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Supporting Information for

Cerium Separation with NaBiO$_3$ Nanoflower Material via Oxidation Adsorption Strategy

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Experimental section

Synthesis of NaBiO$_3$ nano-sheet (NBS)

The synthesis of NBS is based on the reported method. [1] Firstly, 10 g NaOH was added into 50 mL NaClO solution under stirring at 70 °C, and a uniform white suspended solution was obtained. Then, 1.5 g Bi(NO$_3$)$_3$*5H$_2$O was dissolved into 5 mL 4 M HNO$_3$, and the solution was slowly droped into the suspended solution at stirring. A yellow product was generated in the solution and the solution was sitrring for 12 h at 70 °C. The precipitate (NBS) was rinsed with 1 wt% NaOH solution for several times and collected by centrifuging. Finally, the resulting NBS was dried in vacuum at 60 °C for 24 h.

Extraction Ce^{3+} from dilute Ln^{3+} mixtures

The mixtures consisting of 10 mg L^{-1} of all Ln^{3+} ions and Sc^{3+}, Y^{3+} were prepared with different concentration of nitric acid solutions. For the mixed Ln solution (10ppm, pH=2), 1 mL standard solutions of each lanthanides were mixed in a 50mL glass beaker, 1mL Sc^{3+} standard solution (1000ppm, 0.5 M HNO$_3$, Alfa Aesar) and 1mL Y^{3+} standard solution (1000ppm, 0.5 M HNO$_3$, Alfa Aesar) were also added to the mixture. The mixture was heated and evaporated to near dry, then dissolved with 0.01 M HNO$_3$. Finally, the solution was transferred to a 100mL volumetric flask and diluted to 100ml with 0.01 M HNO$_3$. The concentrations of metal ions in the initial solution were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinEmer Optima 8300). The pH of the initial solution was determined by meter pH (PHSJ-5, INESA).

In a typical static sorption experiment, 10 mg NBF was mixed with the multi-ion test solution (20 mL), and the mixtures were shaken at 300 rpm for 30 min. Then, the suspension was centrifuged at 10000 rpm for 5 minutes. The supernatant was separated from the suspension by using a 0.22 μm nylon membrane filter. The concentrations of metal ions in the supernatant and initial solution were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinEmer Optima 8300) or inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700x). All values represent the average of three experiments with a mean variation of less than 5%. The removal efficiency or extraction rate (E, %) , equilibrium Ce^{3+} uptake (q$_e$, mg g^{-1}) , distribution coefficients (K$_d$, mL g^{-1}), separation factor (SF) between two metal ions were calculated using the following equations:

$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

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

$$SF_{M1/M2} = \frac{K_d(M1)}{K_d(M2)} \qquad (4)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of Ce^{3+} in the aqueous phase, respectively, V (L) is the volume of the solution, and m (g) is the dry mass of the NaBiO$_3$ samples.

Extraction rates and distribution coefficients (K$_d$) values were calculated following the equations (1) and (3), shown in Figure 3 and Figure S5.

Binary uptake experiments

Fifteen combinations of mixtures (Ce/Ln, Ce/Sc, Ce/Y) were prepared with different concentration of nitric acid solutions. Then, 10 mg NBF was mixed with the multi-ion test solution (20 mL), and the mixtures were shaken at 300 rpm for 30 min at 25 °C. The distribution coefficients (K$_d$) values and separation factors (SFs) were calculated following the equations (3) and (4). As shown in Figure S6, NBFs exhibit excellent selectivity for Ce over other lanthanides under wide acidity conditions (0.001–2 M HNO$_3$), and the best selectivity is obtained at pH 2.

Multi-ion uptake experiments

Firstly, the mixtures consisting of 10 mg L^{-1} of uranyl, transition metals (Cu, Ni, Zn, Pd, Au, Ag, and Fe) and main group metals (Al, Ca, Ba, Mg, K, and Li) were prepared with different concentration of nitric acid solutions. Then, 10 mg NBF was mixed with the multi-ion test solution (20 mL), and the mixtures were shaken at 300 rpm for 30 min at 25 °C. Extraction rates were calculated following the equations (3). The adsorption performances of the NBF toward these metals were shown in Figure S7a.

For radionuclides, the test solution consisting of 100 Bq/mL of radionuclides (such as ^{241}Am, ^{244}Cm or ^{242}Pu was prepared with the appropriate amounts of tracer (~1000 Bq/mL ^{241}Am, ^{244}Cm or ^{242}Pu in 0.1 M nitric acid), water, and concentrated nitric acid. Then, 5 mg NBF was mixed with the test solution (1 mL), and the mixtures were shaken at 300 rpm for 30 min. The suspension was centrifuged at 10000 rpm for 5 minutes. The supernatant was separated from the suspension by using a 0.22 μm nylon membrane filter. The resulting solutions were analyzed using alpha spectrometry and liquid scintillation counting. The removal efficiency or extraction rate (E, %) , the weight distribution ratio (D$_w$, mL g^{-1}), separation factor (SF) between two metal ions were calculated using the following equations: [2,3]

$$E = \frac{(A_0 - A_{aq})}{A_0} \times 100\%$$ (5)

$$D_w = \frac{(A_0 - A_{aq})}{A_{aq}} \times \frac{V}{m}$$ (6)

$$SF_{M1/M2} = \frac{D_w(M1)}{D_w(M2)}$$ (7)

where A_0 and A_{aq} (Bq/mL) are the initial and equilibrium specific activities of the tracer in the aqueous phase, respectively, V (L) is the volume of the solution, and m (g) is the dry mass of the NBF. The adsorption performances of the NBF toward these radionuclides were shown in Figure S7b.

Am/Cm separation experiments

Firstly, the test solution consisting of 100 Bq/mL of radionuclides ([41]Am and [244]Cm) was prepared with the appropriate amounts of tracer (~1000 Bq/mL [241]Am, and [244]Cm in 0.1 M nitric acid), water, and concentrated nitric acid. Then, 5 mg NBF was mixed with the test bimetal solution (1 mL), and the mixtures were shaken at 300 rpm for 30 min at 25 °C. The suspension was centrifuged at 10000 rpm for 5 minutes. The supernatant was separated from the suspension by using a 0.22 μm nylon membrane filter. The resulting solutions were analyzed using alpha spectrometry and liquid scintillation counting. The weight distribution ratio (D_w, mL g^{-1}), and separation factor (SF) between Am and Cm were calculated following the equations (6) and (7), shown in Figure S8.

Extraction of cerium from bastnaesite

The bastnaesite power (0.5 g) was placed in 250 mL Teflon beaker, and mixed acid (HF: HNO$_3$: HClO$_4$ = 3:2:1) was added to Teflon beaker, which was then digested at 350 °C. And mixed acid should be added several times until the digestion was completed. Finally, the bastnaesite sample solution was prepared by 0.1 M HNO$_3$ solution. The concentrations of metal ions in initial solution were determined by ICP-OES. The concentrations of main metal ions are as follows: La^{3+} (34 ppm), Ce^{3+} (48 ppm), Pr^{3+} (0.3 ppm), Nd^{3+} (9 ppm).

NBF (50mg) and microporous silica beads (450mg) were mixed uniformly by stirring in 0.1 M HNO3, and the mixture was then used for chromatographic separation. Empty polypropylene columns (2 mL) and vacuum box (AR-12-BOX, TrisKem International, France) were used for the experiments. Columns were slurry packed using 0.1 M nitric acid and 0.5 g column material (10% NBF by weight), then placed on the vacuum box and washed with 5 mL of 0.1 M nitric acid to ensure acidification of the mixture. The bastnaesite sample solution was loaded onto the

column followed by 50 mL of 0.1 M nitric acid to elute the La, Pr, and Nd. The Ce was then eluted with 90 mL of mixed solution (1.0 M nitric acid and 5% H_2O_2), and was collected in a single fraction. The effluents from the column were collected with the volume of 5 mL and determined by ICP-OES. The elution curve was shown in Figure 7a.

Recovery of cerium from simulated glass residue

The simulated glass residue prepared with standard solution of metal ions, and the concentrations of ions are as follows: La^{3+} (24 ppm), Ce^{3+} (49 ppm), Al^{3+} (28 ppm), Ca^{2+} (62 ppm). The chromatographic separation procedure is similar to that of Figure 7a. The simulated sample solution was loaded onto the column followed by 50 mL of 0.1 M nitric acid to elute the La, Al, and Ca. The Ce was then eluted with 70 mL of mixed solution (1.0 M nitric acid and 5% H_2O_2), and was collected in a single fraction. The effluents from the column were collected with the volume of 5 mL and determined by ICP-OES. The elution curve was shown in Figure S11, cerium was washed using 1 M nitric acid and H_2O_2 with 99% recovery.

Am/Cm separation in simulated high-level liquid waste solution

The simulated high-level liquid waste solution was prepared with 0.2 mL Am^{3+} (1 mCi/mL) and Cm^{3+} (1 mCi/mL), and adjusted the acidity to pH 1. The chromatographic separation procedure is similar to that of Figure 7a. The Am was eluted with 5 mL 0.1 M nitric acid, then Cm was eluted with 5 mL 2 M nitric acid. The effluents from the column were collected with the volume of 1 mL and determined by alpha spectrometry. The elution curve and alpha spectra were shown in Figure 7b and Figure S12.
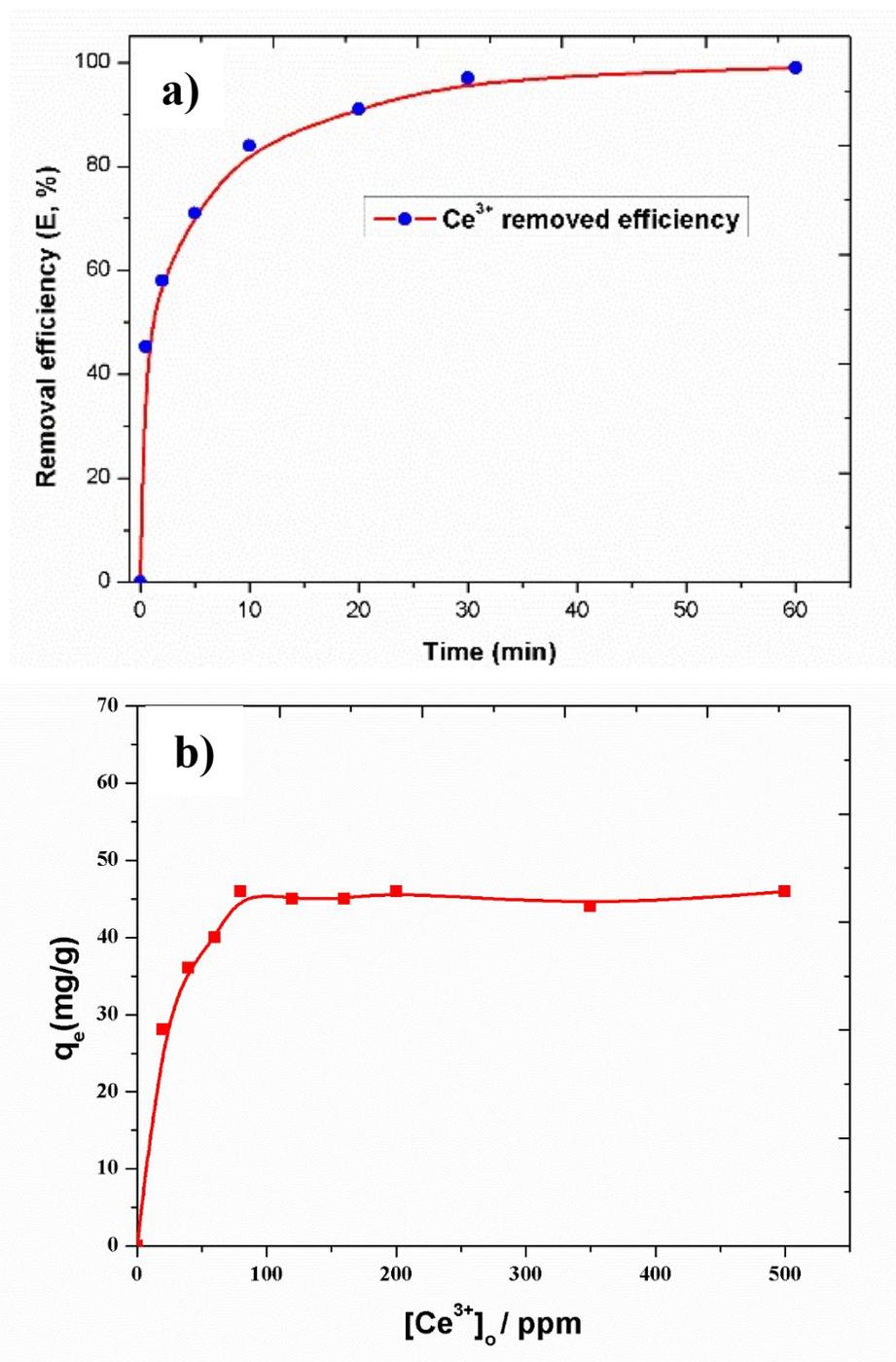
Figure S1 (a) Removal of Ce^{3+} ions by commercialized $NaBiO_3$ with different time. The commercialized $NaBiO_3$ (10 mg) and the Ce^{3+} nitric acid solution (pH=2, 10 ppm, 20 mL) were used. The mixtures were shaken at 300 rpm for 0.5, 2, 5, 10, 20, 30, 60 min, respectively. The temperature was 25 °C. (b) Removal of Ce^{3+} ions by commercialized $NaBiO_3$ with different Ce^{3+} concentrations. The commercialized $NaBiO_3$ (10 mg) and the Ce^{3+} nitric acid solution (pH=2, 20 – 500 mg L^{-1}, 20 mL) were used. The mixtures were then shaken at 300 rpm for 30 min. The temperature was 25 °C.
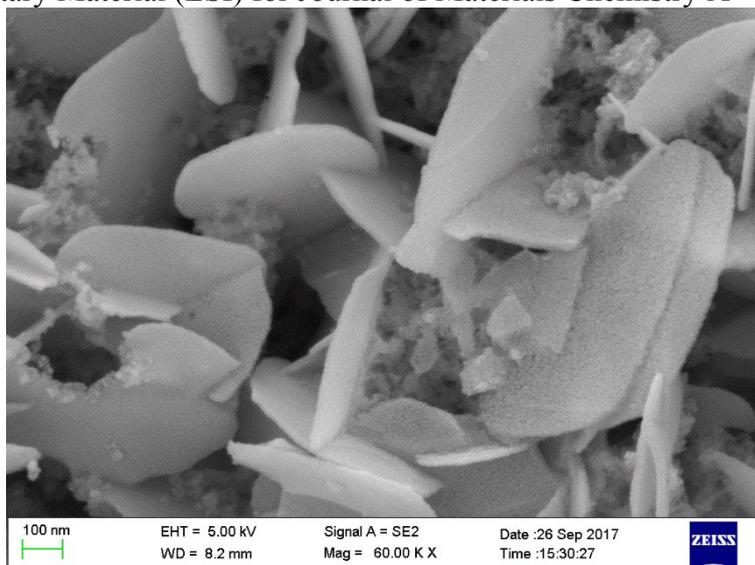
Figure S2 SEM image of NBS.
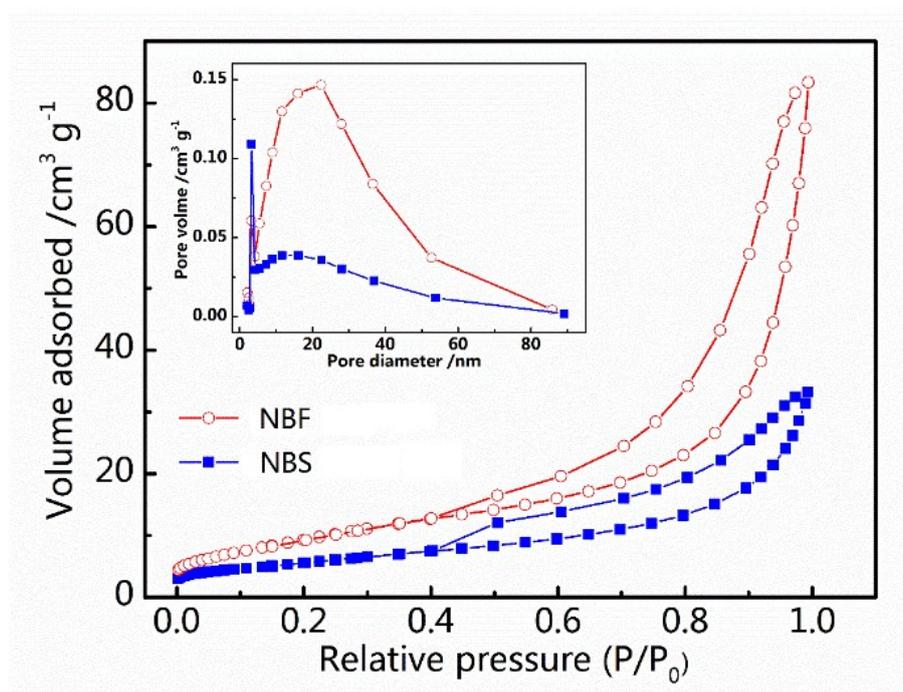
Figure S3 Nitrogen adsorption–desorption isotherms and the corresponding pore-size distribution curves (inset) of NBF and NBS samples.
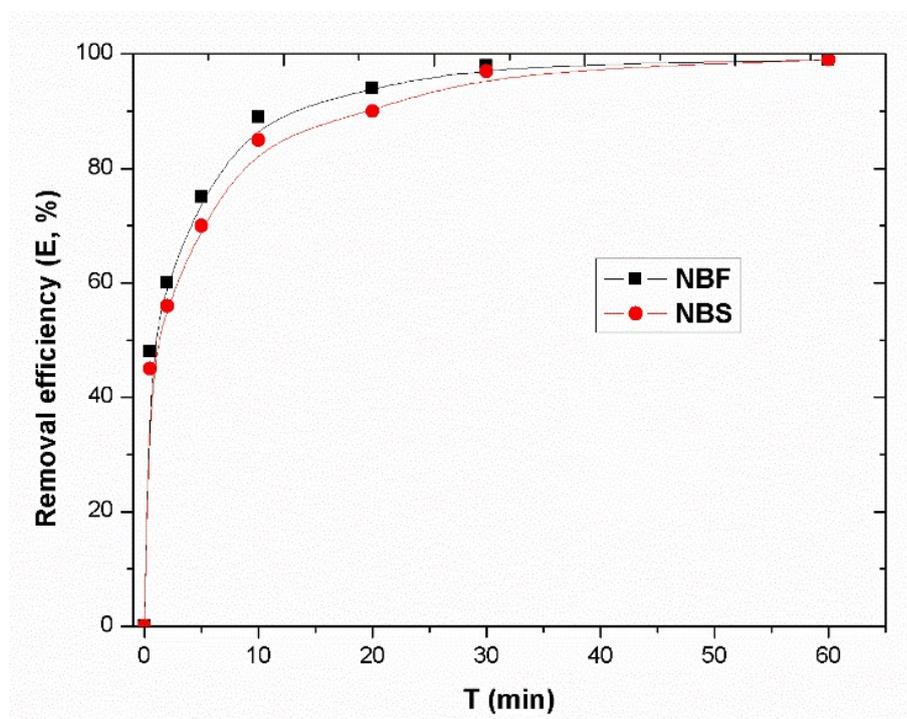
Figure S4 Removal of Ce^{3+} ions by NBF and NBS. 10 mg NBS or NBF and the Ce^{3+} nitric acid solution (pH=2, 50 ppm, 20 mL) were used. The mixtures were then shaken at 300 rpm for 0.5, 2, 5, 10, 20, 30, 60 min, respectively. The temperature was 25 $^{\circ}$C.
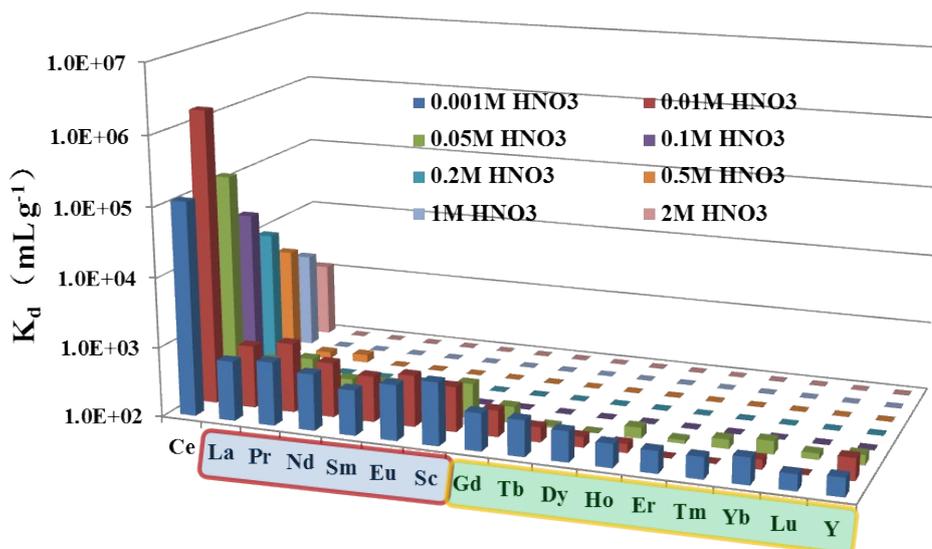
Figure S5. Extraction from dilute Ln^{3+} mixtures by NBF: distribution coefficients (K_d). NBF dosages: 0.5 g L^{-1}, shaking times: 30 min, temperature: 25 °C. All data points represent the average of three experiments with a mean variation of less than 5%. The maximum K_d value in the study is presented as 199 8000 mL g^{-1}, calculated from the detection limit (10 μg L^{-1}).
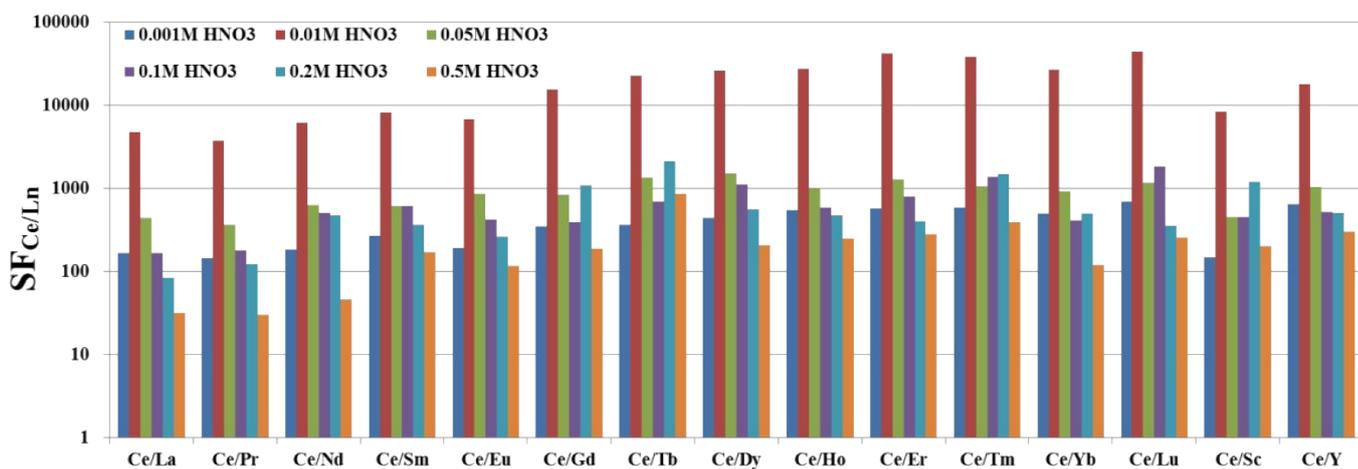

Figure S6 Separation factors (SFs) between the Ce^{3+} and Ln^{3+} combinations as a function of acid concentration. NBF dosages = 0.5 g L^{-1}, shaking times = 30 min, temperature = 25 °C, Initial solution composition: 0.2 mM equimolar mixture of the selected Ln^{3+} pair.
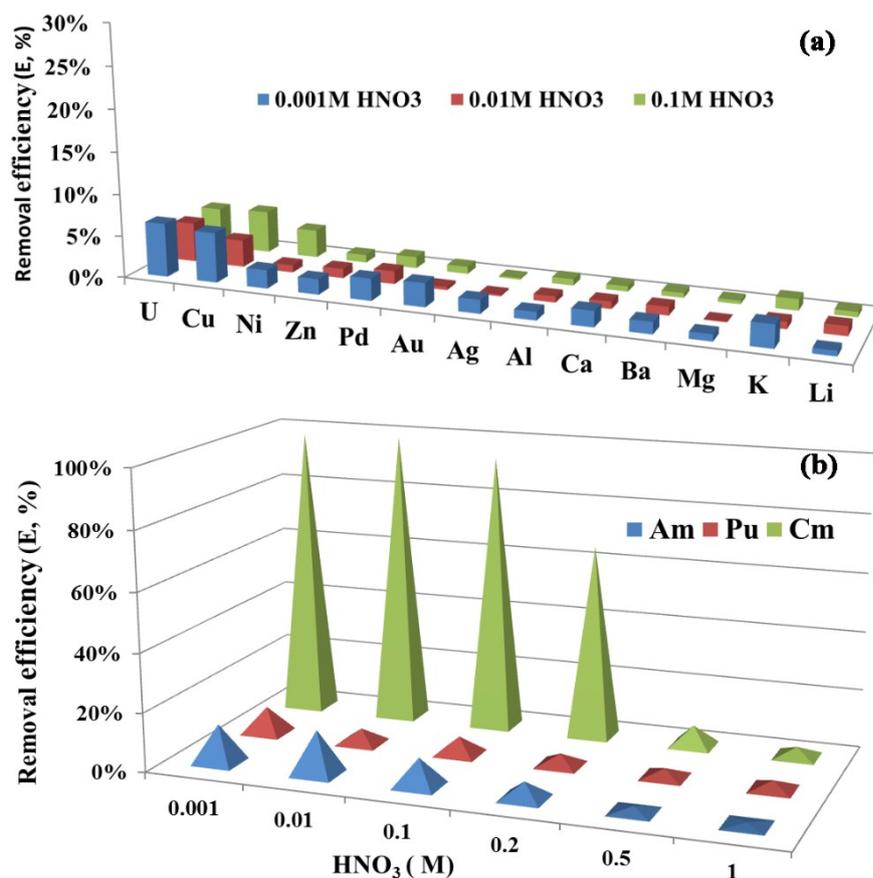
Figure S7 (a) Removal of metal ions by NBF. NBF:10mg, shaking times: 30 min, temperature: 25 $^{\circ}$C. (b) Removal of radionuclides by NBF. NBF:5mg, shaking times: 30 min, temperature: 25 $^{\circ}$C. All data points represent the average of three experiments with a mean variation of less than 5%.
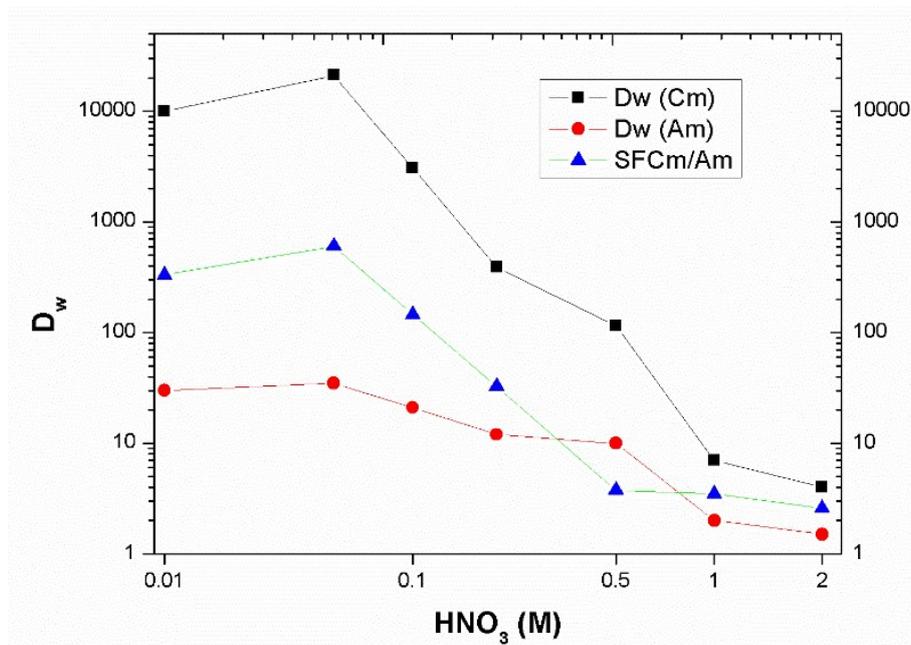

Figure S8 Weight distribution ratio (D_w) and separation factor (SF) between the Am^{3+} and Cm^{3+}

combinations as a function of acid concentration. NBF:5mg, shaking times: 30 min, temperature: 25
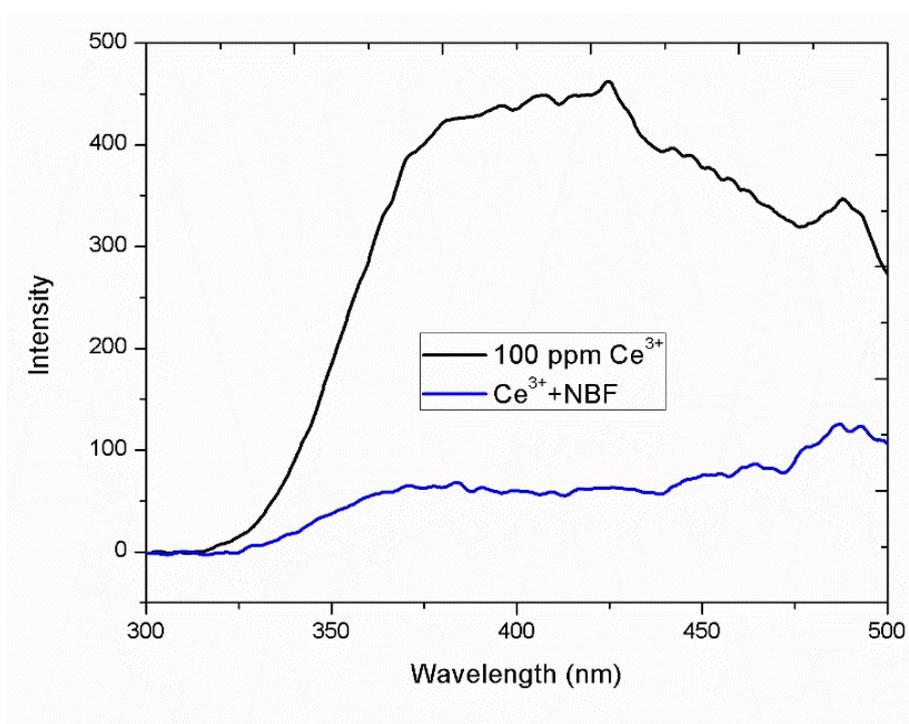
°C.

Figure S9 Fluorescence spectra of Ce^{3+} ions before and after NBF addition. The Ce^{3+} nitric acid solution (pH=2, 100 ppm) was tested firstly. 20 mg NBF was added into the Ce^{3+} solution, the mixtures were stirred for 0.5 min, and the fluorescence spectrum was tested.
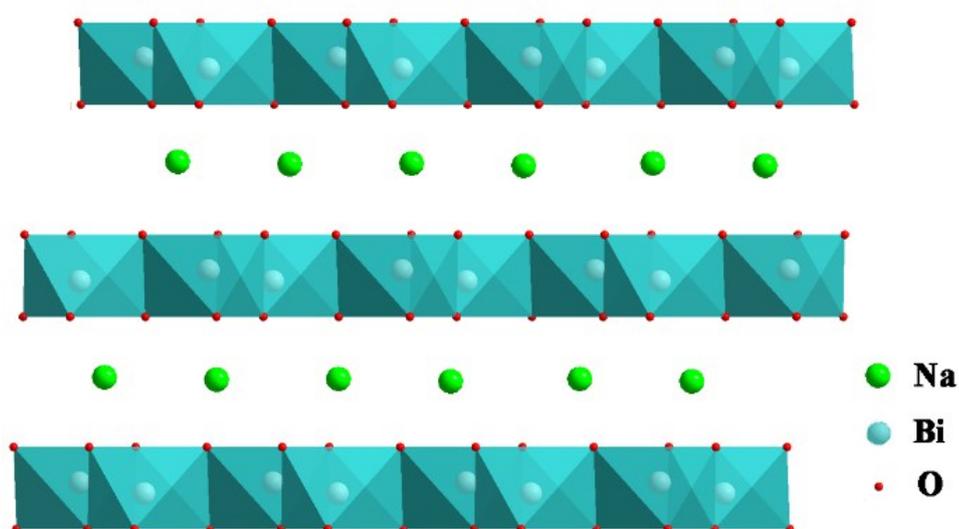

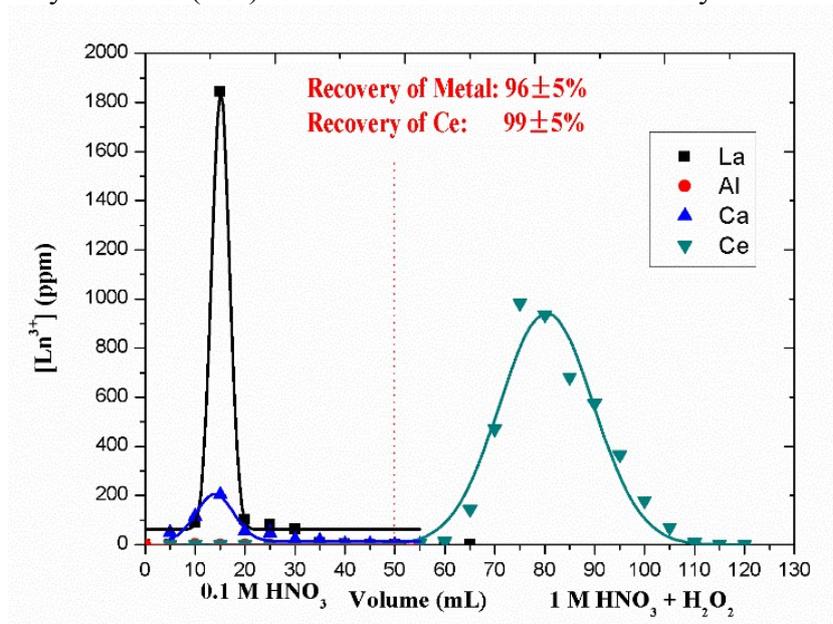**Figure S10** Crystal structure representation of typical $NaBiO_3$. [4]

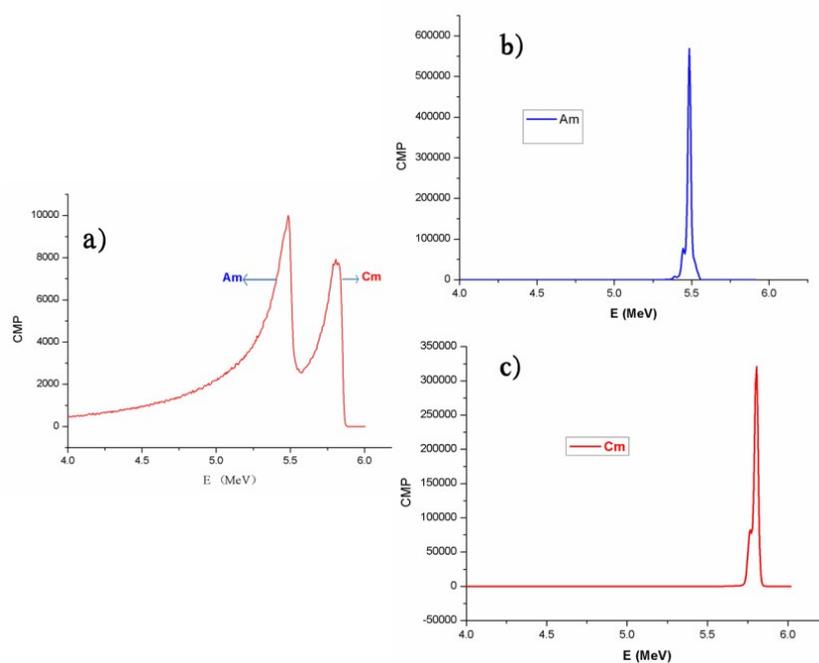**Figure S11** Elution curves of the simulated glass residue solution.

Figure S12 Alpha spectra of (a) the simulated high-level liquid waste solution, (b) the Am fraction, and (c) the Cm fraction.
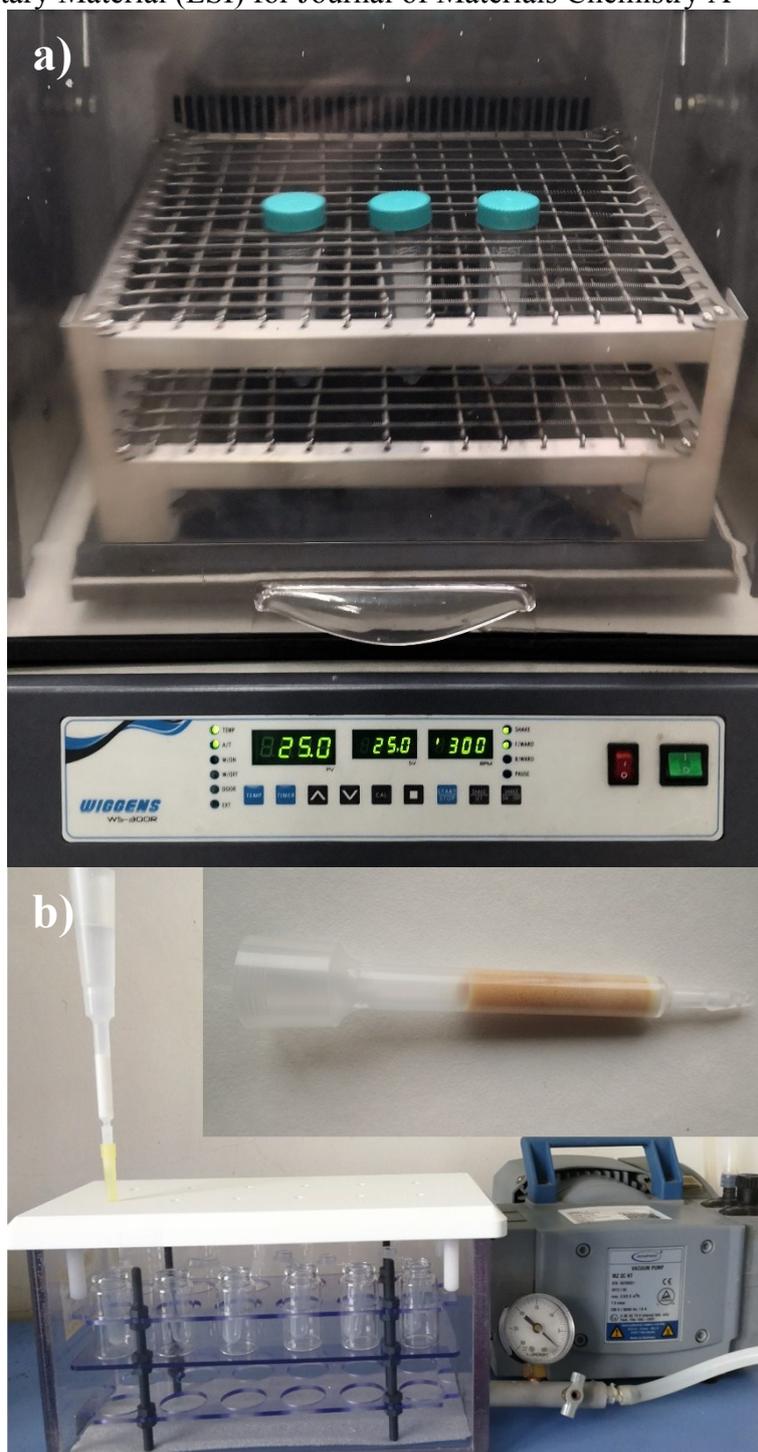
Figure S13 (a) the experimental set up for the extraction experiments and (b) the experimental set up for chromatographic separation

Table S1. Physical properties of NBF and NBS.

Samples	BET surface area m² g	Average pore size nm	Total pore volume cm³ g⁻¹
NBF	35.96	14.33	0.13

NBS	20.59	9.98	0.051

Table S2 Crystallographic parameters of $Ce_{0.39}Bi_{3.45}O_7$ deduced from Rietveld refinement of NPD pattern

$Ce_{0.39}Bi_{3.45}O_7$	Fdm				
	a = 10.97				
Atom	Site	x	y	z	Occ.
Ce1	16d	0.50	0.50	0.5	0.1947
Bi1	16d	0.50	0.50	0.5	0.7247
Bi2	16c	0	0	0	1
O1	48f	0.3637	0.125	0.125	1
O2	8b	0.375	0.375	0.375	1

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