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

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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·g^{-1}) and larger *d*-spacing of adsorption resultant (3.4 nm) than the control system with no co-existing anion (3.64 mmol·g^{-1}, 3.25 nm) and the NO_3^- system (3.82 mmol·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-}.

Keywords: Calcium based layered double hydroxide (CaAl-LDH-Cl), Sodium dodecylsulfate (SDS), Co-existing anions, Sulphate, Nitrate, Removal mechanism

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 sulfate 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.

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

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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 $[DS^-] = 0.005$ to 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

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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 $0.7mL\cdot min^{-1}$, 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 $K\alpha$ (40 kV, 100 mA) radiation at a scanning

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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).

Results and discussion

3.1 Sorption isotherm with/without nitrate or sulphate

The sorption isotherms of SDS by CaAl-LDH-Cl with/without nitrate or sulphate

were shown in Fig.1 and Table S1. It is noted that all three isotherms fit the Langmuir

model. In the SDS-alone system, the adsorbed DS$^-$ amount increases significantly

from 0.58 to 3.03 mmol·g^1 at a relatively low SDS concentration (5 to 40 mM), then

gradually reaches a plateau. The maximum adsorption amount (Q_m) as 3.64 mmol·g^{-1},

which is much higher than that of other LDHs (~1 mmol·g^{-1}), as reported elsewhere

[20, 23, 24]. In the case of nitrate system, the Q_m value as 3.82 mmol·g^{-1}, which is

quite similar to that in the SDS-alone system. The slightly higher DS$^-$ adsorption in

the presence of nitrate is in accordance to what Caragheorgheopol et al. reported [25].

Nitrate, known as the strong electrolyte, can enhance the affinity capacity of SDS by

reducing the repulsive forces between the polar groups in organic molecules and

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favouring the formation of aggregation [26, 27]. Though sulfate is also a strong electrolyte, the Q_m value in the sulphate system (4.43 mmol·g^{-1}) is significantly higher than those in the SDS-alone and nitrate system. Affirmatively, such a difference implies that the removal mechanism of SDS co-existing with sulphate is different from that with nitrate, as will be discussed shortly.

3.2 Phases change of solids with/without nitrate or sulphate

To elucidate the SDS removal behaviour in the presence of nitrate or sulphate, the solid products before and after the sorption in different systems were analysed by XRD, FT-IR and SEM as exhibited in Figs. 2-4, respectively.

As shown in Fig. 2a, the XRD pattern of as-prepared CaAl-LDH-Cl is identified as $Ca_4Al_2(OH)_{12}Cl_2(H_2O)_4$ with a typical Friedel phase (PDF card No. 78-1219). Sharp reflections ascribed to (002), (004), and (006) indicate a layered structure with $d_{(002)}$ as ca. 0.78 nm. The detail information has been already reported in our previous studies [13, 14]. After sorption, the characteristic peaks at low angles from 2° to 15° are investigated (Fig. 2b). For all samples, two different series of reflections are clearly observed (marked with "*" and "#" in Fig.2b). As previously reported, these two types of frameworks contained in the obtained materials are organic layered double hydroxide with intercalated SDS (LDH-SDS, marked with "*") and Ca-SDS precipitation (marked with "#") resulted from the self-dissolution of CaAl-LDH-Cl combined with SDS, respectively [14].

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Very interestingly, in the sulphate coexistence system, it is worth mentioning that a new series of peaks at 33.14°, 47.58° and 59.22° are identical as Kuzelite (CaAl-LDH-SO$_4$, Ca$_4$Al$_2$ (OH)$_{12}$(SO$_4$)·6H$_2$O, PDF card No. 50-1607, marked as ** in Fig 2), suggesting that SDS is not significantly involved. CaAl-LDH-SO$_4$ is a typical kind of Ca-based LDH with SO$_4^{2-}$ as the interlayer ion, and its d-spacing is 0.89 nm [28], which is much larger than that of CaAl-LDH-Cl. The phenomenon implies that sulphate ion takes over the positions of Cl$^-$ ion between the layers of LDH. It thus is summarized that there is the third resulting product of CaAl-LDH-SO$_4$ in the presence of sulphate system besides two resulting products of LDH-SDS and Ca-SDS. Additionally, the calculated d value from Ca-SDS peaks in the pattern of sulphate system (3.4 nm) is higher than those of nitrate system (3.27 nm) and SDS-alone system (3.25 nm), which further confirms the results of the sorption isotherms. This observation infers that the presence of sulphates enlarges the interlayer distance of resulting product, and consequently increases the amount of adsorbed SDS. Thus, it is reasonable to imply that the nitrate and SDS-alone system show similar removal behaviours of SDS while the sulphate system has another reaction approach, as discussed shortly.

Fig. 3 shows the FT-IR spectra of reacted samples with/without the co-existent anions. As reported elsewhere [29, 30], CaAl-LDH-Cl is identified by the metal-oxygen-metal stretching (400-800 cm^{-1}), the bending vibration of the interlayer water (1620-1660 cm^{-1}), the overlapping stretching vibrations of the interlayer water,

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the hydroxyl groups at 3500 cm^{-1}, and a weak band at 1400-1500 cm^{-1}. After the adsorption of SDS, the overlapping stretching vibrations of the interlayer water and hydroxyl groups at ca. 3500 cm^{-1} and the bending vibration of the interlayer water at ca.1640 cm^{-1} shift to higher wavenumber in all three spectra of [LDH-SDS], [LDH-SDS-N] and [LDH-SDS-S]. This indicates less hydrogen-bonding interaction with the increasing adsorption amount of SDS [31].

In addition, the sample of [LDH-SDS] is also characterized by the C-H bending vibration at 1470 cm^{-1}, the symmetric and asymmetric stretching vibrations of the methyl group at 2920 and 2851 cm^{-1}, and the stretching and bending vibrations of -OSO$_3^-$ group at 1247, 1213 and 1066 cm^{-1}, respectively [32]. These characteristics are also illustrated in the IR spectra of [LDH-SDS-N] and [LDH-SDS-S]. It is found that the bands of -OSO$_3^-$ group at 1247 and 1213 cm^{-1} shift to lower wavenumber than that of SDS, which confirmed that the SDS was successfully intercalated into the interlayer of CaAl-LDH-Cl. Noting that the vibrations of the free sulphate group at 1104 cm^{-1} in the spectra of [LDH-SDS-S] is detected with weak signal while no characteristic of nitrate is found in the spectra of [LDH-SDS-N], indicating that a small amount of sulphate directly react with CaAl-LDH-Cl, while nitrate does not participate in the chemical reaction of SDS removal.

The SEM images of CaAl-LDH-Cl and the products after SDS sorption in the presence of different anions were displayed in Fig. 4. For CaAl-LDH-Cl (Fig. 4a), the sample reveals hexagonal plate-like crystallites with sharp particle edges as well as

uniform particle sizes. The thickness of CaAl-LDH-Cl is around several hundred nanometers with the lateral dimension around 0.5-1.0 μm, which is in good agreement with the previously reported morphology of LDHs [33]. After the adsorption of SDS, some platelets aggregate and become small particles whereas the sheet-like morphology still remains consistent. Compared to the CaAl-LDH-Cl, the particle sizes of [LDH-SDS], [LDH-SDS-N] and [LDH-SDS-S] are significantly increase to 3.0, 2.8 and 1.4 μm, respectively. Generally, it is known that strong electrolytes can reduce the repulsive forces between the polar groups in organic molecules, which is favourable to the formation of aggregation and the enhancement in the affinity of organic materials [26, 27]. In other word, the more SDS aggregate, the more the particle size of the resulting products decreases. The higher SDS concentration leads to higher aggregation degree [26]. Therefore, in terms of particle sizes, we can easily deduce that the loading amount of SDS in [LDH-SDS-S] is the highest among all three systems, which is further identical with adsorption results as discussion above.

3.3 Reaction mechanism

Based on our previous works, it is found that Ca-based LDHs can spontaneously interact with SDS anions via two approaches [14]: *i*) the anion-exchange to form organic LDHs (i.e. DS$^-$ ion interacted into the interlayer of CaAl-LDH-Cl); and *ii*) the self-dissolution followed re-precipitation to assemble organic salt (i.e. Ca-SDS) due to the partial dissolution of Ca-based LDHs. Actually, the concentration of released Ca^{2+} and Al(OH)$_4^-$ ions in aqueous solution play a vital role in these two mechanisms.

Therefore, to better understand the mechanism between CaAl-LDH-Cl and SDS in the presence of nitrate or sulfate ion, the released concentration of Ca^{2+}, $Al(OH)_4^-$ and Cl^- ions in the adsorption process with various initial SDS concentration were investigated in Fig.5

In the case of the SDS-alone system (Fig.5), the released concentration of Cl^- increases rapidly and reaches a plateau (17.6 mM) at the initial SDS concentration of 40mM, while the released concentrations of Ca^{2+} decreases during this process, which confirms that LDH-SDS is formed by re-precipitation. With the increasing initial concentration of SDS (>40 mM), the released concentration of $Al(OH)_4^-$ slightly rises again and Ca^{2+} decreases, then reaches their plateau at the initial concentration of SDS (80 mM), which ascertains that the dissolved Ca^{2+} ions prefer to combine with DS^-, forming Ca-SDS. In the nitrate system, the whole variant trend of every ion is similar to that in the SDS-alone system. Yet the re-precipitation of LDH-SDS brings forward at the initial concentration of SDS (20 mM), and the equilibrium released concentrations of $Al(OH)_4^-$ ions is around 4.5 mM, which slightly exceeds that in the SDS-alone system. In addition, it is found that the residual concentrations of NO_3^- ions in the systems with different initial SDS concentration are around 40 mM (Fig.6), which is close to the initial concentration of NO_3^- (40 mM), revealing that NO_3^- ion do not participate in SDS removal. Accordingly, it confirms that the enhancement of SDS adsorption on CaAl-LDH-Cl is mainly subject to the strong electrolysis from nitrate.

The sorption behaviour in the sulphate system is found different from the SDS-alone and nitrate systems, as shown in Figs 5 and 6. At the very beginning of the reaction (i.e. without SDS), the released concentration of Cl^- instantly increases to 17.6 mM, which is close to the theoretical maximum concentration of Cl^- calculated from 0.1 g CaAl-LDH-Cl in 20 mL aqueous solution. Meanwhile, the concentrations of Ca^{2+}, $Al(OH)_4^-$ and SO_4^{2-} are 0.40, 5.45, and 0.90 mM (Fig.6), respectively. In terms of mass conservation before and after reaction, all Cl^- ions from CaAl-LDH-Cl are completely released. Combining with the XRD patterns shown in Fig. S1, it is found that the resulting products from sulphate system consist of LDH with sulphate ion as the interlayer anion (marked with **) and Ettringite (Aft, $[Ca_3Al(OH)_{12} \cdot 12H_2O]_2(SO_4)_3 \cdot 2H_2O$, PDF card No. 41-1451, marked as ●). It is ascertained that the major process in the sulphate system is the ion-exchange, in which all Cl^- ions is replaced by sulphate ions.

In Figs. 5 and 6, noted that the trends of all curves vary at a specific point at DS^-/SO_4^{2-} molar ratio = 2, which represents the balance of charge between the monovalent DS^- and divalent SO_4^{2-}. Before the DS^-/SO_4^{2-} molar ratio reaches 2 ($DS^-/SO_4^{2-} \leq 2$), Cl^- concentration has no change whereas the concentration of released Ca^{2+} increases as well as that of sulphate ions, accompanying with the decrease of $Al(OH)_4^-$ concentration. Yet the concentration of sulphate ion does not reach 0.2 mM, the maximum level. Moreover, CaAl-LDH-SO4 and LDH-SDS are both observed in the XRD pattern (Fig. S1), and the *d*-value of [LDH-SDS] from this

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system is slightly higher than those of the other two systems, which leads to the increase of SDS adsorption.

As the DS^-/SO_4^{2-} molar ratio exceeds 2 ($DS^-/SO_4^{2-}>2$), the concentrations of Ca^{2+} and $Al(OH)_4^-$ gradually decrease then reach plateaus at 0.80 mM and 5.20 mM, respectively, while the concentration of sulphate ions remains at 6.50 mM. The total negative charge from DS^- and SO_4^{2-} in the precipitation is far beyond the available positive charge from $[Ca_2Al(OH)_6]^+$, the main layer of LDH. Consequently, Na^+ ions from Na_2SO_4 are needed to enter the interlayer space and balance the redundant negative charge, which is known as intersalation. In fact, the intersalation occurs during the intercalation between organic matters and LDHs in coexistence of inorganic salt, in which the cations from the coexisting salts (i.e. Na_2SO_4) mingle with anion to make the *d*-value of LDHs far larger than that in the pure organic matter system [22], enhancing the adsorption capacity of LDHs. Therefore, intersalation may contribute to the higher adsorption amount of SDS in the presence of sulphate system than those in SDS-alone and nitrate system. Besides, the concentration of released $Al(OH)_4^-$ are higher than those of SDS-alone and nitrate systems, i.e. less Al in the precipitate of the sulphate system. This could be attributed to less LDH formation as the consequence of more Ca-SDS precipitation, promoted by increasing ionic strength [34].

Furthermore, to check whether the formation of [Ca-SDS] involves intersalation in presence of Na_2SO_4, $CaCl_2$ instead of CaAl-LDH is adopted to treat the SDS-alone

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and sulphate coexistence system. the XRD patterns of the products are shown in Fig.7. The products are denoted as [Ca-SDS] and [Ca-SDS-S], respectively. Strong peaks from [Ca-SDS] and [Ca-SDS-S] at similar positions are observed, revealing that both products have similar crystal phase and layered structure. Moreover, the FT-IR spectra of [Ca-SDS] and [Ca-SDS-S] display the similar characteristic vibrations of SDS (Fig. 8). The peaks at 1246 and 1470 cm^{-1} correspond to S=O group and C-H bending vibration, respectively, which are similar to those in the spectra of [LDH-SDS] and [LDH-SDS-S] (Fig. 3), suggesting that the similar re-precipitation reaction occurred between SDS and the Ca^{2+} ions from CaAl-LDH, irrelevant sulphate coexistence.

As discussed above, both modes of ion exchange and self-dissolution followed by precipitation exist in the SDS adsorption process, regardless of the presence of nitrate/sulfate ion. Yet the SDS adsorption amounts mainly depend on the functional mechanism of coexisting ions, including the ion-exchange capacity with SDS and the combination capacity with CaAl-LDH-Cl. We can now draw general schemes for the interaction between SDS with CaAl-LDH-Cl with/without nitrate and sulphate in Fig.9. For nitrate, due to the poor combination capacity with LDH-Cl, it only enhances SDS adsorption slightly by means of the strong electrolysis. While in the case of sulphate, when DS^{-}/SO$_4^{2-}$ is below 2, the ion-exchange process occurs between SDS and sulfate ion in the interlayer space of LDH. When DS^{-}/SO$_4^{2-}$ is much

more than 2, the intersalation occurs besides ion-exchange and self-dissolution followed by precipitation to further enhance the SDS adsorption amount.

Conclusions

To summarise, the presence of nitrate in SDS sorption process do not influence the solid phase of sorption product, though the particle sizes are lower. Though SDS intercalation into LDH is the common reaction route in all three systems, anion exchange between sulphate in solution and chloride in LDH occurred, increasing the interlayer distance before SDS initiated anion exchange with sulphate. Hence, the DS and sulphate anions co-exist in the interlayer region of the resulting LDH product. Potential mechanisms are investigated by analyzing the ion concentrations during the SDS removal process. NO_3^- ions have no obvious influence on the SDS removal efficiency, while SO_4^{2-} ions are involved in the SDS removal by LDH. At low molar ratio ($DS^-/SO_4^{2-}<2$), part of SO_4^{2-} ions are replaced by SDS, and the absorbed amount of SO_4^{2-} and SDS keep steady under high molar ratio ($DS^-/SO_4^{2-}>2$).

Acknowledgments

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

double hydroxide

Ping Zhang [a,b], Sida Ouyang [a], Peng Li [b], Zi Gu [d], Yun Huang [a*], Shuguang Deng [a,c *]

Fig. 1 Adsorption isotherms for SDS by CaAl-LDH-Cl in SDS aqueous solutions with/without
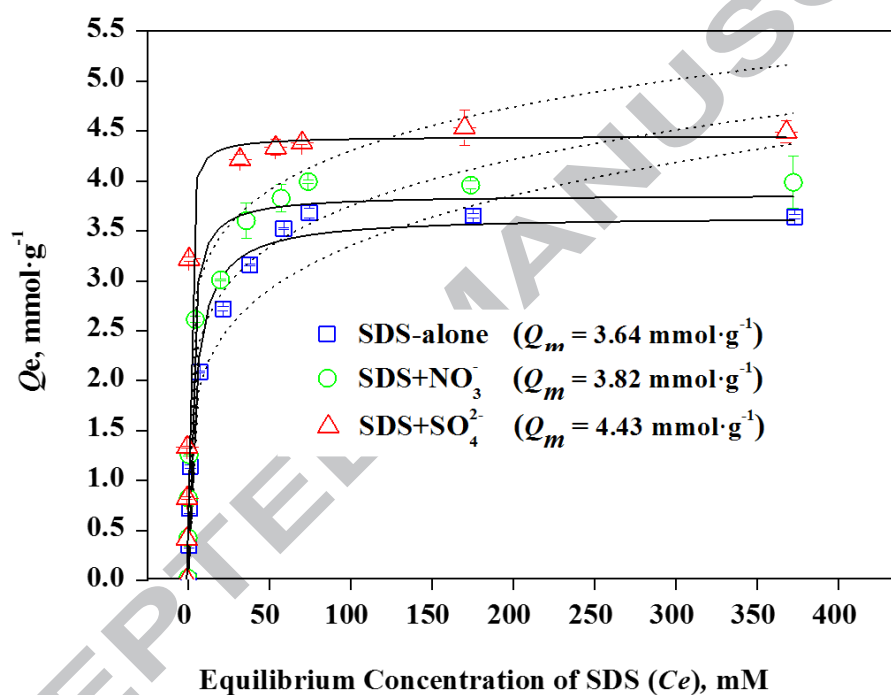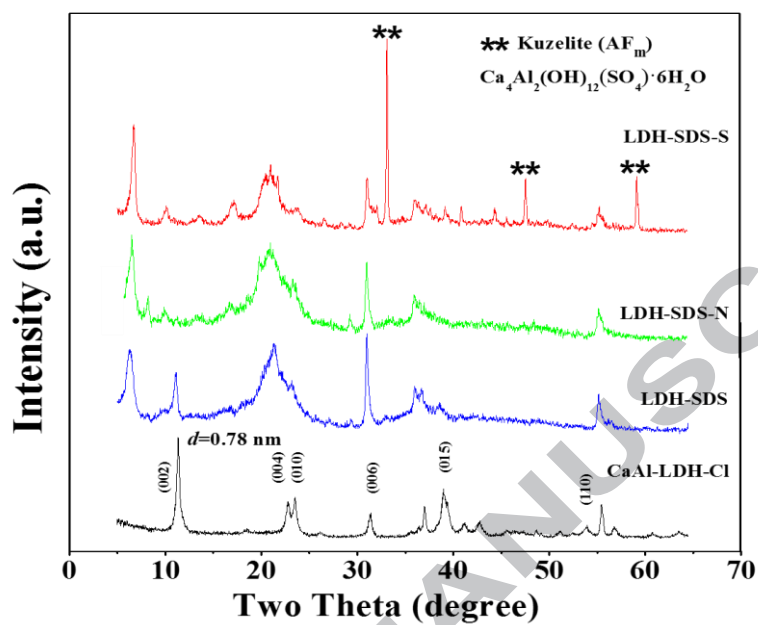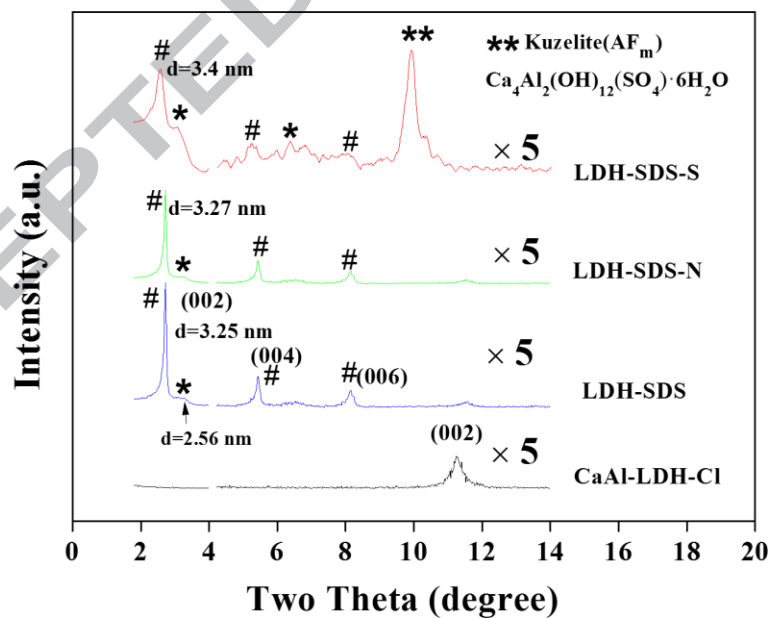
nitrate ions and sulphate ions.

Fig. 2 XRD patterns of CaAl-LDH-Cl, [LDH-SDS], [LDH-SDS-N], and [LDH-SDS-S] scanned

from (A) 5-65° and (B) 2-15°.

(A)

(B)

Fig. 3 FT-IR spectra of CaAl-LDH-Cl, [LDH-SDS], [LDH-SDS-N], and [LDH-SDS-S].

21
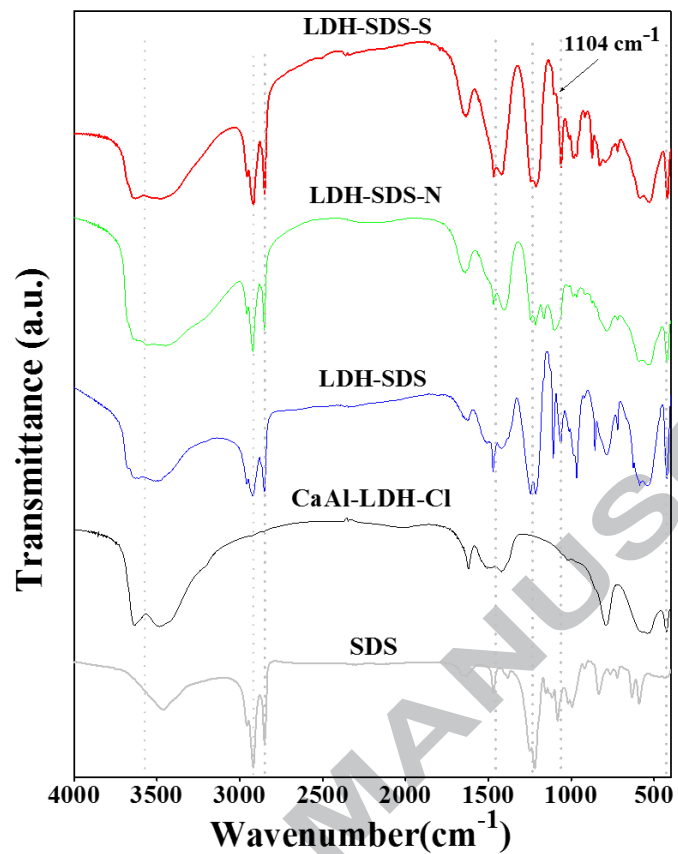
Fig. 4 SEM images of (A) CaAl-LDH-Cl; (B) [LDH-SDS]; (C) [LDH-SDS-N]; and (D) [LDH-SDS-S].
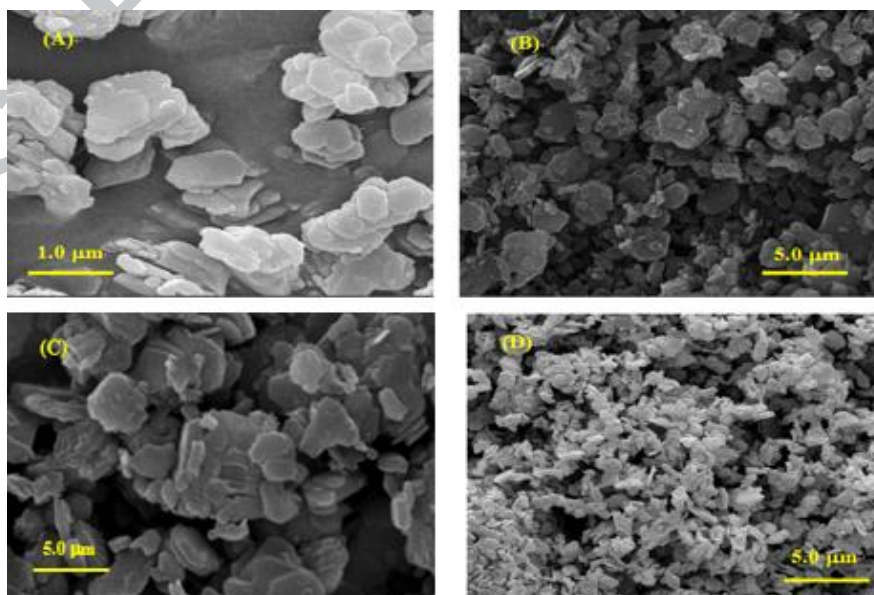
Fig. 5 Released concentration of Cl^-, Ca^{2+} and $Al(OH)_4^-$ ions of the resulting products during

adsorption process in SDS aqueous solutions coexisting with/without nitrate ions or sulphate ions.
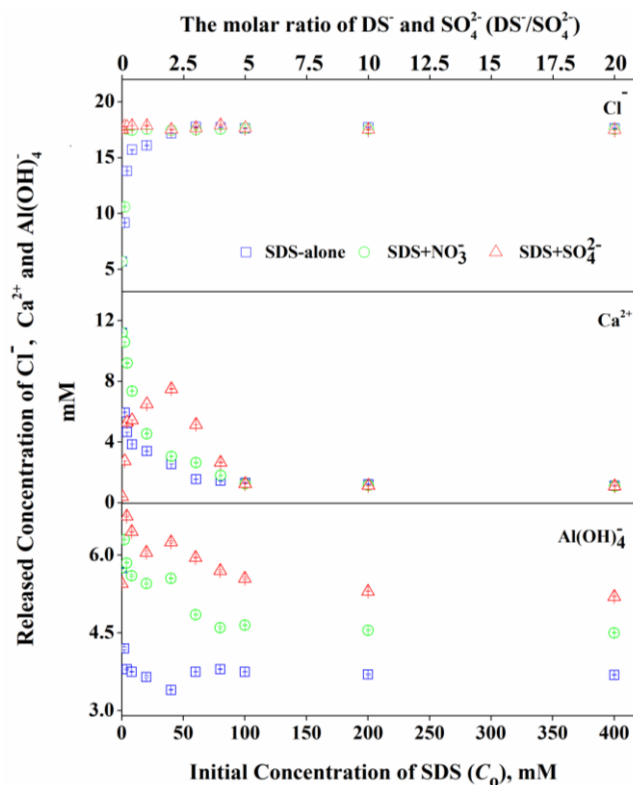
Fig. 6 Concentrations of NO_3^- ions and SO_4^{2-} ions during adsorption process in SDS aqueous

solutions coexisting with nitrate ions or sulphate ions.

23
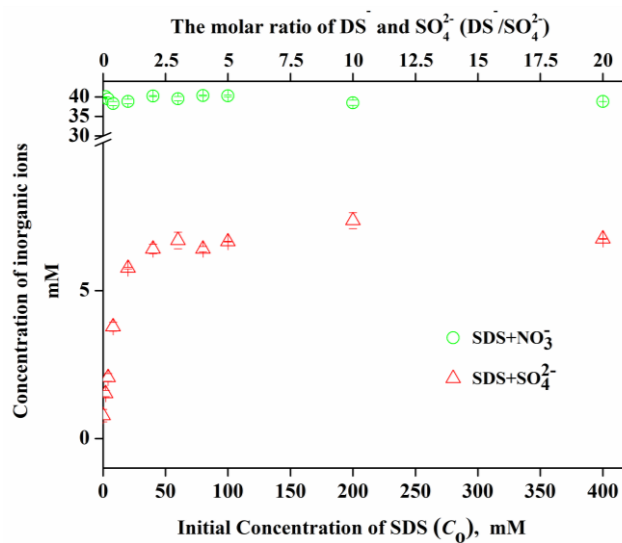
Fig. 7 XRD patterns of the phases obtained from the SDS adsorbed by $CaCl_2$ in 0.2 mol·L^{-1} SDS aqueous solution with/without sulphate ions scanned from 2-15° (The diffraction peaks marked with '■' are attributed to Ca-SDS).
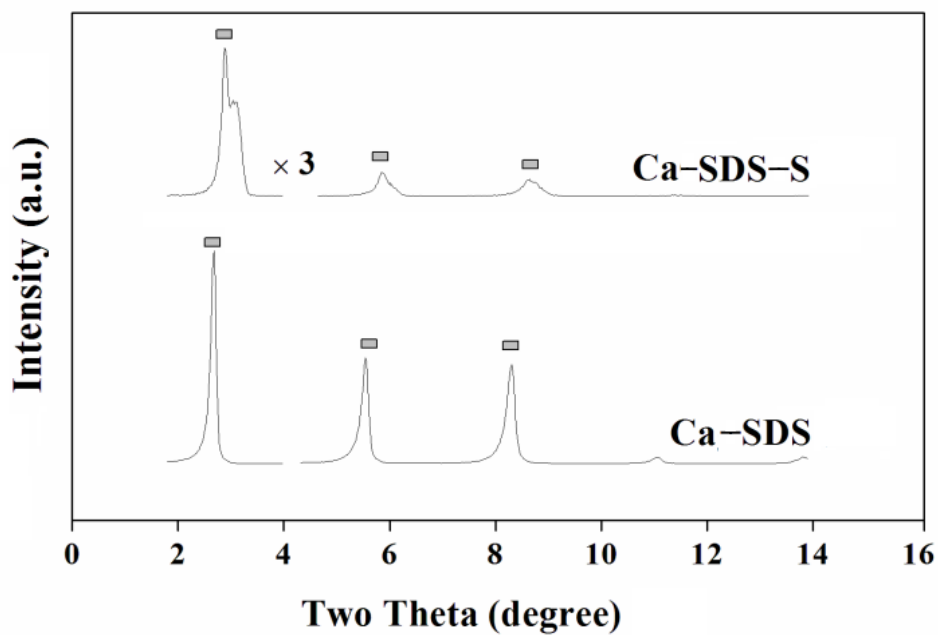
Fig. 8 FT-IR spectra of the phases obtained from the SDS adsorbed by $CaCl_2$ in 0.2 mol·L^{-1} SDS aqueous solution with/without sulphate ions.

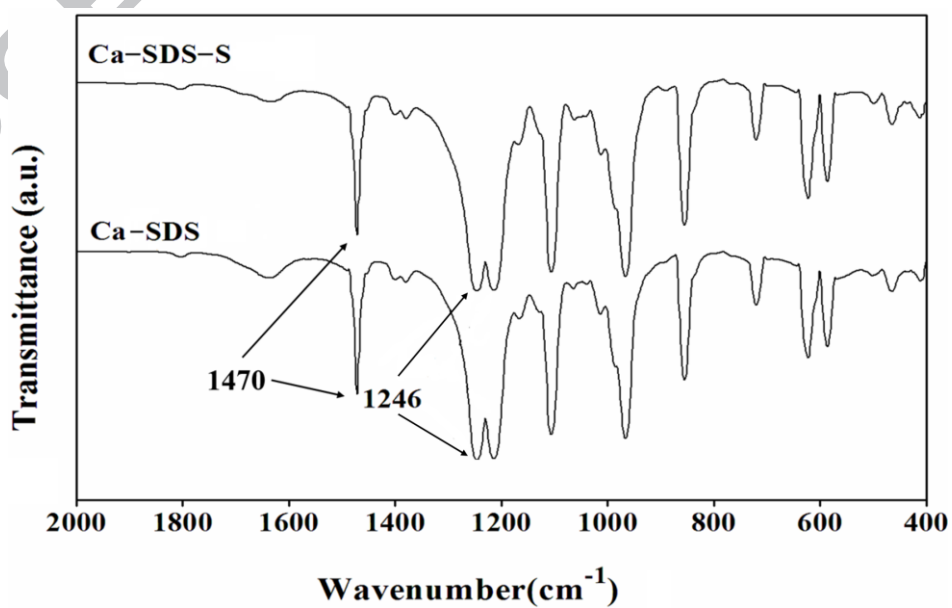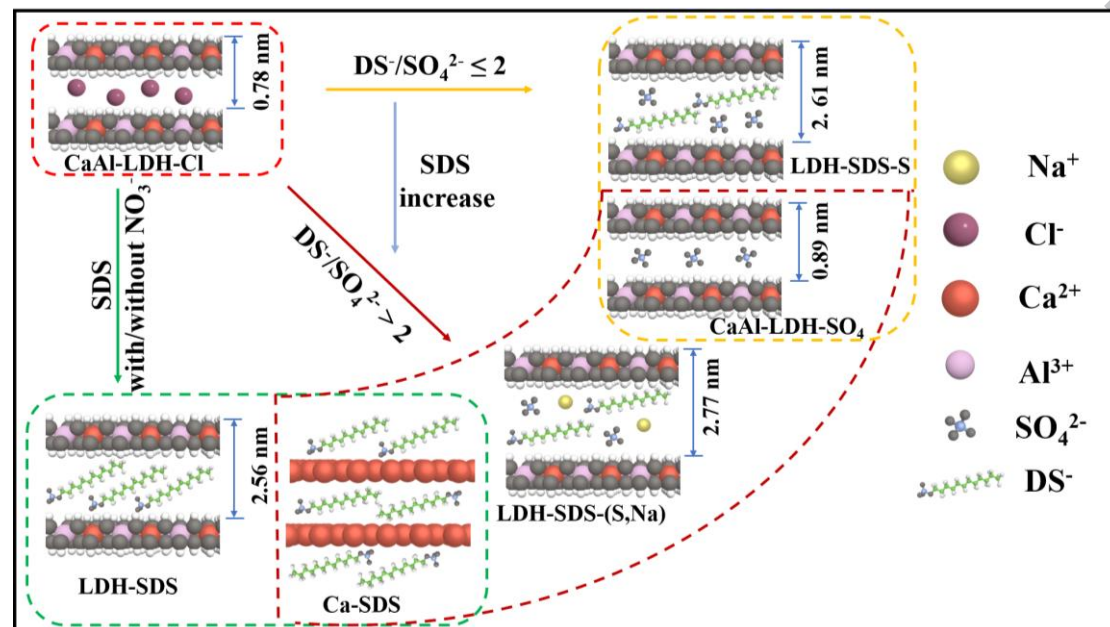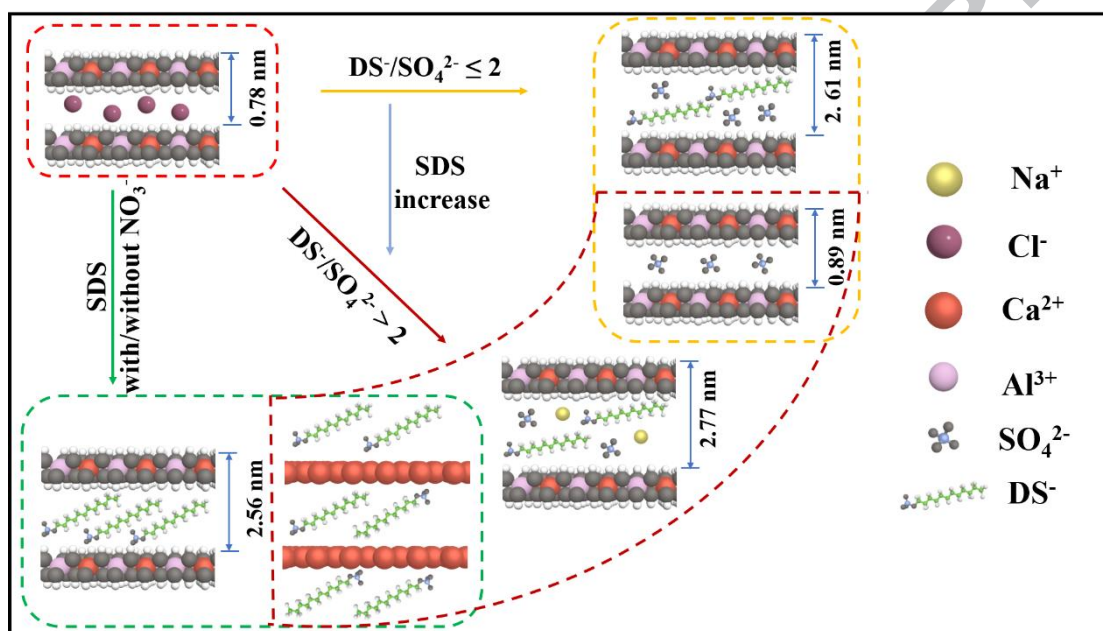Fig. 9 The schematic illustration for the adsorption mechanism for SDS on CaAl-LDH-Cl

coexisting with nitrate and sulphate ions.

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

Ping Zhang [a,b], Sida Ouyang [a], Peng Li [b], Zi Gu [d], Yun Huang [a*], Shuguang Deng [a,c*]

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 sulfate (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-}.