

Electronic supplementary information

**Confinement effect of layered double hydroxide on intercalated
pyromellitic acidic anions and highly selective uranium extraction
from simulated seawater**

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1.1 Chemicals and reagents

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Tianjin Damao Chemical Reagent Co., Ltd, 99.0%), aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd, 99.0%), hexamethylene tetramine (*abbr.* HMT, Xilong Chemical Industry Reagent Co., Ltd, 99.0%), 1,2,4,5-benzenetetracarboxylic acid, also named pyromellitic acid (*abbr.* PMA, Bide Pharmatech Co., Ltd, 99.96%), uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Shanghai Acme Biochemical Co., Ltd, 99%), formamide (*abbr.* FM, with a chemical formula of HCONH_2 , Xilong Scientific Reagent Co., Ltd, 99.0%). All solvents and chemical reagents in the present work were analytical reagents and were used without further purification.

1.2 Characterization techniques

X-ray diffraction (XRD) patterns of solid samples were collected using a PANalytical X'pert Pro MPD diffractometer with $\text{Cu-K}\alpha$ radiation at room temperature, with step size of 0.0334° , scan time 20 s per step, and 2θ ranging from 5 to 80° . Fourier transformed infrared (FT-IR) spectra of the samples were recorded on a Nicolet-380 FT-IR spectrometer using the KBr pellet method. Scanning electron microscopy (SEM) were carried out using a Hitachi S-4800 microscope. X-ray photoelectron spectroscopy (XPS) of the solid samples after the adsorption experiments were performed using an ESCALAB 250Xi spectrometer (ThermoFisher). The peaks were fitted using the software Avantage.

The metal ion contents in solid samples were determined by ICP-AES (Jarrel-ASH, ICAP-9000). The metal ion concentrations in supernatant solutions before and after adsorptions were measured using ICP-AES technique, and for extra low concentrations, ICP-MS (NexION 300X) was used. C, H and N contents of the solid samples were determined using an Elementar Vario EL elemental analyzer. The pH of the solution was monitored before and after the adsorption using a Sartorius universal type pH meter (PB-10).

1.3 Adsorption isotherm

The equilibrium adsorptions were fitted using isothermal equations of Langmuir¹ and Freundlich² models, which are depicted by (eq. 1) and (eq. 2), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_e K_L} \quad (\text{eq. 1})$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{eq. 2})$$

where q_e (mg g⁻¹) and q_m (mg g⁻¹) are adsorption capacity at equilibrium time and the maximum adsorption capacity of sorbate, respectively. K_L (L mg⁻¹) and K_F (mg¹⁻ⁿ·Lⁿ/g) represent the constants of Langmuir and Freundlich models, separately. The n is an estimate of isotherm nonlinearity related with adsorption intensity.

1.4 Adsorption kinetics

Pseudo-first-order (eq. 3) and pseudo-second-order (eq. 4) kinetics models³ are used to fit the experimental data to investigate the adsorption kinetics.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (\text{eq. 3})$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (\text{eq. 4})$$

In the formula, q_e (mg g⁻¹) is adsorption capacity at equilibrium time, q_t (mg g⁻¹) is adsorption capacity at the time of t , k_1 (min⁻¹) and k_2 (g (mg min)⁻¹) are pseudo-first-order and pseudo-second-order rate constants, respectively.

Table S1 Chemical compositions of NO₃-LDH precursor and PMA-LDH composite.

| Samples | Chemical formula | Wt%, <i>found</i> (<i>calcd</i>) | | | | |
|----------------------|--|------------------------------------|--------|--------|--------|--------|
| | | Mg | Al | C | H | N |
| NO ₃ -LDH | Mg _{0.66} Al _{0.34} (OH) ₂ (NO ₃) _{0.30} | 16.79 | 9.24 | 0.44 | 3.28 | 4.83 |
| | (CO ₃) _{0.02} ·0.64H ₂ O | (17.45) | (9.99) | (0.39) | (3.57) | (4.27) |
| PMA-LDH | Mg _{0.68} Al _{0.34} (OH) ₂ (C ₁₀ H ₂ O ₈) | 16.86 | 9.89 | 9.85 | 3.52 | 0.53 |
| | _{0.075} (NO ₃) _{0.038} ·0.60H ₂ O | (17.21) | (9.85) | (9.66) | (3.60) | (0.57) |

The *found* data were obtained by CHN and ICP, and the *calcd* data were determined based on the chemical formula.

Table S2 Adsorption data of NO₃-LDH for U(VI).

| C_0 (ppm) | C_f (ppm) | q_m (mg g ⁻¹) | Removal (%) |
|-------------|-------------|-----------------------------|-------------|
|-------------|-------------|-----------------------------|-------------|

| | | | |
|------|------|------|------|
| 55.4 | 35.2 | 20.2 | 36.5 |
| 104 | 80.6 | 23.4 | 22.5 |

Table S3 Langmuir and Freundlich isotherm parameters for U(VI) sorption on PMA-LDH.

| q_{exp} | Langmuir | | | Freundlich | | |
|------------------|-----------------------------|-----------------------------|-------|---|------|-------|
| | q_m (mg g ⁻¹) | K_L (L mg ⁻¹) | R^2 | K_F (mg ¹⁻ⁿ L ⁿ g ⁻¹) | n | R^2 |
| 352 | 355 | 0.202 | 0.999 | 109.95 | 4.77 | 0.988 |

Table S4 Pseudo-first-order and pseudo-second-order kinetics parameters for U(VI) sorption on PMA-LDH.

| q_{exp} | Pseudo-first-order model | | | Pseudo-second-order model | | |
|------------------|-----------------------------|----------------------------|-------|-----------------------------|---|-------|
| | q_e (mg g ⁻¹) | k_1 (min ⁻¹) | R^2 | q_e (mg g ⁻¹) | k_2 (g mg ⁻¹ min ⁻¹) | R^2 |
| 112.7 | 2.76 | 0.0084 | 0.48 | 112.9 | 0.012 | 1 |

Table S5 Effect of competitive ions on U(VI) sorption by PMA-LDH.

| Ions | C_0 (ppm) | C_f (ppm) | Removal (%) | K_d (mL g ⁻¹) | SF _{U/M} |
|-------------------------------|-------------|-------------|-------------|-----------------------------|----------------------|
| UO ₂ ²⁺ | 105 | 0.16 | 99.8 | 6.55×10 ⁵ | - |
| K ⁺ | 112 | 110 | 1.79 | 18.2 | 3.60×10 ⁴ |
| Na ⁺ | 102 | 97.8 | 4.09 | 42.9 | 1.53×10 ⁴ |
| Ca ²⁺ | 106 | 105.6 | 0.37 | 3.79 | 1.73×10 ⁵ |
| Mg ²⁺ | 108 | 102 | 5.56 | 58.8 | 1.11×10 ⁴ |
| Sr ²⁺ | 103 | 102 | 0.97 | 9.80 | 6.68×10 ⁴ |
| Co ²⁺ | 99.5 | 96.2 | 3.32 | 34.3 | 1.91×10 ⁴ |
| Ni ²⁺ | 98.9 | 94.9 | 4.04 | 42.1 | 1.55×10 ⁴ |
| Mn ²⁺ | 102 | 101 | 0.98 | 9.90 | 6.62×10 ⁴ |

pH = 6, m = 0.02 g, V = 20 mL, contact time: 12 h.

References

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2. H. Freundlich, *Phys. Chem.*, 1906, **57**, 385-470.
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