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Effect of anion co-existence on ionic organic pollutants removal over Ca based layered double hydroxide

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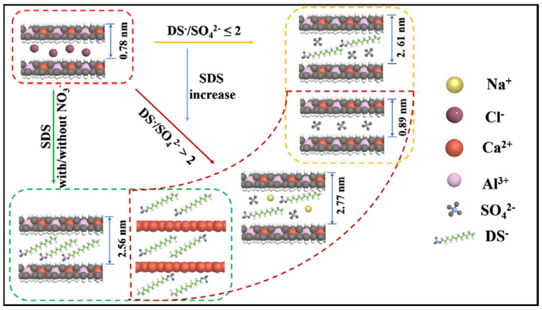
GRAPHICAL ABSTRACT

The effects of anion co-existence on ionic organic pollutants removal by calcium based layered double hydroxide (CaAl-LDH-Cl) were discussed, taking sodium dodecyl sulphate (SDS) as the representative. The nitrate ions have a little influence in SDS removal due to strong electrolysis, while in the case of SO_4^{2-} system, the resultants vary depending on the molar ratio of DS^-/SO_4^{2-}.



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ABSTRACT

The effects of co-existing anions (NO_3^- or SO_4^{2-}) on the removal of sodium dodecylsulfate (SDS), representing anionic organic pollutants, by Ca-based layered double hydroxide (CaAl-LDH-Cl) are investigated to provide fundamental insights on the ionic surfactant removal in the presence of co-existing anions, and facilitate the establishment of a practical and advanced water treatment for environmental remediation. The SO_4^{2-} system shows higher adsorption capacity (4.43 $mmol \cdot g^{-1}$) and larger *d*-spacing of adsorption resultant (3.4 nm) than the control system with no co-existing anion (3.64 $mmol \cdot g^{-1}$, 3.25 nm) and the NO_3^- system (3.82 $mmol \cdot g^{-1}$, 3.27 nm). The macroscopic and microscopic analyses reveal that, NO_3^- had a little influence on the SDS removal due to strong electrolysis, while SO_4^{2-} could significantly promote the SDS removal. Moreover, the reaction mechanism varies under different molar ratios of DS^-/SO_4^{2-}.

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1. Introduction

Ionic organic compounds, especially ionic surfactants, are widely used in industrial processes and commercial products, such as colloid stabilization, metal treatments, mineral flotation, daily-used detergents and pesticides [1,2]. The ubiquitous and persistent presence of ionic surfactants in the environment directly threatens human and animals due to their allergenicity, toxicity, and hemolysis [3–5]. At present, perfluorooctane sulfonate (PFOS) and sodium dodecyl sulphate (SDS) have been classified as persistent organic pollutants (POPs) [6]. Therefore, it is of great significance to efficiently remove these pollutants before discharging them to water system. Among the common treatment methods, sorption technology is simple, safe, economic, easy to operate, highly efficient, and using soil, activated carbons, or silicate-based clays as absorbents. Unfortunately, these adsorbents exhibited low removal capacity, hindering their applications in practice [7–9]. To amend such crucial disadvantage, layered double hydroxides (LDHs) as efficient adsorbent of ionic surfactants have attracted interests from researchers and industries [10–12]. In our previous works, Ca-based layered double hydroxide (Ca-LDHs) showed outstanding removal capacity for SDS through the ion-exchange and the self-dissolution followed re-precipitation [13,14].

Ca-based LDHs, ascribed as a kind of LDHs, consist of main layers [$Ca_2Al(OH)_6^+$] and interlayer anions (such as Cl^-, NO_3^- or SO_4^{2-}) with H_2O molecules. [15]. Besides the hierarchical pore structure, high surface area, and interlayer ion exchange capacity of LDHs' characteristics, Ca-LDHs release Ca^{2+}, $Al(OH)_4^-$ and OH^- ions once added to water due to a specific behaviour called self-dissolution [16,17]. Ca-LDHs demonstrate higher adsorption capacity than other kinds of LDHs, as reported elsewhere [14,18–20]. However, the adsorption capacity of Ca-LDHs would be influenced by factors like co-exist anions, pH and temperature etc. Rojas investigated that the treatment of heavy metal pollutants by CaAl-LDHs was strongly affected by pH [21]. Plank et al. reported that sulphate ions significantly influence the adsorption of polycarboxylate by CaAl-LDHs [22]. Generally, large amounts of inorganic anions, typically NO_3^- or SO_4^{2-}, exist in practical water system. However, there are little concerns on the effects of these anions during the removal of ionic surfactants from aqueous solution by Ca-LDHs.

Herein, we choose to investigate the effect of nitrate and sulphate ions co-existence on the SDS removal, to date the most studies anionic surfactant, by CaAl-LDH-Cl. The objectives of this research are to (1) investigate the SDS removal behaviours from aqueous solution over CaAl-LDH-Cl with/without co-existing anions; and (2) understand the adsorption mechanism of SDS over this adsorbent in the presence of nitrate and sulphate ion.

2. Materials and methods

2.1. Synthesis of CaAl-LDH-Cl

CaAl-LDH-Cl was synthesized by hydrating the freshly prepared tricalcium aluminate (C_3A) in $CaCl_2$ solution. Tricalcium aluminate (C_3A) was synthesized through a solid phase reaction by heating $CaCO_3$ (reagent grade) and low-alkali Al_2O_3 with a molar ratio of 3:1 at 300–1350 °C. The heating process was conducted in a quartz crucible until the free lime content was reduced to below 0.5%, evidenced by X-ray powder diffraction and a modified Franke test. During the hydration process, the suspension was continuously shaken for more than 18 h under N_2 at 55 ± 1 °C. After cooling to room temperature, the suspension was filtered and the filter cake was thoroughly washed with double distilled CO_2-free water until the filtrate was free of Cl^- ion (examined by $AgNO_3$ test). The filter cake was dried at 105 °C overnight, and then ground and stored in a plastic bottle.

2.2. Sorption of SDS by CaAl-LDH-Cl

To understand essentially the interaction between the adsorbate and adsorbent and determine the adsorption capacity of the adsorbent, the sorption isotherms were obtained by measuring the adsorption amounts of DS^- after mixing 5 $g{\cdot}L^{-1}$ of CaAl-LDH-Cl with SDS solutions at $[DS^-] = 0.005–0.2$ M with/without nitrate or sulphate for 24 h. The concentration of inorganic anions was adjusted to 0.04 M for $NaNO_3$ or 0.02 M for Na_2SO_4. The mixed suspensions were shaken in a series of 20 mL centrifuge tubes with the screw cap and aluminium foil liners at 25 ± 1 °C and 150 rpm in a reciprocal shaker to reach the adsorption equilibrium. After centrifugation, concentrations of SDS, NO_3^-, SO_4^{2-}, Cl^-, Ca^{2+} and $Al(OH)_4^-$ in the supernatant were determined accordingly. The amounts of DS adsorbed by CaAl-LDH-Cl (Q_e) was calculated from the difference between the initial (C_0) and the finial equilibrium concentration (C_e) per gram of adsorbent. The initial concentration of DS and that in the supernatants were measured in a Liquid Phase Total Organic Carbon analyser (Multi N/C 2100). NO_3^-, SO_4^{2-} and Cl^- concentrations were determined by an ion-chromatography (METROSEP A SUPP 5–250) at a flow rate of 0.7 $mL{\cdot}min^{-1}$, and the eluent used was 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$. The concentrations of Ca^{2+} and $Al(OH)_4^-$ in supernatants were measured by an Inductively Coupled Plasma-Atomic Emission Spectrometer (Perkin Elmer Optima DV 2000 ICP-AES).

2.3. Preparation of the sorption products

Typically, CaAl-LDH-Cl was added into SDS aqueous solution with [DS] = 0.2 M in the presence of 0.04 M $NaNO_3$ and 0.02 M Na_2SO_4, respectively. The mixture was stirred under N_2 atmosphere at 25 °C for 24 h, and centrifuged. The precipitate was washed and dried at 70 °C for 24 h, ground, passed through 100-mesh sieve, and stored in a plastic bottle. The samples could be denoted as [LDH-SDS], [LDH-SDS-N] and [LDH-SDS-S], respectively. In addition, the samples were prepared by adding 0 and 0.02 M SDS in the presence of 0.02 M Na_2SO_4, marked as [LDH-S] and [LDH-SDS_{02}-S], respectively. And $CaCl_2$ instead of CaAl-LDH-Cl was used to prepare the precipitates with/out sulphate (named as [Ca-SDS] and [Ca-SDS-S], respectively), followed by the same post treatment.

2.4. Materials characterization

Powder X-ray diffraction (XRD) patterns were collected at room temperature on a D/max RBX diffractometer with Cu Kα (40 kV, 100 mA) radiation at a scanning rate of 6° per minute in the 2θ range of 5-65°. In addition, DS^-incorporated samples were also scanned with 2θ range of 1–5° at a rate of 0.5° per minute. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet Avatar 370 in the range 4000–400 cm^{-1} with 4 cm^{-1} resolution. The morphology images were collected by a scanning electron microscope (Hitachi S-4800) with the electric tension of 30 kV and the working distance of 7 mm. The elemental analysis for CaAl-LDH-Cl were determined by ICP-AES using dilute aqua regia as the dissolving agent and a Eurovector EA 3000 automatic elemental analyzer (Eurovector, Milan, Italy).