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Cu–Al layered double hydroxides intercalated with 1-naphthol-3,8-disulfonate and dodecyl sulfate: adsorption of substituted phenols from aqueous media

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Abstract

Cu–Al layered double hydroxides (Cu–Al LDHs) intercalated with 1-naphthol-3,8-disulfonate (1-N-3,8-DS^{2-}) and dodecyl sulfate (DS^{-}) were prepared by coprecipitation. Based on X-ray diffraction patterns, the 1-N-3,8-DS^{2-} and DS^{-} are most likely oriented perpendicularly to the brucite-like Cu–Al LDH layers. The 1-N-3,8-DS•Cu−Al LDH was able to adsorb substituted phenols from aqueous solution, with the degree of uptake decreasing in the following order: 3-nitrophenol (N-phe) > 3,5-dichlorophenol (DCl-phe) > 4-chlorophenol (Cl-phe) > 2-methoxy-4-methylphenol (MM-phe) ≈ 4-methoxyphenol (Me-phe). The preferential uptake of the substituted phenols by 1-N-3,8-DS•Cu−Al LDH is attributed to π–π stacking interactions between the phenolic aromatic ring and the naphthalene core of the intercalated 1-N-3,8-DS^{2-}. The DS•Cu−Al LDH also adsorbed substituted phenols from aqueous solution, albeit randomly. This random uptake is attributed to hydrophobic interactions between the alkyl groups of the DS^{-} intercalated in the interlayer and the aromatic rings of the aqueous adsorbates.

Introduction

Layered double hydroxides (LDHs) are represented by the chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where A^{n-} is an anion and x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio ($0.20 \leq x \leq 0.33$).[1–6] LDHs exhibit anion exchange properties[7] and have been shown to intercalate a variety of anions in their interlayer spaces. Recently, the modification of LDHs with organic anions and their application to the uptake of hazardous organic materials from aqueous solution have been investigated. For example, LDHs modified with dodecyl sulfate and sebacate were examined for the uptake of non-ionic pesticides.[8] An LDH modified with dodecylbenzenesulfonate was examined for the adsorption of pentachlorophenol;[9] the adsorption isotherm implied a partitioning sorption process. A dodecyl sulfonate-modified LDH could take up humic acid, and the sorption process was well described by a pseudo-second order model.[10] The dodecyl sulfate-modified LDH adsorbed naphthalene, nitrobenzene, and acetophenone, and the sorption mechanism was the partition between water and the organic interlayer phase composed of the alkyl chains of the dodecyl sulfate.[11] The dodecyl sulfate-modified LDH was also able to remove various dyes from water.[12]

We have shown previously that Mg–Al LDHs intercalated with dodecyl sulfate, 2-naphthalenesulfonate, and 2,6-naphthalenedisulfonate can adsorb bisphenol A from aqueous solutions.[13–15] Furthermore, Mg–Al LDHs intercalated with 2,7-naphthalenedisulfonate (2,7-NDS^{2-}), 1,3,6-naphthalenetrisulfonate (NTS^{3-}), and 3-amino-2,7-naphthalenedisulfonate (ANDS^{2-}) were found to preferentially take up aromatic compounds from aqueous solutions.[16–18] The amount of material adsorbed by the organically modified Mg–Al LDHs depended on the electron-donating or -withdrawing properties of the functional groups on the adsorbate. The adsorption mechanism was dependent on π–π stacking interactions[19] between the aromatic rings of the adsorbates and the naphthalene moieties of 2,7-NDS^{2-}, NTS^{3-}, and ANDS^{2-}. Furthermore, the Mg–Al LDH modified with 1-naphthol-3,8-disulfonate (1-N-3,8-DS^{2-}, Fig. 1) preferentially adsorbed 1,3-dinitrobenzene over 1,2-dimethoxybenzene based on π–π stacking interactions.[20] Size-matching effects have been well discussed in LDH chemistry.[21] In these systems, we have examined the effect of the interlayer spacing of the Mg–Al LDH on its ability to take up a nonionic organic material (NOC). Mg–Al LDH, which has numerous large interlayer spacings when intercalated with organic acid anions, could take up large amounts of NOCs from aqueous solution.[22] In mechanistic terms, a Grotthuss-type proton migration process is sometimes discussed.[23]

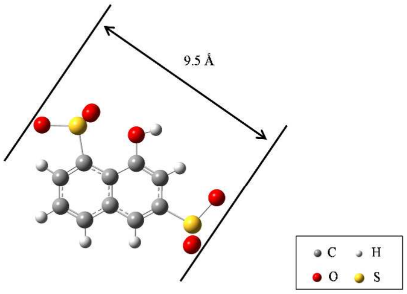


Fig. 1. Molecular structure of 1-naphthol-3,8-disulfonate (1-N-3,8-DS^{2}).

In our system, however, that mechanism does not appear to apply because of less heating and cooling.

In this study, we prepared Cu–Al LDHs intercalated with 1-N-3,8-DS^{2-} and dodecyl sulfate (DS^{-}, Fig. 2), and examined their uptake behaviors toward five substituted phenols in aqueous solution. Because of the strongly electron-donating OH substituent in its intercalated naphthalene core, the Cu–Al LDH incorporating 1-N-3,8-DS^{2-} was expected to preferentially adsorb substituted phenols via π–π stacking interactions. Furthermore, differences in the uptake of the substituted phenols would also be anticipated. The DS^{-}-intercalated Cu–Al LDH was examined as a reference material, because the DS^{-} moiety appears to operate through hydrophobic rather than π–π stacking interactions. Thus, the effects of π–π stacking interactions and hydrophobic interactions on uptake can be distinguished.

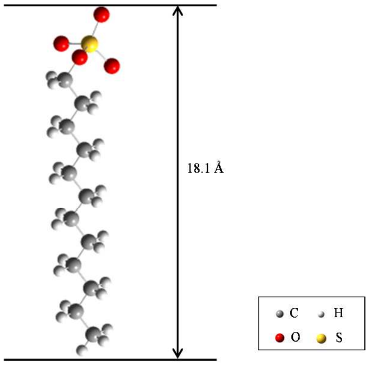


Fig.2. Molecular structure of dodecyl sulfate (DS^{-}).

In aqueous solution, a Mg–Al LDH slurry maintains a constant pH of around 10,[24] whereas with Cu–Al LDH, a constant pH of 6–7 is observed due to the buffering action of Cu^{2+}.[25] For this reason, the latter was used in this study: Cu–Al LDH, with its lower pH, is expected to prevent ionization of the substituted phenols. This study also broadens the scope of adsorbates from aromatic compounds to substituted phenols.

Experimental

All compounds were chemical reagent grade (Kanto Chemical, Ltd. and Wako Pure Chemical Industries, Ltd., Tokyo, Japan) and used without further purification.

Preparation

Cu–Al LDH intercalated with 1-N-3,8-DS^{2-} (1-N-3,8-DS•Cu–Al LDH) [theoretical formula: $Cu_{0.75}Al_{0.25}(OH)_2(C_{10}H_6O_7S_2)_{0.125}$] was prepared by the dropwise addition of a Cu–Al solution to a 1-N-3,8-DS^{2-} solution at a constant pH of 8.0, a constant pH of 9.0, or a constant pH of 10.0. The coprecipitation reaction can be expressed by Eq. (1) below. A stoichiometric coefficient of 0.125 for 1-N-3,8-DS^{2-} ($C_{10}H_6O_7S_2{}^{2-}$) was calculated based on the neutralization of the positive charge of the Al-bearing brucite-like octahedral layers that arises from the replacement of Cu with Al at a Cu/Al molar ratio of 3.0:

$$0.75\ Cu^{2+} + 0.25\ Al^{3+} + 0.125\ C_{10}H_6O_7S_2{}^{2-} + 2\ OH^{-}$$

$$\rightarrow Cu_{0.75}Al_{0.25}(OH)_2(C_{10}H_6O_7S_2)_{0.125}. \qquad (1)$$

In a typical procedure, a Cu–Al solution was prepared with $Cu(NO_3)_2{\bullet}3H_2O$ (0.15 mol/L) and $Al(NO_3)_3{\bullet}9H_2O$ (0.05 mol/L) in deionized water. The 1-N-3,8-DS^{2-} solution was prepared in deionized water at 2.0−4.0 times the stoichiometric quantities defined in Eq. (1). Subsequently, the Cu–Al solution (500 mL) was added dropwise to the 1-N-3,8-DS^{2-} solution (500 mL) at a rate of 10 mL/min at 30°C with gentle agitation. The pH was maintained in the range 8.0–10.0 by adding NaOH solution (1.25 mol/L). The resulting suspensions were allowed to settle at 30°C for 1 h. The 1-N-3,8-DS•Cu–Al LDH particles were recovered by filtration, repeatedly washed with deionized water, and then dried under reduced pressure (133 Pa) at 40°C for 40 h. N_2 was bubbled through the solutions throughout the procedure to minimize the effects of dissolved CO_2.

Cu–Al LDH intercalated with DS^{-} (DS•Cu–Al LDH) [theoretical formula: $Cu_{0.75}Al_{0.25}(OH)_2(C_{12}H_{25}O_4S)_{0.25}$] was also prepared by the dropwise addition of a Cu–Al solution to a DS^{-} solution at a constant pH of 8.0. The coprecipitation reaction can be expressed by Eq. (2) below.

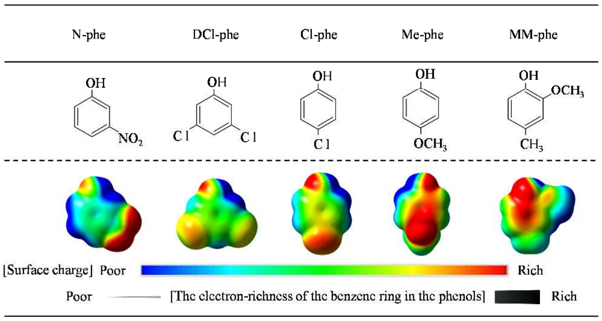
$$0.75\ Cu^{2+} + 0.25\ Al^{3+} + 0.25\ C_{12}H_{25}O_4S^{-} + 2\ OH^{-}$$

$$\rightarrow Cu_{0.75}Al_{0.25}(OH)_2(C_{12}H_{25}O_4S)_{0.25}. \qquad (2)$$

The DS^{-} solution was prepared in deionized water at a stoichiometry equivalent to that defined in Eq. (2).

Uptake of substituted phenols from aqueous solution

Table 1 Chemical structures and surface charges of substituted phenols.



Five substituted phenols, as shown in Table 1, were assessed for uptake: 3-nitrophenol (N-phe), 3,5-dichlorophenol (DCl-phe), 4-chlorophenol (Cl-phe), 4-methoxyphenol (Me-phe), and 2-methoxy-4-methylphenol (MM-phe). Single-compound solutions were prepared at 0.25 mmol/L for each phenol using deionized water. A mixed solution contained 0.25 mmol/L of each component (N-phe, DCl-phe, Cl-phe, Me-phe, and MM-phe) in deionized water. In these cases, the pH of the aqueous phenol solutions was not adjusted. In 50-mL conical flasks, 1-N-3,8-DS•Cu–Al LDH and DS•Cu–Al LDH were each mixed with 20 mL of each single-compound solution or the mixed solution. The quantity of the Cu–Al LDH added was such that the molar ratio of intercalated 1-N-3,8-DS^{2-} or DS^{-} to each compound was 100:1. Each mixture was shaken at 20°C for 2 h. The resulting suspensions were filtered, and the filtrate was analyzed for phenol content.

Characterization methods

X-ray diffraction (XRD) data for the 1-N-3,8-DS•Cu–Al LDH, DS•Cu–Al LDH, and Cu–Al LDHs loaded with the different substituted phenols were acquired using a RINT 2200 diffractometer (Rigaku, Tokyo, Japan) (Cu Kα radiation, 40 kV, 20 mA, and 2°/min scan rate). The Cu and Al contents of the materials were determined after dissolution in 1 mol/L HNO_3 followed by inductively coupled plasma–atomic emission spectrometry (ICP–AES). The quantity of 1-N-3,8-DS^{2-} in the dissolved solution was determined by high-performance liquid chromatography (HPLC). The C, H, and S contents of DS^{-} in DS•Cu–Al LDH were determined by combustion analysis, allowing the calculation of the DS content. For each adsorption experiment, the concentrations of the substituted phenols in the filtrates were determined by HPLC. Furthermore, the pH of the filtrates was measured, and the degree of electrolytic dissociation (ϕ_{ions}) of the substituted phenol was calculated based on Eq. (3).[26]

$$\emptyset_{ions} = \frac{1}{1+10^{\mathrm{p}K_a-\mathrm{pH}}} \times 100 \qquad (3)$$

In addition, the specific surface areas of 1-N-3,8-DS•Cu–Al LDH and DS•Cu–Al LDH were determined by the Brunauer-Emmett-Teller (BET) method using N_2 adsorption-desorption isotherms.

Theoretical calculations

The molecular geometries and sizes of the isolated 1-N-3,8-DS^{2-}, DS^{-}, and the substituted phenols in the ground state were calculated by an *ab initio* Hartree–Fock method utilizing an STO-3G basis set in Gaussian 03.[27]

Results and discussion

Preparation

Table 2 shows the chemical compositions of the 1-N-3,8-DS•Cu−Al

Table 2 Chemical compositions of 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with an R^a value of 2.0 at various pH values.

	pH	wt%			molar ratio	
		Cu	Al	1-N-3,8-DS	Cu/Al	1-N-3,8-DS/Al
(a)	8.0	35.9	4.6	12.3	3.3	0.24
(b)	9.0	36.3	4.5	17.1	3.5	0.34
(c)	10.0	39.0	4.6	14.8	3.6	0.29

^{a}*R* represents the ratio of the actual amount of 1-N-3,8-DS^{2-} in solution to the stoichiometric quantity defined by Eq. (1).

LDHs prepared from solutions with an R value of 2.0 at various pH values, where R represents the ratio of the actual amount of 1-N-3,8-DS^{2-} in solution to the stoichiometric quantity defined by Eq. (1). For all samples, the Cu/Al molar ratios were over 3.0, which was the value theoretically predicted from Eq. (1). In particular, the Cu/Al molar ratio increased with increasing pH, suggesting the dissolution of Al^{3+} from the 1-N-3,8-DS•Cu−Al LDH. This type of dissolution has been already reported by Yamaoka et al.[28] The actual 1-N-3,8-DS/Al molar ratios were less than the value of 0.5 theoretically predicted from Eq. (1). We assumed that the actual content of 1-N-3,8-DS^{2-} in the samples was governed by the electric charge balance in the Cu–Al LDH, and hence, we expected that 1-N-3,8-DS^{2-} was intercalated in the interlayer spaces.

Figure 3 shows the XRD patterns for the CO_3•Cu−Al LDH and 1-N-3,8-DS•Cu−Al LDH prepared from solutions with an R value of 2.0 at pH 8.0, 9.0, and 10.0. The XRD peaks for CO_3•Cu–Al LDH (Fig. 3a) were ascribed to copper aluminum carbonate hydroxide hydrate (JCPDS card 37-630), formulated as $Cu_6Al_2(OH)_{16}CO_3$•$4H_2O$ with a layered double hydroxide structure. The

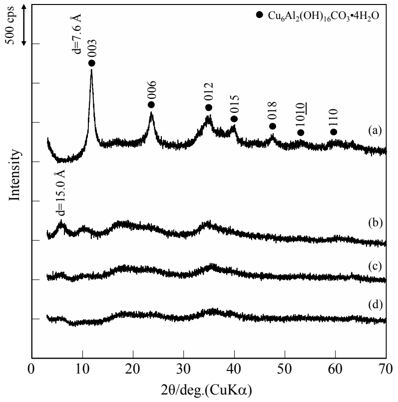


Fig.3 XRD patterns for (a) CO_3•Cu−Al LDH and the 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with an R value of 2.0 at (b) pH 8.0, (c) pH 9.0, and (d) pH 10.0.

XRD peaks corresponding to LDHs are generally indexed on the basis of a hexagonal unit cell with a basal spacing equivalent to $1/n^{\text{th}}$ of the c parameter, where n is the number of repeat layers in the unit cell.[29] The basal spacing results from the Al-bearing brucite-like octahedral layers, and the interlayer spacing is affected by the size and orientation of the intercalated anions. For CO_3•Cu–Al LDH, the observed basal spacing d_{003} was 7.6 Å, with an LDH host layer thickness of approximately 4.8 Å and an interlayer spacing of 2.8 Å. The XRD patterns for the 1-N-3,8-DS•Cu–Al LDHs (Figs. 3b–d) and CO_3•Cu–Al LDH (Fig. 3a) were similar, although the peaks were broader for the former. This suggests that 1-N-3,8-DS•Cu–Al LDH has the same basic structure as Cu–Al LDH. The basal spacing of 15.0 Å in Fig. 3b, with an interlayer spacing of 10.2 Å, is larger than that observed in CO_3•Cu–Al LDH. The data shown in Table 2 suggest that this difference is most likely caused by the intercalation of 1-N-3,8-DS^{2-}, which is larger than CO_3^{2-}, into the interlayer space of the Cu–Al LDH. The XRD peaks for the 1-N-3,8-DS•Cu–Al LDHs prepared at pHs of 9.0 and 10.0 were much broader than those at pH 8.0, indicating their lower crystallinity. This is attributed to the dissolution of Al^{3+} from the 1-N-3,8-DS•Cu–Al LDH at higher pH. In sum, preparation at pH 8.0 is considered to be the most appropriate of the three pH conditions, because the 1-N-3,8-DS•Cu–Al LDH has higher crystallinity and the Cu/Al molar ratio is closer to the expected value, 3.0.

Table 3 shows the chemical compositions of 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with various *R* values at pH 8.0. For all samples, the Cu/Al molar ratio was approximately 3, as expected, given the preparation procedure outlined above. The 1-N-3,8-DS/Al molar ratio increased with increasing *R* value from 2.0 to 3.0, but was constant even with an increasing *R* value from 3.0 to 4.0. The full intercalation of 1-N-3,8-DS^{2-} in the interlayers of Cu–Al LDH occurred at a 1-N-3,8-DS/Al molar ratio of 0.38.

Table 3 Chemical compositions of 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with various *R*[a] values at pH 8.0.

	R[a]	wt%			molar ratio	
		Cu	Al	1-N-3,8-DS	Cu/Al	1-N-3,8-DS/Al
(a)	2.0	35.9	4.6	12.3	3.3	0.24
(b)	3.0	35.1	5.5	23.3	2.7	0.38
(c)	4.0	36.8	5.0	20.9	3.2	0.38

[a] *R* represents the ratio of the actual amount of 1-N-3,8-DS^{2-} in solution to the stoichiometric quantity defined by Eq. (1).

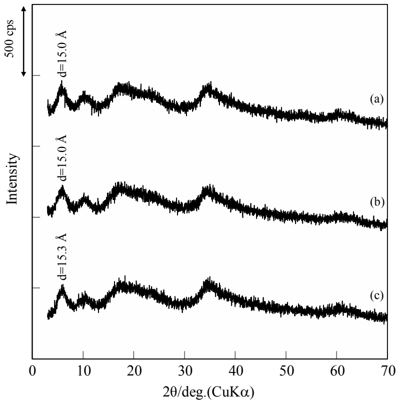


Fig.4 XRD patterns for 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with *R* values of (a) 2.0, (b) 3.0, and (c) 4.0 at pH 8.0.

Figure 4 shows the XRD patterns for the 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with *R* values of 2.0, 3.0, and 4.0 at pH 8.0. All the samples showed similar XRD patterns, indicating the basic Cu–Al LDH structure. The basal spacing was 15.0–15.3 Å, suggesting the intercalation of 1-N-3,8-DS^{2-}. Basal spacings of 15.0 and 15.3 Å give interlayer spacings of 10.2 and 10.5 Å. From the molecular structure shown in Fig. 1, the length of 1-N-3,8-DS^{2-} was calculated as 9.5 Å. This value is less than the abovementioned interlayer spacing, and therefore, the 1-N-3,8-DS^{2-} is most likely oriented perpendicularly to the brucite-like Cu–Al LDH layers, as illustrated in Fig. 5. However, Fig. 4 indicates that the crystallinity of the 1-N-3,8-DS•Cu−Al LDHs is very low. This suggests an irregular arrangement of 1-N-3,8-DS^{2-} in the Cu-Al LDH interlayers, which is attributed to the limited mobility of the 1-N-3,8-DS^{2-} resulting from the immobilization of the two anionic –SO_3^- groups on either side of the interlayer.[11]

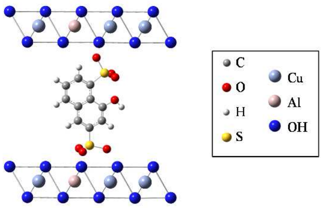


Fig.5 Proposed molecular orientation of 1-N-3,8-DS^{2} intercalated in the Cu−Al LDH interlayer.

In summary, Cu–Al LDH intercalated with 1-N-3,8-DS^{2-} was prepared by dropwise addition of a Cu–Al solution to a 1-N-3,8-DS^{2-} solution. For the adsorption experiments described below, 1-N-3,8-DS•Cu–Al LDH was prepared from a solution with an *R* value of 3.0 at pH 8.0, as this yielded higher crystallinity and the largest 1-N-3,8-DS/Al molar ratio.

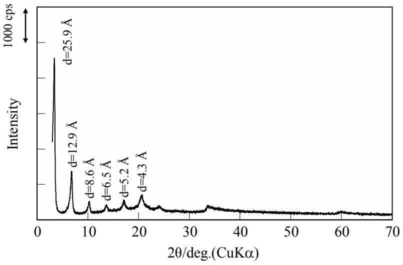


Fig.6 XRD pattern for DS•Cu−Al LDH.

Figure 6 shows the XRD patterns for DS•Cu−Al LDH. The peaks for this compound at 2θ values above 30° were similar to those for CO_3•Cu–Al LDH shown in Fig. 3(a). This suggests that DS•Cu−Al LDH has the same basic structure as Cu–Al LDH. The XRD patterns also show diffraction peaks at low peak angles corresponding to d = 25.9 Å, with higher reflections, which indicate the formation of layered materials. The XRD patterns consist of peaks at 2θ values of 3°, 7°, 10°, 14°, 17°, and 21°, corresponding to the basal spacings d = 25.9, 12.9, 8.6, 6.5, 5.2, and 4.3 Å, respectively. These results suggest that the DS•Cu−Al LDH has an expanded basal spacing with a d_{001} of 25.9 Å.

Table 4 shows the chemical composition of DS•Cu−Al LDH. The Cu/Al molar ratio is 3.0, which is similar to the theoretical value. The DS/Al molar ratio was more than the value of 1.0 theoretically predicted from Eq. (2). This implies that Cu^{2+} and Al^{3+} in the starting nitrate solution were not completely precipitated, leading to the DS^{-} remaining in the solution. This remaining DS^{-} was probably taken up in the interlayer more than expected on the basis of the electric charge balance. These results suggest that the additional DS^{-} is stably incorporated in the LDH through dissolution in the DS^{-}-filled interlayers via hydrophobic interactions between the alkyl groups of the intercalated and free DS^{-} species. Figure 6 shows that a basal spacing of 25.9 Å affords an interlayer spacing of 21.1 Å. From Fig. 2, we see that the length of a DS^{-} molecule is 18.1 Å. This value is lower than the abovementioned interlayer spacing. Therefore, the DS^{-} is most likely perpendicularly oriented to the brucite-like Cu–Al LDH layers, as illustrated in Fig. 7. This DS•Cu−Al LDH was also used for the adsorption experiments described below.

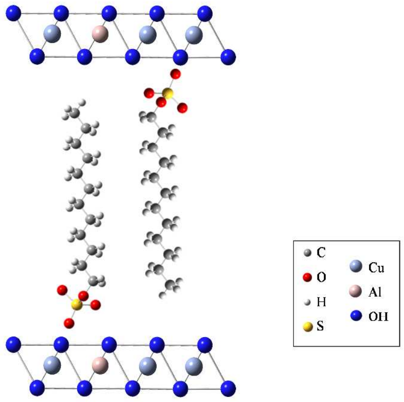


Fig.7 Proposed molecular orientation of DS^{-} intercalated in the Cu−Al LDH interlayer.

Uptake of substituted phenols from aqueous solution

Table 5 shows the pH after the uptake of substituted phenols by 1-N-3,8-DS•Cu−Al LDH and the degrees of electrolytic dissociation (ϕ_{ions}) of the phenols. The ϕ_{ions} was 4.67% for N-phe, suggesting that the phenols were mostly neutral in the aqueous solution, and further indicates that uptake by the 1-N-3,8-DS•Cu−Al LDH was not principally via anion exchange reaction.

Table 5 pH after the uptake of substituted phenols by 1-N-3,8-DS•Cu−Al LDH and degree of electrolytic dissociation (ϕ_{ions}) of the phenol.

	N-phe	DCl-phe	Cl-phe	Me-phe	MM-phe
pH	6.76	6.74	6.76	6.72	6.73
pK_a[a]	8.09	8.18	9.14	10.1	10.3
Φ_{ions} / %	4.67	3.50	0.415	0.0417	0.0288

[a] Cited from Refs. [30,31].

Table 6 Percentage uptake of each substituted phenol from single-compound solutions by different Cu-Al LDHs.

Interlayer anion	Uptake / %				
	N-phe	DCl-phe	Cl-phe	Me-phe	MM-phe
1-N-3,8-DS^{2-}	78.0	50.9	24.0	14.4	15.0
DS^{-}	23.2	62.8	17.4	0	11.0

Table 6 shows the percentage uptake of each substituted phenol from single-compound solutions by different Cu-Al LDHs. The 1-N-3,8-DS•Cu−Al LDH was able to take up each substituted phenol from single-compound solutions. The DS•Cu−Al LDH was also able to take up the substituted phenols except for Me-phe from the single-compound solutions. For DS•Cu−Al LDH, the largest degree of adsorption was 62.8% for DCl-phe, but was below 25% for the other four phenols. This random uptake is attributed to hydrophobic interactions[32] between the alkyl groups of the intercalated DS^{-} and the aromatic rings of the substituted phenols in the aqueous solution. The partition coefficients are known: 2.00, 3.68, 2.39, 1.34, and 1.82 for N-phe, DCl-phe, Cl-phe, Me-phe, and MM-phe, respectively.[33–37] The partition coefficient for DCl-phe is the largest of the five phenols. Therefore, the largest degree of uptake for DCl-phe is attributed to a stronger hydrophobic interaction caused by its larger hydrophobicity. On the other hand, the lower degree of uptake for Me-phe is in agreement with its lower hydrophobicity. For 1-N-3,8-DS•Cu−Al LDH, the degree of uptake decreased in the following order: N-phe > DCl-phe > Cl-phe > MM-phe ≈ Me-phe. The maximum and minimum degrees of uptake were 78.0% for N-phe and 14.4% for Me-phe. These results indicate that the uptake is highly dependent on the type of substituted phenol being adsorbed. However, in the uptake experiments of the substituted phenols, the molar ratio of intercalated 1-N-3,8-DS^{2-} or DS^{-} to each compound was 100:1. The maximum uptake was 78% for N-phe in the case of intercalated 1-N-3,8-DS^{2-}. This is a very low amount in terms of the 1-N-3,8-DS^{2-} intercalated in the interlayer of the Cu-Al LDH, and suggests that adsorption must nearly always occur by the accessible anionic species at the entry of the galleries. The preferential uptake of substituted phenols by 1-N-3,8-DS•Cu−Al LDH is attributed to π–π stacking interactions between the aromatic ring of the substituted phenol and the naphthalene core of the 1-N-3,8-DS^{2-} intercalated in the Cu–Al LDH interlayer spaces. The adsorption probably depends on the electron-richness of the benzene ring in the adsorbate, which is dependent on the attached functional groups. N-phe, DCl-phe, and Cl-phe bear electron-withdrawing groups. The electron-withdrawing effect occurs strongly under the influence of *meta*-directing NO_2 groups and *ortho*- and *para*-directing Cl groups. N-phe has a *meta*-directing NO_2 group, but DCl-phe has a *meta*-directing Cl group. The strength of electron withdrawal by the NO_2 group is probably greater than that of the *meta*-directing Cl group. Although the DCl-phe has two Cl groups, the benzene ring of N-phe is more electron-deficient than that of DCl-phe. Table 1 shows the surface charges of the substituted phenols. The change of color in the order of blue, green, yellow, and red expresses the change in the surface charge from electron-poor to electron-rich. Table 1 supports that the benzene ring of N-phe is the most electron-poor among the substituted phenols. The benzene ring of DCl-phe is more electron-poor than that of Cl-phe due to the difference in the number of Cl groups. The comparative electron-richness of Me-phe and MM-phe can be considered similarly. The benzene ring of MM-phe, with both OCH_3 and CH_3 electron-donating groups, is more electron-rich than that of Me-phe, with a single OCH_3. Table 1 also validates the higher electron-richness of MM-phe among the phenol substrates. Thus, the electron-richness of the benzene ring in the substituted phenols increases in the following order: N-phe < DCl-phe < Cl-phe < Me-phe < MM-phe.

The electron-rich nature of the naphthalene cores of 1-N-3,8-DS^{2-} intercalated into the interlayers of Cu–Al LDH can also be considered in terms of the attached substituents. The aromatic core of 1-N-3,8-DS^{2-} has one OH group and two SO_3^- groups, which are electron donating and weakly electron withdrawing, respectively. The naphthalene core is more electron-rich than benzene; therefore, the naphthalene core of 1-N-3,8-DS^{2-} is probably more electron-rich than the benzene ring, as the SO_3^- group is only weakly electron withdrawing. The high uptake of substituted phenols, which occurs in the decreasing order N-phe > DCl-phe > Cl-phe > Me-phe ≈ MM-phe, definitely results from the π–π stacking interactions between the electron-rich naphthalene cores of 1-N-3,8-DS^{2-} intercalated into the Cu-Al LDH interlayers and the benzene rings of the substituted phenols. In sum, the electron-poor aromatic rings of the phenols interact strongly with the electron-rich naphthalene cores of the intercalated 1-N-3,8-DS^{2-}, and these interactions result in the high uptake of substituted phenols by 1-N-3,8-DS•Cu−Al LDH.

The specific surface areas of 1-N-3,8-DS•Cu−Al LDH and DS•Cu−Al LDH were determined to be 2.1 and 0.6 m^2/g, respectively. The larger specific surface area of 1-N-3,8-DS•Cu−Al LDH compared to DS•Cu−Al LDH is attributed to the lower crystallinity of the former, as shown in Fig. 4(b) and Fig. 6. This may be related to the fact that the maximum uptake by 1-N-3,8-DS•Cu−Al LDH (i.e. 78.0% of N-phe) is larger than that by DS•Cu−Al LDH (i.e. 62.8% of DCl-phe), as shown in Table 6.

Figure 8 shows the XRD patterns for 1-N-3,8-DS•Cu−Al LDH after uptake of the five individual substrates. Comparing these with the XRD patterns for the original 1-N-3,8-DS•Cu−Al LDH (Fig. 4b), no detectable shifts of the diffraction peak at the angle corresponding to the basal spacing of 15 Å were observed, indicating that the uptake of substituted phenols did not disrupt the interlayer spacing in the LDH. The uptake of substituted phenols by this LDH probably occurs by their incorporation into the openings between the perpendicularly oriented naphthalene rings of the intercalated 1-N-3,8-DS^{2-}.

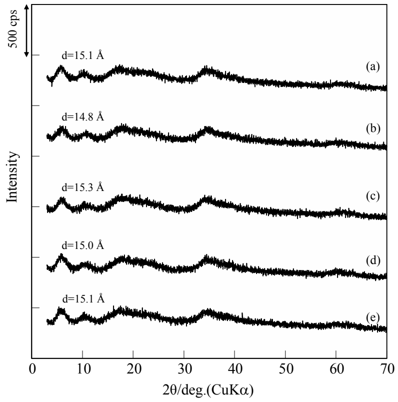


Fig.8 XRD patterns for 1-N-3,8-DS•Cu−Al LDH after uptake of (a) N-phe, (b) DCl-phe, (c) Cl-phe, (d) Me-phe, and (e) MM-phe.

Figure 9 shows the XRD patterns for DS•Cu−Al LDH after uptake of the five phenols. Comparing the XRD patterns for the original DS•Cu−Al LDH (Fig. 6) and DS•Cu−Al LDH loaded with the substituted phenols (Fig. 9), no detectable shifts of the diffraction peak at the angle corresponding to the basal spacing of 26 Å were observed, also indicating that the uptake of substituted phenols did not disrupt the interlayer spacing of DS•Cu−Al LDH. Table 7 shows the percentage uptake from the mixed substituted phenols by 1-N-3,8-DS•Cu−Al LDH. This LDH showed good uptake of the substrates from the mixed solution, in the decreasing order N-phe > DCl-phe > Cl-phe > Me-phe > MM-phe. This order was almost same as that for the uptake of substituted phenols from the single-compound solutions (Table 6). The 1-N-3,8-DS•Cu−Al LDH was found to preferentially take up electron-deficient substituted phenols from the mixed solution.

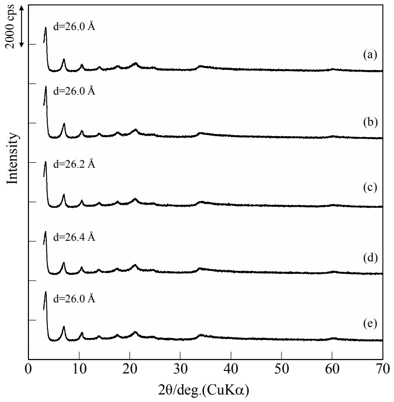


Fig.9 XRD patterns for DS•Cu−Al LDH after uptake of (a) N-phe, (b) DCl-phe, (c) Cl-phe, (d) Me-phe, and (e) MM-phe.

Table 7 Percentage uptake of multiple substituted phenols from mixed solution by 1-N-3,8-DS•Cu−Al LDH.

Uptake / %				
N-phe	DCl-phe	Cl-phe	Me-phe	MM-phe
73.9	56.1	14.0	7.1	4.6

Conclusions

A Cu–Al layered double hydroxide intercalated with 1-naphthol-3,8-disulfonate (1-N-3,8-DS•Cu−Al LDH) and a Cu–Al layered double hydroxide intercalated with dodecyl sulfate (DS•Cu−Al LDH) were prepared by a coprecipitation technique. The intercalated 1-N-3,8-DS^{2-} and DS^{-} species were most likely oriented perpendicularly to the brucite-like Cu–Al LDH layers. The 1-N-3,8-DS•Cu−Al LDH was able to take up each substituted phenol from single-compound solutions, and the degree of uptake decreased in the order 3-nitrophenol (N-phe) > 3,5-dichlorophenol (DCl-phe) > 4-chlorophenol (Cl-phe) > 2-methoxy-4-methylphenol (MM-phe) ≈ 4-methoxyphenol (Me-phe). The DS•Cu−Al LDH was also able to take up the substituted phenols from single-compound solutions, albeit non-preferentially. This random uptake is attributed to the hydrophobic interactions between the alkyl groups of the DS^{-} intercalated in the interlayer and the benzene rings of the substituted phenols in the aqueous solution. The preferential uptake of substituted phenol by 1-N-3,8-DS•Cu−Al LDH is attributed to the π–π stacking interactions between the benzene rings of the substituted phenols and the naphthalene core of the intercalated 1-N-3,8-DS^{2-}. In sum, the electron-deficient benzene rings of some of the substituted phenols interacted strongly with the electron-rich naphthalene cores of the intercalated 1-N-3,8-DS^{2-}. The 1-N-3,8-DS•Cu−Al LDH was also found to preferentially take up substituted phenols with electron-poor benzene rings from the mixed solution.

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Figure captions

Figure 1.

Molecular structure of 1-naphthol-3,8-disulfonate (1-N-3,8-DS^{2-}).

Figure 2.

Molecular structure of dodecyl sulfate (DS^{-}).

Figure 3.

XRD patterns for (a) CO_3•Cu−Al LDH and the 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with an *R* value of 2.0 at (b) pH 8.0, (c) pH 9.0, and (d) pH 10.0.

Figure 4.

XRD patterns for 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with *R* values of (a) 2.0, (b) 3.0, and (c) 4.0 at pH 8.0.

Figure 5.

Proposed molecular orientation of 1-N-3,8-DS^{2-} intercalated in the Cu−Al LDH interlayer.

Figure 6.

XRD pattern for DS•Cu−Al LDH.

Figure 7.

Proposed molecular orientation of DS^- intercalated in the Cu−Al LDH interlayer.

Figure 8.

XRD patterns for 1-N-3,8-DS•Cu−Al LDH after uptake of (a) N-phe, (b) DCl-phe, (c) Cl-phe, (d) Me-phe, and (e) MM-phe.

Figure 9.

XRD patterns for DS•Cu−Al LDH after uptake of (a) N-phe, (b) DCl-phe, (c) Cl-phe, (d) Me-phe, and (e) MM-phe.

Table captions

Table 1

Chemical structures and surface charges of substituted phenols.

Table 2

Chemical compositions of 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with an R^a value of 2.0 at various pH values.

Table 3

Chemical compositions of 1-N-3,8-DS•Cu−Al LDHs prepared from solutions with various R^a values at pH 8.0.

Table 4

Chemical composition of DS•Cu−Al LDH.

Table 5

pH after the uptake of substituted phenols by 1-N-3,8-DS•Cu−Al LDH and degree of electrolytic dissociation (ϕ_{ions}) of the phenol.

Table 6

Percentage uptake of each substituted phenol from single-compound solutions by different Cu-Al LDHs.

Table 7

Percentage uptake of multiple substituted phenols from mixed solution by 1-N-3,8-DS•Cu−Al LDH.