mg–Al LDH ($R_{2,7\text{-NDS}} = 2.0$) loaded with (a) DNB, (b) NB, (c) BA, (d) AS, (e) DMA, and (f) DMB.

Figure 5 shows the variation in the uptake of DNB with time during the suspension of 2,7-NDS•Mg–Al LDH ($R_{2,7\text{-NDS}} = 2.0$) in the solution. The molar ratio of intercalated 2,7-NDS^{2-} to each compound was 10, 20, 50, and 100. At 50 and 100, the uptake of DNB increased rapidly within a 10 min period and was then almost constant with time. At 10 and 20, the uptake of DNB increased rapidly within 10 min and then gradually leveled off with time. 2,7-NDS•Mg–Al LDH was found to take up DNB rapidly from an aqueous solution. The uptake of DNB increased with increasing molar ratio of intercalated 2,7-NDS^{2-} to each compound from 10 to 50 at any time, but it was around 80% despite the increase in molar ratio from 50 to 100. The progress of DNB uptake lead to a low concentration of remaining DNB in solution; this low amount of DNB remaining in solution makes further uptake by 2,7-NDS•Mg–Al LDH difficult.

Table 4 shows the uptake of multiple aromatic compounds from mixtures of aqueous solutions by 2,7-NDS•Mg–Al LDH.

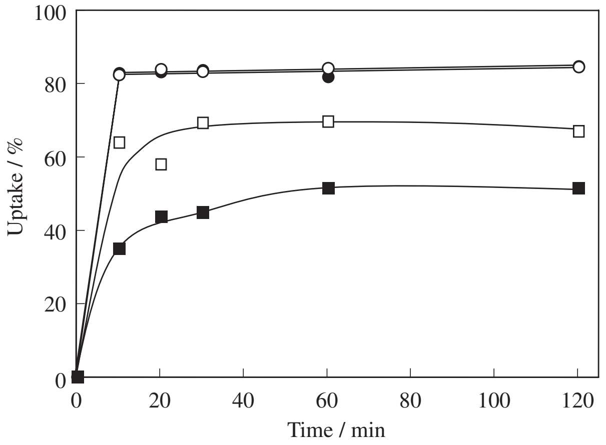

Figure 5. Variation in the uptake of DNB with time during the suspension of 2,7-NDS•Mg–Al LDH ($R_{2,7\text{-NDS}} = 2.0$) in the solution. The molar ratio of intercalated 2,7-NDS^{2-} to each compound was 10 (■), 20 (□), 50 (●), and 100 (○).

Table 4. Uptake of Multiple Aromatic Compounds from Mixtures in Aqueous Solution by 2,7-NDS•Mg–Al LDH, Prepared with $R_{2,7\text{-NDS}} = 2.0$[a)]

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

a) The molar ratio of intercalated 2,7-NDS^{2-} to total compound: 50. Time: 120 min.

Even with 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 2). 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.

Conclusion

2,7-NDS•Mg–Al LDH, which contains 2,7-NDS^{2-} intercalated in the interlayer space, was prepared by coprecipitation. The naphthalene ring of 2,7-NDS^{2-} was probably oriented parallel to the brucite-like host layers of Mg–Al LDH with $R_{2,7\text{-NDS}} = 0.5$ and 1.0. The 2,7-NDS^{2-} was also assumed to orient in an irregular manner in the interlayer of Mg–Al LDH with $R_{2,7\text{-NDS}} = 2.0$ and 3.0. 2,7-NDS•Mg–Al LDH was observed to be capable of absorbing large amounts of aromatics from aqueous solutions, in the decreasing order DNB > NB > BA > AS, DMA > DMB. This is attributed to the different extents of π–π stacking interactions between the naphthalene ring of the intercalated 2,7-NDS^{2-} and the benzene ring of the aromatics (aromatics with different electronic states were examined). In conclusion, Mg–Al LDH intercalated with aromatic anions has the potential to selectively take up hazardous aromatics from waste water due to π–π stacking interactions between the aromatic rings of the hazardous aromatics and those of Mg–Al LDH.

References

1 a) L. Ingram, H. F. W. Taylor, *Mineral. Mag.* **1967**, *36*, 465. b) S. Miyata, *Clays Clay Miner.* **1983**, *31*, 305. c) F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* **1991**, *11*, 173.

2 a) T. Kameda, Y. Miyano, T. Yoshioka, M. Uchida, A. Okuwaki, *Chem. Lett.* **2000**, 1136. b) Y. W. You, H. T. Zhao, G. F. Vance, *Environ. Technol.* **2001**, *22*, 1447. c) Y. You, G. F. Vance, H. Zhao, *Appl. Clay Sci.* **2001**, *20*, 13. d) T. Kameda, T. Yoshioka, M. Uchida, Y. Miyano, A. Okuwaki, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 595. e) J. Orthman, H. Y. Zhu, G. Q. Lu, *Sep. Purif. Technol.* **2003**, *31*, 53. f) T. Yoshioka, T. Kameda, M. Miyahara, M. Uchida, T. Mizoguchi, A. Okuwaki, *Fresenius Environ. Bull.* **2007**, *16*, 928. g) T. Yoshioka, T. Kameda, M. Miyahara, M. Uchida, T. Mizoguchi, A. Okuwaki, *Chemosphere* **2007**, *69*, 832.

3 a) M. V. Villa, M. J. Sánchez-Martin, M. Sánchez-Camazano, *J. Environ. Sci. Health, Part B* **1999**, *34*, 509. b) R. Celis, W. C. Koskinen, M. C. Hermosin, M. A. Ulibarri, J. Cornejo, *Soil Sci. Soc. Am. J.* **2000**, *64*, 36. c) Y. You, H. Zhao, G. F. Vance, *Colloids Surf., A* **2002**, *205*, 161. d) H. Zhao, K. L. Nagy, *J. Colloid Interface Sci.* **2004**, *274*, 613. e) Y. H. Chuang, Y. M. Tzou, M. K. Wang, C. H. Liu, P. N. Chiang, *Ind. Eng. Chem. Res.* **2008**, *47*, 3813.

4 a) T. Kameda, M. Saito, Y. Umetsu, *J. Alloys Compd.* **2005**, *402*, 46. b) T. Kameda, M. Saito, Y. Umetsu, *Mater. Trans.* **2006**, *47*, 923. c) T. Kameda, M. Saito, Y. Umetsu, *Mater. Trans.* **2007**, *48*, 2225.

5 B. W. Gung, J. C. Amicangelo, *J. Org. Chem.* **2006**, *71*, 9261.

6 T. Kameda, T. Yamazaki, T. Yoshioka, *Chem. Lett.* **2009**, *38*, 522.

7 S. P. Newman, W. Jones, *New J. Chem.* **1998**, *22*, 105.