

Novel layered double hydroxides for uranium removal: a review

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Abstract: In recent years, due to the rapid development of China's nuclear industry, the need for uranium has been expanding, while the environmental pollution of water caused by uranium is also receiving more and more attention. Laminated double hydroxide (LDH) is favored by researchers in water pollution removal due to its special layered structure, good adsorption performance, regeneration and easy recycling. The mechanism of adsorption of uranium by the new LDH is summarized, the preparation process and removal effect are introduced, the removal mechanism and influencing factors are analyzed, and on this basis, the future development and research of adsorbent materials are proposed.

1. Introduction

The demand for uranium has increased rapidly due to its role as a key fuel for nuclear energy development. This has led to more frequent uranium mining activities, which inevitably result in the release of uranium wastewater into the environment, especially during the processes of mining, smelting, and nuclear power plant accidents. Uranium-containing wastewater is highly radioactive and chemically toxic, and has a continuous negative impact on the subenvironment^[1-2]. Additionally, uranium(VI) can accumulate in the human body through the food chain^[3], posing a significant risk to human health. Therefore, the discharge of uranium wastewater is a potential threat to both the environment and human health^[4-5]. Addressing the urgent need to effectively treat and recycle uranium wastewater has become a significant nuclear environmental issue.

Currently, there exist several proposed methods for the removal of uranium, including ion exchange^[6], flocculation^[7], reverse osmosis^[8], bioreduction^[9-10], precipitation^[11], and adsorption^[12], among others. The advantages of the adsorption method include its simplicity, high efficiency, and selectivity, with the key factor being the selection of an optimal adsorbent. Laminated double hydroxides (LDH) are known for their excellent physicochemical properties, modifiability, and strong anion exchange capacity, making them a common material for pollutant removal in water. This review paper presents a detailed account of the research progress, preparation process, adsorption mechanism, and adsorption effectiveness of new LDH materials. Suggestions and future outlooks for research applications and development directions are also discussed.

2. Preparation and Properties of Layered Double Hydroxide Materials (LDHs)

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Layered double hydroxide materials can be synthesized using various methods, including hydrothermal, co-precipitation, ion exchange, and roasting reduction.

2.1 Hydrothermal method

The hydrothermal method involves synthesizing materials under high-temperature and high-pressure conditions. The method involves increasing the solubility of insoluble materials in water by elevating the temperature and pressure, followed by cooling and crystallization to further precipitate the material out of the solution. This approach allows for the controlled preparation of LDHs with regular microcrystalline morphology. By adjusting the reaction temperature and time, different morphologies and sizes of LDHs can be synthesized in a controlled manner^[13].

For instance, Peng Li et al.^[14] have used the hydrothermal method to synthesize magnesium-iron layered double hydroxides (Mg-Fe LDHs) for the removal of uranium from wastewater. The optimal preparation conditions involved a molar ratio of Mg to Fe of 4:1, pH of 12.0, and a hydrothermal reaction time of 4.0 hours at 180°C. The resulting adsorbent exhibited excellent crystal structure and high uranium adsorption capacity. The optimum adsorbent synthesized had a well-defined hierarchical amorphous hydroxide LDH morphology with a particle size of approximately 80 nm and a uranium adsorption capacity of 710.0 mg/g. Uranium was removed in the form of UO_2^{2+} through the chelation reaction with interlayer anions.

Peng Lyu et al.^[15] developed a novel phosphorus-modified bamboo biochar (PBC) cross-linked layer double hydroxide (LDH) composite material ("PBC@LDH") through phosphate pre-impregnation and hydrothermal synthesis. Compared to the original biochar (BC), PBC@LDH significantly increased the BET specific surface area and surface functional groups abundance. Indoor cultivation

experiments demonstrated that 10% PBC@LDH exhibited good fixing ability for uranium in soil. In column leaching tests simulating acid rain, PBC@LDH treatment significantly reduced the cumulative loss and leaching rate of U(VI), reaching 53% and 54%, respectively. The adsorption and fixation mechanisms of PBC@LDH for U(VI) are mainly surface complexation, co-precipitation, and reduction.

2.2 Co-precipitation method

The co-precipitation method involves adding a mixed solution containing a certain proportion of metal cations to an alkaline solution under certain temperature conditions, controlling the pH of the solution to reach a target value during the reaction, stirring the solution until co-precipitation occurs, continuing to age the product for a certain period of time, and finally filtering, washing and drying to obtain LDHs^[16].

Xiuling Guo et al.^[17] employed the co-precipitation method to synthesize a binary layered double hydroxide (Ni-Co LDH_{w-7}) for the efficient adsorption of U(VI) from wastewater. The study revealed that the maximum adsorption capacity of U(VI) by Ni-Co LDH_{w-7} was 201.09 mg/g at pH=6.0 and 298 K. Furthermore, Fourier infrared spectroscopy and x-ray photoelectron spectroscopy measurements were performed to elucidate the adsorption mechanism of U(VI) by Ni-Co LDH_{w-7}. The results showed that the electrostatic interactions on the inner surface and complexation, which is dominated by abundant oxygenated M-OH and interlayer OH⁻ ions, played a major role in the U(VI) extraction by Ni-Co LDH_{w-7}. The abundant M-OH functional groups contributed to the complexation of U(VI) with Ni-Co LDH_{w-7}.

Jingwei Tu et al.^[18] synthesized magnesium binary layered double hydroxide (MgAl-LDH) and its iron-induced ternary hydroxide (MgAlFe-LDH) by co-precipitation method to extract U(VI) at simulated concentrations in brine systems in saline lakes. The results showed that both LDHs had a strong affinity for U(VI) at different stages. Specifically, MgAl-LDH

exhibited strong affinity at lower U(VI) concentrations (0.2 mg/L to 5 mg/L), while MgAlFe-LDH had a stronger affinity at higher U(VI) concentrations (5 mg/L to 30 mg/L). Hence, both LDHs are suitable for U(VI) extraction from salt lakes at different concentrations. Furthermore, the adsorption mechanism of U(VI) by both LDHs was investigated through X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) studies. The results indicated that the adsorption mechanism was mainly surface complexation and interlayer carbonate co-precipitation.

2.3 Ion-exchange method

Ion exchange method is mainly based on the exchangeability of interlayer anions of layered bimetallic hydroxide. It is a method to exchange the required anions with interlayer anions. This method can not only maintain the original structure between the metal plates of layered bimetallic hydroxide. The layered bimetallic hydroxide with different functions can also be obtained according to the requirements of self-design. The advantage of the ion exchange method is that the reaction time is short and the number and type of anions between layers can be assembled while maintaining the original layered structure of LDHs.

Lixiao Yang et al.^[19] prepared NO₃-LDH using the NO₃⁻/CO₃²⁻ anion exchange method and then synthesized the MgAl-PMA-LDH composite material (referred to as PMA-LDH) through complete anion exchange between PMA⁴⁻ and NO₃⁻ using NO₃-LDH as a precursor, followed by swelling/reduction. The excellent adsorption performance of the composite material for U(VI) is attributed to the hydrogen bond interaction between the deprotonated PMA⁴⁻ -COO⁻ and LDH, as well as the π - π stacking interaction between the PMA⁴⁻ phenyl rings, which further enhances the structural stability. The maximum adsorption capacity of PMA-LDH for U(VI) was found to be 352 mg/g. The schematic diagram of the preparation principle of PMA-LDH and the interaction mode between UO₂²⁺ and PMA⁴⁻ are shown in Figure 1.

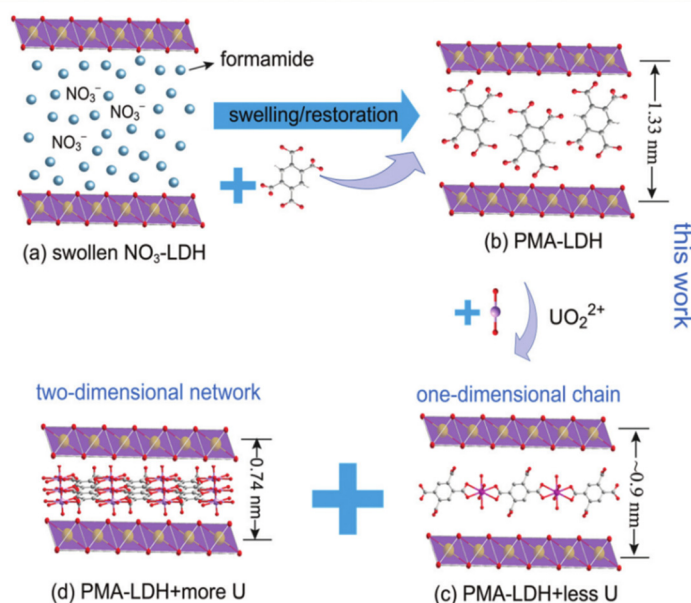


Figure 1 depicts a schematic representation of the preparation process for PMA-LDH, and also illustrates the interaction pattern of UO_2^{2+} with PMA⁴[19].

Hui Wang et al.^[20] synthesized MgAl-BAO-LDH composites (referred to as BAO-LDH) via an ion exchange method, by introducing benzamidoxime (BAO) into the interlayer of MgAl-LDH, for the purpose of uranium extraction in seawater and nuclear wastewater treatment. The incorporation of BAO into the LDH interlayer, and the consequent substitution of the starting NO_3^- anion, was verified through X-ray diffraction (XRD) spectra. The BAO-LDH exhibited a remarkable maximum adsorption capacity of 327 mg/g and an exceptionally high selectivity towards UO_2^{2+} due to the coordination of interlayer BAO (N and O as ligands) with UO_2^{2+} and the synergistic interaction between the hydroxyl groups of the LDH layer and UO_2^{2+} .

2.4 Roasting reduction method

The calcination-reduction method can eliminate the competition between metal salt inorganic anions and organic anions for intercalation, and achieve the repeated utilization of LDHs by utilizing the "memory effect". After calcination at 300-500 °C, LDHs are transformed into layered double metal oxides (LDOs), which can reconstruct the layered structure and reform LDHs when they come into contact with water or solutions containing suitable anions. The reconstruction process is facilitated by the presence of residual metal cations and the memory effect of LDHs, resulting in the restoration of the original layered structure and intercalated anions. This method provides a promising approach for the preparation and regeneration of LDHs with high efficiency and sustainability^[21].

Meiqing Chen et al.^[22] employed this method to prepare MgAl-LDO-500 by calcining MgAl-LDH in air at 500 °C. MgAl-LDO-500 showed remarkable adaptability to immobilize U(VI) in a broad pH range (3-10) and different aqueous matrices, with coexisting ions. The adsorption of U(VI) by MgAl-LDO-500 was found to have an equilibrium time of 15 minutes and a

maximum adsorption capacity of 1098.90 mg/g. The insertion of the anionic form of U(VI) into the layers of MgAl-LDO-500 led to a reorganization of the layered structure. XRD, SEM, FTIR, and XPS analyses revealed that the memory effect and surface complexation were the primary mechanisms responsible for the enhanced U(VI) fixation observed in MgAl-LDO-500.

Xiuling Guo et al.^[23] have successfully synthesized Ni-Co layered double hydroxides (Ni-Co LDO-X, where X represents the calcination temperature) with favorable electrostatic attraction and complexation through calcination of Ni-Co LDH under air atmosphere. Their study reveals that the amount of uranium adsorbed on Ni-Co LDO-X is significantly influenced by the calcination temperature, with Ni-Co LDO-500 exhibiting the highest adsorption capacity (707.91 mg/g) followed by Ni-Co LDO-650, Ni-Co LDO-350 and Ni-Co LDH (201.09 mg/g). Moreover, Ni-Co LDO-500 demonstrates superior adsorption capacity compared to Ni-Co LDH for U(VI). The good adsorption capacity of Ni-Co LDO-500 for U(VI) is mainly attributed to the memory effect, electrostatic interactions, and complexation on the outer sphere surface. These findings have broadened the application range of hydrotalcite materials in uranium removal and facilitated the reuse of these materials.

Based on the provided material, it can be inferred that the calcination of layered double hydroxides (LDH) to layered double oxides (LDO) leads to a further improvement of U(VI) adsorption capacity compared to LDH, and the memory effect plays a crucial role in its good U(VI) adsorption ability. The conversion between LDH and LDO can expand the application range of hydrotalcite-like materials in uranium removal and enable the repeated use of the materials.

3. Mechanism of U(VI) adsorption by LDH

Pang Hongwei et al.^[24] prepared a Ca-Mg-Al ternary hydroxalcalite material, CMAL-SNZVI, using a hydrothermal synthesis method, and studied its U(VI) removal efficiency under different pH and solution ion concentrations. The results indicated that its action mechanism belongs to inner surface complexation. The adsorbent and pollutant were bound by chemical bonds and were affected by electrostatic interactions. Lichao Tan et al.^[25] prepared an rGO/NiAl-LDH composite material with a uranium(VI) adsorption capacity that was higher than that of most other reported materials. The study summarized that the functional groups (such as C-H, -OH, and -COOH) on the surface of reduced graphene oxide (rGO) ensured the capture of metal cations (UO_2^{2+}) by surface complexation mechanism. Xin Wang et al.^[26] synthesized a three-dimensional flower-like phos-LDH functionalized layered double hydroxide (3D flower-like phos-LDH) and found that at pH 5.0, there was an electrostatic attraction between UO_2^{2+} and phos-LDH, and the -OH on the surface of phos-LDH sheets also had a complexation effect with UO_2^{2+} . In summary, the adsorption of LDH materials on U(VI) depends on ion exchange, coordination, physical adsorption caused by electrostatic effects, and other factors. To improve the adsorption performance of materials, modification methods such as grafting and intercalation can be used to increase the active sites of the adsorbent, improve stability, and enhance the adsorption performance of the material, depending on the situation.

4. Conclusion and outlook

The adsorption mechanism of LDH mainly consists of ion exchange, coordination and electrostatic interactions. It has the characteristics of high ion exchange capacity, radiation resistance and low cost, but also has the problems of complex functionalisation modification and structural instability. The preparation of LDH with good structural stability is one of the current research priorities, but the properties of the materials are often more complex after modification. These materials may have disadvantages such as being toxic, causing secondary contamination, being costly or complex to synthesise, which need to be explored in more depth for subsequent research and improvement.

At the same time, most of the research at this stage is based on simulated wastewater, with fewer interfering ions to consider, whereas the situation in practical applications will be more complex, with various organic substances and other metal ions having a certain impact on the adsorption effect, and the preparation of highly selective LDH is also an important direction to be put into practical industrial use in the future.

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