Adsorption of chlorinated hydrocarbons by Mg-Al layered double hydroxides with intercalated surfactant ions: characteristics and sorption studies

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Introduction

Chlorinated hydrocarbons (CHCs) are used extensively in industry as solvents [1]. Despite their desirable properties for industrial uses, CHCs are not easily biodegraded, as their degradation requires very specific conditions; hence they are frequently found as pollutants in soil and groundwater.

Environmental stakeholders (e.g., government agencies, research centers, universities, and consultancy firms) are always looking for cheap and more effective remediation technologies that can be successfully implemented *in situ* for polluted soil and water. In recent years, research efforts have focused on activated carbon and the preparation, characterization, and adsorption properties of surfactant-modified-LDHs (i.e. organo-LDHs) and their potential remediation application as sorbents for CHCs such as trichloroethylene (TCE) [2, 3], tetrachloroethylene (PCE) [2, 3], and 1,1,1 trichloroethane (1,1,1-TCA) [4].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are a family of synthetic or natural inorganic-lamellar hydroxides compounds formed by two different metal cations (M^{III}/M^{II}) in the main layer and containing anionic species in the interlayer domain [5, 6]. Their high anionic exchange capacity enables the exchange of the interlayer anions with organic species (e.g., surfactants), making them hydrophobic and improving their organic contaminant removal efficiency [3, 7 ,8].

The aim of this research is to synthesize and characterize two organo-LDHs, and asses their sorption capacities for two persistent CHCs, TCE and 1,1,2-trichloroethane (1,1,2-TCA), that are commonly found in polluted groundwater.

Experimental

Organo-LDHs with Mg/Al ratio of 3:1 were synthesized at a constant pH of 9 by addition of 1 M NaOH solution by incorporating anionic surfactants sodium dodecyl sulfate (SDS) ($NaC_{12}H_{25}SO_4$) and sodium 1-dodecane sulfonate (1-SDF) ($NaC_{12}H_{25}SO_3$) into the Mg/Al-LDH via co-precipitation. A solution containing $Mg(NO_3)_2.6H_2O$ (0.75 M) and $Al(NO_3)_3.9H_2O$ (0.25 M) was dropwise added (1-2 ml/min) to a 0.25 M aqueous solution of the surfactant (SDS or 1-SDF) to be intercalated. Mg_3Al-1-SDF was synthesized at 40±5 ℃ to enhance surfactant dissolution. The suspension was stirred for 24 h at room temperature, centrifuged, and the supernatant solution decanted. The solid material was washed 3-4 times with distilled water. The synthesized material was oven dried at 45 ℃ for 48 h, ground with an agate mortar and pestle, and stored in capped-plastic bottles.

Atomic absorption spectroscopy (AAS) was used to determine the amounts of Al, Mg, S, and Na in the solid phase. Al Ultima 2 (Jovin Yvon Horiba) instrument was used. The amount of interlayer water was derived from thermogravimetric (TG) curves recorded in a SDT Q 600 instrument from TA. The basal spacing, d_{003}, and crystalline structure were obtained by powder X-ray diffraction (PXRD) analysis using a Siemens D-5000 apparatus. The FT-IR spectra were recorded in a Spectrum One spectrometer from Perkin-Elmer. Specific surface areas (S_{BET}) were determined using the BET equation applied to the nitrogen (N_2) adsorption-desorption isotherms recorded in a Gemini VI apparatus from Micromeritics. The particle size distribution was analyzed by measuring in Mastersizer 2000 equipment from Malvern.

The adsorption isotherms were determined using batch equilibration at 20±1 ℃. Known amounts of Mg_3Al-SDS and Mg_3Al-1-SDF were placed into 10 ml PTFE-lined screw-caps glass vials and stock solutions of chlorinated hydrocarbons were spiked. After 24 h of shaking, vials were centrifuged and the concentration in the supernatant measured by gas chromatography-mass spectrometry (GC-MS) analyzer. For each sample a blank (without solid) was run to ensure data quality.

Results

The main characteristics of the synthesized organo-LDHs are summarized in Table 1. Element chemical analysis confirms that the Mg/Al and Al/S ratios are close to 3:1 and 2:1, respectively. The PXRD diffraction patterns and FTIR spectra of pure surfactants (SDS and 1-SDF) and the synthesized compounds (Mg_3Al-SDS and Mg_3Al-1-SDF) show the intercalation of the surfactant ions into the hydrotalcite interlayer (Figure 1), in agreement with results reported elsewhere-[9–11]. The basal spacing for $Mg_3Al(CO_3)$ is 7.8 Å [6, 12]. When SDS and 1-SDF are intercalated, $d_{(003)}$ increases to 26.4 Å for Mg_3Al-SDS and 23.9 Å for Mg_3Al-1-SDF. Considering a thickness of 4.8 Å for the brucite-like sheets the heights of the interlamellar distances, calculated as (d_{003}-4.8 Å) [13], are 21.6 Å and 19.1 Å for Mg_3Al-SDS and Mg_3Al-1-SDF, respectively. This suggests a monolayer vertical arrangement for the SDS and slightly tilted arrangement for 1-SDF in the interlayer [10]. The presence of the $d_{(110)}$ diffraction at 1.53 Å, corresponding to one half of dimension *a* [6, Ch. 8],

confirms the presence of the hydrotalcite phase. The FT-IR spectra of samples Mg₃Al-SDS and Mg₃Al-1-SDF show characteristic absorption bands of a hydrotalcite compound with strong bands at 500-700 cm^{-1} due to metal-oxide-metal stretching modes. Intercalation of surfactants is confirmed by the absorption bands at 1220, 1186, 1064, and 1050 cm^{-1}, characteristic of S=O antisymmetric and symmetric stretching, C-H stretching (ca. 3000 cm^{-1}), and C-H bending (1469 cm-1) modes [9, 11, 14]. The BET specific surface areas for the synthesized organo-LDHs are around 0.2-0.4 m^2/g.

Table 1- Element chemical analyses and selected properties of synthesized Mg/Al organo-LDHs.

Sample name	Mg₃Al-SDS	Mg₃Al-1-SDF
Mg/Al molar ratio[a]	2.6	2.7
Surfactant/Al molar ratio[a]	0.9	0.8
Empirical formula[a,b]	$Mg_{0,75}Al_{0,25}(OH)_2(SDS)_{0,27}.0,9\ H_2O$	$Mg_{0,75}Al_{0,25}(OH)_2(1\text{-}SDF)_{0,30}.0,9\ H_2O$
Basal spacing (d_{003}) (Å)[c]	26.4	23.9
Interlamelar distance (Å)[c,d]	21.6	19.1
S_{BET} (m^2/g)	0.2	0.4
Particle aggregated size (μm)	~ 200	~ 200
Individual particle size (μm)	~ 50	~ 50

[a] ICP analysis
[b] Themogravimetric analysis
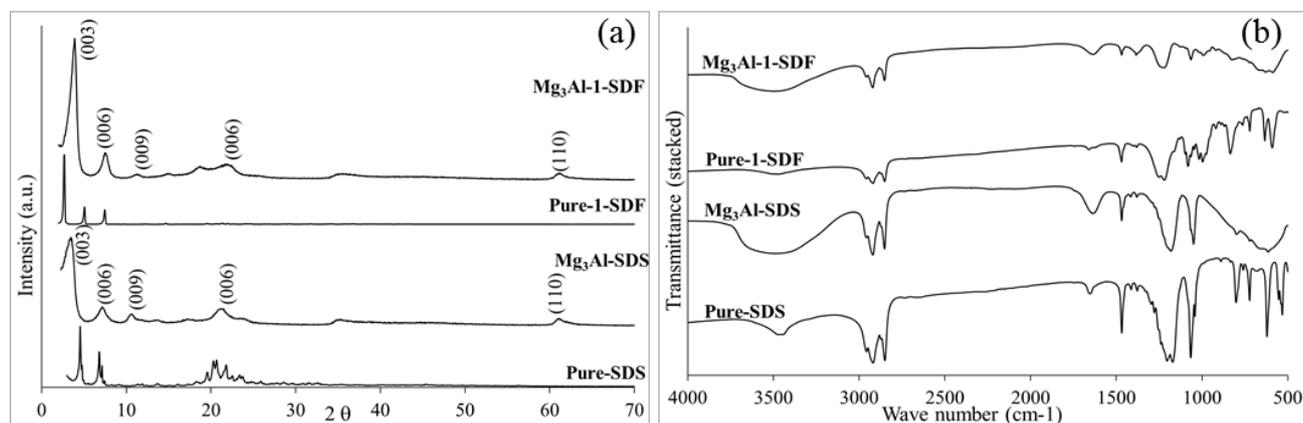c PXRD data
[d] Calculated as d_{003} – 4.8 Å [13].

Figure 1- (a) PXRD patterns of Mg₃Al-1-SDF, pure 1-SDF, Mg₃Al-SDS, and pure-SDS. (b) FT-IR spectra of Mg₃Al-1-SDF, pure 1-SDF, Mg₃Al-SDS, and pure-SDS.
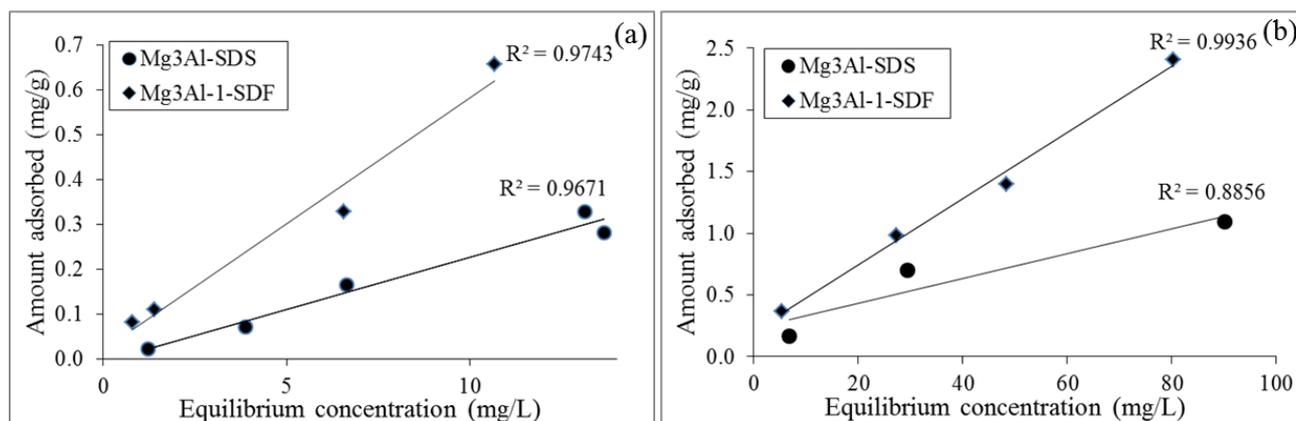
Figure 2- Equilibrium adsorption isotherms of (a) TCE and (b) 1,1,2- TCA on Mg_3Al-SDS and Mg_3Al-1-SDF.

The isotherm adsorption curves were determined by plotting the amount of chlorinated compound uptake (q_e) (mg of adsorbate/g of adsorbent) vs. equilibrium concentration (C_e) (Figure 2). Preliminary results showed highly linear adsorption isotherms. Log adsorption coefficient (log K_d) (L/kg), calculated as the log data from q_e by C_e, for Mg_3Al-SDS are 1.40 (TCE), 1.2 (1,1,2-TCA), and for Mg_3Al-1-SDF they are 1.8 (TCE), 1.5 (1,1,2-TCA).

Discussion

Dodecyl sulfate and 1-dodecane sulfonate were successfully intercalated into Mg_3Al-LDH. PXRD and FT-IR data are similar to those in reported previously [10, 11]. The BET specific surface area of inorganic hydrotalcites (e.g., Mg_3Al-CO_3) is reported to be 50-100 m^2/g [10]. However, when ion surfactants are intercalated the surface dramatically decreases to 0.2-0.4 m^2/g. This can be explained by the presence of surfactant molecules at the external surface of the organo-LDH, generating aggregation of particles and minimizing the access of nitrogen molecules to the internal surface [4, 15]. This is also confirmed by the remnant of trace amounts of Na detected by AAS.

Highly linear adsorption isotherms relate to a partitioning absorption mechanism and were previously reported for CHCs adsorption into organo-LDHs [4, 16]. K_d results suggest that Mg_3Al-1-SDF has a better affinity for TCE and 1,1,2-TCA when compared to Mg_3Al-SDS. However, the log K_d in this work are lower than previously reported values [4]. It is hypothesized that increasing the specific surface area and reducing the particle size could enhance CHCs sorption into organo-LDHs. Therefore, further research is needed to understand which are the optimal parameters/steps to be used in the synthesis to reduce particle size and increase the specific surface area to enhance chlorinated hydrocarbon sorption into the organo-LDHs.

Conclusions

Organo-LDHs were synthesized by co-precipitation and characterized by different techniques to assess the intercalation of two surfactants, and evaluate their possible application as sorbents for TCE and 1,1,2-TCA. The BET specific surface area of organo-LDHs decreased compared to MgAl-CO_3, due to the presence of ion surfactants on the solid surface, which might enhance particle aggregation. TCE and 1,1,2-TCA are partitioned into the organo-LDHs, following a Langmuir model. Mg_3Al-1-SDF shows a higher adsorption capacity for both CHCs compared to Mg_3Al-SDS.

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