Supporting materials for

Effective and Selective adsorption of La^{3+} by Poly-N-isopropylacrylamide phosphoric modified cellulose aerogel

Xudong Zheng*, Ang Li, Jie Hua, Yuzhe Zhang, Jian Rong, Jinfeng Mei, Man Zhou,Zhongyu Li *

[a] School of Environmental and Safety Engineering, Changzhou University, Changzhou 213164, PR China

* Corresponding author.

Mail address: zhengks@outlook.com

Postal address: 417 Mingxing Building, Science and Education City, Wujin District, Changzhou, Jiangsu, China

1. Instruments

A scanning electron microscope (SEM, JEOL, Japan) was used to observe the surface morphology of the aerogel. The automatic specific surface area and porosity analyzer (BET, ASAP 2460, USA) is used to analyze the specific surface area (S_{BET}) of aerogels. The samples are tested by Fourier transform infrared spectrophotometer (FT-IR, IS50, USA). Under N_2 atmosphere, thermogravimetric analysis of the aerogel was performed using a thermogravimetric analyzer (Q600-TGA/DSC, USA). The residual concentration of La^{3+} was measured by inductively coupled plasma atomic emission spectrometer (ICP-OES, Vista-AX, USA) at a wavelength of 379.478nm.

2. Adsorption experiment

Effect of pH on adsorption: $La(NO_3)_3$ was used to prepare a stock solution with La^{3+} concentration of 50 mg L^{-1}. At room temperature, 10 mg of adsorbents were immersed in La^{3+} stock solution (10 mL) with different pH (2.0 to 7.0) for 24 hours. The pH value was adjusted by 0.1 M NaOH and 0.1 M HCl. After adsorption was completed, the mixture was centrifuged (10000 r min^{-1}, 15 min) and the absorbents were removed using a 0.22 μm filter. The residual concentration of La^{3+} in the mixed solution was measured by the ICP-OES. The adsorption capacities Q_t (mg g^{-1}) were calculated by the following formula(Cristiani et al., 2021):

$$Q_t = \frac{V(C_0 \middle| C_t)}{m} \tag{1}$$

Where C_0 and C_t (mg L^{-1}) are initial concentration and the residual concentration of La^{3+} in mixed solution, respectively. V (L) is the volume of La^{3+} stock solution, and m (g) is the mass of aerogel.

Adsorption dynamics: At room temperature, 10 mg of adsorbents separately immersed in La^{3+} stock solution (10 mL, 50 mg L-1, pH=4.0), separately. The residual concentrations of La^{3+} in mixed solution were determined at different contact times (0 minutes to 24 hours). We used the pseudo-first-order kinetic model (PFOKM, equations (2)), pseudo-second-order kinetic model (PSOKM, equations (3)) respectively to fit the adsorption kinetic data, and then analyzed the adsorption mechanism(Maruthapandi, Luong, & Gedanken, 2020):

$$Q_t = Q_e - Q_e e^{-k_1 t} \tag{2}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{3}$$

Where, Q_t (mg g^{-1}) and Q_e (mg g^{-1}) are the adsorption amount of aerogels at time t and equilibrium, respectively. k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) represent the rate constants of PFOKM, PSOKM, respectively.

Adsorption isotherms: At room temperature, 10 mg of adsorbents were immersed in the La^{3+} stock solutions (10 mL, pH=4.0) with different initial concentrations (0, 25, 50, 100, 150 and 200 mg L^{-1}). The residual concentrations of La^{3+}

in the solution were determined after 24 hours. Langmuir (Eq. (4)) and Freundlich (Eq. (5)) models were used to fit the experimental equilibrium data(Di et al., 2019):

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (4)$$

$$Q_e = K_F C_e^{1/n} \quad (5)$$

C_e (mg L^{-1}) is the concentration of La^{3+} in solution at equilibrium, Q_m (mg g^{-1}) is the maximum adsorption capacity of aerogels for La^{3+}. K_L (L mg^{-1}) is the Langmuir parameter denoted the energy of adsorption and affinity of binding sites. K_F (mg g^{-1}) is the Freundlich sorbent adsorption strength, while $1/n$ is the heterogeneity factors.

Adsorption thermodynamics: 10 mg of adsorbents were immersed in La^{3+} stock solution (10 mL, pH=4.0) with different initial concentrations (25, 50 and 100 mg L^{-1}). Adsorption tests were carried out at 298.15 K, 308.15 K and 318.15 K, respectively. The residual La^{3+} concentrations in the solution was determined after 24 hours. The values of Gibbs energy (ΔG°) are calculated by equation Eq. (6)(Zheng, Sun, Li, Wang, & Li, 2021):

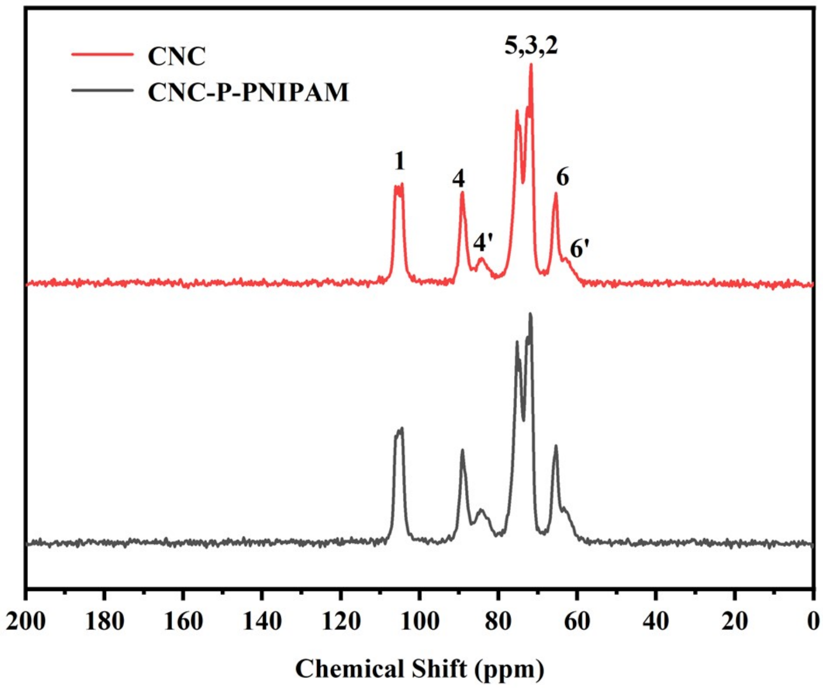
$$\Delta G^{\circ} = -RT \ln K^{\circ} \quad (6)$$

Where thermodynamic equilibrium constant K° is calculated by plotting the function of $\ln(C_s/C_e)$ versus C_s. Wherein, C_s (mmol g^{-1}) is the adsorption amount per gram of aerogels, and C_e is the concentration of La^{3+} in the mixed solution at adsorption equilibrium. R (8.314 J mol^{-1} K^{-1}) is the universal gas constant, and T is the given temperature. Eventually, entropy (ΔS°) and the enthalpy (ΔH°) values are obtained from van't Hoff equation Eq. (7)(Zhang, Zheng, Bian, Zhang, & Li, 2020):

$$\ln K^{\circ} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

Reusability tests: After the adsorption process was over, the adsorbents were eluted, and the adsorbents were soaked in a 10% glacial acetic acid solution for 24 hours to remove the adsorbed La^{3+}. Then at room temperature, these adsorbents (10 mg) were re-injected into the La^{3+} stock solution (10 mL, pH=4.0) for 24 hours, and the remaining concentration of La^{3+} in the solution was measured. The whole adsorption-desorption experiment was repeated 5 times. The reusability of the aerogels was verified by the changes of five adsorption capacities of the aerogels(Zhang et al., 2020).

3. Solid state nuclear magnetic resonance



References:

Cristiani, C., Iannicelli-Zubiani, E. M., Bellotto, M., Dotelli, G., Stampino, P. G., Latorrata, S., . . . Finocchio, E. (2021). Capture Mechanism of La and Cu Ions in Mixed Solutions by Clay and Organoclay. *Industrial & Engineering Chemistry Research, 60*(18), 6803-6813.

Di, T., Tan, D., Yu, Q., Lin, J., Zhu, T., Li, T., & Li, L. (2019). Ultra-high performance of hyper-crosslinked phosphate-based polymer for uranium and rare earth element adsorption in aqueous solution. *Langmuir, 35*(43), 13860-13871.

Maruthapandi, M., Luong, J. H., & Gedanken, A. (2020). Nitrogen-enriched porous benzimidazole-linked polymeric network for the adsorption of La (III), Ce (III), and Nd (III). *The Journal of Physical Chemistry C, 124*(11), 6206-6214.

Zhang, Y., Zheng, X., Bian, T., Zhang, Y., & Li, Z. (2020). Phosphorylated-CNC/MWCNT thin films-toward efficient adsorption of rare earth La(III). *Cellulose, 27*(6).

Zheng, X., Sun, W., Li, A., Wang, B., & Li, Z. (2021). Graphene Oxide and Polyethyleneimine Cooperative Construct Ionic Imprinted Cellulose Nanocrystals Aerogel for Selective Adsorption of Dy(III).