

## Supporting Information

### Phosphate-rich cellulose beads for efficient cesium extraction from aqueous solutions: a novel approach for cellulose utilization

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## 1. Experimental

**Reagents:**  $\alpha$ -cellulose was purchased from Tianjin Xiensi Biochemical Technology Co., LTD. N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAC), urea and phosphoric acid ( $H_3PO_4$ , 85%) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. Ethyl alcohol ( $C_2H_5OH$ ), nitric acid ( $HNO_3$ ) and hydrochloric acid (HCl) were obtained from Tianjin Beichen Founder Reagent Factory. Sodium hydroxide (NaOH) was purchased from Sinopharm Group Chemical Reagent Co., LTD. Cesium chloride (CsCl, 99%) was supplied by Shanghai Aladdin Biochemical Technology Co., LTD.

All reagents used in this experiment were analytical grade and have not been purified again.

**Characterization:** The surface morphology and elemental distribution of the CBPs were obtained by scanning electron microscopy (SEM) and energy spectroscopy (EDS) analyses with a TESCAN MIRA scanning electron microscope. The surface-anchored functional groups of the CBPs were analyzed by infrared spectroscopy (FT-IR) using a Fourier transform infrared spectrometer (NICOLET 6700, USA).

**Synthesis of CBs:** CBs were prepared by a reported method<sup>[1]</sup>. First,  $\alpha$ -cellulose (3.0 g) and DMAC (89.0 g) were dissolve completely in the deionized water (50 mL). After heating this solution to 150 °C for 30 min, the temperature of the solution was lowered to 100 °C. Then, the lithium chloride (8.0 g) was added and stirred for another 30 min. As a result, the cellulose solution was obtained after by natural cooling down to 25 °C for 12 h. Finally, this cellulose solution was added dropwise into ethanol by syringe to obtain the CBs.

**Synthesis of CBPs:** CBPs were prepared by the reported method<sup>[2]</sup>. First, CBs were gradually rinsed with volume ratios of 20%, 40%, 60%, 80% and 100% DMF aqueous, and finally soaked in DMF solution. Subsequently, the pre-treated CBs (4.0 g,

wet weight) were immersed in 150 mL DMF solution dissolved with 3.0 g urea. The mixture was stirred at 100 °C for 1 h with a condensing reflux device, then 20.0 g 85 % H<sub>3</sub>PO<sub>4</sub> was added drop by drop, and the temperature was raised to 150 °C for 8 h. After cooling down to room temperature, the orange microspheres were cleaned several times with deionized water to obtain CBPs.

**Adsorption experiment:** The adsorption performance of the adsorbent on Cs<sup>+</sup> was assessed by a typical intermittent adsorption experiment. The batch adsorption experiments were carried out in a closed beaker, and a certain amount of CBs/CBPs were used for the adsorption of Cs<sup>+</sup>-containing solution. The closed beaker was placed into the thermostatic bath at desired temperatures with a shaking speed of 200 rpm to accelerate the adsorption equilibrium. In certain interval, 2 mL of the solution sample was taken out for measurement of Cs<sup>+</sup> concentration. The concentrations of metallic ions were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman Corporation, America). All the experiments were analyzed in triplicate for data accuracy and the average was taken for subsequent calculations.

**Adsorption selectivity experiment:** Binary solutions with different molar ratios of monovalent ions Na<sup>+</sup>/Cs<sup>+</sup>, K<sup>+</sup>/Cs<sup>+</sup>, Li<sup>+</sup>/Cs<sup>+</sup> (1-20) were respectively prepared for the study of adsorption selectivity of CBPs. Experiments were carried out at 298.15 K and pH 7 using 25 mg CBPs and 50 mL of the above binary solutions.

**Recyclability:** The adsorption-desorption cycling experiments were conducted to test the reusability of CBPs. After adsorption experiments, the desorption and regeneration for the Cs-loaded CBPs were achieved using 0.1 M HNO<sub>3</sub>. After that, the adsorbents were washed with distilled water for several times and used for the next adsorption-desorption process.

## 2. Equations used in this work

The basic experimental parameters of adsorption capacity ( $q_t$ , mg/g), adsorption

efficiency ( $E$ , %) distribution coefficient ( $K_d$ , mL/g) and separation factor ( $S_F$ ) were calculated by the following Eqs. S1-S4.

$$q_t = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \quad (2)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} = \frac{q_e}{C_e} \quad (3)$$

$$S_{FM}^{Cs} = \frac{K_d(Cs)}{K_d(M)} \quad (M = Li^+, Na^+, K^+) \quad (4)$$

Where  $C_0$ ,  $C_t$  and  $C_e$  (mg/L) are the concentrations of  $Cs^+$  at initial, time  $t$  and equilibrium, respectively.  $V$  (L) is the volume of the solution used for adsorption and  $m$  (g) is the weight of the adsorbent.

The kinetic fitting equations are shown below:

$$q_t = q_e [1 - e^{-k_1 t}] \quad (5)$$

$$q_t = \frac{k_2 t q_e^2}{1 + k_2 t q_e} \quad (6)$$

The pseudo-first-order kinetic model rate parameter  $k_1$  ( $\text{min}^{-1}$ ) and the pseudo-second-order kinetic model rate parameter  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) are usually used to judge the adsorption rate.

The thermodynamic parameters including enthalpy ( $\Delta H^0$ ,  $\text{kJ} \cdot \text{mol}^{-1}$ ), entropy ( $\Delta S^0$ ,  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) and Gibbs free energy ( $\Delta G^0$ ,  $\text{kJ} \cdot \text{mol}^{-1}$ ) can be calculated by Eqs. S7-S8 as followings:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

where  $K_d$  is the equilibrium distribution coefficient,  $T$  (K) is the temperature,  $R$

(8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>) is the ideal gas constant, respectively.

Langmuir, Freundlich isothermal adsorption equations:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (9)$$

$$q_e = K_F C_e^{1/n} \quad (10)$$

Where  $q_e$ ,  $C_e$  represent the adsorption capacity and the concentration of cesium ions when the adsorption reaches equilibrium, respectively, and  $K_L$  and  $K_F$  are the model constants of the Langmuir model Freundlich model.  $q_m$  (mg/g) denotes the theoretical maximum adsorption capacity. The  $n$  value is related to the adsorption strength of the adsorbent.

### 3. Adsorption kinetics.

**Table S1.** Pseudo-first-order and Pseudo-second-order model kinetic parameters.

Type	$q_e(\text{exp})$ (mg·g <sup>-1</sup> )	pseudo-first-order model			Pseudo-second-order model		
		$q_e$ (mg·g <sup>-1</sup> )	$K_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg·g <sup>-1</sup> )	$K_2$ (min <sup>-1</sup> )	$R^2$
CBPs	95.48	94.34	0.4575	0.9983	96.15	0.0171	0.9996

### 4. Adsorption isotherms.

**Table S2.** Fitting parameters of two isothermal adsorption models.

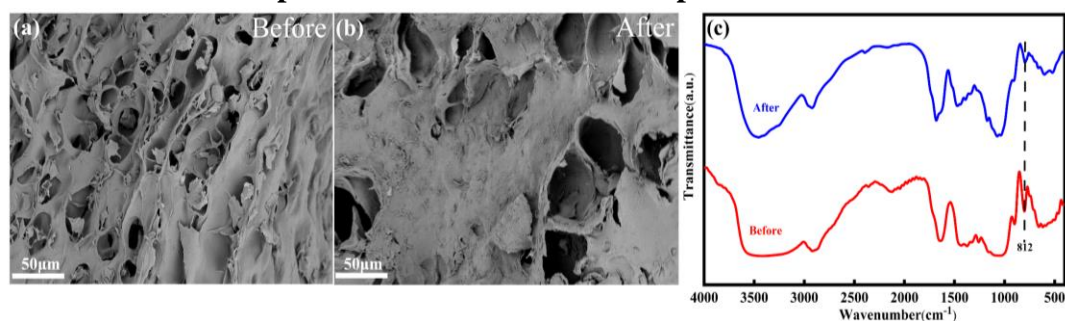
Type	Langmuir	$q_{max}$ (mg/g)	115.06
		$K_L$ (L/mg)	$2.01 \times 10^{-4}$
		$R^2$	0.9892
Type	Freundlich	$K_F ((\text{mg/g}) \cdot (\text{L/mg})^{1/n})$	12.24
		$1/n$	0.4891
		$R^2$	0.9346

## 5. Adsorption thermodynamic.

**Table S3.** Thermodynamic parameters of CBPs adsorption process.

	$T$ (K)	$\Delta G^0$ (kJ·mol <sup>-1</sup> )	$\Delta H^0$ (kJ·mol <sup>-1</sup> )	$\Delta S^0$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
CBPs	298.15	-2.64	5.56	27.49
	308.15	-2.91		
	318.15	-3.19		
	328.15	-3.46		

## 6. SEM and FT-IR spectra before and after adsorption



**Figure S1.** The SEM images and FT-IR spectrums of CBPs before and after five times adsorption.

## 7. Distribution coefficient and separation factor

**Table S4.** Distribution coefficient and separation factor of CBPs.

	Li <sup>+</sup> /Cs <sup>+</sup>	Na <sup>+</sup> /Cs <sup>+</sup>	K <sup>+</sup> /Cs <sup>+</sup>
$K_d$ (mL/g)	2447	2357	2022
$S_F$	32.80	22.52	8.111

## 8. Geothermal water adsorption

**Table S5.** Cs<sup>+</sup> removal efficiency and the composition of geothermal water used in this work.

pH	Concentrations (mg/L)									$E(\text{Cs}^+)\%$	$K_d$ (mL/g)
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Cl <sup>-</sup>	B <sub>2</sub> O <sub>3</sub>		
8.80	25.78	682.00	137.90	3.08	-	3.45	17.58	973.10	360.20	54.35	$2.38 \times 10^3$

## References

- [1] M. Gericke, J. Trygg, P. Fardim, *Chem. Rev.*, 2013, **113**, 4812.
- [2] T. Oshima, K. Kondo, K. Ohto, K. Inoue, Y. Baba, *React. Funct. Polym.*, 2008, **68**, 376.