Characteristics and mechanisms of sorption of organic contaminants onto sodium dodecyl sulfate modified Ca-Al layered double hydroxides

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A series of calcium aluminum layered double hydroxides (LDHs) modified with sodium dodecyl sulfate (SDS) (Ca/Al-SDS-LDHs) were synthesized by co-precipitation, and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, and elemental analysis. The Ca/Al-SDS-LDHs enhanced sorption of nitrobenzene and naphthalene from water compared with inorganic LDH (Ca/Al-Cl-LDH). The sorption isotherms for sorption of organic contaminants onto the Ca/Al-SDS-LDHs were linear for the concentration range tested, which implies that the sorption mechanism is mainly by partition. The sorption of naphthalene onto Ca/Al-SDS-LDH was apparently stronger than that of nitrobenzene, but this order reversed after eliminating the hydrophobic effect of these two contaminants. Because naphthalene is non-polar and nitrobenzene is polar, the results indicate that the Ca/Al-SDS-LDHs were selective for polar organic contaminants.

layered double hydroxide, SDS, sorption, nitrobenzene, naphthalene, co-precipitation

Layered double hydroxides (LDHs) or hydrotalcite-like compounds are a class of natural and synthetic lamellar compounds with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$ $[A^{n-}_{x/n}]$ mH_2O, where $M^{2+} = Mg^{2+}$, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and $M^{3+} = Al^{3+}$, Fe^{3+}, Cr^{3+}; and A^{n-} is an anion such as CO_3^{2-}, SO_4^{2-}, NO_3^-, or an organic anion [1]. Some of the M^{2+} ions in LDHs are substituted by M^{3+} ions, which produces positively charged layers with the composition $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$. To compensate for the positive charges on these layers, A^{n-} are intercalated in the structure. LDHs have been investigated because of their potential applications as ion-exchangers [2–6] and catalysts [7].

LDHs can be used to remove contaminants from the environment. However, hydrophilic hydroxyl groups on the LDH surface reduce the sorption performance for hydrophobic non-ionic organic contaminants [8,9]. To enhance the sorption of non-ionic organic contaminants, anionic surfactants such as the anions of dodecyl sulfate (DS⁻) and dodecylbenzenesulfonic acid (DBS⁻) have been inserted into Mg-Al/Li-Al/Zn-Al LDHs [10–18]. Anionic surfactant intercalated LDHs can be prepared by the ion exchange method, using LDH-Cl or LDH-NO₃ as the precursors. The carboxylic acids are believed to assist the intercalation process by facilitating the elimination of carbonate ions [19]. The intercalation capacity of DBS⁻ into Mg/Al-NO₃-LDH was greater than that of DS⁻, which indicates that increasing the SO₃⁻ content on the surfactant will increase its intercalation capacity [20].

Modification of anionic surfactants has been used to improve the removal efficiencies of organic contaminants by LDHs. Excellent sorption of 2-naphthol onto SDS-modified Mg-Al-Cl-LDH was used to propose a solubilization theory, in which the solubility of the organic compounds increased after sorption onto LDHs and this increased transfer of the organic compounds from water to the LDHs [21]. For example, the sorption of carbetamide and metamitron onto

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SDS modified Mg-Al LDH was enhanced when the quantity of intercalated DS$^-$ increased [22]. The sorption of the dye Green Bezanyl-F2B on Mg/Al-SDS-LDH by the calcination-rehydration method has also been studied, and the sorption isotherms were fitted to the Langmuir and Freundlich equations [23]. The mechanism for the adsorption of chlorpyrifos (CPF) onto DBS-LDHs was believed to be related to the hydrophobicity of the DBS-LDHs, but π-π interactions between the pyridine ring of CPF and the benzene ring of DBS may also be important [24]. Intercalation of surfactants into Mg-Al LDH was found to decrease the specific surface area of Mg-Al LDH, whereas surfactants dramatically enhanced the LDH affinity for 1,2,4-trichlorobenzene and 1,1,1-trichloroethane in aqueous solutions. The sorption characteristics of 1,2,4-trichlorobenzene and 1,1,1-trichloroethane onto organo-LDH indicated that sorption occurred by the partition mechanism [25]. 2,4-Dichlorophenol was considerably solubilized in the anionic surfactant layers intercalated in hydrotalcite. The bis[2-ethylhexyl] sulfosuccinate-hydrotalcite complex appeared to be a more effective adsorbent for 2,4-dichlorophenol than the dodecyl sulfate-hydrotalcite complex [26].

Many studies have investigated the sorption of organic contaminants by anionic surfactant-modified LDHs with different M^{2+}/M^{3+} ratios. The results have shown that the sorption of organic contaminants onto organic LDHs is influenced by the M^{2+}/M^{3+} ratio. For example, the sorption of trichloroethylene and tetrachloroethylene by Mg/Al-SDS-LDHs was stronger on Mg$_3$Al-SDS-LDH than on Mg$_2$Al-SDS-LDH [27]. However, there are many different kinds of organic contaminants in the environment, and the effect of the different properties of these organic contaminants on their sorption by LDHs has not been investigated. Further research is required in this area.

To optimize the use of LDHs for contaminant removal from the environment, it is necessary to understand how the characteristics and mechanisms of sorption are affected by different contaminants. In this work, the sorption of polar (nitrobenzene) and non-polar (naphthalene) organic contaminants by Ca/Al-Cl-LDH and Ca/Al-SDS-LDHs were studied.

1 Materials and methods

1.1 Materials

All the chemicals used in this study, including CaCl$_2$, AlCl$_3$·6H$_2$O, NaOH, sodium dodecyl sulfate, nitrobenzene, and naphthalene, were analytical grade. All the aqueous solutions were prepared in double-distilled water.

1.2 Methods

(1) Samples preparation. A series of Ca/Al-SDS-LDHs were prepared by co-precipitation. Aqueous solutions of CaCl$_2$ and AlCl$_3$ with various Ca/Al amount-of-substance ratios (Ca/Al=2:1, 1:1, 1:2, and 1:3) were prepared. These solutions were added dropwise with NaOH solution (100 mL, 1.5 mol/L) to a 500 mL flask containing 0.2 mol/L SDS with vigorous stirring at 25°C. The mixture was shaken at 60°C for 24 h, aged at 65°C for 24 h [28], and then filtered. The residue was washed with double-distilled water three times, then dried at 105°C for 24 h and ground to 100 mesh. The samples prepared from Ca/Al=2:1, 1:1, 1:2, and 1:3 were labeled S1, S2, S3, and S4, respectively.

A Ca/Al-Cl-LDH sample was prepared by the same method using 100 mL of NaOH solution (1.5 mol/L) and an aqueous solution of CaCl$_2$ and AlCl$_3$ (Ca/Al=2:1).

All the samples were stored in a vacuum desiccator.

(2) Sample characterization. The samples were analyzed by powder X-ray diffraction (XRD) using a Rigaku D/MAX2200 X-ray diffractometer (Rigaku, Tokyo, Japan) under the following conditions: 40 kV, 40 mA, and Cu Kα (λ = 0.15406 nm) radiation. The samples, as unoriented powders, were scanned in 0.02° (2θ) steps from 1° to 15° at 1°/min.

Elemental analysis was performed on a Eurovector EA3000 automatic elemental analyzer (Eurovector, Milan, Italy).

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet 380 FT-IR spectrometer (Thermo Fischer Scientific, Waltham, MA). Samples were analyzed as KBr discs with a 1% compound loading. The spectra were recorded between 4000 and 400 cm^{-1}.

(3) Sorption experiments. Sorption experiments were conducted in 25 mL centrifuge tubes. After adding 0.1 g of sorbent and 20 mL of an aqueous solution containing various quantities of organic contaminants (nitrobenzene and naphthalene), the tubes were shaken at 25°C for 4 h to attain equilibrium. After centrifugation, the concentrations of the organic contaminants in the supernatant were determined by UV-Vis spectroscopy (Unic UV-4802H) using the peaks at 270 nm (nitrobenzene) and 219 nm (naphthalene). All samples were analyzed in triplicate.

2 Results and discussion

2.1 Characteristics of the Ca/Al-SDS-LDHs

The Ca/Al-SDS-LDHs were characterized by XRD, FT-IR spectroscopy, and elemental analysis (EA). The XRD patterns of the LDH samples are shown in Figure 1. The three peaks observed for the samples indicated that all these samples had layered structures. The d_{003} value of Ca/Al-Cl-LDH was 0.76 nm. However, the d_{003} values of S1, S2, S3 and S4 were 3.31, 3.12, 3.98 and 4.18 nm, respectively. Compared with Ca/Al-Cl-LDH, the interlayer spacings of the Ca/Al-SDS-LDHs were much larger because of the SDS modification.
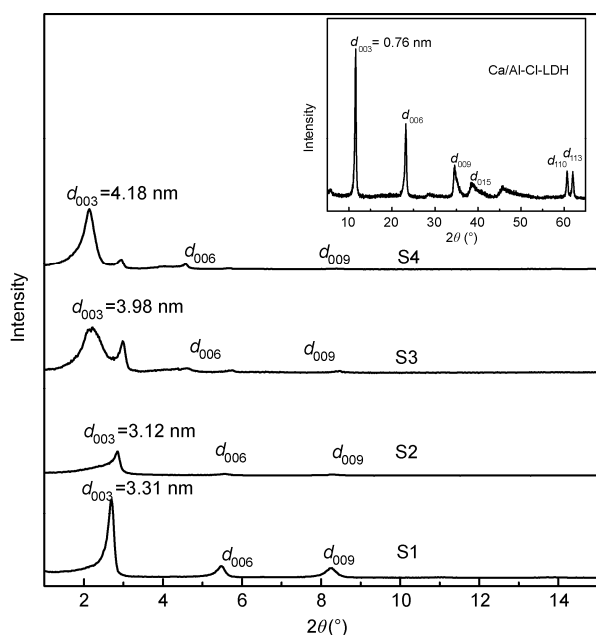
Figure 1   XRD patterns of the Ca/Al-LDHs.

Table 1   FT-IR spectral data for the samples

Sample	2900–3000(cm^{-1})	2800–2900(cm^{-1})	1200–1300(cm^{-1})
Pure SDS	2918.7, 2956.7	2850.5	1221.2
S1	2922.4, 2959.0	2852.7	1219.9
S2	2923.6, 2959.0	2853.3	1219.9
S3	2923.6, 2959.0	2853.2	1219.9
S4	2923.8, 2959.1	2853.4	1219.9
Ca/Al-Cl-LDH	–	–	–

Table 2   Element analysis of the Ca/Al-SDS-LDHs

Sample	Ca /Al ratio	C_C (%)	C_S (%)	$f_{DS}^{-\ a)}$ (%)
S1	2:1	30.4	5.7	47.1
S2	1:1	41.5	7.9	65.3
S3	1:2	41.4	7.8	64.7
S4	1:3	40.4	7.4	61.2

a) $f_{DS}^{-} = C_S$ (%)/(M_S/M_{DS}^{-}).

The XRD pattern of S1 appeared to be much more crystalline than the other samples. This ordered layer structure of S1 might aid sorption of aqueous organic contaminants. As shown in Figure 1, the crystal structure of S3 was the least ordered and the d_{003} value of S2 was the lowest. Sample S4 had the largest d_{003}, which indicates that this sample has the largest interlayer spacing, which would provide a space for intercalation of organic molecules in the LDHs during the sorption process.

The presence of anionic surfactants in the organic LDH structure can be further supported by the FT-IR spectra (Table 1). Pure SDS showed four characteristic bands. The bands at around 2959 and 2850 cm^{-1} were v_{C-H} antisymmetric stretching and symmetric stretching bands for –CH$_3$, the band at around 2920 cm^{-1} was from v_{C-H} antisymmetric stretching of –CH$_2$, and the band at around 1220 cm^{-1} was from $v_{S=O}$ stretching. There were no similar bands in the spectrum of Ca/Al-Cl-LDH . For S1, S2, S3 and S4, the FT-IR spectra showed three bands at around 2959, 2920, 2850 and 1220 cm^{-1}. These results indicate that DS$^-$ was successfully loaded in these samples.

The EA results for the Ca/Al-SDS-LDHs samples are shown in Table 2. Using the sulfur contents (C_S (%)) of the samples and the molecular weight of SDS, the mass contents of DS$^-$ (f_{DS}^-) in the organic LDH samples were calculated. The mass of DS$^-$ loaded on the LDH samples was in the

following order: S1<S2 $\approx$ S3 $\approx$ S4.

The EA, FTIR and XRD analyses demonstrate that DS$^-$ was successfully inserted into the interlayer of all the Ca/Al-SDS-LDHs (S1–S4).

2.2   Sorption isotherms

The physical and chemical properties of nitrobenzene and naphthalene are listed in Table 3. These two compounds have similar molecular weights, but very different solubilities, octanol-water partition coefficients (K_{ow}), and polarity. The K_{ow} of naphthalene is 1995.3, and the K_{ow} of nitrobenzene is 70.8, which indicates that naphthalene is more hydrophobic than nitrobenzene. The greater dipole moment of nitrobenzene (3.98) than naphthalene (0) shows nitrobenzene is more polar than naphthalene.

The sorption isotherms for nitrobenzene and naphthalene sorption from water by the Ca/Al-SDS-LDHs and Ca/Al-Cl-LDH are shown in Figure 2. The stronger sorption of nitrobenzene and naphthalene onto the Ca/Al-SDS-LDHs than Ca/Al-Cl-LDH illustrated that organic modification of the LDHs can enhance their sorption for aqueous organic contaminants.

From the sorption isotherms in Figure 2, the sorption of naphthalene was shown to be greater than that of nitrobenzene for all the LDH samples. This result is consistent with the hydrophobicities of these two compounds. The sorption strengths the Ca/Al-SDS-LDHs for nitrobenzene were in the order S1>S4>S3>S2, and those for naphthalene were in the

Table 3   The basic physical and chemical properties of the organic pollutants in this study

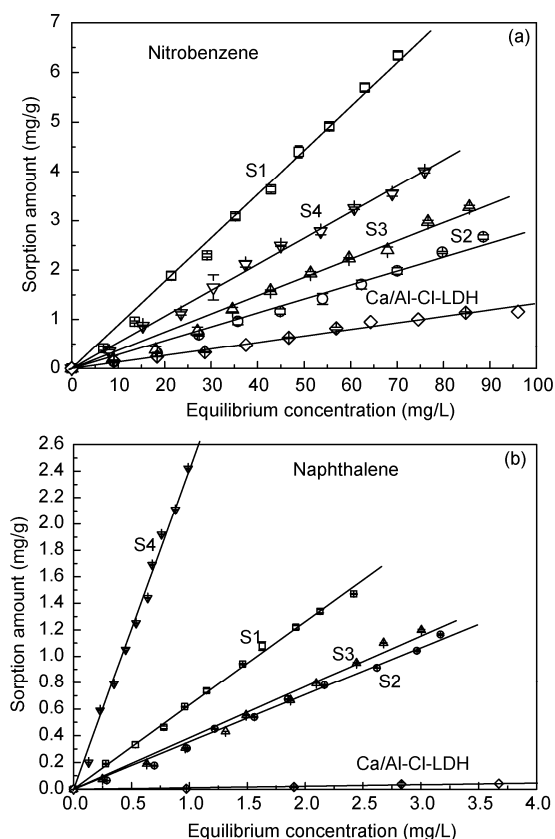| Organic material	Molecular weight	Solubility in water (mg/L)	K_{ow}	Polarity	Dipole moment
Nitrobenzene	123.11	2090	70.8	Polar	3.98
Naphthalene	128.18	31.8	1995.3	Non-polar	0

Figure 2 Sorption isotherms of nitrobenzene (a) and naphthalene (b) by the Ca/Al-SDS-LDHs and Ca/Al-Cl-LDH. The standards deviations are shown by the error bars.

order S4>S1>S3>S2. The XRD patterns of the Ca/Al-SDS-LDHs (Figure 1), showed the crystal structure of S3 was not ordered, and the d_{003} value of S2 was the low. These structure characteristics of S3 and S2 might contribute to their weak sorption of the organic contaminants. The good crystalline structure of S1 and the large interlayer spacing of S4 could assist their sorption of the organic contaminants. However, for nitrobenzene, the sorption by S1 was stronger than that by S4, while for naphthalene, the sorption by S4 was greater than by S1. Therefore, in addition to the hydrophobicity, other physical and chemical properties of the organic contaminants must affect their sorption by the Ca/Al-SDS-LDHs.

2.3 Partition coefficients

The sorption isotherms of nitrobenzene and naphthalene onto Ca/Al-SDS-LDH were almost linear within the investigated concentration range of the solute. The shape of the sorption isotherm implied that the sorption was mainly controlled by the partition mechanism. This can be expressed by the following equations:

$$Q_p = K_p C_e , \tag{1}$$

$$K_{oc} = K_p / f_{oc} , \tag{2}$$

where Q_p (mg/g) is the sorption mass; C_e (mg/g) is the equilibrium concentration in the water; K_p is the partition coefficient; K_{oc} is the organic carbon standardized partition coefficient; and f_{oc} is the percentage content of organic carbon of Ca/Al-SDS-LDHs, which can be calculated from f_{DS^-} of the Ca/Al-SDS-LDHs. The values of K_p and K_{oc} were calculated using eqs. (1) and (2), and are listed in Table 4.

The K_p values for nitrobenzene sorption by the different Ca/Al-SDS-LDHs were in the order S1>S4>S3>S2, and those for naphthalene were in the order S4>S1>S3>S2. These results are consistent with the sorption isotherms. However, for the K_{oc} values both nitrobenzene and naphthalene sorption by the different Ca/Al-SDS-LDHs were in the order S1>S4>S3>S2. The K_{oc} value decreased as the f_{oc} value of the Ca/Al-SDS-LDHs increased. This phenomenon was also reported for the sorption by organobentonites [29]. In the sorption of organic compounds onto organobentonites, where bentonite is intercalated by surfactant cations, the K_{oc} increased as the f_{oc} increased, until K_{oc} reached a maximum at a particular f_{oc} value. After that point, K_{oc} decreased with further increases in the f_{oc}, which was thought to be caused by steric hindrance of surfactant cations in the interlayer of organobentonites [29]. This may occur because organic LDHs and organobentonites form organic phases in their interlayer. The similarity of their interlayer structures might result in the similar sorption mechanisms for organic contaminants. The greater K_{oc} value of S1 than S4 might also result from the steric hindrance of DS$^-$ in the interlayer because the f_{oc} of S4 was higher than that of S1.

2.4 Polarity effects

Sorption isotherms of organic contaminants onto Ca/Al-SDS-LDHs (Q-C_e/S_w plots) (Figure 3) were plotted, where C_e/S_w is the ratio of equilibrium concentration to solute aqueous solubility (S_w).

In Figure 3, C_e/S_w was used to eliminate the effect of hydrophobic organic contaminants on sorption, and this was used to determine the interactions between the sorbents and

Table 4 K_p and K_{oc} of different Ca/Al-SDS-LDHs

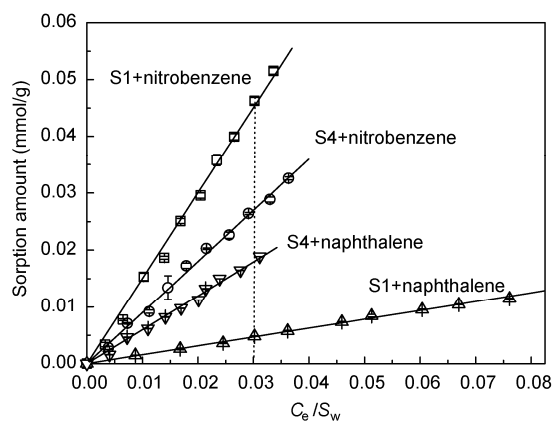| Sample	f_{oc} (%)	K_p (nitrobenzene)	K_p (naphthalene)	K_{oc} (nitrobenzene)	K_{oc} (naphthalene)
S1	30.4	0.09	0.63	0.29	2.08
S2	41.5	0.03	0.36	0.07	0.86
S3	41.4	0.04	0.39	0.09	0.93
S4	40.4	0.05	0.73	0.13	1.82

Figure 3 Sorption isotherms of nitrobenzene and naphthalene by S1 and S4 (Q-C_e/S_w plots). The standard deviations are shown by the error bars.

the organic contaminants. After eliminating the hydrophobic effect, it was obvious that both S1 and S4 had stronger sorption of nitrobenzene than naphthalene. A similar polarity effect was observed for the sorption of organic compounds by organobentonites [30]. After eliminating the hydrophobic effect, the sorption of strongly polar compounds (aniline or phenol) was greater than that of a weakly polar compound (toluene) by organobentonites [30]. For the contaminants used in this study, the polarity of nitrobenzene (D=3.98) is greater than naphthalene (D=0). Therefore, it can be inferred that the sorption of nitrobenzene and naphthalene by Ca/Al-SDS-LDHs was dependent mainly on polar effects after elimination of the hydrophobic effect. The stronger sorption of nitrobenzene and the weaker sorption of naphthalene onto S1 relative to the sorption onto S4 (Figure 2) might be caused by the co-effect of the polarities and hydrophobicities of these two contaminants.

As shown in Figure 3, the difference between the sorption of nitrobenzene and naphthalene for S1 was much greater than the difference for S4. For example, for S1 at C_e/S_w=0.03, the sorption of nitrobenzene (0.045 mmol/g) was almost 10 times greater than the sorption of naphthalene (0.004 mmol/g). However, for S4 at C_e/S_w=0.03, the sorption of nitrobenzene (0.026 mmol/g) was only 1.5 times greater than the sorption of naphthalene (0.017 mmol/g). These results imply that the difference in S1's affinity to nitrobenzene and naphthalene is much greater than that of S4 to the same compounds. Figure 3 exhibited a polarity effect for the sorption of organic contaminants onto S1 and S4, and it can be concluded that S1 was more polarity-selective than S4.

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