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Actinides selective extractants coated magnetite nanoparticles for analytical applications

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Abstract *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) and bis(2-ethylhexy)phosphoric acid (HDEHP) were coated on Fe_3O_4 nanoparticles under different chemical conditions. The TODGA-coated magnetite nanoparticles (Fe_3O_4@TODGA) captured representative actinides Am(III) and Pu(IV) at 3–4 M HNO_3 with high efficiency. However, the HNO_3 induced pre-organization of TODGA, before coating on the magnetite nanoparticles, was found to be important for the sorption of Am(III) and Pu(IV) ions. The Fe_3O_4@HDEHP particles exhibited selectivity toward Pu(IV), and Am(III) did not sorb from 3 to 4 M HNO_3. The quantification of Pu(IV) preconcentrated on coated particles was carried out by removing the extractant coating in dioxane based scintillator, followed by liquid scintillation counting.

Keywords *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) · Bis(2-ethylhexy)phosphoric acid (HDEHP) · Actinide · Preconcentration · Coated magnetite · Liquid scintillation counting

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Introduction

Functionalized nanoparticles (NPs) have many potential applications in analytical chemistry based on their unique magnetic, optical and electrochemical properties [1]. The functionalized superparamagnetic particles offer many advantages for the sample preparation and analyte pre-concentration such as higher surface area, easy dispersion in a larger volume sample, and retrieval from sample using an external magnetic field without retaining residual magnetization after withdrawal of magnetic field [2, 3]. It is important that the magnetic particles should be easy to prepare, cheaper, nontoxic, stable under ambient conditions, should be superparamagnetic with higher magnetic saturation value, and easy to functionalize for the analyte specific applications. The magnetite (Fe_3O_4) NPs and its products of oxidation maghemite (γ-Fe_2O_3) have such properties and, therefore, used extensively not only in analytical chemistry but also for hosting the NPs for many other applications [4–7]. In general, the Fe_3O_4 NPs can be used after coating/anchoring desired functionality directly on their surfaces [8–11], immobilization in polymer matrix [12–16], or formation of ferrofluid [17, 18]. However, the most popular method appears to be the direct functionalization of the Fe_3O_4 NPs by physical coating or anchoring of functional groups by covalent linking [2, 3, 19–21].

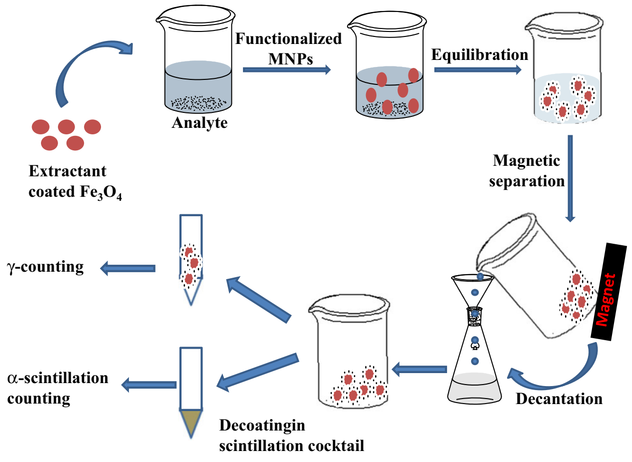
Argonne National Laboratory has developed a magnetically assisted chemical separation (MACS) process for removal of transuranic elements for the waste management objectives [22]. Thereafter, several research papers have been published for the removal of actinides using different design and strategy of MACS [23–30]. However, the quantification of actinide requires the reproducible high extraction efficiency, selectivity towards the target analyte or a group of analytes, and reusability in a prevailing chemical environment. The quantification of the analyte preconcentrated on the Fe_3O_4 NPs is done either subjecting directly to tailored instrumental methods [31, 32], or eluting analyte in an appropriate solution which is subjected to conventional instrumental methods such as alpha spectrometry, ICP-AES etc. [33–35]. The radiation measurement based analytical methods are highly sensitive to radionuclides but lacks chemical selectivity, require constant radiation courting geometry, and often subjected to the sample preparation steps to avoid interferences and lowering detection limit by preconcentration [36, 37].

In the present work, the *N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) and bis(2-ethylhexy)phosphoric acid (HDEHP) coated Fe_3O_4 NPs have been developed for the preconcentration of actinides from large volume samples followed by magnetic separation. These extractants are well known for their promising separation of lanthanides and actinides [38–40]. The coated particles are characterized by thermogravimetry, vibrating sample magnetometry, and their actinide sorption efficiencies. The amounts of actinides preconcentrated have been quantified either by decoating of the extracting phase on Fe_3O_4 NPs in scintillation cocktail which is subjected to alpha liquid scintillation counting, or by direct γ-spectrometry. The outline of the present work is shown in Scheme 1.

Experimental

Materials and methods

TODGA and Fe_3O_4 NPs (20–30 nm) were procured from Thermax, Pune, India and J. K. Impex, Mumbai, India, respectively, dodecane and tetra ethoxy silane (TEOS) from Sigma-Aldrich, methanol from S. D. Fine Chemicals, India, nitric acid (69–70%) received from Beaker chemicals Pvt. Ltd, Mumbai, India and liquid scintillation cocktail-O from Sisco Research Laboratory, India. JASCO 420 spectrometer was used for recording FTIR, and STARe system METLER TOLEDO instrument was used for thermo gravimetric analysis (TGA).



Scheme 1 The Outline of different steps involved in quantifications of actinides using extractants coated Fe_3O_4 NPs

Coating of extractants on Fe_3O_4 NPs

The coating of TODGA on Fe_3O_4 (Fe_3O_4@TODGA) was carried out with and without pre-HNO_3 treatment. For acid treatment, TODGA in dodecane (0.1 mol L^{-1}) was equilibrated with equal volume of HNO_3 (0.1–3 mol L^{-1}) for 30 min prior to coating. It was then centrifuged and aqueous layer was discarded. Thereafter, Fe_3O_4 NPs (0.1 g) were dispersed in 10 mL of acid treated as well as in without acid treated solutions containing 0.1 mol L^{-1} TODGA in dodecane. These solutions containing Fe_3O_4 particles were subjected to constant agitation for 24 h at room temperature and 40 °C using a constant temperature shaking bath. Subsequently, the coated Fe_3O_4 particles were separated from solutions using an external magnet. Finally, the coated Fe_3O_4 particles (Fe_3O_4@TODGA) were washed 4–5 times with 5 mL of methanol, and dried under vacuum at room temp for overnight.

The coating of HDEHP was carried out in a similar fashion except that acid treatment was not given. Typically, 0.1 g of Fe_3O_4 NPs were dispersed in 10 mL of 0.1 mol L^{-1} HDEHP in ethanol and equilibrated under shaking condition for 24 h. Then the coated Fe_3O_4 was removed and washed 3 times with 5 mL methanol. It was then dried overnight at room temp.

Extraction experiments

The sorption/desorption of actinides in Fe_3O_4@TODGA was studied using ^{241}Am and ^{mix}Pu as representatives of actinides. Weighed amounts of Fe_3O_4@TODGA coated under different chemical conditions were equilibrated with 5 mL solution containing known activity of Am and Pu in 3 mol L^{-1} HNO_3 for 2 h with a constant shaking at room temp. After equilibration, the aqueous phase and Am/Pu loaded Fe_3O_4@TODGA were separated by applying external magnet, and counted by γ-spectrometer consisting of NaI(Tl) detector coupled to a multichannel analyzer for ^{241}Am, and a home built liquid scintillation counter was used for ^{mix}Pu. The radioactivity of the aqueous phase before and after equilibration was used to determine the D value using following equation:

$$D = \frac{(A_i - A_f)}{W} \times \frac{V}{A_f} \tag{1}$$

where A_i and A_f represent γ/α -activity of radionuclide in aqueous phase initial and after equilibration, W and V are weight of the functionalized Fe_3O_4 and volume of equilibrating aqueous phase (5–10 mL), respectively. The uptake efficiency was calculated using following relation:

$$\text{Uptake efficiency} = \frac{[A_i - A_f]}{[A_i]} \times 100 \tag{2}$$

where A_i and A_f are same as given in Eq 1. To study the reproducibility of coating procedure, four batches of Fe_3O_4@TODGA were prepared by the same procedure and equilibrated with ^{241}Am as described above. Standard deviation was calculated on percentage extraction from different batches. Similar extraction experiments were also carried out with HDEHP coated Fe_3O_4 for Plutonium extraction at 3 mol L^{-1} HNO_3.

Analytical applications

To explore analytical applications of TODGA@Fe_3O_4, the known amounts of ^{241}Am activity (5.7–57 μCi) spiked in the 3 mol L^{-1} HNO_3 and loaded in fixed weights of TODGA@Fe_3O_4 (100 mg) as described above for the sorption experiments. The ^{241}Am activity loaded in Fe_3O_4 was counted by γ-spectrometry. For alpha liquid scintillation counting, the ^{mix}Pu loaded TODGA@Fe_3O_4 particles were dispersed in 5 mL of different solvents like toluene, toluene based scintillator, isopropyl alcohol (IPA) and dioxane based scintillator for 24 h to remove TODGA coating in a scintillating glass vials. Toluene based scintillator contained 5% HDEHP in cocktail-O; whereas dioxane based scintillator contained 1% TOPO in cocktail-W.

Results and discussion

Characterizations of extractant coated Fe_3O_4 NPs

The morphology of the Fe_3O_4 NPs did not change after coating the extractant (TODGA/HDEHP) as shown in the representative FE-SEM image in Fig. 1. The size of particles were 20 ± 5 nm. In order to stabilise the magnetite nanoparticles in high nitric acid medium, the magnetite nanoparticles were coated with silica using tetra ethoxy silane (TEOS). The presence of extractant on Fe_3O_4 NPs was confirmed by FTIR spectroscopy. The absorption peaks at around 638 and 580 cm^{-1} observed in FTIR spectrum of the pristine Fe_3O_4 could be assigned to stretching mode of Fe–O. The absorption peaks at 1095 and 1210 cm^{-1} corresponds to Si–O bond, which shows that silica layer was successfully coated on Fe_3O_4 see Fig. 2. The additional absorption bands appeared at 2920 and 1375 cm^{-1} in Fe_3O_4@TODGA were due to C-H stretching and bending modes of the alkyl group, respectively, 1640 cm^{-1} was assigned to carbonyl group, and 1105 cm^{-1} assigned to stretching vibration of C–O–C groups present in TODGA see Fig. 2b. The characteristic phosphate bands were observed at 1370 and 960 cm^{-1} along with C–H stretching vibrations at 2926 and 1060 cm^{-1} in FTIR spectrum shown in Fig. 2c of the Fe_3O_4@HDEHP particles.

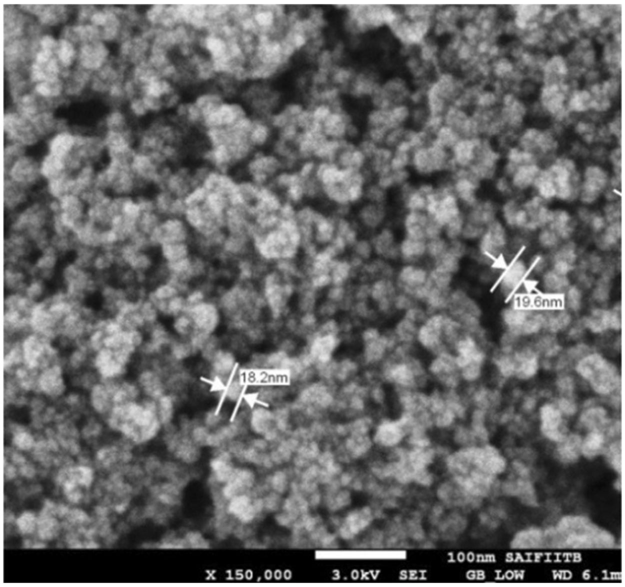


Fig. 1 FE-SEM image of extractant (TODGA) coated Fe_3O_4 particles

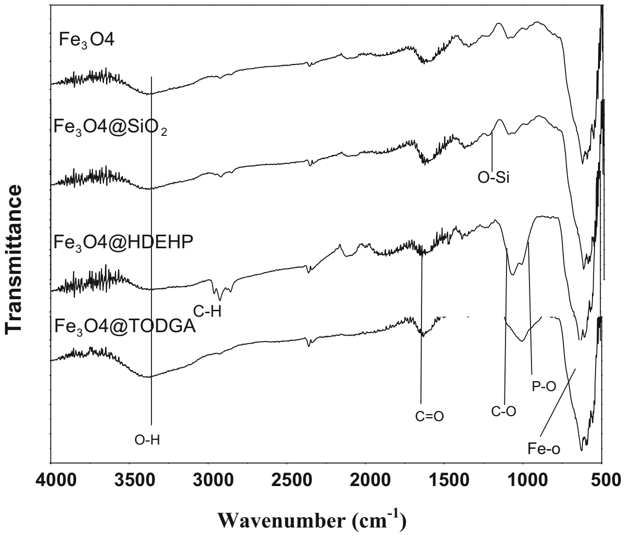


Fig. 2 FTIR spectra of pristine Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@HDEHP and Fe_3O_4@TODGA nanoparticles respectively

The effect of extractants coatings on the superparamagnetic properties of Fe_3O_4 was studied by using vibrating sample magnetometer (VSM). It is seen from the magnetization curves given in Fig. 3 that the TODGA and HDEHP

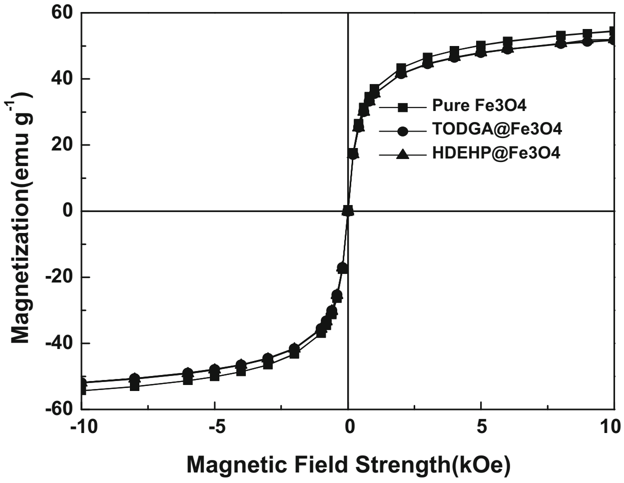


Fig. 3 VSM magnetization curves of pristine Fe_3O_4, and TODGA/HDEHP coated Fe_3O_4 particles

coatings did not reduce the saturation magnetization to a significant extent with respect to that of the pristine Fe_3O_4 particles. This seems to suggest that the extractants coating on Fe_3O_4 was thin as expected from the FE-SEM images.

The amounts of extractants coated on the Fe_3O_4 particles were determined by thermo gravimetric analysis (TGA) performed under nitrogen atmosphere with the heating rate of 15 °C min^{-1}, and thus obtained thermograms are given in Fig. 4. As can be seen from Fig. 4, 3% weight loss was observed because of adsorbed water in the pristine Fe_3O_4. For HDEHP and TODGA coated Fe_3O_4 particles, the initial weight loss about 3 wt% was observed below 200 °C attributed to the loss of water molecules and additional weight losses of 6 wt% from 200 to 600 °C for TODGA coated Fe_3O_4 and 8% weight loss from 200 to 700 °C for HDEHP coated Fe_3O_4 were observed. The organic extractants were burned to gases during analysis. Thus, 6 and 8 wt% losses could be correlated to the amounts of extractants coated on the Fe_3O_4 particles. The higher coating of HDEHP on the Fe_3O_4 particles could be due to mono acidic phosphate group in HDHEP which has higher affinity towards Fe^{3+}/Fe^{2+} sites of Fe_3O_4.

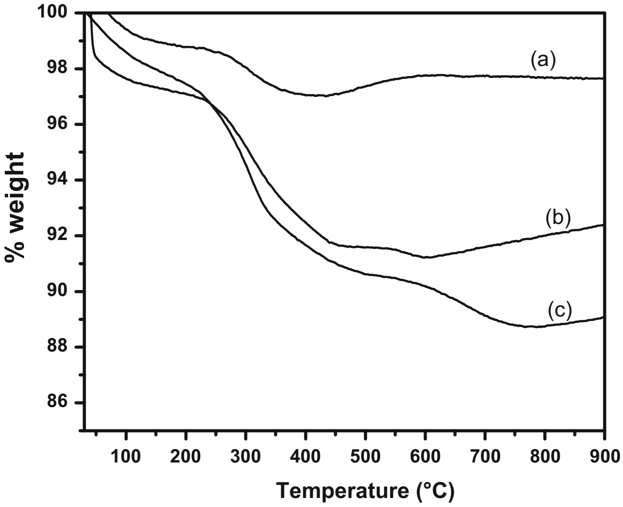


Fig. 4 TGA curves of pure Fe_3O_4 (*a*), Fe_3O_4@TODGA (*b*) and Fe_3O_4@HDEHP (*c*) nanoparticles

Actinide sorptions and desorptions

The actinide extraction properties of diglycolamides are attributed to their aggregations induced by HNO_3 [41–45]. These class of extractants take up tri and tetravalent actinides such as Am(III) and Pu(III,IV) from 3 to 4 mol L^{-1} HNO_3 solutions [46, 47]. To understand effect of HNO_3 induced aggregation of TODGA, 0.1 mol L^{-1} TODGA in dodecane was pre-equilibrated with HNO_3 and then coated on the Fe_3O_4 particles at different temp. As can be seen from distribution coefficients values (D) given in Table 1, the pre-acid treated Fe_3O_4@TODGA extracted Am^{3+} quantitatively irrespective of coating temp but no extraction was observed for non-acid treated TODGA coated particles. It was also evident from data given in Table 2 that the Fe_3O_4@TODGA formed by the coatings of lower concentration of HNO_3 acid pre-equilibrated TODGA did not have significant extraction efficiency toward Am^{3+} ions. This is in accordance with the literature which reported the critical concentration of acid required for 0.1 mol L^{-1} TODGA in *n*-alkane to form TODGA reverse micelles was 0.7 M mol L^{-1} HNO_3 [48]. HDEHP exists normally in a dimer form without any pre-treatment [49, 50], therefore was coated as such using conditions described in experimental section. The depicted chemical structure and schematic representation of HDEHP/TODGA coatings is shown in Scheme 2. But in aqueous solution the hydrocarbon chains collapses and coils around magnetite nanoparticles.

To study the reproducibility of TODGA coating, four batches of Fe_3O_4@TODGA were prepared by the same procedure. Fe_3O_4@TODGA (0.1 g) was equilibrated with 25 mL solution containing ^{241}Am in 3 mol L^{-1} HNO_3 for 3 h under constant shaking at 25 °C. The extraction efficiency was found to quite reproducible as 87 ± 3%. It was also observed that Pu(III,IV) sorption in Fe_3O_4@TODGA was similar as expected from literature [41–47].

Unlike Fe_3O_4@TODGA particles, the Pu(IV) ions were selectively adsorbed in the Fe_3O_4@HDEHP particles at higher HNO_3 concentration as shown in Table 3. Thus, it is possible to quantify Pu(IV) selectively in the presence of Am(III) using the Fe_3O_4@HDEHP particles. The reusability of Fe_3O_4@TODGA particles was tested for Am(III) ions. First the Fe_3O_4@TODGA particles were loaded with Am(III) ions from 25 mL of 3 mol L^{-1} HNO_3 for 3 h; and subsequently de-loaded quantitatively (>99%)

Table 1 Extraction behaviour of Fe_3O_4@TODGA NPs toward ^{241}Am(III) from 3 mol L^{-1} HNO_3 under different coating conditions of 0.1 mol L^{-1} TODGA in *n*-dodecane

Coating temp. (°C)	Pre-treatment	Extraction (%)	*D* (g mL^{-1})
25	No	7 ± 1	8
25	With 3 mol L^{-1} HNO_3	88 ± 4	684
40	No	8.7 ± 1	9
40	With 3 mol L^{-1} HNO_3	87 ± 3	672

with 3 mL of 0.02 mol L^{-1} disodium salt of EDTA. The cycle of extraction and stripping was repeated for three times. It was observed that the percentage of extraction remains same even after three cycles. The same is also true for Fe_3O_4@HDEHP particles toward Pu(IV) ions. Where Pu was deloaded with 0.02 mol L^{-1} disodium salt of EDTA and again equilibrated with same amount of plutonium. The re-usability cycles given in Fig. 5. Which indicates the extractant coatings on Fe_3O_4 particles did not deteriorate after multiple uses.

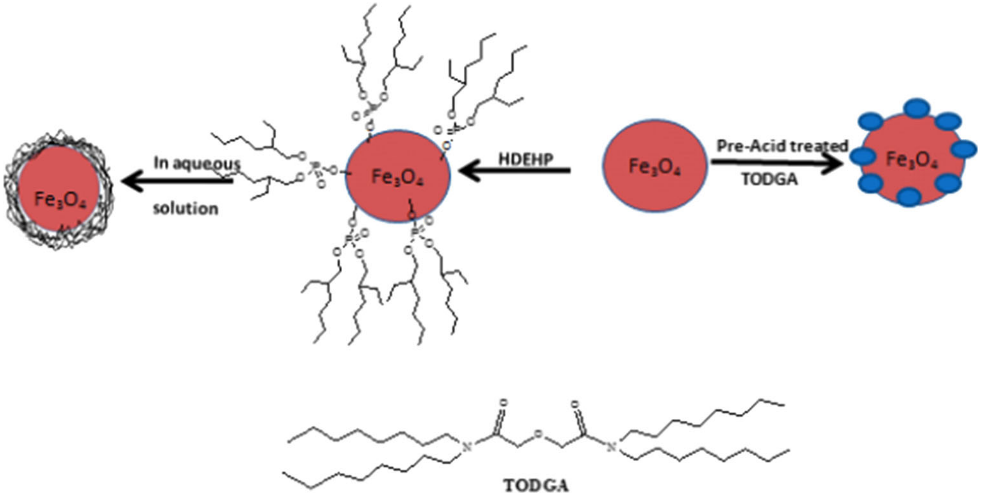
Table 2 Extraction behavior of Fe_3O_4@TODGA formed by coating TODGA in dodecane pre-equilibrated with different acidity towards ^{241}Am(III) from 3 mol L^{-1} HNO_3

Acidity for pre-treatment (mol L^{-1})	Extraction (%)	*D* (g mL^{-1})
0.01	11 ± 1	12
0.1	2 ± 1	3
1	75 ± 1	306
3	87 ± 3	636

Analytical applications

The quantification of ^{241}Am, which emits 59.54 keV γ-rays with 35.9% abundance, was carried out by direct γ-spectrometry of ^{241}Am(III) loaded Fe_3O_4@TODGA particles. For this, the Fe_3O_4@TODGA particles (0.01 g) were equilibrated with different amount of ^{241}Am activity (5.7–57 μCi) spiked in the 3 mol L^{-1} HNO_3 and kept under shaking condition for 2 h at room temp. As can be seen from Fig. 6, the gamma activity in Fe_3O_4@TODGA particles varied linearly as a function of amount of activity spiked. Thus, the direct γ-spectrometry of ^{241}Am(III) loaded Fe_3O_4@TODGA particles could be used for Am(III) quantification using calibration plot or by the standard comparison method.

The isotopes of Pu are weak γ-emitters and, therefore, their quantification with γ-spectrometry at ultra trace conc is not feasible. However, the α-counting using alpha spectrometry, proportional counters and scintillation counters etc. could be used for the quantification of Pu after appropriate sample manipulation [36, 37, 51–53]. In the



Scheme 2 Surface modifications of Fe_3O_4 with TODGA and HDEHP

Table 3 Extraction behaviour of Fe_3O_4@HDEHP particles toward Pu(IV) and Am(III) ions as a function of HNO_3 conc

HNO_3	Am(III)		Pu(IV)	
Mol L^{-1}	Extraction (%)	*D* (g mL^{-1})	Extraction (%)	*D* (g mL^{-1})
0.5	1.17	2.36	85 ± 3	1192
1	0.46	0.93	87 ± 3	1408
3	0.80	1.62	92 ± 2	2547

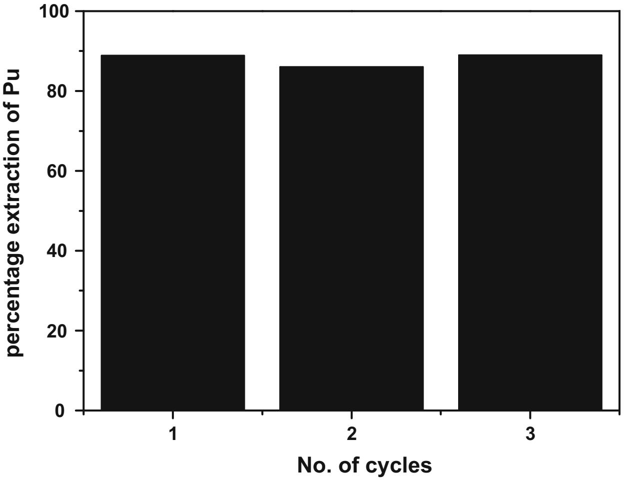


Fig. 5 The reusability cycles of Fe_3O_4@HDEHP particles towards Plutonium

present work, the Pu(IV)-loaded Fe_3O_4@TODGA particles were dispersed in a liquid scintillation cocktail and subjected to scintillation counting. It was observed that Fe_3O_4@TODGA particles did not remain homogeneously distributed and settled at bottom of the vial. This made alpha scintillation counting non-reproducible and lower than that obtained by spiking the same quantity of Pu in the liquid scintillation cocktail. Therefore, the removal of coating in the liquid scintillation cocktail having different solvents was studied. For this, ^{241}Am was used as it is good γ and α emitter which make it possible to corroborate liquid scintillation counting results with γ-spectrometry.

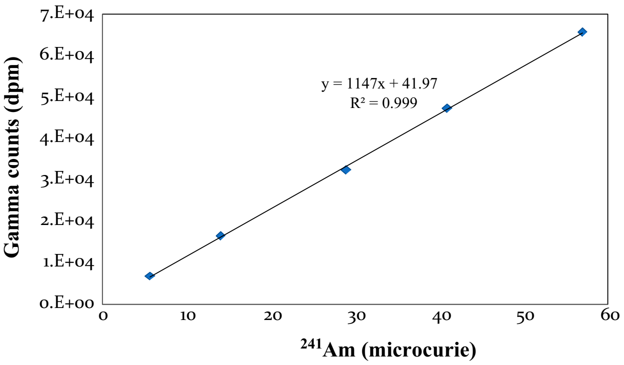


Fig. 6 Variation in γ-activity of ^{241}Am loaded on Fe_3O_4@TODGA nanoparticles as a function of Am(III) amount spiked in the solution. Fe_3O_4@TODGA nanoparticles were equilibrated with different amount of ^{241}Am activity (5.7–57 μCi) spiked in the 3 mol L^{-1} HNO_3 for 2 h under shaking conditions at room temp

Table 4 Decoating of TODGA bearing organic phase from the ^{241}Am(III) loaded Fe_3O_4@TODGA in different organic solvents. Am(III) was loaded from 3 mol L^{-1} HNO_3

Solvent	De-coating observed by γ-counting	Physical appearance of solvent
Toluene	Nil	Transparent
Dioxane	>99%	Transparent
Isopropyl alcohol	>99%	White coagulation

The known quantity ^{241}Am(III)-loaded Fe_3O_4@TODGA NPs were dispersed in different organic solvents such as toluene, dioxane and isopropyl alcohol. As can be seen from Table 4, there was no decoating of the TODGA organic phase from ^{241}Am(III)-loaded Fe_3O_4@TODGA after equilibration for 24 h in toluene. However, the quantitative decoating of TODGA bearing organic phase in dioxane as well as isopropyl alcohol was observed. The dioxane decoated solvent was transparent, but white coagulation was observed in isopropyl alcohol. Therefore, dioxane based liquid scintillation cocktail was tested for decoating of organic phase of ^{241}Am(III)-loaded Fe_3O_4@TODGA and subsequent alpha scintillation counting. It was observed that scintillation counts rate thus obtained was within ±1% of that obtained by direct spiking of the same quantity of ^{241}Am in the same dioxane based liquid scintillation cocktail. There was no residual γ-activity in the decoated Fe_3O_4, and did not sorb the Am(III) on reuse.

Finally, the fixed amount (0.1 g) of Fe_3O_4@TODGA and Fe_3O_4@HDEHP particles were equilibrated with solution containing varying amount of Pu(IV) ions and fixed amount of ^{241}Am at 3 mol L^{-1} HNO_3. The scintillation counts rates obtained after decoating in the dioxane based liquid cocktail varied linearly with the Pu(IV) amount spiked in the equilibrating solutions. The scintillation counts rate obtained by using the Fe_3O_4@TODGA particles were systematically higher than that obtained using the Fe_3O_4@HDEHP particles corresponding to fixed amount of ^{241}Am, see Fig. 7. This was attributed to a fact that the Fe_3O_4@HDEHP particles sorbed Pu(IV) ions only, while Fe_3O_4@TODGA takes of both Am(III) and Pu(IV) ions.

Conclusions

TODGA and HDEHP extractants were successfully coated on superparamagnetic Fe_3O_4 nanoparticles using the optimized chemical conditions. The TODGA coated Fe_3O_4 nanoparticles showed quantitative uptake of Am^{3+} and Pu^{4+} ions. However, HDEHP coated Fe_3O_4 nanoparticles were found to take up Pu^{4+} ions only from the solution having 3 mol L^{-1} HNO_3, which are normally encountered in the nuclear reprocessing plants. For liquid scintillation counting, the removal of coating in dioxane based scintillator was found to be suitable for the quantification of preconcentrated actinides

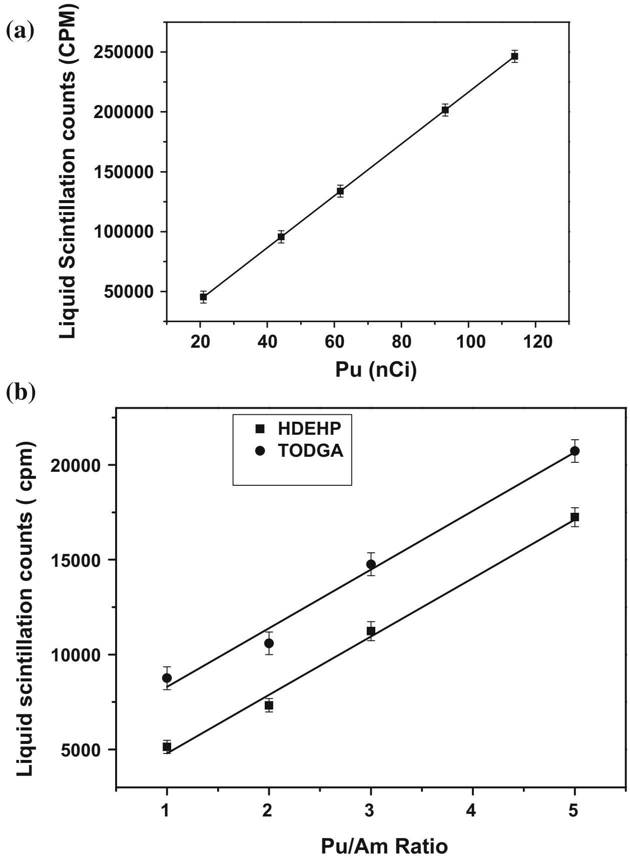


Fig. 7 **a** Variation in α-scintillation count rate of ^{mix}Pu loaded on Fe_3O_4@TODGA nanoparticles as a function of Pu(IV) amount spiked in the solution. Fe_3O_4@TODGA nanoparticles were equilibrated with different amount of ^{239}Pu activity (20–114 nCi) spiked in the 3 mol L^{-1} HNO_3 for 2 h under shaking conditions at room temp. Pu loaded Fe_3O_4@TODGA nanoparticles were then dispersed in 5 mL dioxane based scintillation cocktail and then counted. **b** Variation in α-scintillation count rate obtained by equilibrating Fe_3O_4@TODGA and Fe_3O_4@HDEHP particles in solution having varying amount of Pu(IV) and fixed amount of ^{241}Am (scintillation count rate 35,000 counts min^{-1}) under similar conditions described for Fig. 6a

on the extractant coated Fe_3O_4 nanoparticles. This provides a potential application of this method for monitoring the ultra-trace concentration of radioactivity in large volume of aqueous sample discharges from nuclear facilities using magnetically assisted separation followed by quantification by alpha scintillation counting.

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