

Supplementary Materials for

Preparation of resin-based composites containing Ce and cations polymer with abundant promotional affinity sites for phosphate capture

Xiangcheng Shan^{1a}, Liyu Yang^{1a}, Huarong Yang^a, Guilin Song^a, Zuoyi Xiao^a, Changsik Ha^b, Shangru Zhai^{*a}, Qingda An^{*a}

^a Liaoning Key Lab of Lignocellulose Chemistry and BioMaterials, Liaoning Collaborative Innovation Center for Lignocellulosic Biorefinery, College of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China

^b Department of Polymer Science and Engineering, Pusan National University, Republic of Korea

¹ They contributed equally to this work.

***Corresponding authors.**

Tel: (+86) 411-8632-3649; Fax: (+86) 411-8632-364679

E-mail address: zhairschem@163.com (Shangru Zhai); anqingdachem@163.com (Qingda An)

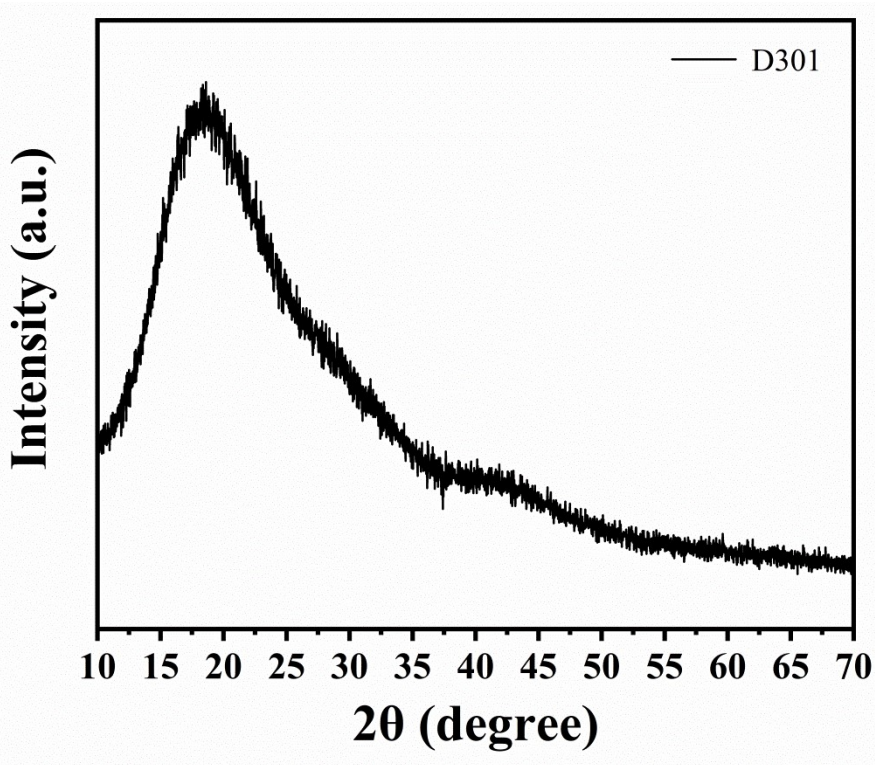


Fig. S1 XRD pattern of D301.

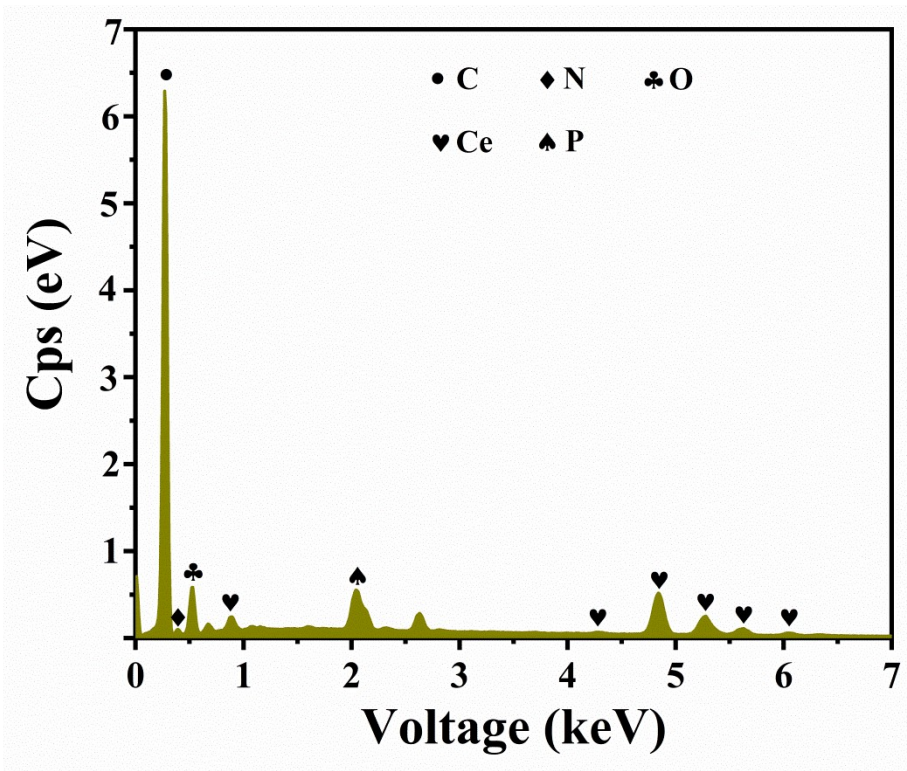


Fig. S2 EDS results of C, N, O, Ce, and P of D301-Ce⁺ after phosphate adsorption.

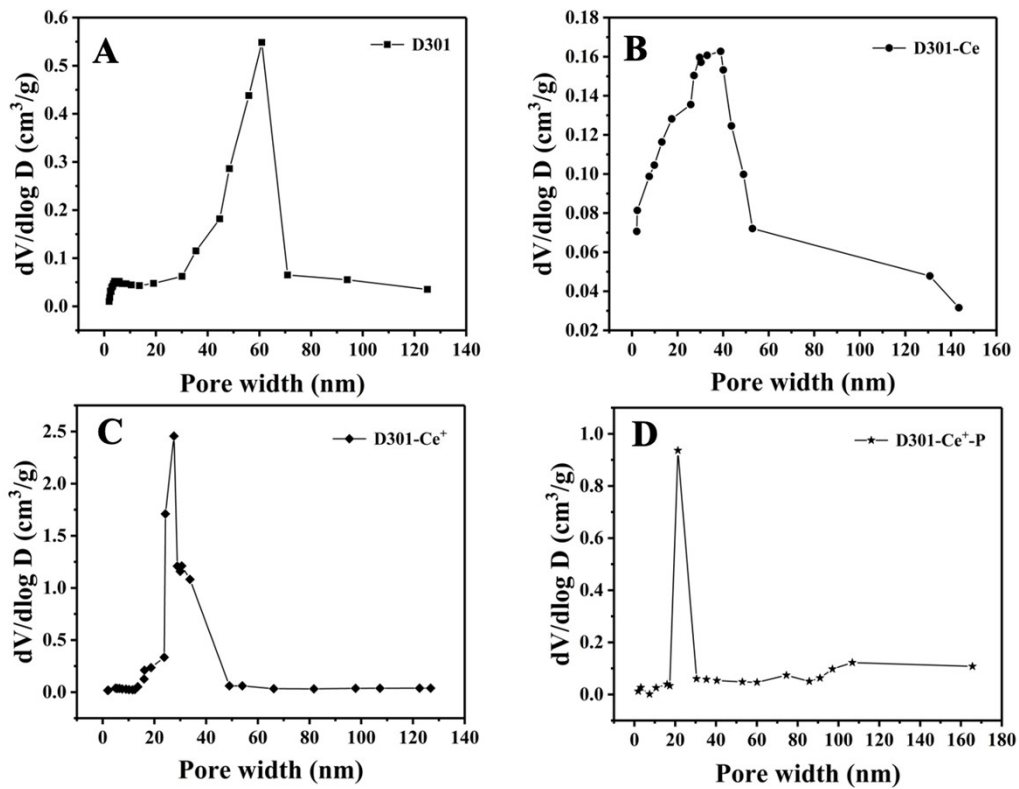


Fig. S3 The pore size distributions of (A) D301; (B) D301-Ce; (C) D301-Ce⁺; (D) D301-Ce⁺-P.

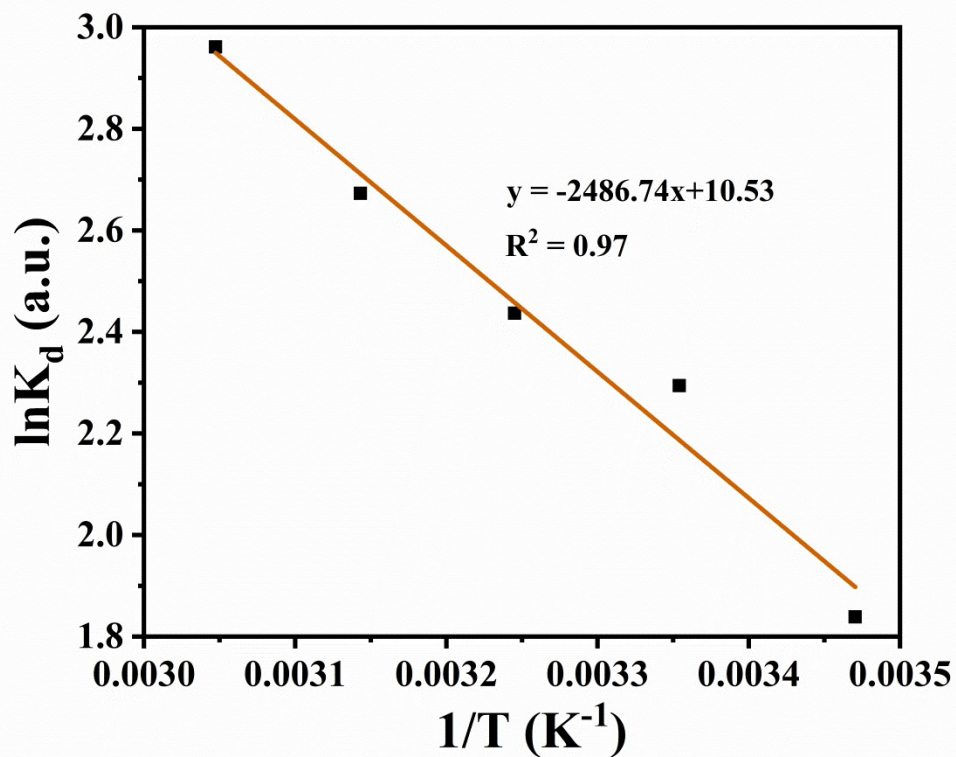


Fig. S4 Point-line graph of $\ln K_d$ and $1/T$ in the adsorption thermodynamic calculations.

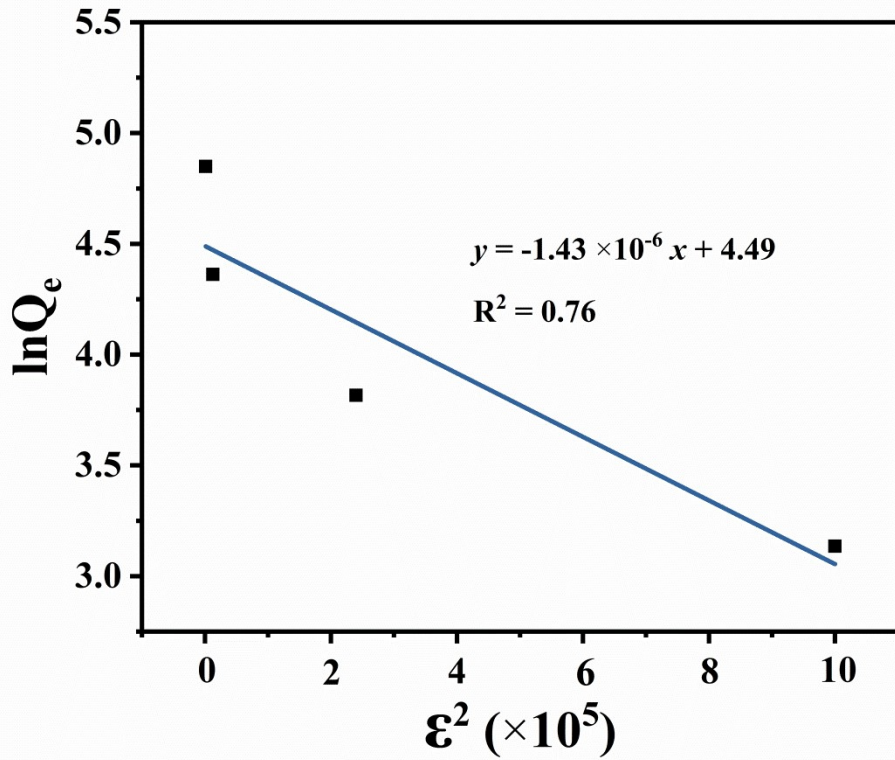


Fig. S5 Fitted point-line figure of $\ln Q_e$ vs ϵ^2 of the D-R model.

Table. S1 Fitted parameters of the Langmuir, Freundlich, and D-R models.

Model	Parameter	Value
Langmuir model	Q_m	397.23
	K_L	0.002
	R^2	0.993
Freundlich model	n	1.65
	K_F	4.83
	R^2	0.974
D-R model	K_{DR}	-1.43×10^{-6}
	X_m	246.74
	R^2	0.76
	E	0.59

Table. S2 Fitted parameters of the Pseudo-first-order, pseudo-second-order kinetic models and

diffusion-based (particle diffusion, and pore diffusion) models.

Model	Parameter	25 mg P/L	50 mg P/L
Pseudo-first-order	Q_e	21.99	40.61
	K_f	5.71×10^{-3}	2.72×10^{-3}
	R^2	0.96	0.94
Pseudo-second-order	Q_e	25.00	50.00
	K_s	6.35×10^{-4}	1.89×10^{-4}
	h	0.40	0.47
	R^2	0.99	0.98
Particle diffusion	K_d	3.81×10^{-3}	1.87
	R^2	0.21	0.97
Pore diffusion	K_i	0.02	1.87
	R^2	0.98	0.97

Table. S3 The chi-square test and the sum of the squares of errors (SSE) of pseudo-first-order and pseudo-second-order models.

Model	Parameter	25 mg P/L	50 mg P/L
Pseudo-first-order	reduced chi-square	2.39	0.23
Pseudo-second-order	SSE	19.20	4.80

Text. S1 Details of characterization methods and instruments.

The functional groups of the samples were detected by a Fourier transform infrared spectrometer (FTIR, Japan). The crystalline phase of the samples was recorded on an X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) (Shimadzu XRD-7000S, Japan). The surface micromorphology of the samples was observed by a thermal field emission scanning electron microscope system (SEM, JSM-7800F,

Japan) equipped with an X-Max50 energy spectrometer and backscattered electron diffraction analyzer (EDS) from Oxford Instruments. The samples' specific surface area and pore structure were analyzed by Brunauer-Emmett-Teller (BET) method with JW-BK222 (China) at 77 K. Thermogravimetric analysis (TGA) was conducted at the temperature ranging from 30 to 800 °C by TGA801 (USA). The samples' element composition and element valence were confirmed by X-ray photoelectron spectroscopy (XPS, ESCALAB250, USA). The surface potentials of the samples at different pH values were detected by a Zetasizer (3000HSA, Japan). The element content in samples and solutions were detected by an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific™, USA)

Text. S2 Calculation equations of the thermodynamic parameters.

Several thermodynamic parameters, viz., several thermodynamic parameters, e.g., enthalpy change (ΔH° , kJ/mol), entropy change (ΔS° , J/(mol·K)) and Gibbs free energy change (ΔG° , kJ/mol) are calculated by the follow equation¹:

$$K_d = \frac{Q_e}{C_e} \quad (S1)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} \quad (S2)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \cdot T \quad (S3)$$

According to the Van't Hoff equation, the equilibrium constant K_d is obtained from the slope of Q_e against C_e at different temperatures. The values of ΔH° and ΔS° are determined from the slope and intercept of a plot of $\ln K_d$ versus $1/T$.

Text. S3 Equations of the Langmuir model, Freundlich model, D-R model, and the calculation

methods of related parameters.

Langmuir isotherm :

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (S4)$$

Freundlich isotherm :

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (S5)$$

Where C_e is the equilibrium concentration (mg/L) and Q_e is the amount adsorbed per unit weight of adsorbent. Q_m (mg P/g) represents the maximum adsorption capacity. Langmuir constant K_L (L/mg) is related to intensity of adsorption. Values of Freundlich constants viz., K_F (mg P/g) and n are calculated from the intercepts and slopes of the linear plots of $\log Q_e$ vs $\log C_e$.

D-R isotherm :

$$\ln Q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (S6)$$

Where X_m is the adsorption capacity (mg P/g) and K_{DR} is the constant related to adsorption energy (mol^2/kJ^2). The values of K_{DR} and X_m are computed from the slope and intercept of the plot $\ln Q_e$ vs ε^2 . Polanyi potential (ε) can be calculated using the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (S7)$$

where T is the temperature (K) and R is the gas constant (8.314 J/(mol·K)). The values of K_{DR} are used to calculate the mean free energy E (kJ/mol) of the adsorption².

$$E = - (2K_{DR})^{-0.5} \quad (S8)$$

Text. S4 Equations of the pseudo-first-order, pseudo-second-order, particle diffusion, intra-particle diffusion, and the calculation methods of related parameters.

Pseudo-first-order:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_f}{2.303}t \quad (\text{S9})$$

where Q_e and Q_t are the adsorption capacity at equilibrium and at time t , respectively (mg P/g), K_f is the rate constant of pseudo-first order adsorption (min^{-1}). Linear plots of $\log(Q_e - Q_t)$ against t gives a straight line that indicates the applicability of pseudo-first-order model. K_f and Q_e can be determined from the slope and intercept.

Pseudo-second-order:

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{t}{Q_e} \quad (\text{S10})$$

in which $Q_t = \frac{Q_e^2 K_s \cdot t}{1 + Q_e K_s \cdot t}$ is the amount of anion on the surface of the sorbents at any time, t (mg P/g), K_s is the pseudo-second-order rate constant ($\text{g}/(\text{mg} \cdot \text{min})$), Q_e is the amount of phosphate adsorbed at equilibrium (mg P/g), and the initial adsorption rate, $h = K_s Q_e^2$. The value of Q_e (1/slope), K_s (slope²/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/Q_t against t .

Particle diffusion :

$$\ln\left(\left|1 - \frac{C_t}{C_e}\right|\right) = -K_p t \quad (\text{S11})$$

where K_p is the particle rate constant (min^{-1}). The value of particle rate constant is obtained by the slope of $\ln(1 - C_t/C_e)$ against t .

Intra-particle diffusion :

$$Q_t = K_i t^{1/2} \quad (\text{S12})$$

where K_i is the intra-particle diffusion coefficient ($\text{mg P/g min}^{1/2}$). The slope of the plot of Q_t against $t^{1/2}$ will give the value of the intra-particle diffusion coefficient³.

Text. S5 The calculation equations of parameters on the adsorption experiment of adsorbent in simulated dynamic wastewater, and details of the Thomas and Adams-Bohart models.

The effluent volume (V_E , mL), total amount of phosphate adsorbed (Q_{total} , mg), empty bed contact time (EBCT, min), adsorbed phosphate amount at equilibrium (Q_e , mg P/g) in the fixed-bed column experiments were calculated by the following equations:

$$V_E = vt_e \quad (\text{S13})$$

$$Q_{\text{total}} = \int_0^{V_E} (c_0 - c_t) dV \quad (\text{S14})$$

$$EBCT = \frac{\text{bed volume}}{v} \quad (\text{S15})$$

$$Q_e = \frac{Q_{\text{total}}}{m} \quad (\text{S16})$$

in which v (mL/min) and t_e (min) are the flow rate through the column and the time of the breakthrough point, m is the mass of D301 or D301-Ce⁺.

The Thomas model assumes that the adsorption process is controlled by mass transfer between phases, the formula is depicted as follow:

$$\frac{c_t}{c_0} = 1 + e^{-\frac{1}{v} \left(\frac{K_T Q_0 m}{v} - K_T c_0 t \right)} \quad (\text{S17})$$

where Q_0 (mg P/g) is adsorption capacity, K_T (L/(min·mg)) is Thomas constant, v (mL/min) is flow rate, c_0 and c_t is the primeval concentration of phosphate and concentration of the effluent solution at time t (min), m (g) is the mass of D301 or D301-Ce⁺.

The Adams-Bohart model is usually applied to describe the front part of breakthrough curve, the formula is depicted as follow:

$$\frac{c_t}{c_0} = e^{-K_{AB} c_0 t - K_{AB} N_0 \frac{Z}{F}} \quad (\text{S18})$$

where N_0 (mg P/L) is the saturated concentration, K_{AB} (L/(min·mg)) represents the dynamic constant, Z (cm) is the height of bed column and F (cm/min) is the superficial velocity⁴.

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