Supplementary Information

Polyethylenimine-cross-linked cellulose nanocrystals for highly efficient recovery of rare earth elements from water and mechanism study

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Table S1 Elemental analysis results of CNC, TEMPO-CNC, and PEI-CNCs.

Sample	Elemental content (wt. %)				N content in adsorbent		PEI content
	N	C	H	S	mg/g	mmol/g	(wt. %)[a]
CNC	0	42.14	6.18	0.73	0	0	0
TEMPO-CNC	0	40.46	5.77	0.37	0	0	0
PEI-CNC1 (0.5:1)	8.64	42.84	7.11	2.57	86.4	6.17	26.54
PEI-CNC2 (1:1)	12.12	43.9	7.51	1.75	121.2	8.66	37.23
PEI-CNC3 (2:1)	15.05	44.49	7.73	1.38	150.5	10.75	46.23
PEI-CNC4 (4:1)	16.35	46.1	8.12	0.91	163.5	11.69	50.22

[a] Calculated from nitrogen content (wt. %) and considered $(C_2H_5N)_n$ as the chemical formula of PEI: $PEI\% = N\% \times M_{C_2H_5N}/M_N$.

Functional cost analysis of PEI-CNCs

Table S2 The wholesale cost of reagents.

Reagent	Cost ($/kg)[a]
Cellulose nanocrystal	7
Polyethylenimine (50 wt. % in H_2O)	5
2,2,6,6-tetramethylpiperidinyloxy	7.2
N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride	12
N-hydroxysuccinimide	16

[a] Prices obtained from wholesale suppliers (metric ton scale).

Table S3 The pilot-scale cost analysis of PEI-CNCs.

	PEI-CNC1	PEI-CNC2	PEI-CNC3	PEI-CNC4
Yield (%)	68	65	59	33
Raw materials ($/kg)[a]	30	30.8	33.4	58.8
Pilot-scale ($/kg)[b]	42.6	43.7	47.4	83.5

[a] Calculated based on the raw materials required to produce 1 kg of PEI-CNC having 1:0.5, 1:1, 1:2, and 1:4 CNC:PEI ratios in quantitative yield, according to Alsbaiee's method.[1]
[b] The costs of the raw materials were scaled by 142% as a rough estimate of the cost associated with an optimized process in a pilot scale manufacturing plant, according to Alsbaiee's method.[1]

Notes and references

1. A. Alsbaiee, B. Smith, L. Xiao, Y. Ling, D. E. Helbling and W. R. Dichtel, *Nature*, 2016, **529**, 190–194.

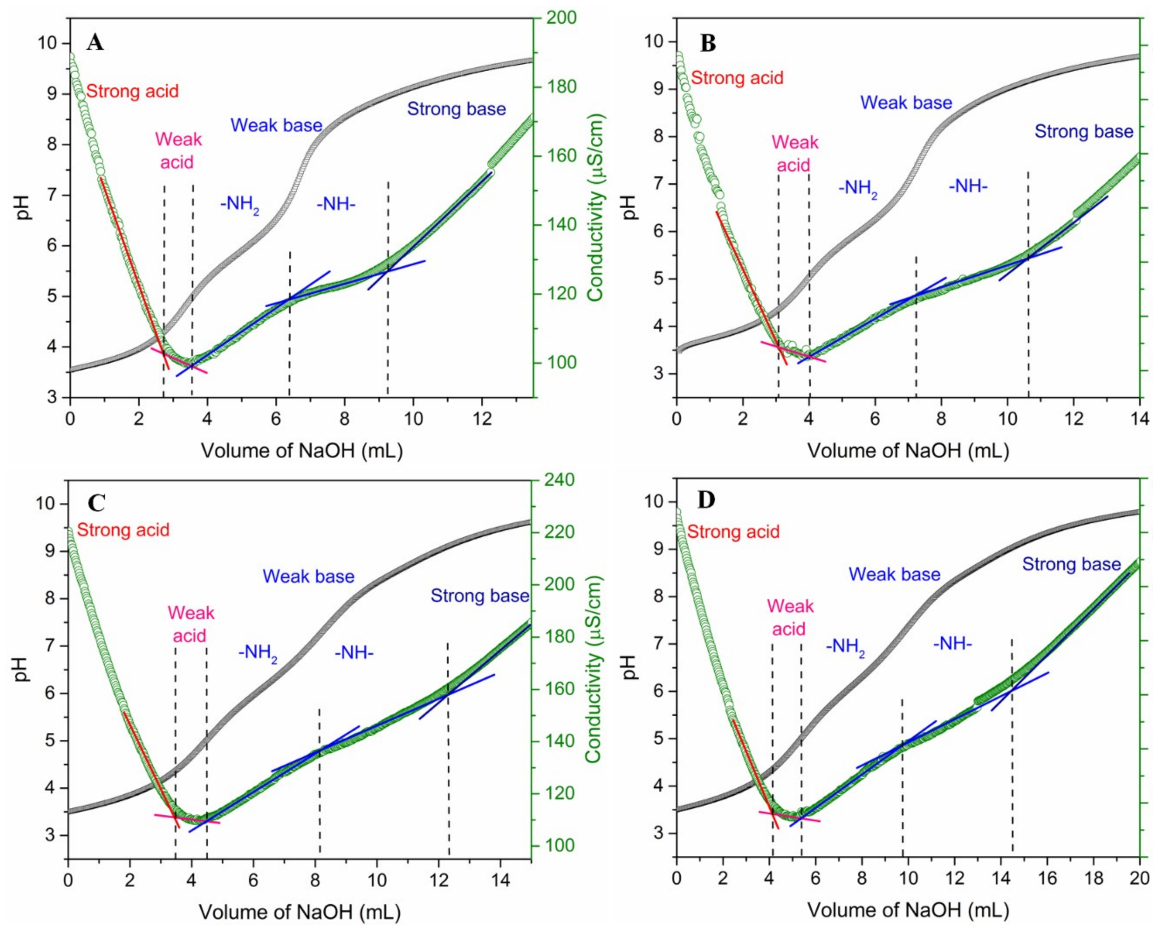

Fig. S1 Simultaneous conductometric−potentiometric titration curves of 0.025 wt. % PEI-CNC1 (A), PEI-CNC2 (B), PEI-CNC3 (C), and PEI-CNC4 (D) by 0.01 M NaOH. Experimental condition: PEI-CNC, 10 mg; solution, 40 mL; initial pH of solution: 3.5; titration speed, 50 μL/min.

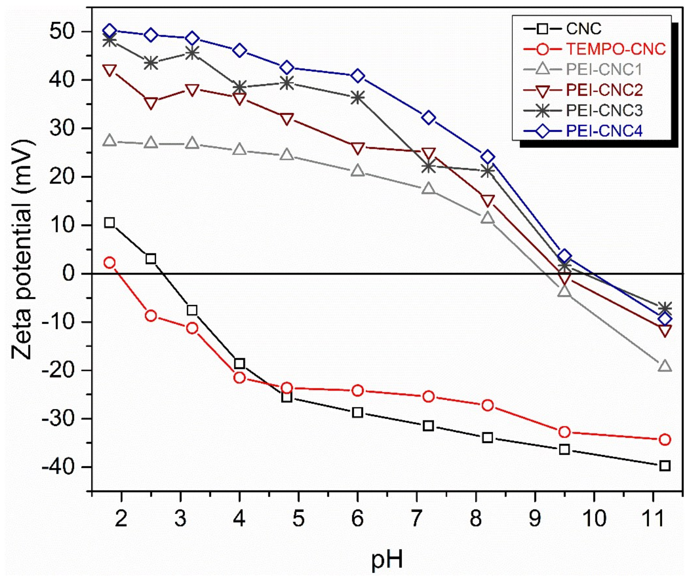

Fig. S2 ζ-potentials of the pristine, modified, and cross-linked CNCs as a function of solution pH.

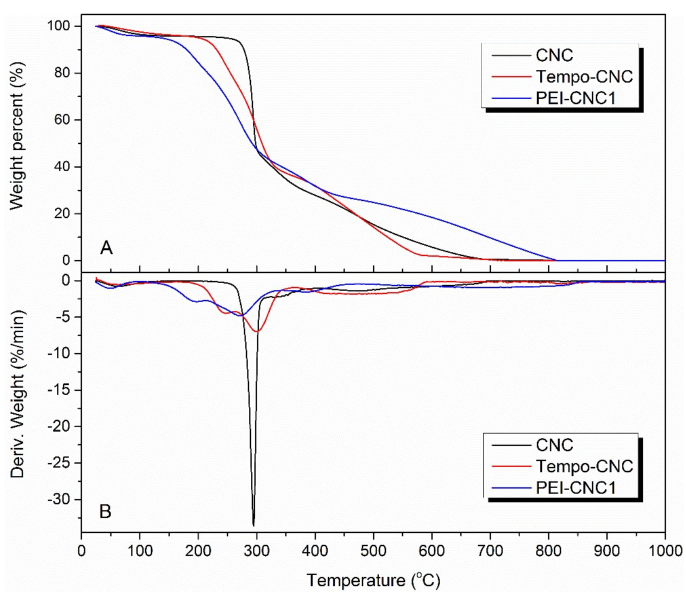

Fig. S3 TGA (A) and DTG (B) curves of CNC, TEMPO-CNC, and PEI-CNC1.

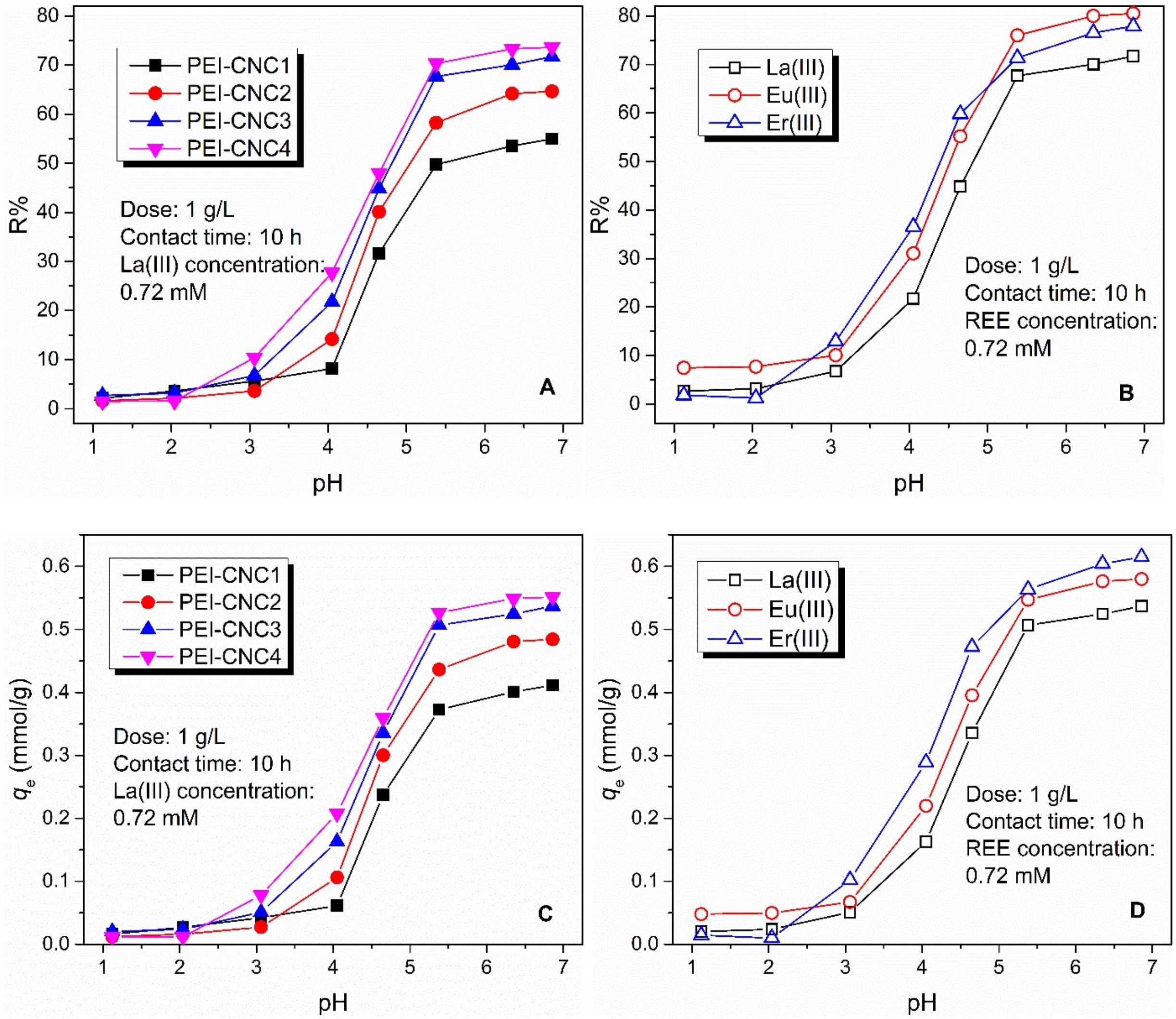

Fig. S4 Effect of pH on the adsorption efficiency (A) and adsorption capacity (C) of La(III) by different PEI-CNCs and effect of pH on the adsorption efficiency (B) and adsorption capacity (D) of different REEs by PEI-CNC3.

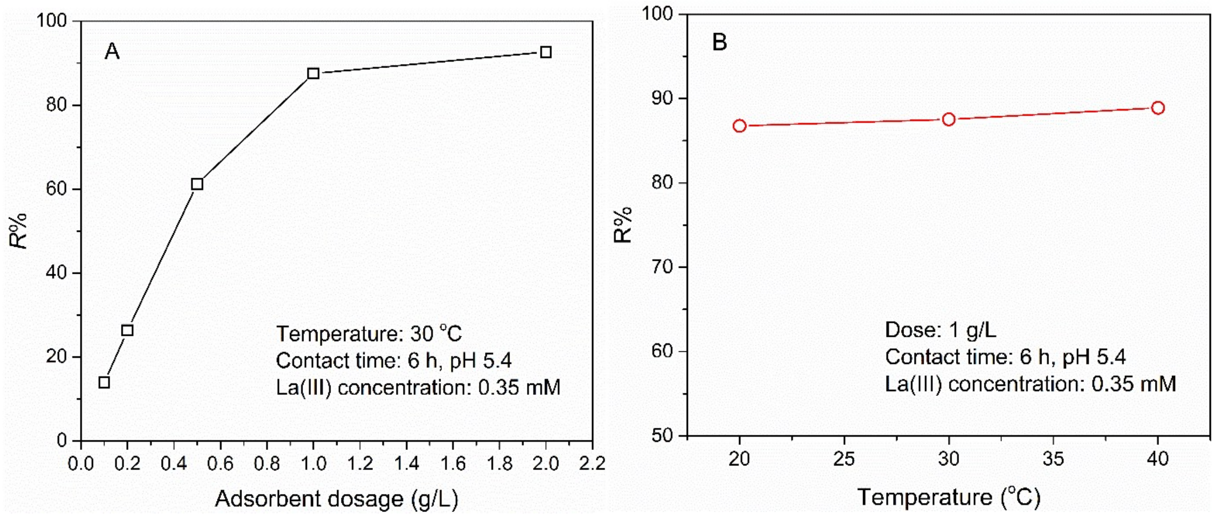

Fig. S5 The effect of amount of adsorbent (A) and the effect of temperature (B) on the adsorption efficiency of La(III) onto PEI-CNC3.

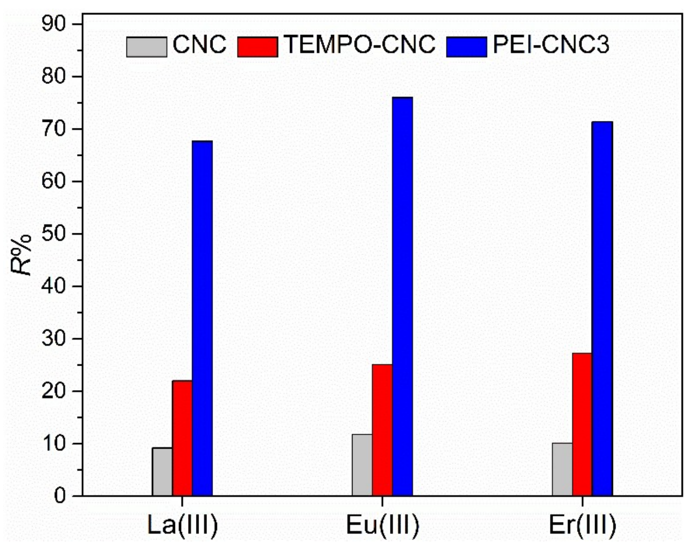

Fig. S6 Comparison of the adsorption efficiency of La(III), Eu(III), and Er(III) onto CNC, TEMPO-CNC, and PEI-CNC3. Experimental condition: dose, 1 g/L; pH 5.4; contact time, 10 h; REE concentration, 0.72 mM.

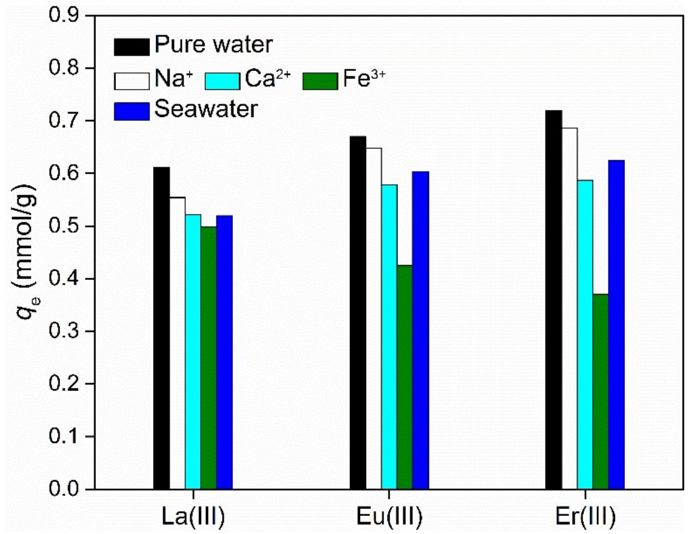

Fig. S7 Effect of competitive ions (Na^{+}, Ca^{2+}, and Fe^{3+}) on the adsorption of La(III), Eu(III), and Er(III) onto PEI-CNC3 (Experimental condition: dose, 1 g/L; pH 5.4; contact time, 10 h; the concentration ratio of competitive ion to REE, 1:2 (mM)), and its application in the adsorption of REEs from seawater, which was collected from Gulf of Finland near Helsinki.