Supplementary Information (SI) for Green Chemistry.

Supporting Information

Molecularly engineering cellulose to functional cellulose-based aerogel adsorbent for precious metals recovery from e-waste

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Includes,

1. Supplementary methods

2. Supplementary figures (Fig. S1~S10) and table (Table S1~S6)

3. Supplementary references

1. Supplementary methods

(1) The preparation of CLE

Cellulose levulinate ester (CLE) was prepared following our prior work.[1] Typically, following a specific ratio, MCC (2 g, 12.34 mmol OH), DMSO (30.8 g), and DBU (5.6 g, 37.2 mmol) were weighed and added to a high-pressure reaction vessel. CO_2 was slowly introduced until reaching 1-2 MPa, followed by a gradual release. This process was repeated three times to exchange gases in both the reaction vessel and the solution. Finally, CO_2 was introduced until the pressure stabilized at 1-2 MPa. The reaction solution was heated to 50 °C and stirred magnetically for 3 h to obtain a 5 wt% homogeneous and transparent cellulose solution. Next, α-AL was slowly added into 28.8 g of the 5 wt% cellulose solution in a flask. α-AL (8.17 g, 83.3 mmol, molar ratio: -OH/α-AL=1/3) was slowly dropped into 28.8 g of the 5 wt% cellulose solution in a flask, the reaction solution was heated up to 120 °C for 0.5 h under mechanical stirring. After completion of the reaction, and a large amount of solid was precipitated by slowly pouring the reaction solution into isopropanol (200 mL), the product was filtered and then continued to be washed with isopropanol (200 mL×3) repeatedly. Finally, the generated CLE (DS=1.3) was dried under vacuum at 60 °C for 48 h.

The DS of CLE was calculated according to the following equation:

$$DS = \frac{I_{Methyl} \times 7}{I_{AGU} \times 3} \#(1)$$

Where I_{Methyl} represents the integration value of the terminal methyl group and I_{AGU} represents the integration value of the cellulose structural units.

(2) Adsorption kinetic

The kinetics experiment involved agitating a mixture of 100 mg CLE@50PEI aerogel adsorbent and 100 mL containing 2000 mg/L solution of Au(III), Pt(IV) and Pd(II) separately. At intervals of 5, 15, 30, 60, 120, 180, 240 and 360 min of agitation, 1 mL of the supernatant was taken out for filtration and dilution, and then the analysis of the metal ions concentrations was conducted using ICP-OES. The kinetics experiment data were fitted by adopting the linear pseudo-first-order model,[2, 3] pseudo-second-order model[4, 5] and intra-particle diffusion model,[6] respectively, with the following equations:

Linear pseudo-first-order model:

$$In(q_e - q_t) = Inq_e - k_1 t\#(2)$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}\#(3)$$

Intra-particle diffusion model:

$$q_t = k_i t^{0.5} + C_i\#(4)$$

Where q_t (mg/g) is the adsorption capacities at given time. k_1 ($\min^{-1}$), k_2 [(g/(mg·min)] and k_i [mg/(g·min$^{1/2}$)] represent the adsorption rate constants. C_i (mg/g) is a constant associated with the depth of the interfacial layer.

(3) Adsorption isotherms

For isothermal experiments, 10 mg of CLE@50PEI aerogel was added into a 40 mL glass vial containing 10 mL precious metal ions with various initial concentrations (ranging from 10-4000 mg/L) in 0.1 M HCl. The mixtures were agitated using a thermostatic shaker for 24 h at temperatures of 298, 308 and 318 K, respectively. The experimental data were fitted using the Linear Langmuir[7] and Freundlich[8] models with the following equations, respectively.

Langmuir model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}\#(5)$$

$$R_L = \frac{1}{1 + K_L C_0}\#(6)$$

Freundlich model:

$$Inq_e = InK_F + b_F InC_e\#(7)$$

Where q_m (mg/g) is the calculated theoretical maximum adsorption capacity. K_L and K_F are the adsorption constants. The dimensionless constant R_L, with values ranging from 0 to 1, indicates the quality of adsorption in the Langmuir isotherm and signifies a favorable process when within this range.[9] b_F is a constant that relates to the adsorption intensity.

(4) Adsorption selectivity

The selective recovery of the CLE@50PEI adsorbent for various precious metals was assessed using a simulated industrial leach solution based on those from Tanaka Kikinzoku Kogyo Co. Ltd. in Japan.[10] This e-waste solution contained a mixture of seven different metal ions dissolved in a 0.1 M HCl medium, including Cu (II) (23.8 mg/L), Zn (II) (5.6 mg/L), Ni (II) (3.0 mg/L), Fe (III) (667.0 mg/L), Au (III) (331.0 mg/L), Pd (II) (121.0 mg/L) and Pt (IV) (743.0 mg/L). Subsequently, a precise 20 mL aliquot of the mixed metal ion solution was added into a 40 mL small glass bottle with 20 mg of CLE@PEI adsorbent. And the bottle was shaken for 24 h at 298 K, after which the mixture was filtered and diluted. Ultimately, the concentrations of the seven metal ions were quantitatively determined through ICP-OES.

(5) Bond dissociation energy

Bond dissociation energy (BDE) is defined as the enthalpy change associated with the homolytic cleavage of a bond in a molecule. The bond dissociation energy of the A-B bond is defined as the enthalpy change when the A-B bond undergoes homolytic cleavage to form two radicals, A• and B•. This can be expressed as:

$$\text{A-B} \rightarrow \text{A}\bullet + \text{B}\bullet$$

The BDE is calculated as the difference in energy between the molecule in its ground state and the total energy of the two radicals formed after bond dissociation:

$$\text{BDE} = E(\text{A}\bullet) + E(\text{B}\bullet) - E(\text{A-B})$$

Where $E(\text{A}\bullet)$, $E(\text{B}\bullet)$ and $E(\text{A-B})$ represent the energies of the radical fragments and the parent molecule, respectively.

2. Supplementary figures and tables

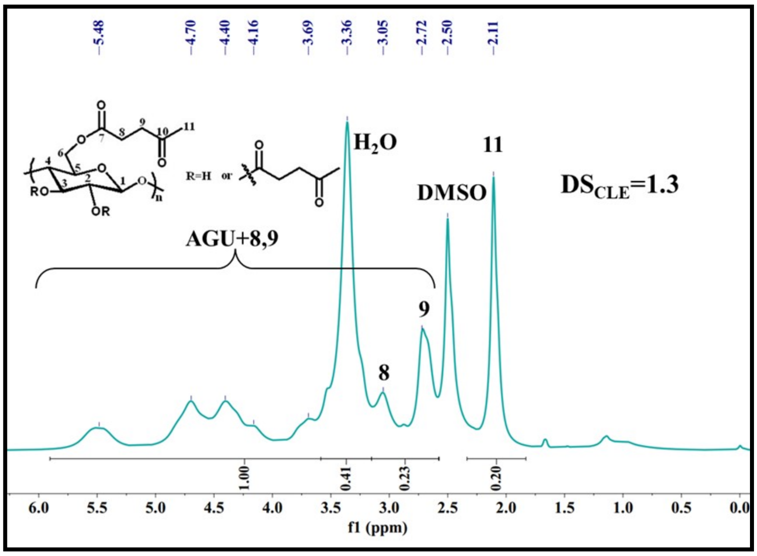

Fig. S1 ^{1}H-NMR of CLE (DS=1.3).

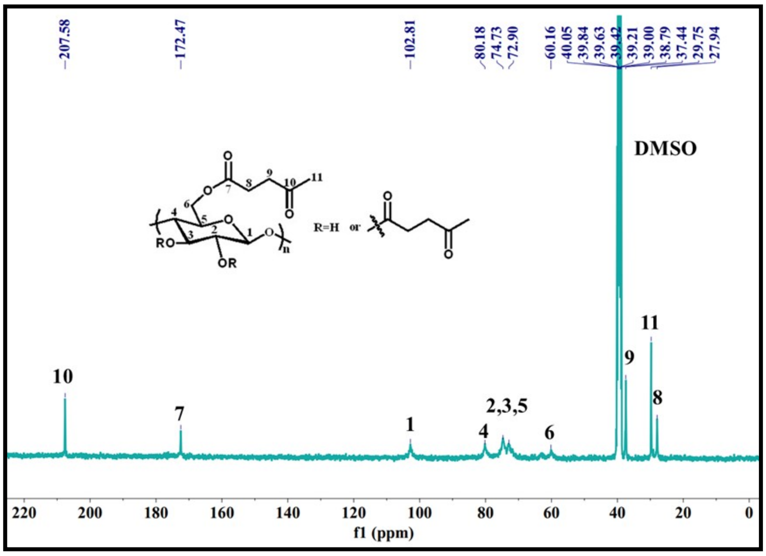

Fig. S2 ^{13}C NMR of CLE.

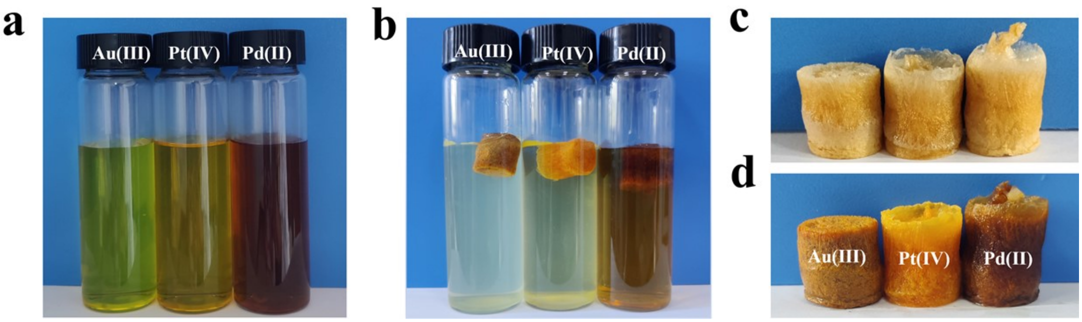

Fig. S3 Digital photographs of (a) Precious metal ions solution (C_0: 2000 mg/L, 0.1M HCl), (b) CLE@50PEI aerogel adsorbing precious metal ions, (c) CLE@50PEI aerogel and (d) CLE@50PEI aerogel after adsorption of precious metals, respectively.

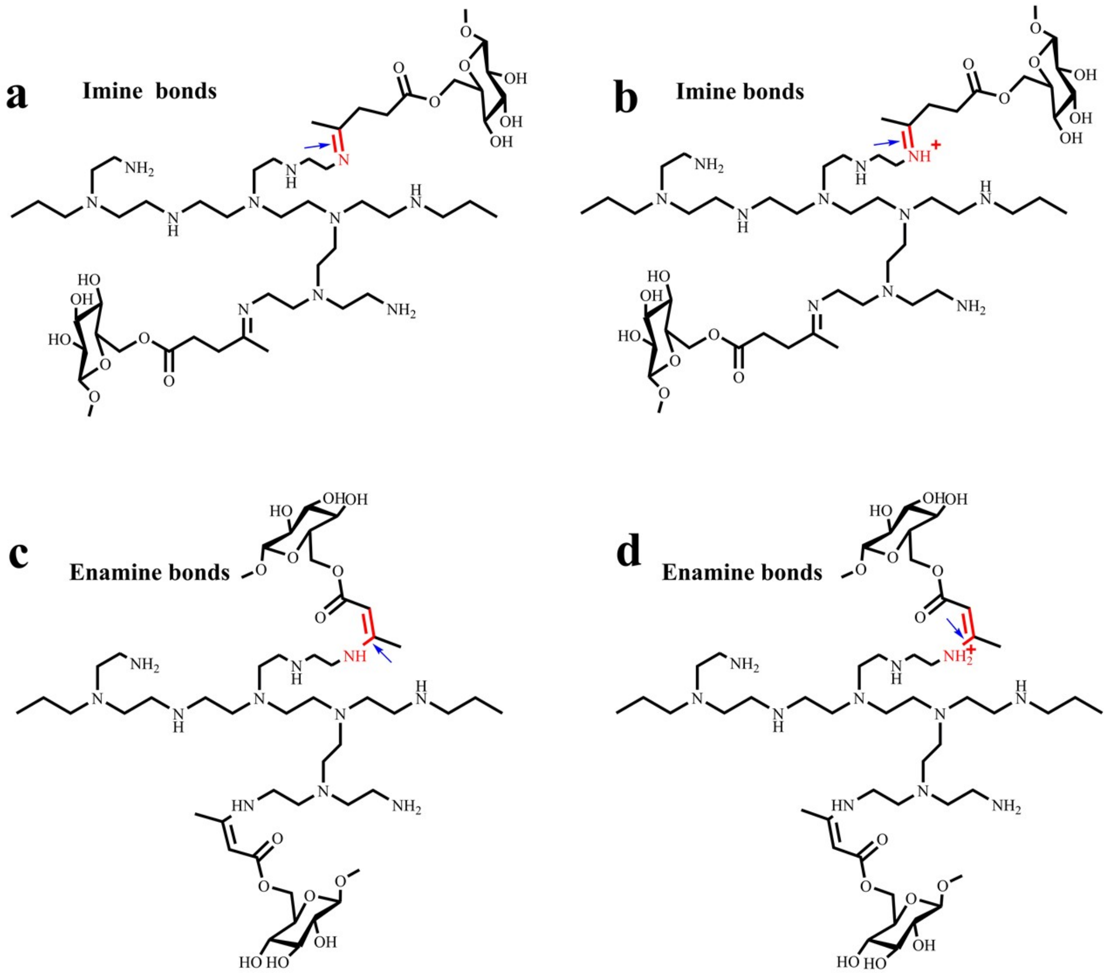

Fig. S4 Structural representations for DFT calculations of bond dissociation energies (BDE) under different conditions: (a) The structure containing imine bonds in vacuum, (b) The structure containing imine bonds under acidic condition, (c) The structure containing enamine bonds in vacuum and (d) The structure containing enamine bonds under acidic condition.

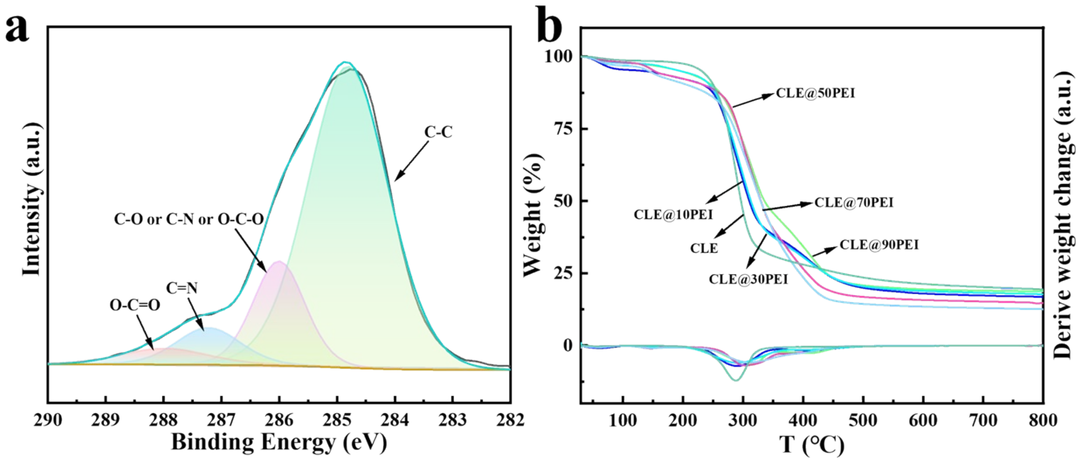

Fig. S5 (a) C1s peaks of the CLE@50PEI aerogel. (b) TGA Spectra of different proportions CLE@PEI aerogel.

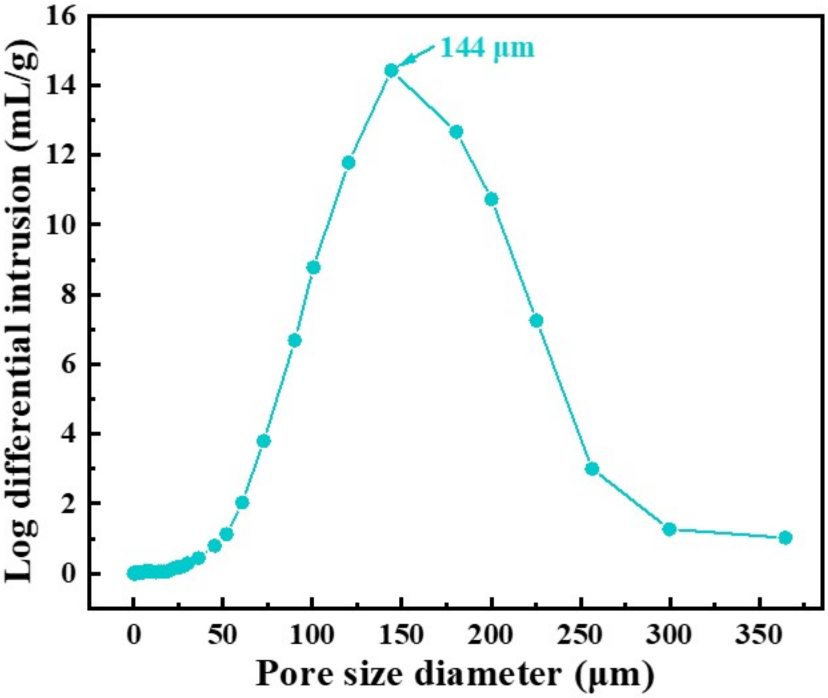

Fig. S6 Pore size distribution of CLE@50PEI aerogel.

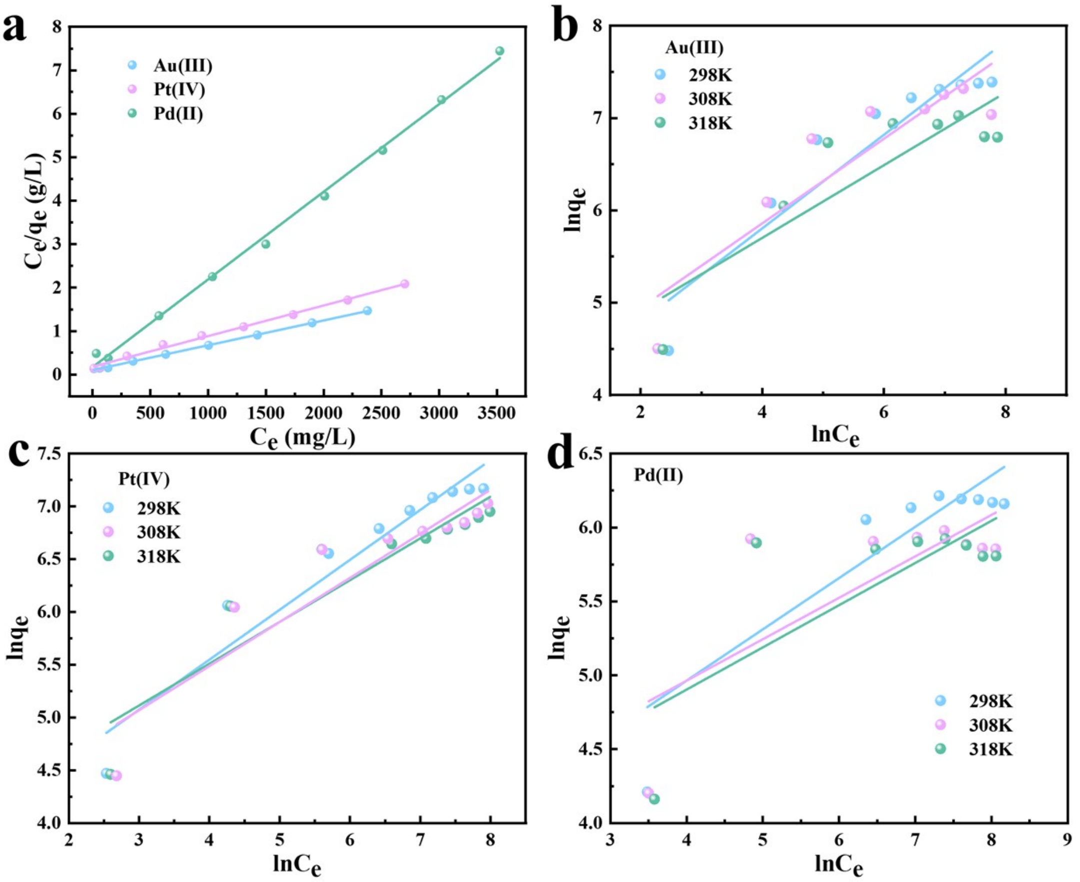

Fig. S7 Adsorption isotherms fitting curve from (a) Langmuir model (*T*: 298 K), Freundlich model for (b) Au(III), (c) Pt(IV) and (d) Pd(II) adsorption on the CLE@50PEI aerogel. Initial concentration of metal ions: 2000 mg/L.

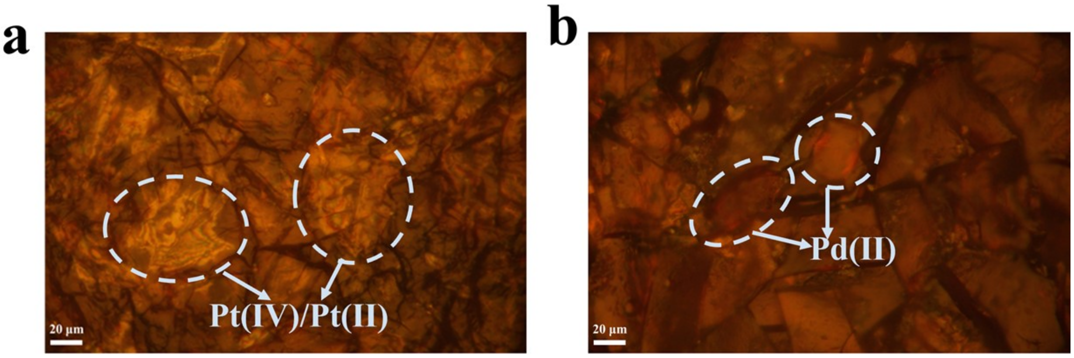

Fig. S8 Digital micrograph image of the CLE@50PEI after adsorption of (a) Pt(IV) and (b) Pd(II). Initial concentration of metal ions: 2000 mg/L.

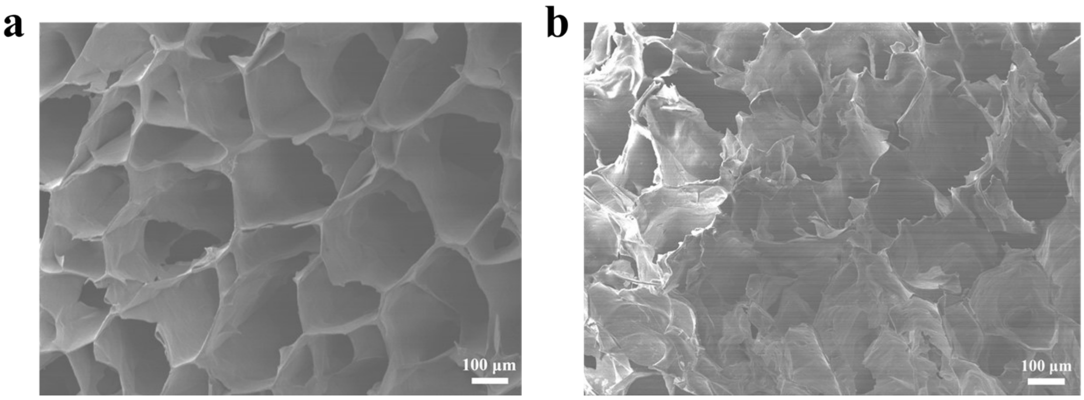

Fig. S9 The SEM images of (a) the CLE@50PEI aerogel, (b) the CLE@50PEI aerogel after five absorption-desorption cycles.

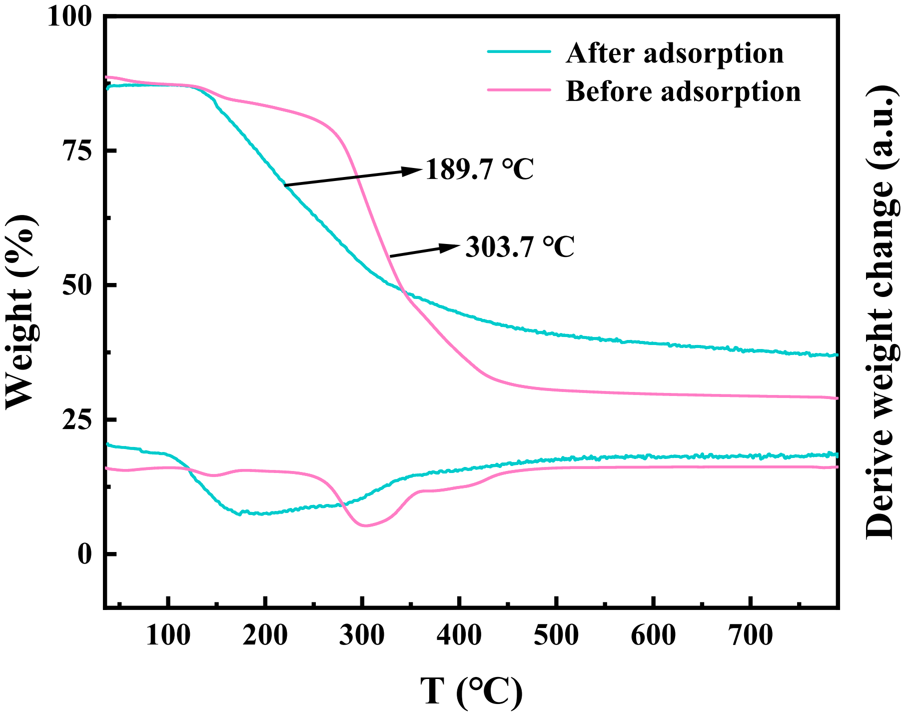

Fig. S10 Comparison of TGA curves for CLE@50PEI adsorbent before and after adsorption.

Table S1. Comparison of the bond dissociation energies (BDE) for imine and enamine bonds under vacuum and acidic conditions.

Bond type[a]	**Environment**	**BDE (kcal/mol)**
-C=N-	vacuum	149.7
-C=NH$^+$-	acidity	148.1
-NH-CH=CH-	vacuum	102.6
-NH+ 2-CH=CH-	acidity	79.3

a. Marked in red are the chemical bonds used to calculate BDE

Table S2 Elemental analysis of CLE and CLE@PEI aerogels with different PEI content

Sample	**Atomic %**		
	C (%)	**O (%)**	**N (%)**
CLE	69.82	30.18	0
CLE@10PEI	66.68	29.30	4.02
CLE@30PEI	67.9	23.84	8.26
CLE@50PEI	70.94	17.04	12.02
CLE@70PEI	71.08	14.17	14.75
CLE@90PEI	71.87	7.94	20.19

Table S3 Parameters derived Pseudo-first-order and Pseudo-second-order models for CLE@50PEI. Initial concentration of metal ions: 2000 mg/L, temperature: 298 K.

Kinetic model	**Parameters**	**Au(III)**	**Pt(IV)**	**Pd(II)**
	$q_{e\text{-}exp}$ (mg/g)	1328.4	1046.5	498.2
Pseudo-first-order $ln(q_e - q_t) = lnq_e - k_1t$	k_1 (min$^{-1)}$	6.6×10^3	4.8×10^3	5.0×10^3
	q_e (mg/g)	454.2	135.4	65.8
	R^2	0.9238	0.6505	0.7326
Pseudo-second-order $t/q_t = 1/k_2q_e^2 + t/q_e$	k_2 [(g/(mg·min)]	7.3×10^5	3.4×10^4	3.4×10^4
	q_e (mg/g)	1335.9	1039.2	663.9
	R^2	0.9998	0.9998	0.9999

Table S4 Parameters derived from intraparticle diffusion model for CLE@50PEI. Initial concentration of metal ions: 2000 mg/L, temperature: 298 K.

Samples	**Stage 1**			**Stage 2**		
	R^2	**k_1 [mg/(g·min$^{1/2}$)]**	**C_i (mg/g)**	**R^2**	**k_2 [mg/(g·min$^{1/2}$)]**	**C_i (mg/g)**
Au(III)	0.8880	57.5	639.7	0.9779	6.4	1159.4
Pt(IV)	0.8485	60.6	683.6	0.9216	1.9	989.7
Pd(II)	0.7868	25.9	334.4	0.9688	1.3	463.8

Table S5 Comparison of the Au(III), Pt(IV) and Pd(II) adsorption performance of CLE@50PEI aerogel with other recently reported biomass adsorbents.

Adsorbents	**Maximum adsorption capacity (mg/g)** [a]			**References**
	Au(III)	**Pt(IV)**	**Pd(II)**	
AF	166.7	-	-	Peydayesh et al.,[11]
LMCCR	70.3	129.3	109.5	Fujiwara et al., [12]
TEPA-PT gel	1168.0	343.3	157.5	Gurung et al., [10]
DMA-PP gel	1103.0	50.7	44.7	Xiong et al., [13]
QAPT gel	819.4	101.4	89.4	Gurung et al., [14]
DMC	998.6	470.1	-	Biswas et al.,[15]
GMCCR	170.0	122.5	120.4	Ramesh et al.,[16]
AG-PT gel	1753.0	107.5	392.1	Gurung et al.,[17]
TC-chitosans	750.5	241.9	365.0	Bratskaya et al.,[18]
EN-lignin	606.8	104.6	22.7	Parajuli et al.,[19]
DMA-CLP	1398.5	121.0	65.9	Parajuli et al.,[20]
DMA-paper gel	906.1	175.6	223.5	Adhikari et al.,[21]
Cellulose-TFN-A	1992.0	-	-	Li et al.,[22]
T-CNF/PEI 2	-	600	-	Hong et al.,[23]
GA-PEI-Alginate	>2300	-	-	Bediako et al.,[24]
CLE@50PEI	1752.0	1420.5	495.1	This work

a. "-" denotes that no data were reported in the reference.

Table S6 Comparison of selectivity and recycles of Au(III), Pt(IV) and Pd(II) with other recent reports.

Adsorbents	Metal ions	Selectivity	Recycles [a]	References
CDF-CS	Au(III)	99.1% (Au, As, Cr, Cd, Mg, Mn, Sb and Co ions)	4	Zhao et al.,[25]
AF	Au(III)	66.8% (Au, Cu, Fe, Pb, Ni, Zn, Cr, and Mn ions)	-	Peydayesh et al.,[11]
TpDa-COF	Au(III)	96.25% (Au, Cu, Ni, Al and Zn ions)	-	Mei et al.,[26]
BIT-POP-15	Au(III)	95% (Ag, Al, Mg, Zn, Fe , Ni, Cu, Sn and Au ions)	-	Shi et al.,[27]
PA6	Pt(IV)	41.3% (Al, Ce, Mg, Pt, and Pd ions)	-	Hsu et al.,[28]
	Pd(II)	25.9% (Al, Ce, Mg, Pt, and Pd ions)	-	
4-AP/PCMS	Au(III)	92.2% (Au, Cu, Ni, Co, Zn, Fe, Cd and Mg ions)	5	Chen et al.,[29]
EDTA-TAB	Au(III)	99.9% (Au, Pt, Al, Zn, Ni, Cd, Co, Cr, Pb and Cu ions)	6	Bian et al.,[30]
	Pt(IV)	99.2% (Au, Pt, Al, Zn, Ni, Cd, Co, Cr, Pb and Cu ions)	6	
AN-AMPS-AAO3	Pd(II)	65.1% (Au, Ca, Cu, Fe, K, Mg, Ni and Zn ions)	5	Wu et al.,[31]
CLE@50PEI	Au(III)	75.7% (Cu, Zn , Ni, Fe, Au , Pd and Pt ions)	5	This work
	Pt(IV)	67.5% (Cu, Zn , Ni, Fe, Au , Pd and Pt ions)	5	
	Pd(II)	97.1% (Cu, Zn , Ni, Fe, Au , Pd and Pt ions)	5	

a. “-” denotes that no data were reported in the reference.

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