Integrated fabrication of CMC@UiO-66-NH₂@PEI composite

sorbents for efficient batch and dynamic phosphate capture

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Text S1 Materials

Lanthanum chloride hexahydrate (LaCl₃· 6H₂O, 99.99%), sodium carboxymethylcellulose (CMC, $C_8H_{16}NaO_8$, viscosity 800-1200 m Pa· s), polyethyleneimine (PEI, (CH₂CH₂NH)n, M.W.600, 99%) were ordered from Aladdin-Reagent (Shanghai, China). N, N-dimethylformamide (DMF, AR, \geq 99.5%), hydrochloric acid (HCl), sodium hydroxide (NaOH, AR, \geq 96.0%) was obtained from Tianjin Cormier Chemical Reagent Co. 2-aminoterephthalic acid (2-NH₂-BDC, \geq 98.0%) and zirconium (IV) chloride (ZrCl₄, \geq 98.0%) was purchased from Macklin. Acetic acid glacial was sourced from Tianjin Guangfu Technology Development Co., Ltd. And potassium phosphate monobasic (KH₂PO₄, AR, \geq 99.5%) was procured from Tianjin Damao Chemical Reagent Factory.

Text S2 Characterization methods

The morphology of 0.2CUI was observed with a JSW-7800F scanning electron microscope (JEOL, Japan), the element composition and content in the adsorbent were analysed using an energy dispersive spectrometer (EDS, Oxford, UK). The functional groups present in the adsorbent were analysed using Fourier transform infrared spectroscopy (FTIR, Spectrum two, Japan). The crystallization properties of the material were investigated using an X-ray diffractometer (XRD, 10KVA, Japan). The specific surface area and pore distribution of the adsorption materials were determined through the utilization of an N₂ adsorption-desorption experiment conducted using the Quantachrome Autosorb NOVA2200e apparatus from the United States. The adsorption mechanism of phosphate was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) and Zeta potential (Malvern ZS 90). The concentration of residual phosphorus after adsorption was measured using a UV-754N Shanghai China Molybdenum Blue Spectrophotometer. The thermogravimetric analysis of 0.2CUI in the temperature range of 35~800°Cwas studied by thermogravimetric analysis.

Text S3 Column adsorption study of phosphate removal by 0.2CUI

Use equations to calculate the water volume ($V_E mL$) and total phosphorus uptake (Q_{total} , mg). Equations were used to calculate the contact time (EBCT, min) and the amount of phosphate adsorbed at equilibrium (Q_e , mg P/g). The corresponding calculation formula is as follows:

$$V_{E}(mL) = Qt_{e} \qquad \qquad \land * \text{ MERGEFORMAT (1.1)}$$
$$Q_{total} = \int_{0}^{V_{E}} (C_{t} - C_{0}) \qquad \qquad \land * \text{ MERGEFORMAT (1.2)}$$

$$EBCT(\min) = bedvolume(mL) / Q$$
 * MERGEFORMAT (1.3)

$$Q_e = \frac{Q_{total}}{m} \qquad \qquad \land * \text{ MERGEFORMAT (1.4)}$$

In order to study the dynamic characteristics of 0.2CUI, the most commonly used Thomas model and Adams-Bohart model were used to fit the experimental data.

The two equations specific to these two models can be found below:

$$\frac{C_{t}}{C_{0}} = \frac{1}{1 + e^{\frac{K_{T}q_{0}M}{Q} - K_{T}C_{0}t}} \qquad (* \text{ MERGEFORMAT (1.5)})$$

$$\frac{C_{t}}{C_{0}} = e^{K_{AB}C_{0}t - K_{AB}N_{0F}^{Z}} \qquad (* \text{ MERGEFORMAT (1.6)})$$

Among them, K_T (L/min/mg) and K_{AB} (L/min/mg) are Thomas model constants and Adams-Bohart model kinetic constants respectively, Ct (mg/L) refers to the phosphate in the effluent within time t concentration, C_0 (mg/L) is the initial concentration of phosphate solution, Q (mL/min) represents the flow rate, Q_e (mg/g) represents the adsorption capacity, M (g) represents the quality of the adsorbent; F (cm/ min) indicates the apparent flow velocity, N_0 (mg/m L) and Z (cm) indicate the saturation concentration and bed length of the phosphate solution, respectively.



Fig.S.1 The initial assessment compares different ratios of adsorbents, with (a) indicating polyethyleneimine (PEI) and (b) representing UiO-66-NH₂.



Fig.S.2. N₂ adsorption–desorption isotherms of UiO-66-NH₂







Fig. S.4. Effect of dosage on phosphate adsorption capacity



Fig. S. 5 (a) Effect of temperature on phosphate adsorption; (b) The point-line graph of $\,\ln K_d\,$ and 1/T.



Fig.S.6. Distribution of phosphorus-containing particles in phosphate solutions at different pH

Table S1 Structural parameters of materials								
Sample	SBET (m²/g)	V _{tp} (cm ³ /g)	Daps (nm)					
UiO-66-NH ₂	613.859	0.368	3.564					
CL	30.759	0.068	12.655					
CLU	64.702	0.070	6.810					
0.2CUI	48.659	0.220	29.018					
0.2CUI-P	2.846	0.025	4.721					

Table S2 Parameters of fitted curves of Thomas and Adams-Bohart models

	Thomas model			Adams-Bohart model		
V (mL/min)	K _T (L/(min [*] mg))	Q₀(mg P/g)	R ²	K _{AB} (L/(min [*] mg))	N ₀ (mg P/L)	R ²
1	5.2986×10 ⁻⁶	257	0.7717	2.1040×10 ⁻⁶	294800	0.7093
3	8.7690×10 ⁻⁶	8.68	0.9705	1.5745×10 ⁻⁶	496210	0.9069