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## Direct separation of minor actinides from high level liquid waste by Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent

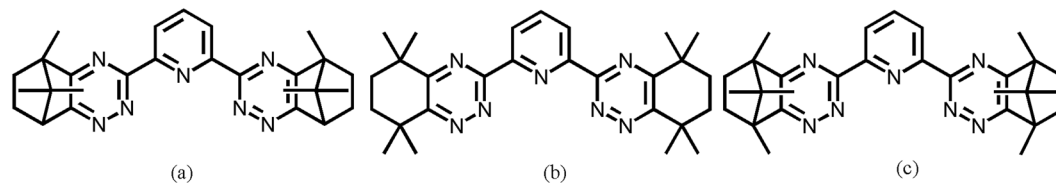
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Directly separating minor actinides (MA: Am, Cm, etc.) from high level liquid waste (HLLW) containing lanthanides and other fission products is of great significance for the whole nuclear fuel cycle, especially in the aspects of reducing long-term radioactivity and simplifying the post-processing separation process. Herein, a novel silica-based adsorbent Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P was prepared by impregnating Me<sub>2</sub>-CA-BTP (2,6-bis(5,6,7,8-tetrahydro-5,8,9,9-tetramethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine) into porous silica/polymer support particles (SiO<sub>2</sub>-P) under reduced pressure. It was found Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P exhibited good adsorption selectivity towards <sup>241</sup>Am(III) over <sup>152</sup>Eu(III) in a wide nitric acid range, acceptable adsorption kinetic, adequate stability against  $\gamma$  irradiation in 1 and 3 M HNO<sub>3</sub> solutions, and successfully separated <sup>241</sup>Am(III) from simulated 3 M HNO<sub>3</sub> HLLW. In sum, considering the good overall performance of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent, it has great application potential for directly separating MA from HLLW, and is expected to establish an advanced simplified MA separation process, which is very meaningful for the development of nuclear energy.

As the development of nuclear energy, spent nuclear fuel in storage has amounted to around 266 000 t of heavy metal (HM) and is accumulating at a rate of around 7000 t HM/year, which has long-term potential radioactivity threats to the environment and must be managed safely and efficiently. Although the industrialized PUREX (Plutonium Uranium Recovery by EXtraction) process based on TBP can recover 99.5% of uranium and plutonium from spent nuclear fuel, the resulting high-level radioactive liquid waste (HLLW) containing most of the fission products (FP) and minor actinides (MA: Am, Cm, etc.) reserves most of the radioactivity, especially the  $\alpha$ -emitters MA, which are the main contributors of radiotoxicity after three centuries storage<sup>1</sup>. Partitioning MA and the other long-lived FP from HLLW and then transmuting them into short-lived or stable nuclides, which is the so-called Partition and Transmutation strategy (P&T), can reduce the time isolated from the environment from over 20,000 years to 300–500 years<sup>2–5</sup>. However, as the content of lanthanides (Ln), which accounts for about 1/3 of the FP, is much higher than that of MA in order of magnitude, and some Ln have large neutron absorption cross sections and are neutron poisons, Ln should be separated from MA before the transmutation step<sup>5,6</sup>. Considering MA and Ln dominantly exist as trivalent cations in solution with comparable radii and coordination numbers, mutual separation of MA(III) and Ln(III) is very difficult, which requires high selectivity for the separation materials<sup>7–11</sup>. Moreover, as the acid in HLLW produced by PUREX process was 2–5 M HNO<sub>3</sub> and HLLW is highly radioactive with  $\alpha$ ,  $\beta$ ,  $\gamma$  radioactivity, it further requires that the materials used for MA separation shall have good acid and irradiation resistance stability.

Processes developed over the past decades are mainly based on the co-extraction of MA(III) and Ln(III) from HLLW followed by the An(III)/Ln(III) group separation<sup>5,12,13</sup>. Firstly, MA and Ln are co-separated from the other FP from high acid (mol/L) HLLW, e.g. the TRPO process using 30% (v/v) mixture of trialkyl phosphine oxides (TRPO) in kerosene<sup>14</sup>, the TRUEX process using [CMPO] = 0.2 M + [TBP] = 1.4 M in n-dodecane<sup>12,15</sup>, the DIAMEX process using DMDBTDMMA or DMDOHEMA in HTP<sup>15</sup> and the DIDPA process using 0.5 M DIDPA-0.1 M TBP in n-dodecane<sup>16</sup>. The oxygen donor ligands, e.g. CMPO, DMDOHEMA, TRPO and DIDPA mentioned above can separate MA(III) and Ln(III) together from fission products in HLLW, but exhibit poor

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**Figure 1.** Chemical structures of (a) CA-BTP, (b) CyMe<sub>4</sub>-BTP and (c) Me<sub>2</sub>-CA-BTP.

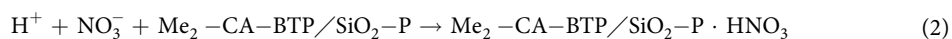
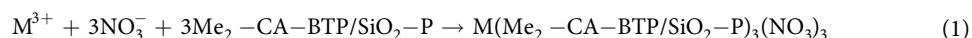
adsorption selectivity between MA(III) and Ln(III). Secondly mutual group separation of MA and Ln are needed, making the integral HLLW separation process very complex. According to the hard and soft acid-base theory, MA(III) and Ln(III) both belong to hard acid, but MA(III) is a little softer than Ln(III) and has better coordination complexation with ligands containing soft coordination atoms N or S<sup>17</sup>. Using ligands containing N or S is expected to achieve the mutual group separation of MA(III) and Ln(III), e.g. BTP (BTBP) and CYANEX 301 used in SANEX<sup>1,18</sup>, CYANEX 301 processes<sup>19</sup> respectively. Among the various N or S donor ligands, 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTPs) and 6,6'-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs) both exhibit high selectivity for MA(III) over Ln(III) in a wide range of nitric acid solutions (HNO<sub>3</sub>: 0.1–4 M, M = mol/L) with the separation factor  $SF_{Am/Eu}$  around 100 and are considered to be a significant breakthrough in MA separation as before that separation MA could be realized only in low acid (pH range)<sup>20–26</sup>. Furthermore, BTPs/BTBPs contain only C, H, N elements and fulfill the CHON principle and thus are completely combustible to gaseous products after use, reducing the second radioactive waste. However, the presently available BTPs used in liquid-liquid extraction suffer from one or more drawbacks, e.g. poor solubility property in traditional solvents (e.g. *i*-Pr-BTP, CyMe<sub>4</sub>-BTBP)<sup>1,26</sup>, slow stability against acid and irradiation (e.g. *n*-alkylated BTPs and BTBPs)<sup>26–28</sup>, low loading capacity (e.g. CA-BTP)<sup>28</sup>, and poor back extraction performance (e.g. CyMe<sub>4</sub>-BTP)<sup>26</sup>, slow kinetic<sup>26</sup> etc. To improve it, we synthesized a new kind of BTP, Me<sub>2</sub>-CA-BTP (2,6-bis(5,6,7,8-tetrahydro-5,8,9,9-tetramethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine) based on the structure of both CyMe<sub>4</sub>-BTP and CA-BTP avoiding -CH<sub>2</sub>- group on the α position of the triazine rings which is the weak spot of the ligand under degradation to make it more stable with their chemical structures shown in Fig. 1<sup>26,29,30</sup>.

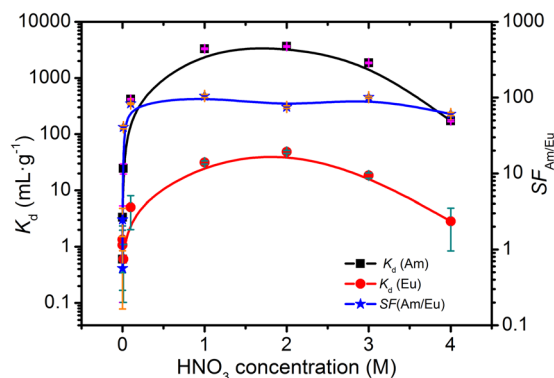
In a word, more challenging processes for directly separating MA from HLLW are eagerly needed to be developed. Separating MA from HLLW by one step process has been proposed, such as 0.2 M CMPO + 1.4 M TBP in *n*-dodecane used in SETFICS process<sup>5</sup>, 0.015 M CyMe<sub>4</sub>-BTBP + TODGA or DMDOHEMA in TPH/Octanol used in the 1-cycle SANEX process<sup>5,13</sup>, TODGA + water-soluble SO<sub>3</sub>-Ph-BTBP in TALSPEAK process<sup>31</sup>. As the processes mentioned above involved more than one kind of extractant, it is inconvenient for the organic phase regeneration. Wei et al. proposed a compact and effective process based on extraction chromatographic technology named MAREC process (Minor actinide extraction by chromatographic process) as shown in Fig. 1S<sup>32</sup> whose purpose is to directly separate MA(III) from PUREX raffinate HLLW containing fission products Ln and other FPs through single column packed with high-efficiency microporous adsorbent, e.g., BTPs/SiO<sub>2</sub>-P. If success, it will significantly simplify the MA separation process and is of great significance for the whole nuclear fuel cycle. Efforts to realize the single-column MAREC process from simulated HLLW have been made by using isoHex-BTP/SiO<sub>2</sub>-P by co-authors<sup>33,34</sup>, but isoHex-BTP/SiO<sub>2</sub>-P turned out to be easy to lose the adsorption ability when it accepted γ irradiation in 3 M HNO<sub>3</sub> solution in our previous research<sup>35</sup>, so more advanced materials are needed to be developed. Furthermore, MAREC process uses almost no organic solvent, avoiding the third phase formation and large amount of secondary organic waste accumulation.

In this work, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent was prepared by impregnating 5 g Me<sub>2</sub>-CA-BTP dissolved in CH<sub>2</sub>Cl<sub>2</sub> into 10 g stable microporous silica/polymer composite support (SiO<sub>2</sub>-P) particles under reduced pressure. The adsorbent properties of selectivity, kinetics, γ-irradiation stability was studied by batch adsorption experiments. Finally, the feasibility of using Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent to directly separate MA(III) from 3 M HNO<sub>3</sub> simulated HLLW through single-column MAREC process was evaluated.

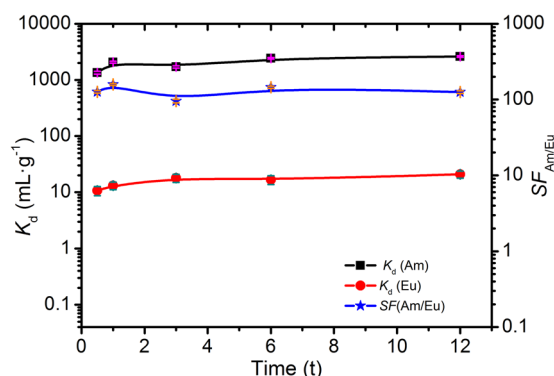
## Results

**Adsorption selectivity.** To study adsorption selectivity, the effects of initial HNO<sub>3</sub> concentration (pH = 4–4 M) on Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorption towards <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) were evaluated. Figure 2 illustrates the distribution coefficients ( $K_d$ ) of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) and the separation factors of <sup>241</sup>Am(III) over <sup>152</sup>Eu(III) ( $SF_{Am/Eu}$ ) changing as a function of HNO<sub>3</sub> concentration. The distribution factors  $K_d$  of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) increased as the HNO<sub>3</sub> concentration increased until up to 2 M HNO<sub>3</sub> solution which are explained by the adsorption of BTP towards <sup>241</sup>Am(III) needing the participation of NO<sub>3</sub><sup>-</sup><sup>28</sup>. Then with further increase of the acid, the distribution factors  $K_d$  of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) decreased. The decreasing distribution factors are explained by metal ions (<sup>241</sup>Am(III) and <sup>152</sup>Eu(III)) and nitric acid competing adsorption for BTP. The whole adsorption mechanism may be as shown in Equation (1) and (2) similar to CA-BTP<sup>28</sup>. Three NO<sub>3</sub><sup>-</sup> complexes are incorporated into the coordination sphere so as to maintain neutral due to metal iron's trivalent oxidation state





**Figure 2.** Effects of HNO<sub>3</sub> concentration on Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorption towards <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) (phase ratio: 0.1 g/5 mL, <sup>241</sup>Am(III): 1000 Bq·mL<sup>-1</sup> (3.27·10<sup>-8</sup> mol/L), <sup>152</sup>Eu(III): 1000 Bq·mL<sup>-1</sup> (1.02·10<sup>-9</sup> mol/L), Temp.: 25 °C, contact time: 24 h, shaking speed: 300 rpm).

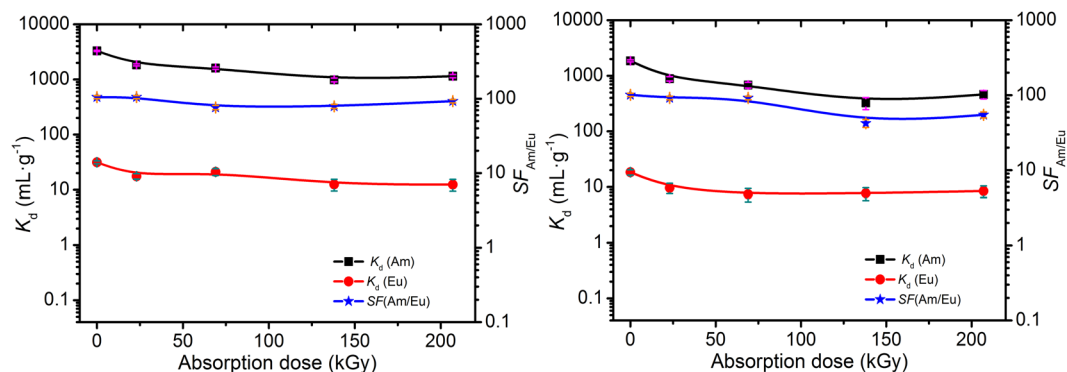


**Figure 3.** Adsorption kinetics of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) on Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P in 1.0 M HNO<sub>3</sub> solution (phase ratio: 0.1 g/5 mL, <sup>241</sup>Am(III): 1000 Bq·mL<sup>-1</sup> (3.27·10<sup>-8</sup> mol/L), <sup>152</sup>Eu(III): 1000 Bq·mL<sup>-1</sup> (1.02·10<sup>-9</sup> mol/L), Temp.: 25 °C, shaking speed: 120 rpm).

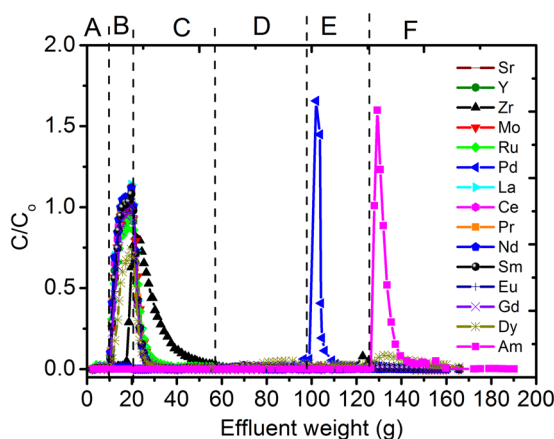
Overall, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P exhibited good adsorption selectivity towards <sup>241</sup>Am(III) with the uptake rate of <sup>241</sup>Am(III) over 96% and  $SF_{Am/Eu}$  over 75 in a wide nitric acid range of 1–3 M, which was high enough for effective separation <sup>241</sup>Am(III) from <sup>152</sup>Eu(III). Furthermore, according to previous work<sup>29,36</sup>, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P showed almost no adsorption ability towards most typical FP except Pd(II) in 3 M HNO<sub>3</sub>. The results above indicates that Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P has the potential to directly separate MA from high nitric acid (3 M) HLLW. The adsorption ability and the applicable acidity range of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P towards Am(III) has been improved and enlarged compared with CA-BTP which only exhibited good adsorption ability towards Am(III) in 0.5–1 M HNO<sub>3</sub> and CyMe<sub>4</sub>-BTBP whose adsorption ability towards Am(III) increased as HNO<sub>3</sub> concentration increased in 0.1–2 M HNO<sub>3</sub> and isoHex-BTP which only exhibited good adsorption towards <sup>241</sup>Am(III) in ≥ 2 M HNO<sub>3</sub> solution<sup>28,37,38</sup>.

**Adsorption kinetics.** The effect of contact time on Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorption towards <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) was studied in 1.0 M HNO<sub>3</sub> solution at 25 °C with the results shown in Fig. 3. Evidently, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbed <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) quickly reaching almost equilibrium within 0.5 h and exhibited much higher adsorption affinity towards <sup>241</sup>Am(III) than <sup>152</sup>Eu(III) with  $SF_{Am/Eu}$  around 100. Considering the equilibrium time for CA-BTP and CyMe<sub>4</sub>-BTBP adsorption towards Am(III) was about 10 min and 30 min in solvent extraction<sup>27,28</sup>, the three systems mentioned above have comparable adsorption kinetic.

**Stability evaluation.** Considering the radioactive nuclides in HLLW emit vast amounts of radiation, e.g., α, β, γ, the adsorbent irradiation stability is a serious concern in practical applications for HLLW reprocessing. Herein, the stability of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent against γ-irradiation in 1 and 3 M HNO<sub>3</sub> solution were evaluated. 0.8 g adsorbent was combined with 40 mL 1 or 3 M HNO<sub>3</sub> solution in 50 mL glass vial and irradiated by <sup>60</sup>Co-γ source with the absorbed radiation dose rate of 1 kGy·h<sup>-1</sup>. After being irradiated to the predetermined doses, vacuum filter was used for solid-liquid separation. After drying the Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent in room temperature, the Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent was used to adsorb <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) in 1 and 3 M HNO<sub>3</sub> solution respectively with the results shown in Fig. 4. The  $K_d$  of <sup>241</sup>Am(III) decreased as the absorbed dose increased in both 1 M and 3 M HNO<sub>3</sub> solution but was still kept in a high level over 983 and 325 mL/g respectively when the absorbed dose was up to 207 kGy. Meanwhile Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent maintained good adsorption selectivity towards <sup>241</sup>Am(III) over <sup>152</sup>Eu(III) with  $SF_{Am/Eu}$  over 76 and 42 in 1 M and 3 M HNO<sub>3</sub> solution



**Figure 4.** Effect of  $\gamma$  irradiation absorbed dose in (a) 1 M HNO<sub>3</sub> (b) 3 M HNO<sub>3</sub> on Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorption towards <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) in (a) 1.0 M (b) 3 M HNO<sub>3</sub> solution (irradiation conditions: <sup>60</sup>Co- $\gamma$  source, 1 kGy/h, phase ratio: 0.8 g/40 mL; adsorption conditions: phase ratio: 0.1 g/5 mL, Temp.: 25 °C, contact time: 24 h, <sup>241</sup>Am(III): 1000 Bq·mL<sup>-1</sup> (3.27·10<sup>-8</sup> mol/L), <sup>152</sup>Eu(III): 1000 Bq·mL<sup>-1</sup> (1.02·10<sup>-9</sup> mol/L), shaking speed: 120 rpm).



**Figure 5.** Directly separate MA(III) from simulated 3 M HNO<sub>3</sub> HLLW through single-column MAREC process (Temp.: 35 °C, liquid flow rate: about 0.1 mL/min, A: 3 M HNO<sub>3</sub>, B: 3 M HNO<sub>3</sub>, 5 mM [M], 500 Bq/mL <sup>241</sup>Am(III), C: 3 M HNO<sub>3</sub>, D: 0.1 M HNO<sub>3</sub>, E: 0.01 M HNO<sub>3</sub>-0.1 M thiourea, F: 0.001 M HNO<sub>3</sub>-0.01 M DTPA).

respectively in the whole irradiation experiments. Furthermore, considering when isoHex-BTP was irradiated in 3 M HNO<sub>3</sub> under the same irradiation conditions, it quickly lost the adsorption ability<sup>35</sup>, and CyMe<sub>4</sub>-BTBP distribution factors of <sup>241</sup>Am(III) decreased from about 22 to about 12 in 1 M HNO<sub>3</sub> when the absorbed  $\gamma$  dose reached 200 kGy with the absorption dose rate of 0.22 kGy/h<sup>22</sup>, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent exhibited very good  $\gamma$  irradiation stability in 1 M and 3 M HNO<sub>3</sub> solution and are expected to directly separate MA from high nitric acid HLLW.

**Directly separate MA(III) from HLLW by single-column MAREC process.** To examine the separation of MA(III) from fission products, a hot test using simulated 3 M HNO<sub>3</sub> HLLW containing typical FP (Sr, Y, Zr, Mo, Ru, Pd, La, Ce, Nd, Sm, Eu, Gd, Dy, 5 mM respectively) and <sup>241</sup>Am(III) (500 Bq/mL) was carried out at 35 °C using a glass column (5 mm in inner diameter and 500 mm in length) packed with 5 g Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P with the results shown in Fig. 5 and Table 1. As can be seen, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P showed very poor or almost no adsorption towards lanthanides and most other typical fission products, such as Sr, Y, Zr, Mo, Ru. These elements flowed out with the feed solution in step B and the following 3 M and 0.1 M HNO<sub>3</sub> solution in step C and D. On the other hand, Pd, well known as a “soft” metal ion which has strong electron acceptance ability, was adsorbed onto Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P and could not be effectively eluted from the adsorbent by reducing the HNO<sub>3</sub> concentration. A complexing agent, thiourea, which has strong complexation affinity with Pd, was attempted to desorb the adsorbed Pd. As shown in Fig. 5, Pd can be effectively eluted off by 0.01 M HNO<sub>3</sub>-0.1 M thiourea in step E. Meanwhile, <sup>241</sup>Am was strongly adsorbed by Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent, then it was eluted off using 0.001 M HNO<sub>3</sub>-0.01 M DTPA as an eluent with <sup>241</sup>Am recovery yield of 95.87% and the other typical fission products less than 3% except Dy. But considering there is almost no Dy or other Ln heavier than Dy in HLLW, the effects caused by Dy are almost negligible. In a word, a successful separation between Am and the various typical fission products including lanthanides has been achieved, which is an important step toward a simplified direct process for separation MA from HLLW.

Recovery yield (%)	B (%)	C (%)	D (%)	E (%)	F (%)	Total recovery yield (%)
Sr	87.2	9.3	1.8	0.9	0.8	99.9
Y	82.5	10.1	3.2	1.8	2	99.8
Zr	23.5	72.5	0.9	0.9	6.7	104.5
Mo	82.2	15	1.1	1.1	1.7	101.1
Ru	77.5	18.9	2.4	1.1	1.7	101.5
Pd	1.6	1.5	7.3	78.6	2.6	91.6
La	93.2	9.1	0.6	0.2	0.4	103.4
Ce	89.6	9.7	2.3	1.3	0.9	103.8
Pr	92.2	9.8	1.6	0.8	0.7	105.2
Nd	92.4	9.6	0.7	0.1	0.3	103
Sm	86.2	10.5	3.1	1.2	1.6	102.6
Eu	80.6	11.2	4.5	1.8	1.5	99.8
Gd	77.9	11.1	5.5	2.6	2.8	99.9
Dy	50.3	8.5	11	4.5	19.4	93.7
Am	0	0.03	0.13	0.01	95.87	96.04

**Table 1.** Recovery yields of tested elements with Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent.

## Discussion

To directly separate long-lived MA from HLLW, a single-column MAREC process was proposed and a corresponding novel microporous silica-based Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent was prepared with the content of Me<sub>2</sub>-CA-BTP as high as 32 wt%. The research found Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P exhibited good adsorption selectivity towards <sup>241</sup>Am(III) with the uptake rate of <sup>241</sup>Am(III) over 96% and  $SF_{Am/Eu}$  over 75 in a wide nitric acid range of 1–3 M. In 1 M HNO<sub>3</sub> solution, the adsorption of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P towards <sup>241</sup>Am(III) almost reached equilibrium within an hour with the uptake rate of 96% showing rapid adsorption kinetic. With the increase of  $\gamma$  irradiation absorbed dose in 1 M HNO<sub>3</sub> and 3 M HNO<sub>3</sub> solution, the adsorption performance of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P towards <sup>241</sup>Am(III) did not change significantly. When  $\gamma$  irradiation absorbed dose reached to 207 kGy, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P maintained good adsorption selectivity towards <sup>241</sup>Am(III), indicating Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P has good resistance to  $\gamma$  irradiation stability. Furthermore, the continuous column separation experimental results showed that Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P can effectively and selectively separate <sup>241</sup>Am(III) from the other fission products from simulated 3 M HNO<sub>3</sub> HLLW with <sup>241</sup>Am(III) recovery rate of 95.5% in <sup>241</sup>Am(III) elution step.

In a word, Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P has great application potential in the single-column MAREC process, and is expected to establish an advanced simplified MA(III) separation process.

## Methods

**Reagents.** FP element nitrates (FP: Sr(II), Zr(IV) and trivalent rare earths) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O were commercial reagents of analytical grade. Pd(NO<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O was chemical pure with Pd(II)  $\geq$  39.5 wt% and chloride  $\leq$  0.04 wt%. Ru(III) nitrosyl nitrate solution was in diluted nitric acid containing 1.5 wt% of Ru(III) with a density of 1.07 g•mL<sup>-1</sup>. <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) were from laboratory stock solution. Me<sub>2</sub>-CA-BTP was synthesized at laboratory with the purity of 97% according to the HPLC-MS test. All solutions were prepared with deionized water at 18 M $\Omega$ -cm resistance (DI water). Other agents such as nitric acid, dichloromethane, etc. were of analytical grade and used without further treatment.

**Preparation of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent.** The support SiO<sub>2</sub>-P with pore size of 0.6  $\mu$ m, pore fraction of 0.69 and mean diameter of 50  $\mu$ m was developed in the previous work<sup>39</sup>. P refers to macroreticular styrene-divinylbenzene copolymer (SDB) and is immobilized in porous silica (SiO<sub>2</sub>) particles with the content of 17–18 wt% in SiO<sub>2</sub>-P. The synthesis procedure of Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent was the same as ref.<sup>40</sup>. The synthesized Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent overcame the limitation of low solubility of BTP in traditional diluents as the content of Me<sub>2</sub>-CA-BTP was as high as 32.0 wt% in the adsorbent<sup>29</sup>. The synthetic Me<sub>2</sub>-CA-BTP/SiO<sub>2</sub>-P adsorbent was characterized by high resolution field emission scanning electron microscope (SEM, Sirion 200, FEI COMPANY) and the SEM image is shown in Fig. 2S.

**Batch adsorption experiments.** For batch adsorption experiments towards <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), 0.1 g adsorbent was combined with 5 mL aqueous solution in a 12 mL glass vial with screw teflon cap. The mixture in the vial was shaken mechanically at 300 rpm at 25 °C for a certain time and the solid-liquid separation was realized by centrifugation. The radioactivity of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) in solution before and after adsorption were determined by high-purity germanium multichannel gamma spectrometer (CANBERRA) at 59.5 and 121.78 keV respectively, while the concentrations of non-radioactive FP were determined by inductively coupled plasma-optical emission spectrometer atomic emission spectroscopy (ICP-AES: Shimadzu ICPS-7510).

The distribution coefficient  $K_d$  (mL•g<sup>-1</sup>), separation factor  $SF_{A/B}$  and uptake rate  $E$  (%) which are key factors in solid-liquid adsorption are calculated by Equation (3), (4) and (5), respectively.

$$K_d = \frac{A_o - A_e}{A_e} \times \frac{V}{W} \quad (3)$$

$$SF_{A/B} = K_{dA}/K_{dB} \quad (4)$$

$$E = \frac{(A_o - A_e)}{A_o} \times 100\% \quad (5)$$

where  $A_o$ ,  $A_e$  denote the radioactivity of metal ions in the aqueous phase before and after adsorption, respectively,  $Bq \cdot mL^{-1}$ .  $V$  (mL) indicates the volume of aqueous phase and  $W$  (g) is the mass of dry  $Me_2$ -CA-BTP/SiO<sub>2</sub>-P.

**Column separation experiments.** Column separation experiments for simulated HLLW solution were carried out using a glass column with 5 mm in diameter and 500 mm in length. 5 g  $Me_2$ -CA-BTP/SiO<sub>2</sub>-P adsorbent was transferred to the column in the slurry state under atmosphere. The column volume (CV) of the adsorbent bed was 9.8 cm<sup>3</sup>. The column was kept at a constant temperature (35 °C) with water jacket. Prior to the separation experiment, the adsorbent in column was pre-equilibrium by passing 50 mL of 3 M HNO<sub>3</sub>. The simulated HLLW contained 5 m mol/L for each FP (Sr, Y, Zr, Mo, Ru, Pd, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy) and 500 Bq/mL <sup>241</sup>Am(III) in 3 M HNO<sub>3</sub> solution. All the mobile phase was pumped at 0.1 mL/min and the effluents were collected by a fractional collector. The metal concentrations in the effluents without radioactivity were determined by ICP-AES while <sup>241</sup>Am(III) was determined by high-purity germanium multichannel gamma spectrometer.

**Statistical analysis.** Each batch adsorption experiment was conducted in double parallel, and batch adsorption values used are means ± SD.

**Data availability.** The authors declare that all data supporting the findings of this study are available within the article and its Supplementary Information files.

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## Author Contributions

Y.Z. Wei and S.Y. Ning conceived the project. X.P. Wang and W.Q. Shi carried out the synthesis and characterization analysis. S.Y. Ning and Q. Zou Aided in separation work and the radiation stability evaluation. F.D. Tang and L.F. He aided in the radioactivity test. All authors discussed and co-wrote the paper.

## Additional Information

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**Competing Interests:** The authors declare that they have no competing interests.

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