

Selective Uptake of Aromatic Compounds from Aqueous Solutions by Mg–Al Layered Double Hydroxide Intercalated with 2,7-Naphthalenedisulfonate

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Mg–Al layered double hydroxide intercalated with 2,7-naphthalenedisulfonate ions (2,7-NDS•Mg–Al LDH) selectively absorbs aromatic compounds from aqueous solutions. The amount of material absorbed by 2,7-NDS•Mg–Al LDH depends on the electron-donating or electron-withdrawing properties of the functional groups on the molecules to be absorbed. The absorption mechanism is dependent on the 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 $[\text{Mg}^{2+}_{1-x}\text{Al}^{3+}_x(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, 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 wastewater treatment applications, i.e., for the removal of contaminants from wastewater.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 dodecyl sulfate ions (DS^-), 2-naphthalenesulfonate ions (2-NS^-), and 2,6-naphthalenedisulfonate ions ($2,6\text{-NDS}^{2-}$) has been observed to absorb bisphenol A from an aqueous solution.³ The absorption is attributable to hydrophobic interactions between bisphenol A and the intercalated organic anions. In wastewater 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 wastewater stream. To realize this selective uptake, the electronic state of the aromatic intercalated anions can be manipulated by the addition of electron-donating or electron-withdrawing substituents, thereby activating or deactivating the aromatic rings, respectively.⁴ Activated and deactivated systems are highly reactive, and reactions involving these systems generally yield products with a π – π stacking geometry.⁴ Mg–Al LDHs intercalated with aromatic anions are therefore expected to selectively absorb hazardous aromatics from wastewater owing to the strong electrostatic attraction between the aromatic rings of Mg–Al LDHs and those of the hazardous aromatics. In this study, we examine the selective uptake of six aromatic compounds with different functional groups from an aqueous solution containing Mg–Al LDH intercalated with 2,7-naphthalenedisulfonate ion (2,7-NDS^{2–}).

2,7-NDS-intercalated Mg–Al LDH (2,7-NDS•Mg–Al LDH) was prepared by performing a coprecipitation reaction, similar to the preparation of Mg–Al LDH intercalated with 2-NS[–] or 2,6-NDS^{2–}.³ The amounts of Mg^{2+} , Al^{3+} , and 2,7-NDS^{2–} contained in the final 2,7-NDS•Mg–Al LDH product were 19.5, 7.6, and 25.0 wt %, respectively. From these values, the molar ratios of Mg/Al and 2,7-NDS/Al were calculated as 2.9 and 0.31, respectively. The six aromatic compounds considered were 1,2-di-

methoxybenzene (DMB), *N,N*-dimethylaniline (DMA), anisole (AS), benzaldehyde (BA), nitrobenzene (NB), and 1,3-dinitrobenzene (DNB). In a 50-mL Erlenmeyer flask, 2,7-NDS•Mg–Al LDH was added to 20 mL of a 0.5 mM solution of each compound or multiple compounds. The amount of 2,7-NDS•Mg–Al LDH added was such that the molar ratio of intercalated 2,7-NDS^{2–} to each compound was 50. The flask was shaken at 20 °C for 2 h. The resulting suspension was filtered, and the concentration of each compound in the filtrate was determined by high-pressure liquid chromatography (HPLC). X-ray diffraction (XRD) data for 2,7-NDS•Mg–Al LDH before and after the uptake of aromatic compound were acquired using a diffractometer with Cu K α radiation. In order to demonstrate the effect of the interlayer anions on the absorption of aromatics, DS^- -intercalated Mg–Al LDH ($\text{DS}\cdot\text{Mg}\text{--}\text{Al LDH}$)³ and CO_3^{2-} -intercalated Mg–Al LDH ($\text{CO}_3\cdot\text{Mg}\text{--}\text{Al LDH}$) were also used as reference materials. In the case where $\text{DS}\cdot\text{Mg}\text{--}\text{Al LDH}$ was added to the aqueous solutions, the molar ratio of intercalated DS^- to each compound was 50. The amount of $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al LDH}$ was 0.5 g.

As shown in Figure 1a, the XRD peaks observed for 2,7-NDS•Mg–Al LDH were ascribed to hydrotalcite (JCPDS card 22-700), a hydroxycarbonate of magnesium and aluminum ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$), which occurs naturally and has the structure of a layered double hydroxide. Table 1 shows the uptake of each aromatic compound from the aqueous solutions when different Mg–Al LDHs are added. The uptake of each aromatic compound by 2,7-NDS•Mg–Al LDH and $\text{DS}\cdot\text{Mg}\text{--}\text{Al LDH}$ is larger than that by $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al LDH}$. In the case of $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al LDH}$ in which there is no chemical modification of the interlayer, the uptake is attributed to the adsorption of the aromatic compounds on the surface of the particles of $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al LDH}$. The high uptake by 2,7-NDS•Mg–Al LDH and $\text{DS}\cdot\text{Mg}\text{--}\text{Al LDH}$ is therefore 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 $\text{DS}\cdot\text{Mg}\text{--}\text{Al LDH}$, the maximum and minimum uptake

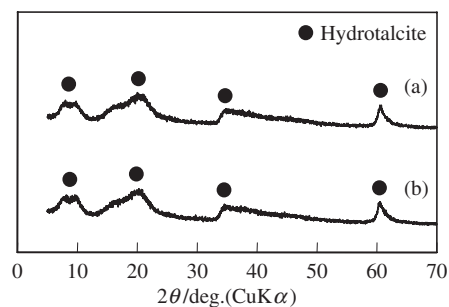


Figure 1. XRD patterns for (a) 2,7-NDS•Mg–Al LDH and (b) NB-loaded 2,7-NDS•Mg–Al LDH.

Table 1. Uptake of each aromatic compound from aqueous solutions by different Mg–Al LDHs

Interlayer anion	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

are 75.0% for DMA and 41.5% for BA, respectively, and the dependence of the uptake on the type of aromatic compound is low. This nonselective uptake is due to the hydrophobic interaction between the alkyl groups of DS⁻ intercalated in the interlayer and the benzene ring of the compound in the aqueous solution.³ On the other hand, in the case of 2,7-NDS•Mg–Al LDH, the uptake decreases in the following order: DNB > NB > BA > AS > DMA > DMB. The maximum and minimum uptake are 84.7% for DNB and 14.2% for DMB, and the dependence of the uptake on the type of aromatic compound is high. This selective uptake is attributable to the 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 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 DMB, DMA, and AS are compared. These compounds are grouped for the comparison because all of them contain electron-donating groups, namely, OCH₃ and N(CH₃)₂ groups. DMB has two OCH₃ groups, and therefore, the benzene ring of DMB has the largest number of electrons among the 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 number of electrons than that of AS. Subsequently, the electronic states of the benzene rings of BA, NB, and DNB are compared. All these compounds contain electron-withdrawing groups, namely, CHO and NO₂ groups. The strength of NO₂ is greater than CHO. This suggests that the benzene ring of NB has a smaller number of electrons than that of BA. DNB has two NO₂ groups, and therefore, the benzene ring of DNB has the smallest number of electrons among the aromatics. In other words, the number of electrons in the benzene ring in the aromatics decreases 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, and therefore, the naphthalene ring of 2,7-NDS²⁻ probably has a large number of electrons due to the poor electron-withdrawing ability of the two SO₃⁻ groups. The high uptake of aromatic compounds in the decreasing order DNB > NB > BA > AS > DMA > DMB is definitely caused by the 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 a smaller number of electrons in the decreasing order DMB > DMA > AS > BA > NB > DNB. That is, the electron-poor benzene ring of aromatics shows strong interactions with the electron-rich naphthalene ring of intercalated 2,7-NDS²⁻, and

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

	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

these interactions result in the large uptake of aromatics by 2,7-NDS•Mg–Al LDH. Figure 1b shows the XRD patterns for NB-loaded 2,7-NDS•Mg–Al LDH. Compared to the XRD patterns for 2,7-NDS•Mg–Al LDH (Figure 1a), 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 such as NB did not cause the detectable change of the interlayer space of 2,7-NDS•Mg–Al LDH. Table 2 shows the uptake of multiple aromatic compounds from mixtures of aqueous solutions containing 2,7-NDS•Mg–Al LDH. Even in the case of the mixtures of aqueous solutions, the uptake is high; the uptake decreases in the order DNB > (NB) > BA > (AS) > DMB. 2,7-NDS•Mg–Al LDH is found to selectively absorb aromatic compounds with electron-poor benzene rings from the mixtures of aqueous solutions.

In summary, 2,7-NDS•Mg–Al LDH is 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 the π – π stacking interactions between the naphthalene ring of the intercalated 2,7-NDS²⁻ and the benzene ring of the aromatics (Aromatics with different electronic states are considered in this study). Activated carbons are widely used to take up aromatic compounds in aqueous solution, but they do not have the uptake selectivity. In contrast, it can be stated that Mg–Al LDH intercalated with aromatic anions has the potential to selectively absorb hazardous aromatics from wastewater owing to the electrostatic attraction between the aromatic rings of the hazardous aromatics and those of Mg–Al LDH.

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