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Arsenic Pollutants Removal from Water by Sulphur Species Functionalized Mg-Al Layered Double Hydroxide

AUTHORS

Zhe LIU / QUEENSLAND UNIVERSITY OF TECHNOLOGY, 70 MARY STREET, BRISBANE, QLD, AUSTRALIA, BRISBANE

Corresponding author : Sarina SARINA / s.sarina@qut.edu.au

PURPOSE OF THE ABSTRACT

Mg-Al layered double hydroxide (Mg-Al LDH) are regarded as an effective adsorbent for contaminant removal from aqueous solutions, which consists charged layers and exchangeable carbanion ion between the layers. In this study, the LDH modified by sulphur species (LDH-S) was prepared by the "memory effect" of LDH, which was found to be more efficient sorbents for the removal of As (V) from an aqueous solution with the adsorption capacity of 45 mg/g (0.6 mmol/g). By the structure characterization for LDH-S via X-ray diffraction, transmission electron microscope and energy-dispersive X-ray spectroscopy, the adsorbent keeps the original layered structure after As absorption. The detailed density functional theory calculation illustrates that the enhanced capture ability of LDH-S for As species is related to the strong affinity between HS⁻ ion (in the layer of LDH) and the HAsO₄²⁻. Furthermore, LDH-S with different ratios of Mg to Al were compared for As absorption in the same condition, the ratio of 2-1 (Mg to Al) shows the best performance and stability in lower pH value condition.

The Mg-Al LDH was fabricated by the standard co-precipitation method. The LDH samples were put into Muffle oven for calcination in air atmosphere at 450 °C for 8 h. The calcined LDH (2.0 g) were mixed with Na₂S aqueous solution (0.02 M, 50 mL) under vigorous stir-ring at room temperature for 16 h. The solid was obtained by centrifuge, then washed with deionized water for three times and dried in oven at 80 °C for 16 h. The product was collected and grinded which was then denoted as LDH-S.

For the subsequent analysis of the absorption capacity of LDH and LDH-S, the removal amount-equilibrium concentration curves for the target ion are plotted. Generally, LDH-S adsorbents are found to outperform pristine LDHs. In this study, 50 mg of LDH (2-1)-S was utilized as adsorbent with increasing concentration of arsenate aqueous solution. When the initial arsenate concentration is 20 ppm, LDH-S adsorbent can completely remove the target ions and in 30 mL solution at room temperature. In comparison, pristine LDH can only remove 37 % of the target ions from the pollutant system under the same condition. Despite the Mg to Al ratio, enhanced arsenate uptake can be observed in LDH-S, which confirms the key function of S species for the absorption of target ions and the necessity of the LDH modification.

To illustrate the adsorption performance of HAsO₄²⁻ in LDH and LDH-S, the adsorption energy (E_{ads}) was calculated based on density functional theory (DFT). We used the fully relaxed LDH structure as a starting point to simulate the local environment of the HAsO₄²⁻. The optimized lattice constants are in good agreement with previous report, indicating the reliability of our calculations. When the HAsO₄²⁻ ion is inserted into pristine LDH, the calculated formation energy of As species (E_{ads1}) is -3.56 eV/supercell. In contrast. The adsorption behavior of HAsO₄²⁻ in LDH-S adsorbent show distinct trait. After the ion-exchange by Na₂S aqueous solution, HS⁻ replace most of the anions between layer spaces of LDH. In order to keep the neutral charge condition, CO₃²⁻ was replaced by two HS⁻ in our simulation. The interaction between HAsO₄²⁻ and HS⁻ is very strong, leading to the movement of H towards O₃ from the As species. Lower adsorption energy value indicates more favorable thermodynamic interaction between LDH-S and As species.

In conclusion, removal of arsenate ion in aqueous solution with high efficiency can be achieved by LDH modified with sulphur species. This is the first time to explain the absorption mechanism by comparing the absorption

energy, which is different from the conventional precipitation mechanism or ion-exchange mechanism. LDH-S materials has been prepared and applied into the As capture from water system, which was regarded as an efficient candidates for the water pollution treatment.

FIGURES

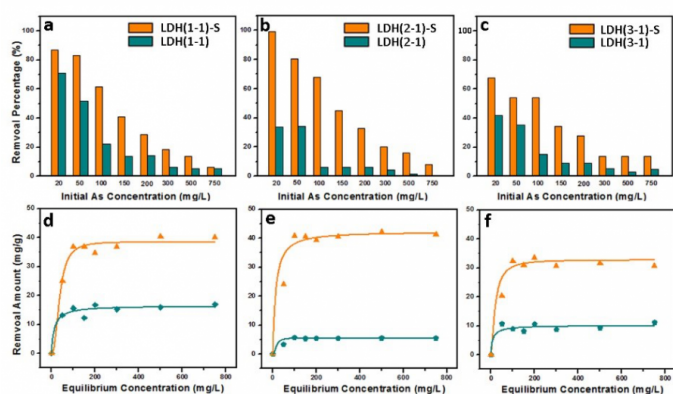


FIGURE 1

Figure 1

Removal capacity of LDH and LDH-S for the target ions are illustrated by the removal percentage and removal amount different concentration. 50 mg LDH or LDH-S was utilized as absorbent in 30 mL target ion aqueous solution for 16 h to confirm the complete

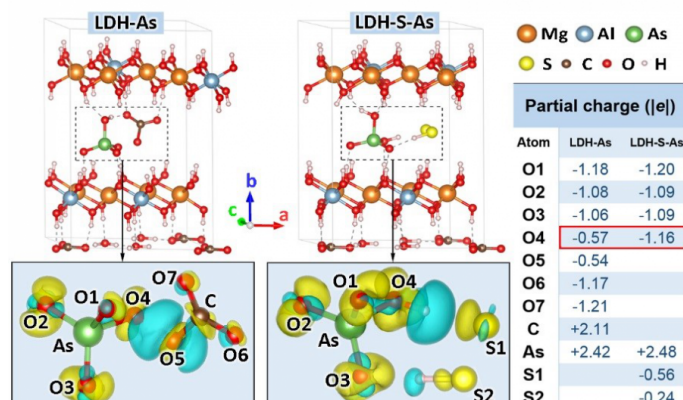


FIGURE 2

Figure 2

Optimized structure of (a) LDH, (b) LDH-S after HAsO₄²⁻ adsorption (the numbers in zoom-in insets denote the calculated partial charges from Bader analysis). Bottom image is the charge density difference where yellow and blue isosurfaces indicate charge a

KEYWORDS

layered double hydroxide | arsenate removal | sulphur modification | water cleaning

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