

Supplementary Materials

Removal of uranium from wastewater through Ni-Al-layered double hydroxide@carbon nanotube functionalized by polyethyleneimine

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1. Batch adsorption experiments

1.1 Effect of pH

A uranium solution (1000 mg/g) was diluted to 200 mg/g; 50 mL of the 1000 mg/g solution was added into 100 mL conical flask, and 0.1 M NaOH and 0.1 M HNO₃ were used to adjust the pH of the solution to 2, 3, 4, 5, 6, 7, 8, and 9. Then, 0.02 g of adsorbent material was added. The conical flask was placed in a constant-temperature water bath shaker and then was allowed to react at 298 K and 180 r/min for 12 h. The product was filtered. ICP-MS was used to measure the filtrate concentration with formula 1-1. The adsorption capacity of the adsorbent at different pH was calculated. The preparation method of CNT/LDH is the same as that of CNT-P/LDH. The tests of CNT-P and CNT/LDH were same as CNT-P/LDH test. It is different, however, 0.01 g of CNT-P was added into 50 mL conical flask which containing 20 mL uranyl ions of 100 mg/L solution.

$$\text{Adsorption capacity: } q_e = (C_0 - C_e) \cdot V/m \quad (1-1)$$

Where m is the mass of the adsorbent (g), V is the volume of the uranium solution (L), C_0 is the initial uranium concentration in the solution (mg/L), C_e the uranium concentration in the solution at adsorption equilibrium (mg/L), and q_e is the adsorption capacity (mg/g).

1.2 Adsorption Kinetic Behavior

The 1000 mg/g uranium solution was adjusted to 200 mg/g; 50 mL of the 1000 mg/g solution was added into 100 mL conical flask, and the pH of the solution was

adjusted with 0.1 M NaOH and 0.1 M HNO₃ to the pH corresponding to the optimal adsorption capacity according to the aforementioned pH effect experiment. Then, 0.02 g of CNT-P was added as-preparation solution. Next, the conical flask placed in a constant temperature water bath shaker, and the adsorption times were 5, 10, 20, 40, 60, 90, 130, 200, 250, and 300 min at 25 °C and 180 r/min. According to previous studies, ten time stages were set to obtain results on the effect of time on adsorption capacity. After the reaction completed, the filtrates were collected in 10-mL centrifuge tubes, and the concentration was determined using ICP-MS. The adsorption capacity at different times was calculated using formula 1-1. During the study of the effect of adsorption time on uranyl ions, the adsorption data were analyzed and fitted using the pseudo-first-order kinetics, pseudo-second-order kinetics, and intra-particle diffusion models to investigate the CNT-P/LDH adsorbent. The fitting equations are as follows:

$$\text{Pseudo-first-order kinetic equation: } q_t = q_e(1 - e^{-k_1 t}) \quad (1-2)$$

$$\text{Pseudo-second-order kinetic equation: } q_t = \frac{q_e^2 k_2 t}{1 + k_2 t} \quad (1-3)$$

$$\text{Intraparticle diffusion model equation: } q_t = k_p t^{1/2} + C \quad (1-4)$$

Where q_t is the adsorption amount at time t (mg/g); q_e is the theoretical equilibrium adsorption amount (mg/g); k_1 is the pseudo-first-order kinetic constant (min^{-1}); k_2 is the pseudo-second-order Kinetic constant ($\text{g/mg}\cdot\text{min}$); k_p ($\text{mg/g}\cdot\text{min}^{1/2}$) is the intra-particle diffusion constant; and C is the constant related to the thickness and the boundary layer. The larger the value of C is, the greater the contribution of the boundary layer to the adsorption is.

1.3 Adsorption isotherm

The 1000 mg/g uranium solution was diluted to 50, 100, 150, 200, 300, 400, 500, and 600 mg/L, and the pH was adjusted with 0.1 M NaOH and 0.1 M HNO₃. Eight values of concentration was set. Some values of concentration were set according the previous studies, and carried out experiment. Final value of concentration could be determined when the adsorption equilibrium was reached. pH influences the pH of the optimum adsorption amount in the experiment. Adding 0.02 g CNT-P/LDH into 100 mL conical flask, and then placing the conical flask in a constant temperature water bath oscillator at 180 r/min, 12 h, at 298 K, 308 K, and 318 K, respectively. After the reaction completed, the filtrates were collected in 10-mL centrifuge tubes, and the concentration was determined using ICP-MS. The adsorption capacity at different times was calculated with formula 1-1.

The assumptions of the Langmuir adsorption isotherm model are as follows: The adsorption is monolayer adsorption, the adsorption energy of each adsorption site is identical, and no interaction occurs between adsorbates. The Freundlich isotherm adsorption model is an empirical model, and its assumption is that adsorption occurs under nonuniform adsorption conditions. Adsorption occurs on the surface and is a multi-molecular layer adsorption. In the Sips isotherm adsorption model, the classical Langmuir model and Freundlich model, a modification of the Langmuir model, are combined, and a correction factor m , which is applicable to a wide range, is introduced. In this paper, these three isotherm adsorption models were used to fit the adsorption data of CNT-P/LDH at different temperatures and concentrations. The fitting formulas are shown in (1-5), (1-6), and (1-7).

$$\text{Langmuir adsorption isotherm model: } q_e = b \cdot q_L \cdot C_e / (1 + bC_e) \quad (1-5)$$

$$\text{Freundlich adsorption isotherm model: } q_e = K_F \cdot C_e^{1/n} \quad (1-6)$$

$$\text{Sips isotherm adsorption model: } q_e = q_s \cdot K_s \cdot C_e^m / (1 + K_s C_e^m) \quad (1-7)$$

Where $b(\text{L/mg})$ is the equilibrium constant; $q_L(\text{mg/g})$ is the monolayer saturated adsorption capacity; $K_F([\text{mg/g}](\text{L/mg})^{1/n})$ is the Freundlich constant; and n is the adsorption strength. In general, the size of $1/n$ is used to indicate the adsorption capacity of the material. The smaller the $1/n$ value, the higher the adsorption performance; when $1/n$ is between 0.1 and 0.5, adsorption is easy; when $1/n$ is higher than 2, adsorption is difficult. q_s is the saturated adsorption capacity, K_s is the Sips constant related to the adsorption energy, and m is the sips constant. The closer the m value to 1, the more uniform the adsorbent surface.

1.4 Ion competition

A 50 mg/L uranium solution containing 0.5 mmol/L anions of Cl^- , SO_4^{2-} , NO_3^- , and HCO_3^- was prepared, and the anions were added in the form of sodium salts. Then, 0.02 g of CNT-P/LDH was added to the solution. The experiment was conducted at 25 °C and 180 r/min for 12 h. After the reaction completed, the filtrates were collected in 10-mL centrifuge tubes, and the concentration was determined using ICP-MS. The removal rate was calculated using formula 1-8 and 1-9 in the presence of different anions.

$$C_{ad} = C_0 - C_e \quad (1-8)$$

$$D = C_{de} / C_{ad} \times 100\% \quad (1-9)$$

Where C_{de} is the concentration of uranyl ions in the desorption solution after desorption (mg/L)

1.5 Cyclic adsorption and desorption

First, 200 mg/L uranyl ion solution was prepared. The pH value corresponding to the optimal adsorption amount was adjusted with 0.1 M NaOH and 0.1 M HNO₃. Next, 50 mL of the prepared uranyl ion solution was added to the conical flask and 0.02 g CNT-P/LDH was added into the conical flask. Adsorption was performed at 180 r/min and 298 K for 12 h. The filtrate was collected in a 10-mL centrifuge tube to determine the concentration through ICP-MS. The adsorbent was dried after adsorption and placed into the desorption solution for desorption. The filtrate was collected in the 10-mL centrifuge tube, ICP-MS was used for concentration determination, and formulas 1-8 and 1-9 were employed to calculate the desorption efficiency. This process was repeated, and the desorption solution with the optimum desorption effect and minimum damage was selected. In this manner, the cyclic regeneration performance of adsorption was studied.

1.6 Effect of salinity

Salt-containing uranium solutions with the concentrations of 1%, 2%, 3%, 3.2%, 3.4%, 3.5%, 3.6%, 3.8%, 4%, 5%, and 6% were prepared. To simulate and test its adsorption capacity in seawater, the uranium concentration was 10 mg/L. The experiment was conducted at 298 K and 180 r/min for 12 h. After the reaction completed, the filtrates were collected in 10-mL centrifuge tubes, and the concentration

was determined using ICP-MS. The removal rate in the presence of different anions was calculated using formula 1-8 and 1-9.

2 Analytical Characterization

2.1 XRD pattern after calcination

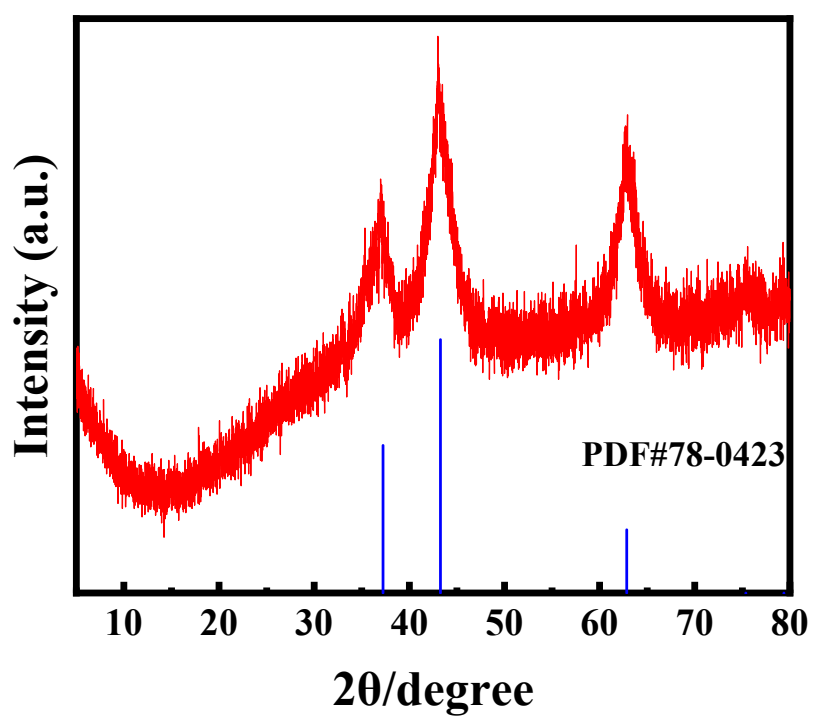


Fig. S1 XRD spectrum after LDH calcination (NiO).

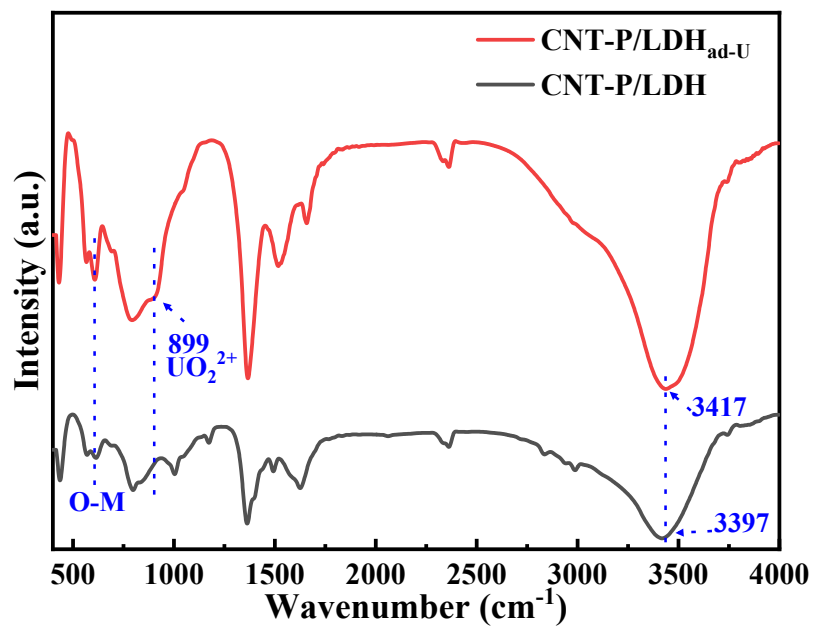


Fig. S2 FT-IR spectra of CNT-P/LDH and CNT-PLDH_{ad-U}.

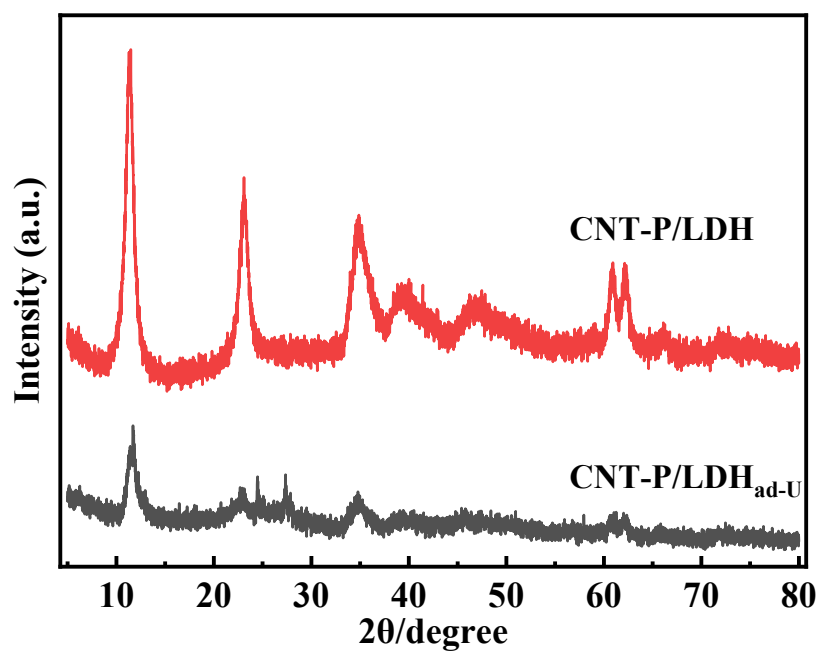


Fig. S3 XRD spectra of CNT-P/LDH and CNT-PLDH_{ad-U}.

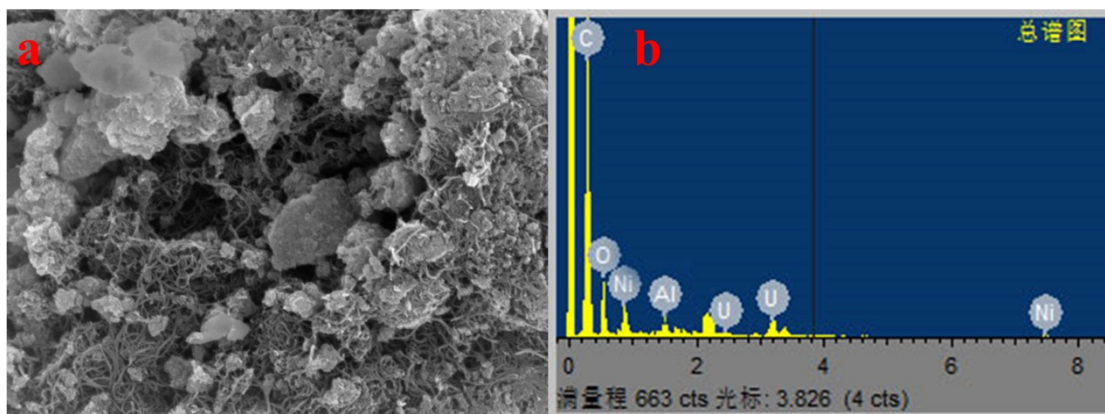


Fig. S4 (a) SEM; (b) EDS spectrum of CNT-P/LDH_{ad-U}.