JOURNAL OF
Materials
CHEMISTRY

Hybrid organic–inorganic derivatives of layered double hydroxides and dodecylbenzenesulfonate: Preparation and adsorption characteristics

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Received 27th July 2001, Accepted 14th December 2001
First published as an Advance Article on the web 22nd February 2002

Layered double hydroxides (LDHs) are anionic clays that can be synthesized under laboratory conditions. In this study, different LDHs were synthesized by a coprecipitation method, with the parent products and calcined derivatives evaluated for their ability to adsorb the anionic surfactant, dodecylbenzenesulfonate (DBS). Adsorption isotherms for DBS retention on LDHs were typical L-type curves, with adsorption data conforming to a simple Langmuir equation. Langmuir maximum adsorption of DBS on calcined-LDH was significantly higher than that on uncalcined-LDHs. Organo-LDHs were also synthesized by incorporating DBS into LDHs *via* ion-exchange, reconstruction of calcined-LDH and *in-situ* synthesis methods. X-ray diffraction analysis of organo-LDHs revealed that DBS was intercalated into LDHs with the mono-layer DBS molecules oriented perpendicularly to LDH surfaces. Intercalation of DBS into LDHs decreased surface area according to BET analysis. The adsorption capacities of organo-LDHs for trichloroethylene (TCE) and tetrachloroethylene (PCE) were substantially greater than the original LDH materials. Adsorption of organic compounds by organo-LDHs was due to a partitioning mechanism.

1. Introduction

Various organic pollutants such as non-ionic hydrophobic organic compounds (HOCs) and anionic surfactants are frequently found in surface- and ground-waters, representing a serious threat to human health and natural ecosystems.[1,2] Removal of these pollutants from aquatic environments is therefore a major focus of wastewater treatment and clean-up efforts. There has been increasing interest in the past decades in developing new adsorbents to remove organic pollutants from aqueous solution. For example, natural layered clay materials, particularly 2 : 1 phyllosilicates, have been studied as environmental adsorbents to remove organic compounds from waters.[3–5]

Recently, layered double hydroxides (LDHs) have received considerable attention due to their unique intercalation properties and their potential technological applications.[6–15] In contrast to clay minerals with negatively charged layers, such as 2 : 1 phyllosilicates, LDHs are host–guest materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules.[8] LDHs can be represented by the general formula: $[M^{II}{}_{1-x}M^{III}{}_{x}(OH)_2]^{z+}A^{n-}{}_{z/n}\cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent cations, respectively, that occupy octahedral positions in the hydroxide layers. A^{n-} is the gallery anion and x is defined as the $M^{III}/(M^{II} + M^{III})$ ratio.[8,16,17]

The lamellar structure and anion exchange capacity of LDHs allow the formation of a wide range of host–guest complexes. Generally, organic anions can be intercalated into LDHs through three methods: (1) an ion-exchange reaction with an LDH containing exchangeable monovalent anions such as NO_3^-, Cl^-;[11,16] (2) the reconstruction of calcined-LDH in organic anion solutions;[18] and (3) *in-situ* synthesis where the LDH sheets form in the presence of the desired organic anion with exclusion of CO_3^{2-}.[19,20] When incorporating organic anions into LDHs, the interlayer spacing of the LDHs increases, which is dependent on the nature, size and geometrical structure of the intercalated species.[11,16,21,22] The incorporation of organic species in LDHs also yields modified organo-LDHs with hydrophobic surface properties, resulting in the modified organo-LDHs that have high adsorption affinities for organic contaminants such as imazamox (2-[4,5-dihydro-4-methyl-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-5-(methoxymethyl)-3-pyridinecarboxylic acid), benzene, toluene and 2-naphthol.[12,13,23–25]

In the present work, different LDHs were synthesized and parent and calcined materials evaluated for their ability to adsorb dodecylbenzenesulfonate (DBS). Organo-LDHs were prepared by intercalation of DBS into LDHs *via* ion-exchange, reconstruction of calcined-LDH and *in-situ* synthesis methods. The surface properties of the organo-LDHs were investigated by powder X-ray diffraction, BET surface-area measurements and total organic carbon determinations. The abilities of organo-LDHs to remove trichloroethylene (TCE) and tetrachloroethylene (PCE) from aqueous solution were also evaluated. The results reported here are instructive towards a better understanding of the potential applications of both LDHs and organo-LDHs for environmental clean-up and remediation of contaminated soils and groundwaters.

2. Experimental methods

2.1. Reagents

Reagent grade metal salts were obtained from Spectrum Quality Products (Gardena, CA, USA). Sodium dodecylbenzenesulfonate and the organic compounds, trichloroethylene

DOI: 10.1039/b106811c

and tetrachloroethylene, were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) and used as received.

2.2. Preparation of Mg–Al and Zn–Al LDHs

Magnesium–aluminum LDHs ($Mg_nAl(OH)_{2n+2}Cl\cdot yH_2O$ with $n = 2–5$) and zinc–aluminium LDH ($Zn_nAl(OH)_{2n+2}Cl\cdot nH_2O$ with $n = 3$) were prepared using the coprecipitation method[14,15] at 25 ± 1 °C by reacting aqueous solutions containing a mixture of divalent and trivalent metal chlorides (total metal concentration equaled 1 M for Mg–Al LDH with molar ratios of Mg/Al ranging from 2.0 to 5.0, and for Zn–Al LDH a molar ratio of Zn/Al of 3.0) with a 2 M NaOH aqueous solution. The pH of the reaction mixtures was maintained at 10 ± 0.3. Nitrogen (N_2) was bubbled throughout the coprecipitation process to minimize CO_3^{2-} in solution. After reaction, the suspensions were continually stirred for 6 h with occasionally adjustment of pH and then aged at 65 °C for 16 days. After cooling to room temperature, the precipitates were isolated by centrifuging and washed extensively with distilled water. The products were again dried at 65 °C, ground and stored in plastic bottles. For the purpose of this study, the products were named Mg–Al LDH 2, Mg–Al LDH 3, Mg–Al LDH 4, Mg–Al LDH 5 and Zn–Al LDH 3, with the number 2, 3, 4 or 5 representing the M^{II}/M^{III} ratio.

2.3. Preparation of calcined-LDH

First, Mg–Al LDH with carbonate ($Mg_nAl(OH)_{2n+2}CO_3\cdot yH_2O$ with $n = 3$) was prepared by a procedure similar to that described above. The mixed aqueous solutions of divalent and trivalent metal chlorides (total metal concentration of 1 M, with a Mg/Al ratio of 3.0) were coprecipitated with an aqueous solution of 2 M NaOH and 1 M Na_2CO_3. The synthesized Mg–Al LDH with carbonate was heated in a muffle furnace at 450 °C for 2 h. The resulting product, hereafter called calcined-LDH, was stored in a desiccator prior to its use.

2.4. Anionic surfactant adsorption isotherms

Dodecylbenzenesulfonate (DBS) adsorption isotherms were determined by the batch equilibration technique. 100 mg of synthesized LDHs were weighed into 25 ml screw-top Corex glass centrifuge tubes which were then filled with 25 ml aqueous solutions of DBS at various concentrations ranging from 0.0 to 4.0 cmol l^{-1}. After the suspensions had been shaken on a reciprocal shaker for 16 h, they were centrifuged and the DBS concentrations determined in the supernatant by measuring aqueous carbon contents using a Shimadzu TOC-5000 (Total Organic Carbon) Analyzer equipped with a Shimadzu ASI-5000 Autosampler.

2.5. Organo-LDH preparation

2.5.1. Ion-exchange method. The synthesized LDHs with chloride were added to 0.1 M DBS solutions at a solid/solution ratio of 1 g/50 ml. The suspensions were shaken on a reciprocal shaker for 16 h, centrifuged and the supernatant solution decanted. The solid material was washed three times using distilled water (~85 ml water/g) and oven dried at 65 °C.

2.5.2. Reconstruction of calcined-LDH method. Calcined-LDH was reconstructed using the same procedure as described above in the ion-exchange method to produce the organo-calcined-LDH.

2.5.3. *In-situ* synthesis method. An organo-LDH was coprecipitated from a mixed Mg/Al chloride (total metal concentration of 1 M, with a Mg/Al ratio of 3.0) and 0.1 M DBS solution by dropwise addition of 2 M NaOH. The solution ratio of DBS to Mg/Al chloride (*v*/*v*) was 3 : 1. The coprecipitation procedure was similar to the Mg–Al and Zn–Al LDH preparation described above.

2.6. Adsorption of hydrophobic organic compounds by organo-LDHs

TCE and PCE adsorption isotherms were obtained by a batch equilibration technique at 25 ± 1 °C as described by Zhao *et al.*[26] Briefly, 100 mg of organo-LDH were weighed into 25 ml Corex glass centrifuge tubes and organic compounds were added as methanol stock solutions using a Hamilton microliter syringe (Hamilton Co., Reno, NV, USA). After organic compounds were added, the centrifuge tubes were immediately closed with foil-lined screw caps to minimize loss of solutes by evaporation. After shaking for 16 h, the tubes were centrifuged and the organic compounds in supernatant solutions were extracted using hexane. A portion of the hexane-containing solutes was analyzed by a Hewlett Packard 5980 series II gas chromatograph (GC) equipped with a HP-5 capillary column and an electron capture detector. The percentage recoveries of TCE and PCE in the blanks were greater than 93%, and the data were not adjusted for these recoveries.

2.7. Characterization of LDHs

The chemical compositions of the synthesized LDHs were determined using inductively coupled plasma (ICP) spectrometry by analyzing diluted solutions of synthesized LDHs dissolved in concentrated HNO_3. Water contents were obtained by heating the LDHs at 250 °C for 2 h.[27] Total organic carbon contents of organo-LDHs were determined by high temperature combustion/alkalinity titration using an Elemental Analyzer Model 1106 (Carlo Erba Strumentazione, Milan, Italy).

Powder X-ray diffraction patterns (PXRD) of synthesized original LDHs and organo-LDHs were recorded using a Scintag XDS 2000TM Diffractometer with Cu-Kα radiation at 40 kV and 30 mV. The data were collected with a scanning rate of 3° min^{-1}.

Surface areas were determined using the BET equation[28] on five-point N_2 gas adsorption isotherms. To avoid the decomposition of intercalated DBS, samples were degassed at 65 °C for 17–19 h under a 20 ml min^{-1} flow of pure N_2. A Tristar 3000 Sorption Meter (Micromeritics Instrument Corp., Norcross, GA, USA) was used to determine the surface areas at temperatures below −196 °C using N_2 as the adsorbate and helium (He) as the carrier gas. Monolayer surface areas were calculated after fitting the five points of each isotherm to the BET equation.

3. Results and discussions

3.1. Properties of synthesized LDHs

Chemical compositions and water contents of the synthesized LDHs are listed in Table 1. The ratio of divalent to trivalent metal of the synthesized LDHs conforms well to the expected ratio in the respective LDHs. This indicates that both divalent and trivalent metal quantitatively precipitated during the coprecipitation processes. Empirical formulae of the synthesized LDHs listed in Table 1 were derived from the chemical composition considering Cl^- as the intercalated anion.

A representative X-ray diffraction pattern of Mg–Al LDH 3 is shown in Fig. 1. X-ray diffraction patterns indicated all the synthesized LDHs have typical, well-order layered structures with a high degree of crystallinity. The X-ray diffraction pattern of calcined-LDH (Fig. 1) indicates that calcination destroyed the brucite layer structure of LDH, resulting in the loss of CO_2 and water, with the detection of Mg oxide.

Table 1 Chemical compositions and selected properties of synthesized LDHs

Sample	Mg (%)	Al (%)	Zn (%)	H_2O^a (%)	Empirical formulae^b	*d*-spacing/Å	Surface area/$m^2\ g^{-1}$
Mg–Al LDH 2	20.1	11.1	—	13.2	$[Mg_{2.0}Al(OH)_{6.0}]Cl\cdot1.8H_2O$	7.91	49.1
Mg–Al LDH 3	22.5	8.73	—	12.9	$[Mg_{2.9}Al(OH)_{7.8}]Cl\cdot2.2H_2O$	7.94	48.9
Mg–Al LDH 4	24.2	6.92	—	13.3	$[Mg_{3.9}Al(OH)_{9.8}]Cl\cdot2.9H_2O$	8.07	47.3
Mg–Al LDH 5	25.5	6.05	—	14.2	$[Mg_{4.7}Al(OH)_{11.4}]Cl\cdot3.5H_2O$	8.09	29.5
Zn–Al LDH 3	—	6.23	47.0	12.2	$[Zn_{3.1}Al(OH)_{8.2}]Cl\cdot2.9H_2O$	7.79	16.4
Calcined-LDH	39.0	14.9	—	–	$Mg_{2.9}AlO_{3.9}(OH)$	–	204

^{a}Weight loss during heating at 250 °C for 2 h. ^{b}Empirical formulae of the LDHs were calculated from the chemical composition with considering Cl^- as the interlayer anion.

Although the layer structure can be destroyed by calcination, the calcined-LDH can re-adsorb water and anions and, in turn, restore to its original structure when rehydrated.[29,30] This phenomenon has been described as the "memory effect" mechanism.[8]

Interlayer spacings (d_{003}) of the synthesized LDHs are also listed in Table 1. The average *d*-spacing value (d_{003}) for the synthesized LDHs is 7.96 ± 0.12 Å, which is as expected for a Cl^- ion-based Mg (or Zn)–Al LDH.[31–33] The *d*-spacing values (d_{003}) increased from 7.91 Å to 8.09 Å as the Mg/Al mole ratio increased from 2 to 5. This may be due to the larger radius of Mg^{2+} compared with Al^{3+}.[8] The *d*-spacing (d_{003}) of Zn-Al LDH was 7.79 Å, which is smaller than that of Mg–Al LDHs. The surface areas of the synthesized LDHs ranked as calcined-LDH > Mg–Al LDH 2 > Mg–Al LDH 3 > Mg–Al LDH 4 > Mg–Al LDH 5 > Zn–Al LDH 3 (Table 1). Calcined-LDH has the highest surface area because of the formation of channels and pores resulting from the removal of water and CO_2[34] and its very small particle size after calcination.

3.2. Adsorption of DBS on synthesized LDHs

Adsorption isotherms for DBS retention by LDHs are shown in Fig. 2. These isotherms indicate that DBS has a high affinity for LDH surfaces, particularly at low surfactant concentrations. The adsorption isotherms are L-type isotherms according to the classification of Giles *et al.*[35] who characterized L-type isotherms as being related to monofunctional solutes adsorbing on specific sites that have high affinity for adsorbates. The L-type isotherms have been reported by other authors for the adsorption of many anions on LDHs, such as NO_3^-, Cl^-, CO_3^{2-}, SeO_3^{2-}, HPO_4^{2-} and trichlorophenol.[14,36,37] Esumi and Yamamoto[23] also reported an L-type adsorption isotherm for adsorption of dodecylsulfate on a Mg–Al LDH.

Isotherms indicated that the adsorption of DBS through reconstruction of the calcined-LDH method is considerably higher than that through the ion-exchange method. Some authors have found that the monovalent anions, Cl^- and NO_3^-, have low affinities for LDHs and are readily displaced *via* ion-exchange reactions.[14,36,38,39] Adsorption of DBS on LDHs with Cl^- is therefore thought to primarily follow an ion-exchange process (Mg–Al LDH 3 as a representative adsorbent):

$$[Mg_3Al(OH)_8]Cl^-\cdot nH_2O + DBS^- \rightarrow [Mg_3Al(OH)_8]DBS^-\cdot nH_2O + Cl^- \qquad (1)$$

On the other hand, adsorption of DBS on calcined-LDH occurred during the reconstruction process, which can be illustrated as follows:

$$Mg_3AlO_4(OH) + (4 + n)H_2O + DBS^- \rightarrow [Mg_3Al(OH)_8]DBS^-\cdot nH_2O + OH^- \qquad (2)$$

Compared with adsorption *via* ion-exchange, the higher DBS adsorption on calcined-LDH may be explained by (1) the loss of H_2O and CO_3^{2-} resulting in a higher anion exchange capacity, (2) "no" competing anions (loss of CO_3^{2-}) during the adsorption process and (3) higher surface area resulting from calcination.

Adsorption isotherms were fitted to the Langmuir equation (Table 2) which indicated that the theoretical Langmuir maximum adsorptions of DBS by LDHs are ranked according to: calcined-LDH > Mg–Al LDH 2 > Mg–Al LDH 3 > Mg–Al LDH 4 > Mg–Al LDH 5 > Zn–Al LDH 3. The Langmuir maximum adsorption of DBS decreased as the Mg/Al ratio increased because as the mole ratio of Mg/Al increases fewer Mg are substituted by Al, thus resulting in both a lower positive charge and anion exchange capacity. The Langmuir maximum adsorption of DBS of Mg–Al LDH 3 was higher than that of Zn–Al LDH 3, which was due to a lower anion exchange capability of Zn–Al LDH 3 than that of Mg–Al LDH 3 because Zn has a larger atomic weight than Mg.

Using the empirical formula of LDHs listed in Table 1, the theoretical anion exchange capacities for the different LDHs

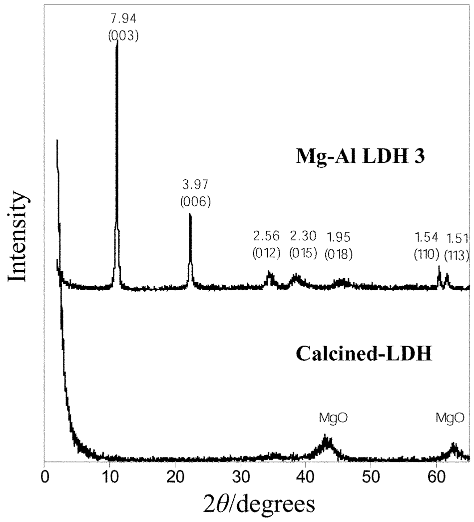

Fig. 1 X-ray diffraction patterns of Mg–Al LDH 3 and calcined-LDH.

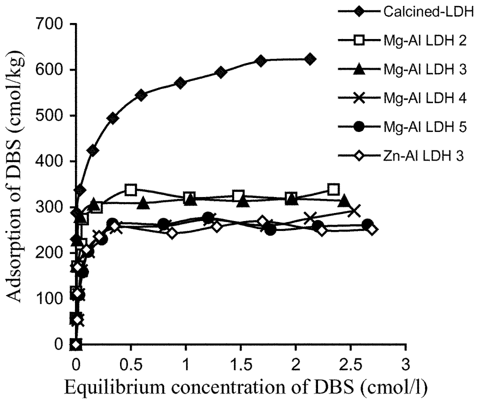

Fig. 2 Adsorption isotherms of DBS retention by synthesized LDHs.

Table 2 Adsorption parameter determined for Langmuir maximum adsorption of DBS (LMAD)[a] and theoretical anion exchange capacities (TAEC)[b] of LDHs

Sample	LMAD/ cmol_c kg^{-1}	r^2	TAEC/ cmol_c kg^{-1}	LMAD/ TAEC (%)
Mg–Al LDH 2	332	0.999	412	81
Mg–Al LDH 3	316	0.999	324	98
Mg–Al LDH 4	287	0.997	256	112
Mg–Al LDH 5	263	0.998	224	117
Zn–Al LDH 3	256	0.998	231	111
Calcined-LDH	622	0.997	NA[c]	NA

[a] Langmuir maximum adsorptions of DBS (b) were calculated from the Langmuir expression: $q = KCb/(1 + KC)$, where q is the DBS adsorbed by LDH, C is the DBS concentration in equilibrium solution and r^2 is the correlation coefficient. [b] Theoretical anion exchange capacities (TAEC) of LDHs were calculated based on the empirical formulae of LDHs listed in Table 1. [c] NA = Not applicable.

were calculated (Table 2). Some of the LDHs have Langmuir maximum adsorptions of DBS slightly higher than their theoretical anion exchange capacities, which was believed to be due to (1) the intercalation of excess DBS *via* non-polar interactions with the hydrophobic alkyl groups of exchanged DBS and (2) adsorption of DBS on external LDH surfaces.

3.3. Properties of organo-LDHs

The representative properties of all organo-LDHs prepared by ion-exchange, reconstruction of calcined-LDH and *in-situ* synthesis are list in Table 3. Organo-calcined-LDHs and *in-situ*-organo-LDHs have higher organic carbon contents than organo-LDHs prepared *via* ion-exchange, suggesting the process of DBS intercalation into LDH *via* reconstruction or *in-situ* synthesis methods is easier than with ion-exchange processes. The organic carbon content of the organo-LDHs ranged from 74to 91% of the theoretical anion exchange capacities of LDHs, which are significantly lower than the Langmuir maximum adsorption of DBS calculated from the adsorption isotherms (Table 2). This inconsistency might have resulted from desorption of adsorbed DBS from the organo-LDHs when washed with distilled water during preparation. Release of intercalated anions in distilled water has been reported by Goswamee *et al.*[40] for adsorbed Cr_2O_7 and You *et al.*[14] for adsorbed SeO_3^{2-}.

BET surface area results provided no consistent relationships between the surface areas of the original LDHs (Table 1) and that of derived organo-LDHs (Table 3). Intercalation of DBS in LDHs decreases surface areas, which were highly variable for the different LDHs and preparation methods. Similar results have been reported by Jaynes and Vance[5] who found that intercalation of long chain cationic surfactants such as dodecyltrimethylammonium and cyclododecyltrimethylammonium into natural clays significantly decreased their surface areas. The decrease in surface area resulted from the intercalated DBS long alkyl tail compact structure, allowing lower access of the internal surface area to N_2 gas. Organo-LDH prepared by the reconstruction process was more aggregated, resulting in the lowest surface area. *In-situ*-organo-LDH had a larger surface area than organo-LDHs prepared by the ion-exchange method.

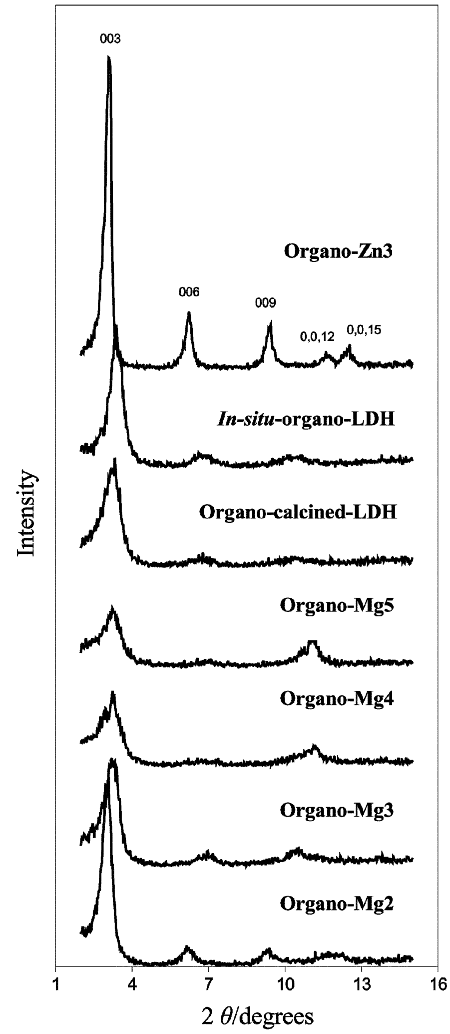

Fig. 3 Representative X-ray diffraction patterns for different organo-LDHs. See Table 3 for a description of the various organo-LDHs.

Powder X-ray diffraction patterns of organo-LDHs indicated that, as DBS was intercalated, there was a progressive increase in basal spacing (Fig. 3). Compared with the X-ray diffraction pattern for the original LDH (Fig. 1), the crystallinity of the organo-LDHs appears to be lower, as shown by the broadening of X-ray lines and decrease in intensity. The lamellar structure of the material is preserved upon intercalation. Meyn *et al.*[16] suggested the smaller equivalent area caused the long chain anionic surfactants to lay perpendicular to the LDH interlamellar surfaces, resulting in monomolecular films. Based on the perpendicular mono-layer structure, the theoretical

Table 3 Selected properties of organo-LDHs

Sample	Preparation precursor	Preparation method	Total organic carbon (%)	Organic carbon fraction of TAEC[a] (%)	Surface area/ m^2 g^{-1}	d-spacing/Å
Organo-Mg2	Mg–Al LDH 2	Ion-exchange	34.9	74.3	25.7	28.7
Organo-Mg3	Mg–Al LDH 3	Ion-exchange	33.5	81.3	10.0	26.6
Organo-Mg4	Mg–Al LDH 4	Ion-exchange	28.5	80.0	13.7	27.4
Organo-Mg5	Mg–Al LDH 5	Ion-exchange	29.5	90.5	9.7	27.4
Organo-Zn3	Zn–Al LDH 3	Ion-exchange	30.0	90.0	14.4	28.4
Organo-calcined-LDH	Calcined-LDH	Reconstruction	36.9	NA	1.2	26.6
In-situ-organo-LDH	NA[b]	*In-situ* synthesis	37.2	NA	25.5	26.4

[a] TAEC is the theoretical anion exchange capacity of the synthesized LDHs (see Table 2). [b] Not applicable.

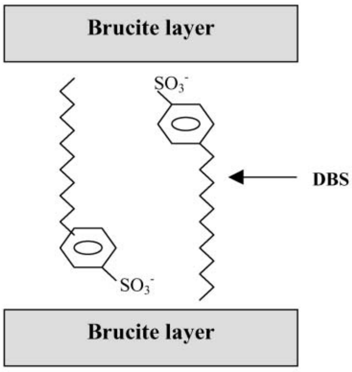

Fig. 4 Possible interlayer arrangement of DBS in LDH (not to scale).

calculated *d*-spacing for DBS was 26.9 Å and the observed *d*-spacing value varied between 26.8 Å and 30 Å.[16] Our observed *d*-spacing conforms well with these values (Table 3). Since the LDH brucite layer is 4.8 Å, the space occupied by DBS would be approximately 22 Å. Possible arrangements for the mono-layer DBS molecules, orienting in the perpendicular direction from the LDH surfaces, are shown in Fig. 4.

3.4. Adsorption of TCE and PCE on organo-LDHs

Isotherms for the adsorption of TCE and PCE in aqueous solutions by organo-LDHs are presented in Fig. 5. The steep slopes of the adsorption isotherms attest to the fact that the adsorptive properties of the original LDHs can be greatly enhanced by intercalation of the anionic DBS surfactant. For the original Mg–Al LDH 3, no organic compounds were adsorbed. In contrast, all organo-LDHs had high retention capacities for both TCE and PCE. Within the concentration range studied, all adsorption isotherms were characterized by relatively high linearity. The adsorption coefficients (K_d), corresponding to the ratio of the amount of the adsorbed organic compounds by organo-LDHs (mg/kg) to its equilibrium solution concentration (mg l^{-1}) were determined from the slope using a zero-intercept, with least-squares fitting to all of the isotherm data (Table 4). A linear regression model was employed to fit the adsorption isotherm data because it provided a better fit than other models such as Langmuir and Freundlich. The linear correlation coefficients for all plots were high ($r^2 > 0.98$). Adsorption linearity has also been observed for commonly studied organo-clays, which indicated a partition mechanism.[4,12,13,41,42] The organo-LDH surface areas (Table 3) and adsorption coefficients (Table 4) were not significantly correlated, suggesting organic compound adsorption was unrelated to surface area because adsorption by partitioning involves dissolution of organic compounds into a three-dimensional organic phase rather than adsorption on a surface.[41,42]

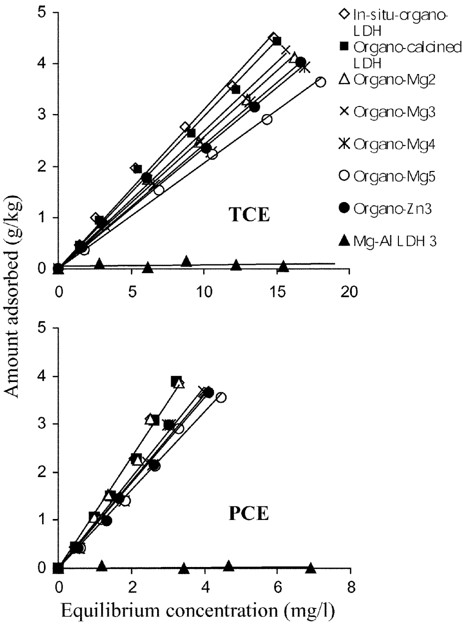

Fig. 5 Adsorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) on organo-LDHs. See Table 4 for additional quantitative adsorption parameters for the various organo-LDHs.

Adsorption coefficients can also be used to provide a relative comparison of the degree of organic compound retention, with higher K_d values corresponding to greater adsorption. Data in Table 4 indicate that adsorption of TCE and PCE by *in-situ*-organo-LDH and organo-calcined-LDH was higher than that by organo-LDHs prepared by the ion-exchange method. For both TCE and PCE, the relationships between adsorption coefficients and the amount of organic carbons intercalated in the organo-LDHs could be expressed in positively linear relationships as:

$$K_{d(TCE)} = 9.17(\%\ \text{organic carbon}) - 42.7 \qquad r^2 = 0.815 \tag{3}$$

$$K_{d(PCE)} = 37.3(\%\ \text{organic carbon}) - 232.5 \qquad r^2 = 0.845 \tag{4}$$

This implies that adsorption of TCE and PCE by organo-LDHs was directly correlated to the amount of intercalated DBS. Adsorption coefficients for PCE were higher than that of TCE (Table 4), indicating that retention of organic compounds on organo-LDHs was inversely proportional to their aqueous solubility. This was also a typical partitioning adsorption characteristic.[41,42]

The adsorption coefficients can be normalized by using the organic carbon content of the organo-LDHs according to the following formula:

$$K_{om} = K_d\ [100/(\%\ \text{organic carbon} \times f)] \tag{5}$$

Table 4 Adsorption coefficients (K_d), organic-matter-normalized adsorption coefficients (K_{om}), water solubility (S_w) and octanol–water partition coefficients (K_{ow}) for the adsorption of trichloroethylene and tetrachloroethylene by different organo-LDHs[a]

Organic compound	Organo-Mg2	Organo-Mg3	Organo-Mg4	Organo-Mg5	Organo-Zn3	Organo-calcined-LDH	*In-situ*-organo-LDH	$S_w{}^c$/ mg l^{-1}
	log$K_d{}^b$							
Trichloroethylene	2.41	2.44	2.37	2.31	2.38	2.47	2.49	1155
Tetrachloroethylene	3.06	2.97	2.95	2.91	2.95	3.06	3.06	150
	log $K_{om}{}^b$							log $K_{ow}{}^{bc}$
Trichloroethylene	2.66	2.71	2.71	2.64	2.70	2.70	2.71	2.61
Tetrachloroethylene	3.31	3.24	3.29	3.24	3.26	3.29	3.28	3.40

[a] See Table 3 for a description of the various organo-LDHs. [b] Coefficients are expressed as l/kg. [c] Water solubility (S_w) and octanol–water partition coefficient (K_{ow}) were adapted from Zhao and Vance[12] and references therein.

where K_{om} is the organic-matter-normalized adsorption coefficients and f equals DBS molecular weight divided by the weight of carbon in DBS. Table 4 shows that the K_{om} values were fairly similar for all organo-LDHs, with K_{om} values also comparable to TCE and PCE octanol–water distribution coefficients (K_{ow}). Thus the enhanced adsorption capacities of LDHs for TCE and PCE after treatment with DBS were due to the alkyl tails and benzene rings of DBS in the interlamellar spaces acting as an organic solvent phase. For TCE, the relative adsorptivity (K_{om}/K_{ow}) of the organo-LDHs was higher than 1, indicating that the DBS forms a better partitioning medium than octanol. However, K_{om}/K_{ow} for PCE was less than 1, which suggests the partitioning medium of DBS-intercalated LDHs are not as effective as octanol.

4. Conclusions

Synthesized LDHs have high retention capacities for DBS, with adsorption of DBS on calcined-LDH being significantly higher than that on uncalcined-LDHs. Organo-LDHs can be prepared by ion-exchange, reconstruction and *in-situ* synthesis methods. X-ray diffraction patterns of organo-LDHs revealed that DBS was intercalated into LDHs with formation of the mono-layer DBS molecules oriented in perpendicular direction to the LDH surfaces. The results clearly demonstrate that the adsorptive properties of LDHs for TCE and PCE can be greatly enhanced by simple intercalation of DBS. The adsorption characteristics strongly suggest that the enhanced adsorption capacities of LDHs for organic compounds after treatment with DBS were due to the alkyl tails and benzene rings of DBS in the interlamellar spaces acting as an organic phase during the partitioning process. The results presented here indicate that organo-LDHs could be used as adsorbents for organic pollutants in surface and groundwaters, and as components of contaminant barriers. In addition, calcined-LDH is a notably effective adsorbent for removing anionic surfactants from aqueous solutions, and should be studied further in *meso-* or field-scaled experiments.

Acknowledgements

Y. W. You is grateful to the Clay Minerals Society (CMS) for a student research grant. We also thank Dr. Steve Boses, University of Wyoming, for the organic carbon and N_2 surface area analyses of organo-LDHs.

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