

Supplementary Informations

Cation exchange studies

0.05 g of HTNT was added to the 5.00 mL of required radiotracer solutions with fixed pH in the range 1.00 to 6.00 with the ionic strength maintained at 0.10 M NaClO₄, except mentioned otherwise, followed by equilibration by stirring with Vortex shaker for the fixed interval of one hour. The solution was then centrifuged at 16,500 rpm for 5 minutes by a high capacity centrifuge (SIGMA). Thereafter suitable aliquot was taken from the supernatant for analysis. ²³³U and ²³⁹Pu were assayed using ZnS(Ag) alpha scintillation counter calibrated with standard ²³⁹Pu. The assay of ²⁴¹Am was done using a high purity germanium detector coupled with 4K multi-channel analyser (ECIL, India). For kinetics study, suitable aliquots were taken from the same extraction vial at different time intervals with the pH of the solution being fixed at 3.00 and the pH was measured using a Metrohome pH meter calibrated with standard buffers (4.00, 7.00 and 9.00 from Merck). The nH⁺ → Mⁿ⁺ (M = Am³⁺, Pu⁴⁺, UO₂²⁺) exchange reactions were determined for HTNT. The cation-exchange capacity was calculated using eq. 4. Following radiometric analyses, ion exchange isotherms and Kielland plots were prepared. Total normality was maintained at 1.01 × 10⁻³ for americium isotherm and Kielland plot, 1.70 × 10⁻³ for uranium isotherm and Kielland plot, and 3.17 × 10⁻⁴ for plutonium isotherm and Kielland plot, respectively.

A few other elements were added separately to the 5.00 mL solution of ²⁴¹Am at a fixed pH (3.00) in varying concentrations for investigating their interference. Feasibility evaluation of HTNT for practical application was carried out in presence of various concentrations of the other elements present simultaneously with americium in the solution. Three combinations were prepared- first combination was composed of 1.00 g/L each of Fe, Sr, Ca, Na and 0.10 g/L Ru. The second combination had 5.00 g/L each of Fe, Sr, Ca, Na and 0.50 g/L Ru. The third combination was comprised of 10.00 g/L each of Fe, Sr, Ca, Na and 1.00 g/L Ru. For sorption isotherms, the concentration of tracer solutions were varied at a fixed pH (3.0) in the batch samples, the concentrations of the targeted radionuclides in the liquid and solid phase were calculated from the sorption data and known initial concentrations in the feed. As HTNT is intended to treat a large volume of the nuclear waste solution, 0.05 g of the synthesized material were added to 5.00 mL, 10.00 mL and 15.00 mL of the ²⁴¹Am tracer solution to find the effective concentration of the HTNT capable of sorption of americium. After the sorption of the radionuclides in HTNT, desorption tests with water and nitric acid was also done in the same way with the used up HTNT by equilibrating it for an hour in the vortex shaker. Examination of "wall absorption" of the extraction vials were carried out with every radiotracers prior to analysis and it was found to be negligible in all cases at all pH. The blank tests (without the radiotracers) of the synthesized HTNT in the acidic pH did not show any changes in the XRD pattern before and after the experiments indicating the material to be stable in the experimental conditions studied. All the experiments were carried out at 25 ± 1 °C. The K_d value, decontamination factor (D.F.) percentage sorption and cation uptake capacities were calculated using the following formulae (Eqs 1-4):

$$K_d = (C_0 - C_e) \times V / (C_e \times M) \quad (\text{mL/g}) \quad (1)$$

$$\text{D.F.} = C_0 / C_e \quad (2)$$

$$\% \text{ sorption} = (C_0 - C_e) \times 100 / C_0 \quad (3)$$

$$\text{Capacity} = (\% \text{ uptake} / 100) \times C_0 \times (V/M) \times Z \quad (\text{meq./g}) \quad (4)$$

where C₀ = Feed concentration/activity, C_e = Effluent concentration/activity, V = volume of the solution in mL and M = mass of the cation exchanger material used in gram and Z is the valence of the exchanged ions.

The solutions were analysed to give the extent of exchange, Q_t, for different times, t. To estimate the equilibrium extent of exchange, Q_∞, from these curves, the area under the curve was found at each of a series of times and was plotted against t. This plot approached a straight line asymptote of slope Q_∞. The ratio Q_t/Q_∞, when plotted against t, approaches a horizontal asymptote when t becomes large and the area between this asymptote and the curve of Q_t/Q_∞, against t is:

$$I_0 = \int_0^{\infty} (1 - Q_t / Q_{\infty}) dt = (r_0)^2 / 15 D \quad (5)$$

Where I₀ is the the area between the asymptote and the curve of Q_t/Q_∞ against time (t). Measurement of I₀ provided a convenient means of estimating D, the interdiffusion coefficient.

The experiments were carried out in duplicate and the precision was within ± 5%.

Langmuir sorption isotherm

The linear form of the equations for Langmuir and Freundlich models are given by Eqs 5 and 6 respectively.

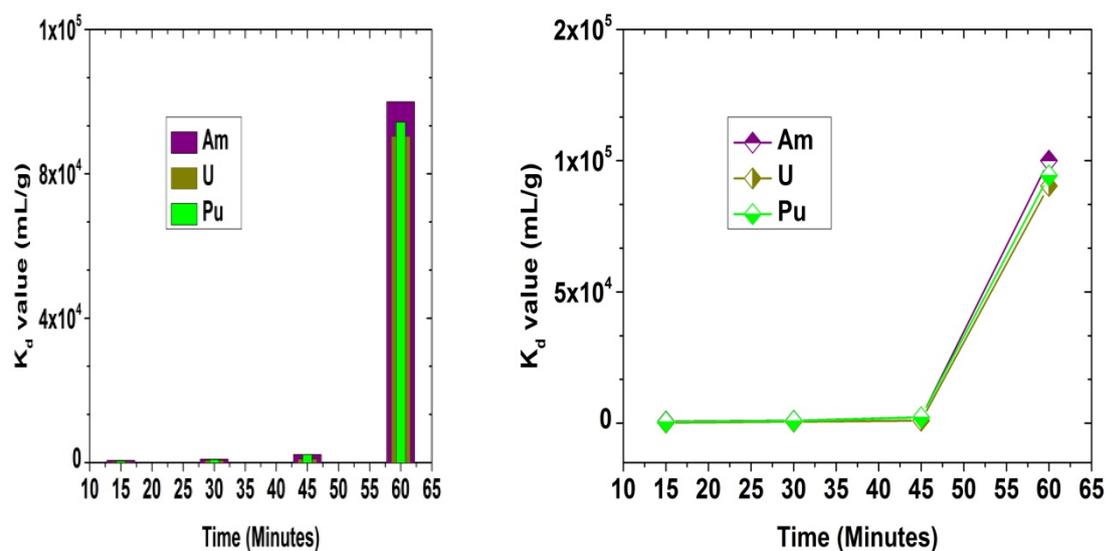
$$\frac{C_e}{q_e} = \frac{1}{Q^o * b} + \frac{C_e}{Q^o} \quad (5)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

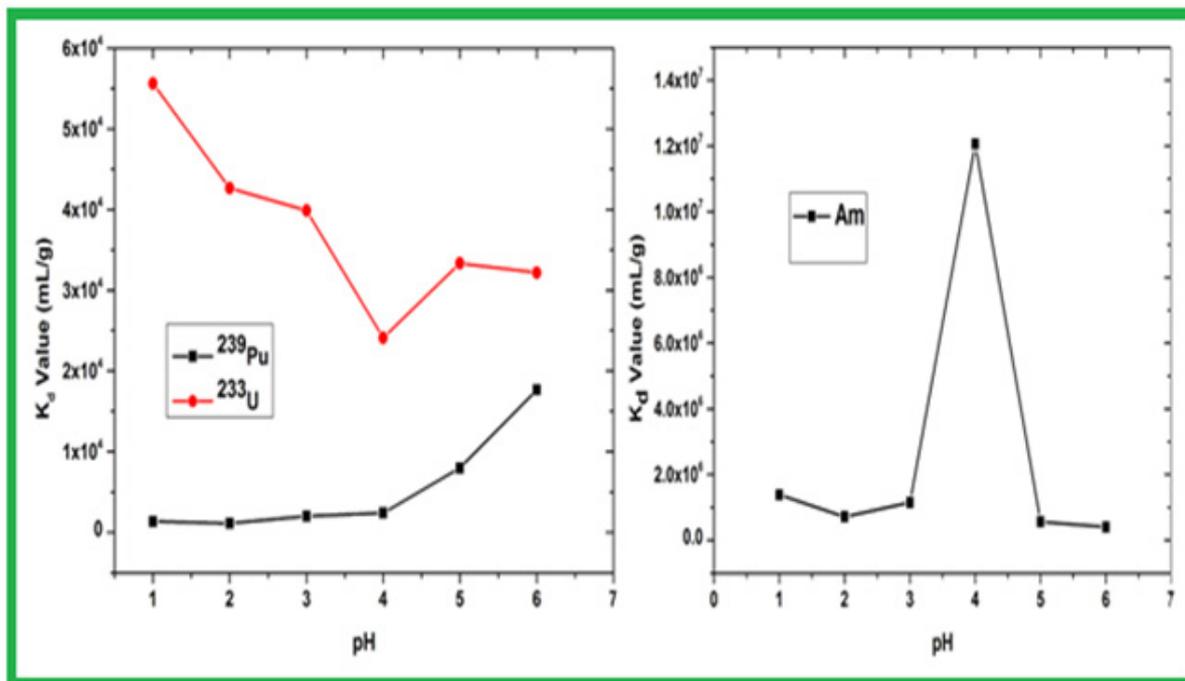
The results of the sorption in the present studies showed that the uptake data can be fitted well in the Langmuir model. The main aspect of Langmuir isotherm can be expressed by R_L , a constant known as the constant separation factor or equilibrium parameter which can be used to predict if an adsorption system is “favourable” or “unfavourable”. The separation factor, R_L is defined by Eq. 7:

$$R_L = \frac{1}{1 + C_o * b} \quad (7)$$

where C_o is the initial solute concentration (mg/L) and b is the Langmuir adsorption equilibrium constant (L/ mg). The values are given in Table 1 and it is seen that R_L values are in the range of $0 < R_L < 1$, indicating that the sorption of the radionuclides on hydrogen titanate nanotubes is favourable.



Supplementary Figure SI-1: Sorption kinetics of radionuclides on nano-titanate



Supplementary Figure SI-2: Variation of K_d Value with pH for ^{233}U , ^{241}Am and ^{239}Pu sorption

Table SI-1: Interdiffusion coefficients for the ion exchange reactions

Exchanging Radionuclide ion	Area (I_0) (minute)	Diameter of spherical crystal of HTNT (μm)	Interdiffusion Coefficient (D) ($\text{m}^2 \text{s}^{-1}$)
Am^{3+}	1212.07	10	1.38×10^{-15}
Am^{3+}	1212.07	15	3.09×10^{-15}
UO_2^{2+}	1072.21	10	1.55×10^{-15}
UO_2^{2+}	1072.21	15	3.50×10^{-15}
Pu^{4+}	1178.75	10	1.41×10^{-15}
Pu^{4+}	1178.75	15	3.18×10^{-15}

Table SI-2: Standard free energy values for the ion exchange reactions

Cation Exchange	$\ln K$	$-\Delta G^\circ$ (kJ/mol)
$3 \bar{\text{H}}^+ \Leftrightarrow \text{Am}^{3+}$	91384.99	75470.97
$2 \bar{\text{H}}^+ \Leftrightarrow \text{UO}_2^{2+}$	1611.08	1995.79
$4 \bar{\text{H}}^+ \Leftrightarrow \text{Pu}^{4+}$	3001.22	1858.94

Table SI-3: Optimization of HTNT concentration

Weight of titanate (g)	Volume of Tracer (²⁴¹Am) (mL)	Conc. Of HTNT (g/L)	Feed ²⁴¹Am concentration (μCi/L)	Effluent concentration (μCi/L)	% Sorption	D.F.	K_d Value (mL/g)
0.05	10.00	5.00	880.36	0.28	99.97	3144.14	6.7×10^5
0.05	15.00	3.33	880.36	13.53	98.46	65.07	1.9×10^4
0.05	20.00	2.50	880.36	118.26	86.57	7.44	2.6×10^3

Table SI-4: Individual interference studies

Interfering element at pH 3.00	concentration of other element (g/L)	Feed ²⁴¹Am concentration (μCi/L)	Effluent concentration (μCi/L)	% Sorption	K_d Value (mL/g)
Ca	1.00	882.82	2.00	86.60	44041.00
Ca	5.00	882.82	-	~100	T.A.
Ca	10.00	882.82	1.31	99.85	67290.84
Na	1.00	882.82	-	~100	T.A.
Na	5.00	882.82	-	~100	T.A.
Na	10.00	882.82	-	~100	T.A.
Ru	0.10	882.82	-	~100	T.A.
Ru	0.50	882.82	-	~100	T.A.
Ru	1.00	882.82	-	~100	T.A.
Sr	1.00	882.82	-	~100	T.A.
Sr	5.00	882.82	-	~100	T.A.
Sr	10.00	882.82	-	~100	T.A.
Fe	1.00	882.82	6.17	99.30	14208.27
Fe	5.00	882.82	238.40	73.00	270.31
Fe	10.00	882.82	347.62	60.62	153.96

Table SI-5: Combined interference studies

Interfering elements	pH	Feed ²⁴¹ Am conc. (mCi/L)	Effluent conc. (μCi/L)	% Sorption	K _d Value (mL/g)
F.C. [§]	1.00	3.09	1440.000	55.14	114.58
F.C.	3.00	3.09	2.879	99.07	1.1 × 10 ⁵
F.C.	4.00	3.09	3.221	98.96	9.6 × 10 ⁴
S. C.	1.00	3.09	1700	47.04	81.76
S. C.	3.00	3.09	2.421	99.24	1.3 × 10 ⁵
S. C.	4.00	3.09	2.762	99.12	1.1 × 10 ⁵
T.C.	1.00	3.09	1730	46.11	78.61
T.C.	3.00	3.09	4.010	98.75	7.7 × 10 ⁴
T.C.	4.00	3.09	1.848	99.42	1.7 × 10 ⁵

[§]F.C.: First Combination, S.C.: Second Combination, T.C.: Third Combination,

T.A.: Total absorption

A few elements were added separately to the 5.00 mL solution of ²⁴¹Am at a fixed pH (3.00) in varying concentrations for investigating their interference. Feasibility evaluation of HTNT for practical application was carried out in presence of various concentrations of the other elements present simultaneously with americium in the solution. Three combinations were prepared- first combination was composed of 1.00 g/L each of Fe, Sr, Ca, Na and 0.10 g/L Ru. The second combination had 5.00 g/L each of Fe, Sr, Ca, Na and 0.50 g/L Ru. The third combination was comprised of 10.00 g/L each of Fe, Sr, Ca, Na and 1.00 g/L Ru. As HTNT is intended to treat a large volume of the nuclear waste solution, 0.05 g of the synthesized material were added to 5.00 mL, 10.00 mL and 15.00 mL of the ²⁴¹Am tracer solution to find the effective concentration of the HTNT capable of sorption of americium.

Table SI-6: Comparison of the various sorbents reported for alpha-emitters in LLW

Sorbent	Targeted Radionuclide	Matrix	pH	Maximum Sorption Capacity (mg/g)	Optimum K_d value (mL/g)	Reference
Nano MnO_2 (powder)	Pu	LLW	3-5	N.R.*	N.R.	1
PAN-Zeolite composite	UO_2^{2+}	Aqueous	5 and 10	0.1517 mg/g (composite X) 0.0429 mg/g (composite C)	$10^{-1} \times 10^5$	2
Zirconium Vanadate (granular)	Am^{3+} , UO_2^{2+}	HCl	2-4	0.1 meq/g for Y^{3+}	1.5-230	3
Amorphous- $Fe_2O_3 \cdot 3.5H_2O$ (HFeO)	Pu, Am^{3+} , UO_2^{2+}	ILW	9-10	N.R.	4.59×10^4	4
Antimonysilicate	Pu, Am^{3+}	LLW	1-2	7.63 meq/g (theoretical cation exchange capacity)	1×10^3 to 7.7×10^5	5
Birnessite	Pu, Am^{3+}	LLW	1-2	3.10 meq/g (theoretical cation exchange capacity)	1×10^2 to 1×10^5	5
Titanium silicates (TiSi)	Am^{3+}	Natural groundwater and fuel pond water	6-7	N.R.	9×10^3 to 2.6×10^5	6
Iron oxides	Pu	Natural groundwater and fuel pond water	6-7	N.R.	4.8×10^3 to 1.6×10^4	6
HTNT	Pu, Am^{3+} , UO_2^{2+}	LLW	1-6	8.14 g/g (U) 1.57 mg/g (Pu) 0.101 mg/g (Am)	1×10^3 to 1×10^7	Present study

N.R.* : Not reported in the publication

References for Table SI-6:

1. K. Bhagyashree, R. K. Mishra, R. Shukla, S. Kasar, A. Kar, S. Kumar, S. Kumar, C. P. Kaushik, A. K. Tyagi, B. S. Tomar, Sorption of plutonium from low level liquid waste using nano MnO₂, DOI 10.1007/s10967-012-1938-0
2. S. Akyil, M. A. A. Aslani, M. Eral, Sorption characteristics of uranium onto composite ion exchangers, *J. Radioanal. Nucl. Chem.* 256:1 (2003) 45–51.
3. K. Roy, P.K. Mohapatra, N. Rawat, D.K. Pal, S. Basu, V.K. Manchanda, Separation of ⁹⁰Y from ⁹⁰Sr using zirconium vanadate as the ion exchanger, *Appl. Radiat. Isot.* 60 (2004) 621–624.
4. N. S. Rathore, A. K. Pabby, A. K. Venugopalan, Removal of actinides and fission products activity from intermediate alkaline waste using inorganic exchangers, *J. Radioanal. Nucl. Chem.* 262:3 (2004) 543-549.
5. L. Al-Attar, A. Dyer, R. Harjula, Uptake of radionuclides on microporous and layered ion exchange materials, *J. Mater. Chem.* 13 (2003) 2963–2968.
6. G. Lujaniene, S. Meleshevych, V. Kanibolotskyy, Application of inorganic sorbents for removal of Cs, Sr, Pu and Am from contaminated solutions, *J. Radioanal. Nucl. Chem.* 282 (2009) 787–791.