



Development of a chelating ion exchange-based radionuclides removal method for the treatment of routine laboratory organic liquid waste

A. S. Suneesh¹ · Alok Rout¹ · T. Prathibha¹ · B. Robert Selvan¹ · M. Amutha Suba¹ · J. S. Brahmaji Rao¹ · G. V. S. Ashok Kumar¹ · N. Ramanathan^{1,2}

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Abstract

In the present work, an ion exchange-based radionuclides removal method for the treatment of radioactive laboratory organic liquid waste was developed. The removal of radionuclides was accomplished with the combined action of an *in-house* developed chelating type polystyrene based weakly acidic cation exchange resin and oxalic acid complexant. The efficacy of the method was investigated based on the results of gamma spectrometry, liquid scintillation counting and alpha spectrometry. The radioactive organic liquid waste treatment was demonstrated finally through column mode of separation method for nearly 1 Litre of the waste.

Keywords Waste management · Plutonium · Americium · Organic waste · Adsorption

Introduction

The industrial-scale deployment of nuclear reactors for commercial power generation evolved after a decade or two post discovery of the nuclear fission process. The spent fuel from the nuclear reactor after its life time in the reactor is generally reprocessed for the recovery of fissile element like plutonium and other valuable materials [1]. This requirement led to the development of liquid–liquid extraction-based large-scale separation of the fissile elements, mainly uranium and plutonium. Treatment and disposal of radioactive organic liquid waste solutions assumes importance because of the chemical toxic nature of the waste in addition to its radio toxicity. The large volumes of liquid waste generation with the above process are associated with the recovery of

uranium from the natural ores and the post-processing of utilized nuclear fuel for the retrieval of fissile elements (uranium and plutonium) and fission product separation. These liquids involve acidic and alkaline solvents used for mineral recovery of uranium, target specific extractants employed for the liquid–liquid separation process-based recovery of fissile elements, and fission products. Organic liquid waste is also a concern from a waste management point of view. Though aqueous and organic wastes pose a substantial radiotoxic danger, managing aqueous liquid waste is relatively undemanding. Several methodologies have been used to process aqueous liquid waste such as evaporation, filtration and pre-concentration to name a few [2–5].

The high radiotoxicity of the organic liquid waste associated with the waste discharged from reprocessing plants demands special attention because of several long-lived alpha-emitting nuclides. Primary attention has been paid to treating liquid waste to mitigate discharge of radiotoxic materials into the biosphere. The worldwide acknowledged notion for remediating the radio-toxicity due to the long-lived radioisotopes is to remove the particularly troublesome radioactive elements and immobilize them in some permanent matrix to restrict the migration of the radiotoxic elements to the biosphere. The international bodies viz. International Atomic Energy Agency (IAEA), International Commission on Radiological Protection (ICRP), etc.,

✉ A. S. Suneesh
suneesh@igcar.gov.in

✉ N. Ramanathan
nram@igcar.gov.in

¹ Materials Chemistry & Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu 603 102, India

² Indira Gandhi Centre for Atomic Research, A CI of Homi Bhabha National Institute, Kalpakkam, Tamil Nadu 603 102, India

authorize the disposal of radioactive waste having less than 37 Bq/L only to the biosphere without regulatory inspection [6]. In this context, the radioactive contaminated organic liquid waste must be adequately treated before its disposal to the environment. However, the treatment processes available for processing organic liquid waste originating from reprocessing plants and several other allied methods is inadequate [7, 8].

The radiotoxicity of the radioactive substance adhered to the organic liquids is not the only concern as the radionuclide-bearing organic solvent also experiences radiation damage up on more extended duration storage before the processing. The prevailing alkaline or acidic environments further enhance this degradation process. The free radical-assisted chemical process further complicates the recovery of the radioactive elements from the organic liquids [9, 10]. The above chemical damage is apart from the usual radiochemical damage of organic solvents used in the liquid–liquid extraction process. Overall, the organic solvents used in reprocessing and other allied separation processes are known to undergo radiation, chemical, and thermal degradation after numerous operations cycles. Though most elements associated with the above organic solvents are removed during the stripping stages, a few radionuclides are held with the organic phase. Radiochemical damage of TBP produces several degradation products such as monobutyl and dibutyl phosphate which could also complex with uranium and plutonium and a few fission products [11]. The presence of these degradation products reduces the stripping of the elements from the organic phase.

Apart from reprocessing plants, a small but sizeable contribution of organic liquid waste originates from various day-to-day experiments in radiochemical laboratories. The decontamination of organic liquid waste facilitates better means to decompose the organic liquids and also provides an opportunity to recover the valuable elements adhered to the organic liquid phase. Wattal et al. reported alkaline hydrolysis for the destruction of spent TBP waste [8]. Similarly, Aly and coworkers reported a wet-oxidation method for the oxidative degradation of TBP diluted with kerosene [12]. All the above processes involve the destruction of the organic liquids followed by the recovery of the adhered radioactive species, which involves cumbersome methods. Apart from the radiotoxic hazard associated with the entrapped radioactive elements, the chemical and environmental hazard associated with the organic liquids also needs special attention. Removal of the radiotoxic elements from the organic liquid wastes makes them suitable for the treatment (by combustion or incineration) so that the treated wastes can be disposed as exempted category (less than 37 Bq/L).

The current paper reports the development of a radionuclide removal method from contaminated organic liquids by a column-based solid phase separation process. The separation process involves the combined action of an in-house

developed chelating polystyrene resin and oxalic acid. Unlike the previously reported procedures, the present method delivers an operationally feasible and effortless decontamination procedure for the contaminated organic liquids that make them amenable for disposal. The radioactive liquid organic waste in our laboratory has been produced due to various laboratory operations/experiments such as solvent extraction experiments, mixer-settler studies and cocktail liquids employed for liquid scintillation counting (LSC)-analysis. Analysis of radionuclides revealed the radioactivity levels in the range from 50,000–100,000 Bq/mL. For the safe disposal purpose as a special category waste, the regulatory agency (Atomic Energy Regulatory Board, AERB) of India and the Centralized Waste Management Facility (CWMF), Kalpakkam has recommended the gross radioactivity of the liquid wastes to be reduced to less than 5000 Bq/mL [13, 14]. The chelating polystyrene based resin that has been developed for the treatment of organic waste is diglycolamic acid anchored polystyrene resin (PS-DVB-DGAH), which is a weak cation exchange resin. We previously reported the PS-DVB-DGAH resin for removing trivalent actinides and lanthanides from a dilute nitric acid medium [15]. Some of our current studies also pointed out the feasibility of utilizing PS-DVB-DGAH for the cation ion exchange-based removal of radionuclides [15, 16]. To the best of our knowledge, it would be a novel attempt to employ a polystyrene based ion exchanger to remove radionuclides from contaminated organic liquids. Besides the advantage of making the organic liquids appropriate for further processing, this method retrieves valuable radioactive elements. The removal of radionuclide from the organic phase was also studied by employing solid state complexants such as oxalic acid, BTP, EDTA and sodium hydroxide. The above treatment methods simplify the treatment procedure for the organic liquid wastes without the need of a prior pre-treatment. Perhaps, this would be a first of its kind attempt to employ a polystyrene based ion exchanger to remove radionuclides from contaminated organic liquids. Besides the advantage of making the organic liquids appropriate for further processing, this method retrieves valuable radioactive elements as well. At the outset, the efficiency of removal of radiotoxic elements from the organic liquid waste solution was studied by batch experiments. A glass column-based demonstration of the feasibility of the process was further demonstrated for 1L of actual laboratory organic liquid waste. An attempt was also made to characterize the treated waste by ATR-FTIR spectroscopy.

Experimental

Materials and methods

Chloromethylated polystyrene divinylbenzene resin (PS-Cl), commercially available under the brand name “Merrifield

Resin” was procured from M/s Aldrich India. Detailed specification of PS-Cl resin is shown in Table Table 1. The resin was used after purification. This involves a series of washings respectively with water, isopropanol and acetone, and finally, the resin was dried in air for 72 h. All the chemicals used for the preparation of the anchored resin i.e. diethylenetriamine (Alfa aesar), pyridine (Merck), diglycolic anhydride (Aldrich) were used without any purification. AR grade sodium hydroxide, sodium carbonate, EDTA and oxalic acid (Merck) were also used as received for the experiments.

The alpha activity of the waste solutions was measured using ZnS(Ag) scintillation counter (M/s Hydex, Finland) after dilution of 0.05 mL of the samples with 5 mL of toluene-based extractive scintillator cocktail (M/s Sisco Research Laboratory, Mumbai). The results were recorded as counts per minute (cpm). Wherever appropriate, it was converted to Bq/mL. Since all the waste solutions were expected to contain a mixture of different alpha-emitting elements such as isotopes of plutonium, americium and uranium, collective (gross) activity of all the isotopes was measured each time. The gamma activity of various samples was assayed using a high purity germanium (HPGe) detector coupled with a multi-channel analyzer (MCA) (M/s Baltic Scientific Instruments, Lithuania). The alpha spectra of the organic samples at different stages were also recorded using Alpha Spectrometer PAS-01 (M/s Electronics Enterprises (I) Pvt Ltd, Mumbai) connected with ion Implanted Silicon detector (Canberra). For recording alpha spectra, the samples were made planchets in a 25 mm stainless steel (SS) disc. The FT-IR spectra of the samples were recorded using M/s Bruker Tensor-2 FT-IR spectrometer coupled with attenuated total reflectance (ATR) accessory installed in a radioactive glove-box.

Preparation of Ion exchange resin PS-DGAH

Preparation and detailed characterization of polystyrene divinyl benzene diglycolamic acid anchored resin (PS-DVB-DGAH) was reported elsewhere [15]. In short, chloromethylated polystyrene divinylbenzene resin (PS-DVB-Cl; Merrifield Resin) was initially converted to amino functionalized resin [16]. 25 g of PS-DVB-Cl (~ 100

mmoles of Cl⁻) was reacted with 14 g of diethylenetriamine (~ 135 mmoles) in presence of 150 mL of pyridine at 90 °C for 16 h, to form an amino modified resin (PS-DVB-NH₂). PS-DVB-NH₂ was washed with isopropanol, water and acetone and was dried in air for 48 h. In the next step, the dried resin was reacted with 15 g of diglycolic anhydride in 10 mL of dichloromethane at 50 °C to form PS-DVB-DGAH. The above prepared resin was washed with isopropanol, water and acetone, followed by drying in air for 48 h. The dried resin was used for batch and column studies to demonstrate the treatment of radioactive organic waste. Figure 1 shows the synthetic scheme for the preparation of PS-DVB-DGAH.

Batch laboratory studies

Feasibility of radionuclides removal by the (i) chelating ion exchange resin and (ii) the inorganic solid phase reagents were investigated by batch extraction experiments. This involves agitation (mixing) of the solid phase reagents (resin or inorganic materials) with the organic liquid wastes. A suitable quantity (0.1 g or 0.5 g) of the resin or solid state substrates was contacted with ~5 mL of the waste solution in a test tube rotator (under 100 rpm) for two hours. After equilibration, the mixture was allowed to settle for half an hour, and alpha counts of the clear solution was recorded. The feed solutions investigated were basically (i) a mixture of amides, diglycolamides, ionic liquids and cocktails, represented as "BATCH-1", (ii) a mixture of trialkylphosphates, phosphonates, phosphine oxides and cocktails, labeled as "BATCH-2" and "BATCH 3". Different batches of waste solutions were basically labeled differently as the sources and compositions were different. All the waste solutions did exhibit a pH of ~ 1 and the average alpha activity (in CPM for 0.05 mL) was ~20,000 for BATCH-1, ~50,000 for BATCH-2 and ~1,10,000 for BATCH 3. BATCH-1 and BATCH-2 were employed for the studies using PS-DVB-DGAH resin while BATCH-3 was employed for the studies with organic and inorganic solid state substrates. For the requirement of separation using column based extraction chromatography experiments, studies were also conducted with different "resin to feed" compositions and all the different batches were evaluated.

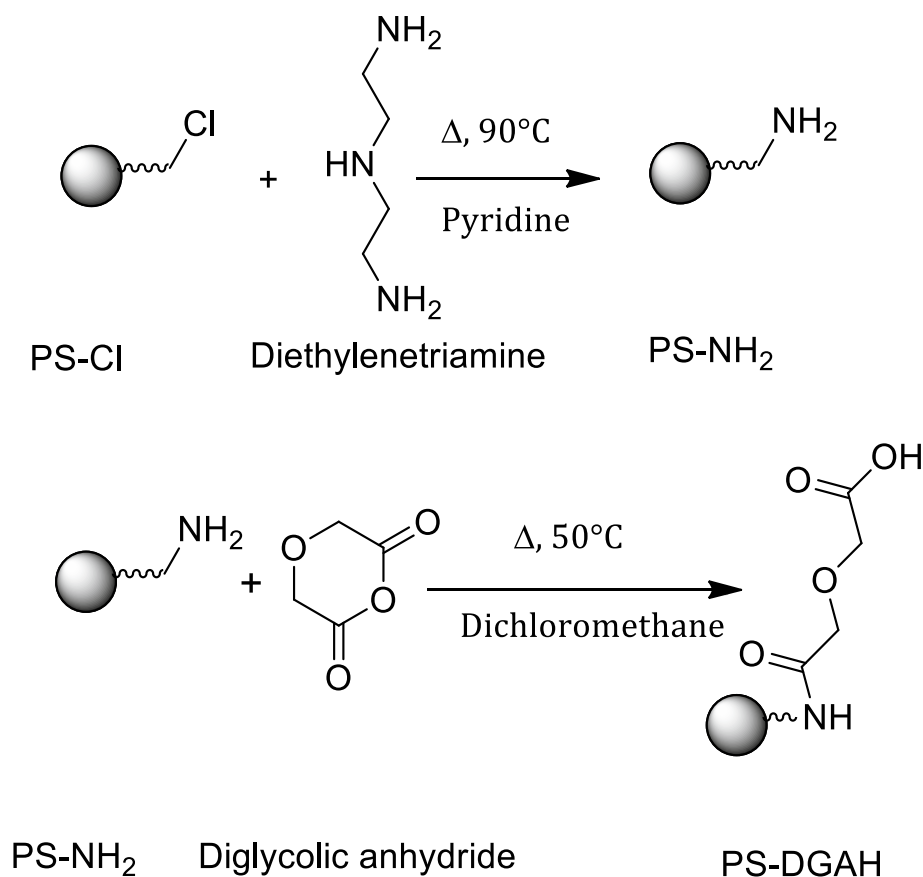
Demonstration by column studies

A thin glass column having 8 mm inner diameter was chosen for the column-based demonstration studies of radionuclides removal by PS-DVB-DGAH resin. The glass column was initially packed with 3 g of dry resin. The resin was initially wetted with 50 mL of n-dodecane (abbreviated as n-DD). 500 mL of the feed solution was passed through

Table 1 Specifications of chloromethylated functionalized polystyrene resin

Functional group	Chloromethylated
Extent of functionality	5 mmol/g (based on chlorine content)
particle size	16–50 mesh
Matrix	Polystyrene
Cross-linking	5.5% divinyl benzene

Fig. 1 Scheme for the preparation of PS-DVB-DGAH



the column at a flow rate of ~ 3 mL per hour. A wider glass filtration column with 15 mm inner diameter was employed during the demonstration studies using solid state complexant. For this purpose, the column was packed with 5 g of solid state complexant and 350 mL of the organic waste solution was directly passed through the column at an average flow rate of ~ 3 mL per hour. The diffusion of the feed through the solid phase adsorbents was maintained via the influence of gravitational force and effluent samples were collected at regular intervals. Each 10 mL fractions of the effluents collected were analyzed by LSC-analysis, alpha spectrometry, gamma and ATR-FTIR spectroscopy. Figure 2 shows the photographs of the column arrangements during the demonstration studies using PS-DVB-DGAH resin and solid state complexant in a radioactive fume hood.

Results and discussions

Batch studies using PS-DVB-DGAH resin

Table 2 shows the results of the batch studies performed with BATCH 1 and BATCH 2 radioactive organic waste solutions. Activity level of BATCH -1 sample was of



Fig. 2 Column demonstration of the organic waste treatment by PS-DVB-DGAH (A) and solid state complexant (B)

the order of $\sim 20,000$ CPM and that of BATCH -2 was $\sim 50,000$ CPM. For these experiments, two different liquid (organic liquid waste) to adsorbent (PS-DVB-DGAH) ratio was maintained. The liquid samples were analyzed before and after the contact with the solid phase (PS-DGAH). The quantitative removal of radionuclides was ascertained

Table 2 Activity of the samples tested during batch studies and performance of the resin under different “resin/feed compositions” in batch study

Batches	Activity measured by gamma spectrum prior to the treatment Bq/mL	Activity measured by LSC-analysis prior to the treatment Bq/mL	Activity measured by LSC-analysis after the treatment Bq/mL
BATCH-1	8633	6333	267
BATCH-2	18,800	16,333	317

based on the analysis of the liquid samples collected after two hours of contact (Refer to experimental section, Section “**Batch laboratory studies**”). The results of LSC-analysis and gamma spectrometry suggest the removal of more than 95 % radionuclides with in single contact with the adsorbent. The radioactivity of the elements that persists after the single contact with the adsorbent did remain less than 500 Bq/mL, indicating that PS-DVB-DGAH is highly suitable for removal of radionuclides from radiotoxic-contaminated organic liquids.

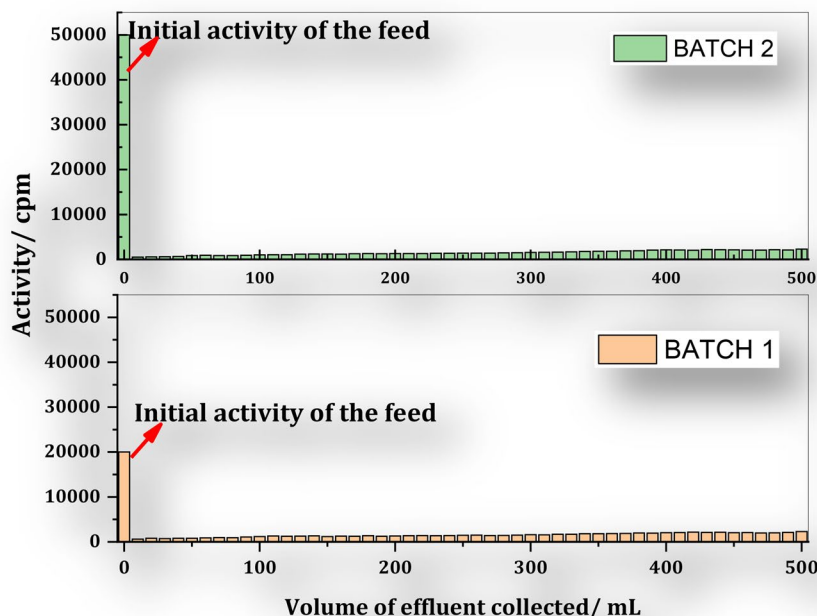
Column studies using PS-DVB-DGAH Resin

Removal efficiency of the radionuclides from organic phase was further enhanced by adopting a column chromatography-based separation module. The larger residence time of the feed solution to the adsorbent (PS-DVB-DGAH) was facilitated by maintaining a slow flow rate

(0.5 mL). Separate experiments were performed for the BATCH-1 and BATCH-2 samples (refer to Table 2 for the composition), and the results are shown in Fig. 3. Figure 3 indicates a reduction in radioactivity of effluent fractions collected from the column even after 500 mL of the effluent, which is less than 1 % break through. For the practical purpose, 5 % break through can be reached, which means that another two liters of the waste can be processed with one gram of the adsorbent. The analysis of effluent samples by LSC-analysis and gamma spectrometry shows that gross activity of the effluent samples was less than 2000 cpm. This indicates that all the radioactive elements present in the feed solution was completely adsorbed on to the column. Total decontamination was achieved for both BATCH-1 and BATCH-2 samples. Photographs of the column demonstration and the collected effluent samples are shown in Fig. 2. The decontamination of the organic liquid waste was achieved and the effluent samples showed negligible activity (< 1000 Bq/mL), which is much lower than the limits (less than 5000 Bq/mL) prescribed by AERB and CWMF for the transportation purpose [13].

Batch studies using solid state substrates

The complexation of alpha-bearing radionuclides with different solid state substrates has been widely studied for their separations from aqueous solutions. The previous studies have shown that aqueous radioactive solutions can be easily treated by the addition of excess of sodium hydroxide, which converts all the dissolved radioactive

Fig. 3 Variation on the activity of the effluent during the column study for different batches

metal ions into insoluble hydroxides, thereby precipitating them as solid waste [13]. The small volume of solid radioactive precipitate can be easily separated from the high volume of liquid and the liquid portion with minimal activity level can be disposed of as low level waste. In a similar way, treatment of organic liquid waste was attempted by using sodium hydroxide, sodium carbonate, ethylene diaminetetraacetic acid (EDTA) and oxalic acid in the current study by batch equilibration procedure. The applicability of an aqueous soluble bis-triazinyl pyridine (BTP) derivative, $\text{SO}_3\text{-Ph-BTP}$ (sulphonated bis-1,2,4-triazinyl pyridine) was also tested for this purpose based on the literature reports of high selectivity of this compound for selective actinide complexation in single cycle minor actinide partitioning process [17]. The results are summarized in Fig. 4 in terms of decrease in alpha counts of 0.05 mL of waste solution (BATCH 3) observed with each of these substrates. Decrease of alpha counts was observed in all the cases and visible change of colour of the solution was noted in some cases after the batch equilibrations (Fig. 5). Though an aqueous solution of $\text{SO}_3\text{-Ph-BTP}$ was highly efficient in the stripping of Am(III) from loaded organic solvents [17], the treatment of organic solvent with solid $\text{SO}_3\text{-Ph-BTP}$ resulted in only a minimal decrease of activity, as nearly 86% of the activity remained in the solvent after the equilibration step. Nearly 72% of the activity remained in the solution after equilibration with 0.5 g

of EDTA, while the equilibration with 0.5 g of sodium hydroxide retained nearly 49% of the activity.

Equilibration of the waste sample with mixture of equal amounts (0.25 g each) of EDTA and sodium hydroxide yielded results similar to that of sodium hydroxide. Sodium carbonate was found to be more effective complexant than sodium hydroxide pellets, as only ~ 13% of the activity of the solution remained after equilibration with 0.5 g of sodium carbonate. The radioactivity levels of the solution was reduced to nearly 6% with the use of 0.5 g of oxalic acid and this system was chosen for further studies based on the superiority in radioactive decontamination.

Operation of a column of solid complexants is not feasible for the treatment of aqueous wastes due to their solubility in aqueous medium. However, the use of a column of solid complexants for the treatment of organic liquid wastes will not suffer from such dissolution problems and further demonstration studies are carried out using a direct oxalic acid column (as shown in Fig. 2).

Column studies using oxalic acid

Figure 5 shows the results of demonstration of the waste treatment by column chromatography for the BATCH 3 radioactive liquid waste solution, treated using 5 g oxalic acid column. The radioactivity of the BATCH 3 waste used for the treatment was approximately ~ 1,10,000 cpm (gross alpha, by LSC-analysis). Initial 150 mL of the effluent of the

Fig. 4 Decrease in alpha counts of the organic waste solution after equilibration with different inorganic substrates. Time of equilibration: 2 h. Volume of solution used for equilibration: 5 mL each. Volume of aliquot used for alpha counting (LSC-analysis): 0.05 mL. Change in colour of the waste solution observed during batch studies with different solid state complexants is shown in inset

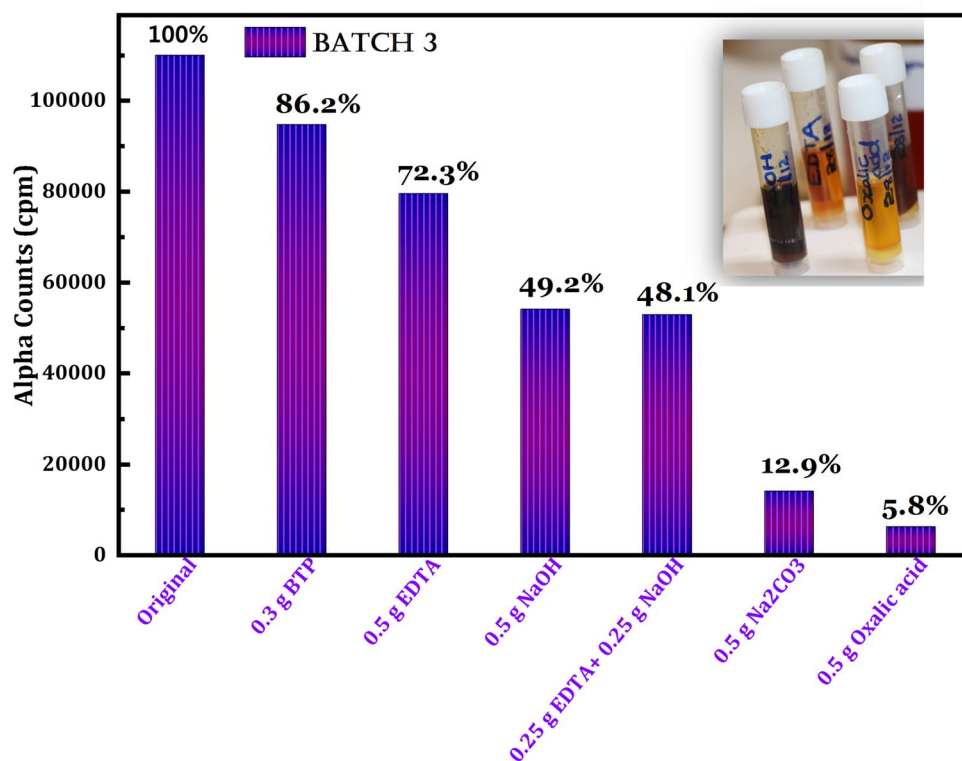
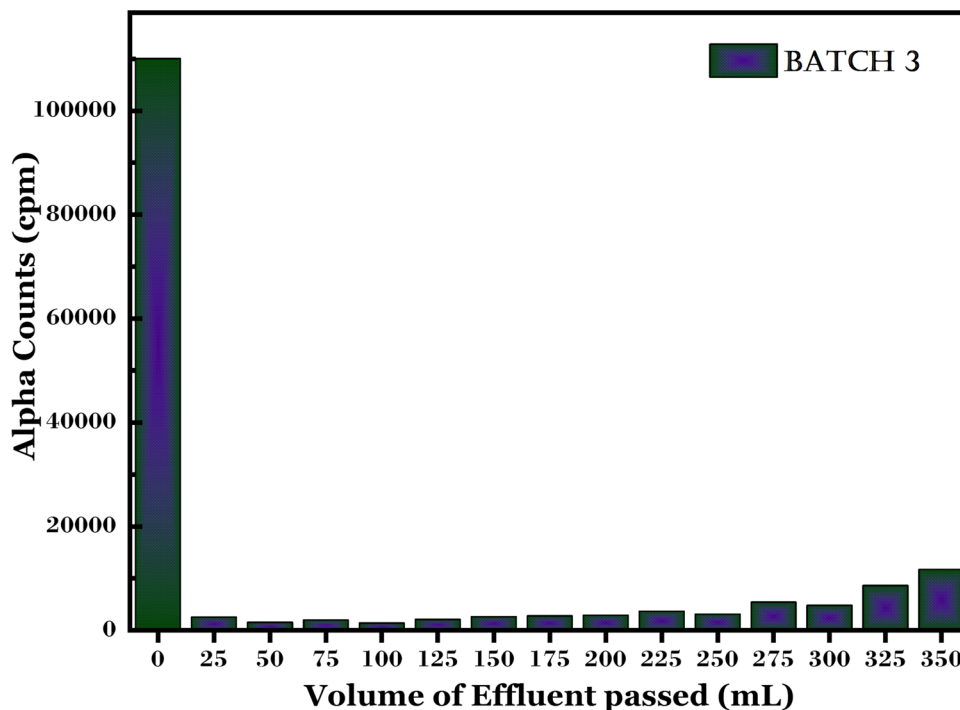


Fig. 5 Alpha activity of the waste solution before and after passing through a column containing 5 g of oxalic acid. The effluent was collected at a rate of ~3 mL per hour. Volume of aliquot used for alpha counting (LSC-analysis): 0.05 mL



above waste demonstrated an activity of ~2,000 cpm (gross alpha, by LSC-analysis). The activity level was ~3,000 cpm for the fractions collected after passing the next 100 mL of the solution. For the subsequent fractions, the activity level gradually increased to ~5,000 cpm and then to ~11,000 cpm, as shown in Fig. 5, which indicates the saturation of oxalic acid in the treatment of the organic waste beyond 100 mL.

The radioactivity value recorded for the final fraction was ~22,000 cpm (gross alpha, by LSC-analysis) in the current study, after passing 350 mL of the radioactive waste solution through a column of 5 g oxalic acid. This value corresponds to ~367 Bq of activity in the 0.05 mL of the sample taken for counting. Therefore, the activity of the treated solution can be estimated as 7333 Bq/mL at this point and nearly 90% of the activity of the original solution was removed. Better decontamination was achieved for initial fractions collected for nearly 300 mL of the waste solution, where the estimated activity levels were less than 5000 Bq/mL, the limits prescribed by AERB for categorization as low level or exempt waste [13].

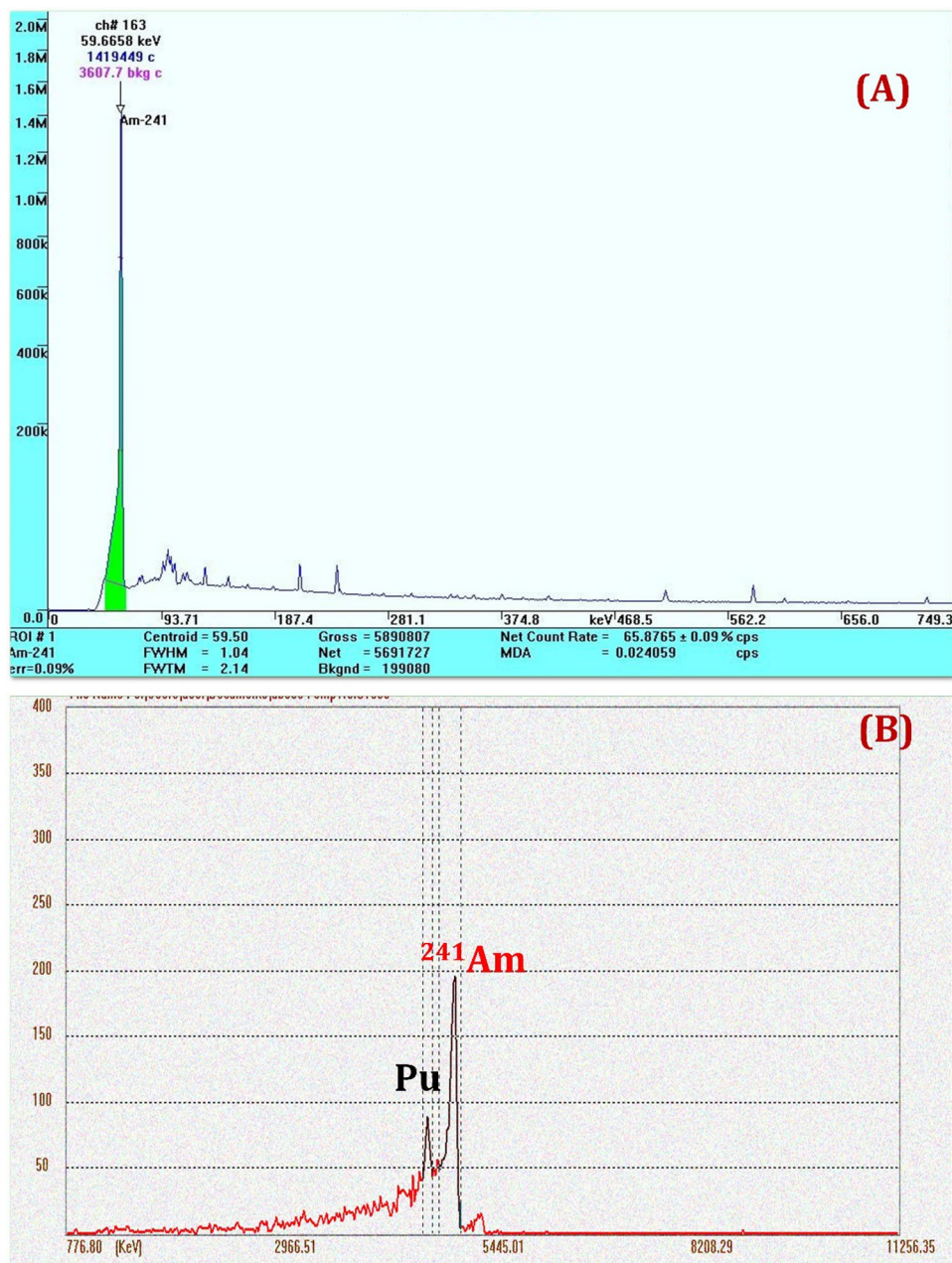
Thus the results of the above column study using 5 g oxalic acid column for BATCH 3 organic waste solution showed that the treatment of nearly 300 mL of the waste solution could be achieved under the conditions of the study. No choking or precipitation problems were noticed during the column operation. Therefore, the results prove the feasibility of column operation on a larger scale with oxalic acid for decontaminating radioactive organic waste.

Gamma assay of the treated and original waste solutions

The radiotoxicity associated with the contaminated liquid samples are predominantly due to the presence of isotopes of Am (mainly ^{241}Am), isotopes of Pu (mainly ^{239}Pu) and uranium. The gamma spectra of organic waste solutions were recorded before and after the column treatment processes to identify the various radioisotopes present in the waste solution. As illustrated already, the waste solutions originated after the various analytical activities involving radioactive tracers of Am, Pu and U isotopes. Less frequently Eu tracer was also used for specific experiments in the laboratory. Other radiotracers of various transition elements and alkaline earth metals (Cs and Sr) were also used, though not regularly. However, studies using Am and Pu have been extensively carried out in the laboratory during the past four decades and it is expected that the waste solutions showing high levels of alpha activity may contain these two elements predominantly.

Figures 6 and 7 show the gamma spectra recorded for the original waste solutions (BATCH-2 and BATCH-3). Interestingly, ^{241}Am was identified as the predominant radionuclide in the gamma spectra of all the waste solutions. The gamma peak at ~60 keV was the only peak found in the spectra of all the samples other than the usual background spectra. Therefore ^{241}Am and ^{239}Pu were followed in gamma spectroscopy to investigate the reduction of radiotoxicity due to the processing.

Fig. 6 Gamma (Grid 'A') and alpha (Grid 'B') spectra of the untreated original waste solution (BATCH-2). Pu peak in the alpha spectrum corresponds to combination of both ^{239}Pu and ^{240}Pu



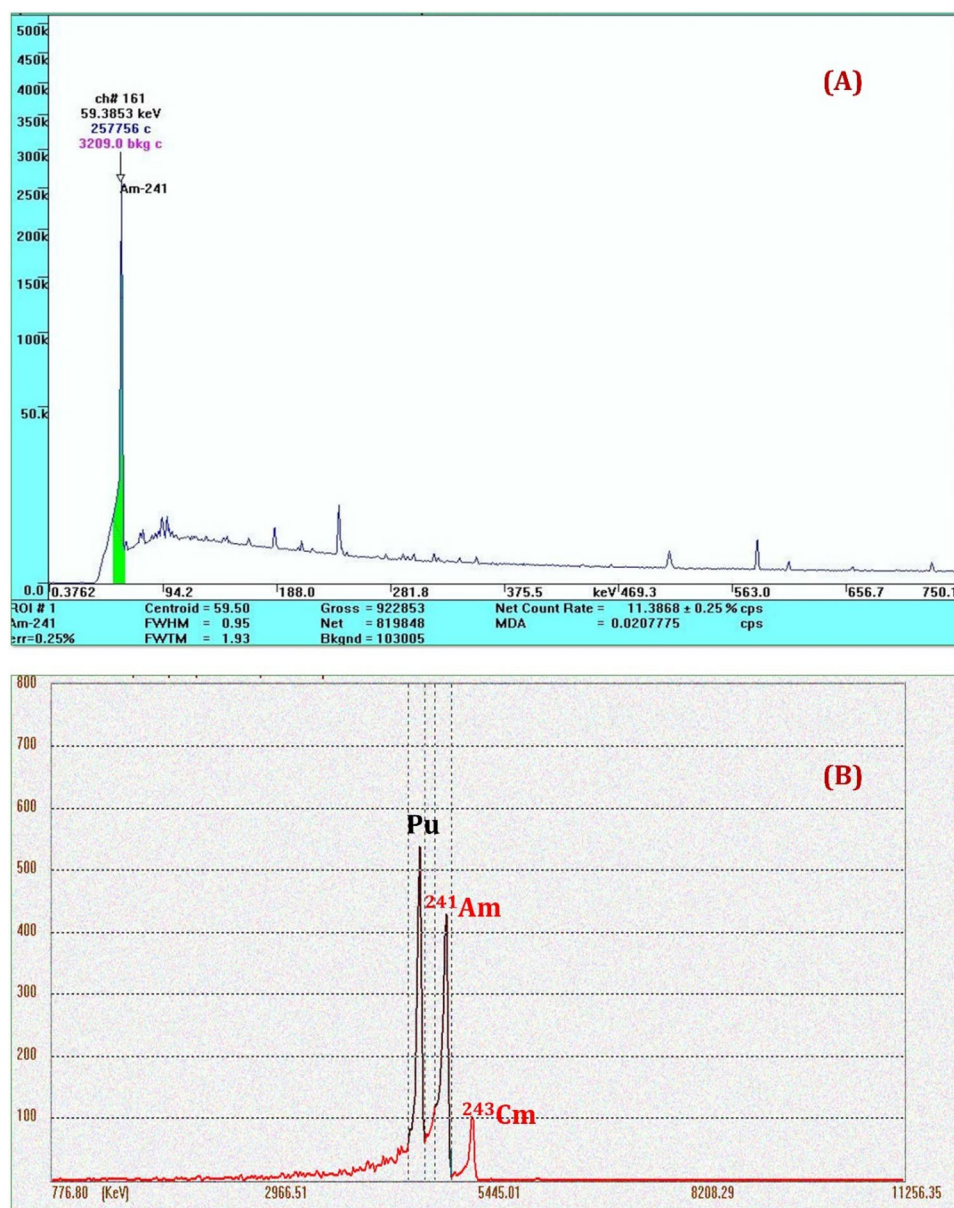
No characteristic gamma peaks of the various plutonium isotopes [18] were recorded for the samples in the current study. Either the organic waste does actually not contain Pu or the intensity of gamma of Pu is so weak to be clearly discerned from gamma spectrometry.

Alpha spectrometry of the treated and original waste solutions

To clearly identify the presence of Pu in the organic waste, alpha spectra of organic waste solutions were recorded.

The radioactive waste fixed on a solid SS disc (known as planchets) was used for recording the alpha spectra. Planchets of organic liquids (especially viscous liquids) usually turn out less efficient. Therefore, the waste was diluted approximately 10 times with *n*-hexane (a less viscous liquid) as the boiling point of *n*-hexane is less than that of DD) and ~ 0.01 mL of the diluted waste was spread around the SS disc and was dried under IR lamp. The alpha spectra of the resultant samples were subsequently recorded. As is evident from Figure 6, Grid 'B' that the weak ^{239}Pu signal was obtained in comparison to

Fig. 7 Gamma (Grid 'A') and alpha (Grid 'B') spectra of the untreated original waste solution (BATCH-3). Pu peak in the alpha spectrum corresponds to combination of both ^{239}Pu and ^{240}Pu



strong ^{241}Am in BATCH-2. Interestingly, in BATCH-3, ^{239}Pu signal is stronger than ^{241}Am lending credence to larger ^{239}Pu content than ^{241}Am in BATCH-3 (Fig. 7B). The shifting of peaks towards lower energy in comparison to the standard spectra of radionuclides (^{239}Pu : 5.15 MeV; ^{241}Am : 5.49 MeV; ^{243}Cm : 5.45 MeV) could be due to the matrix effect of *n*-DD (thickness of the absorber) [19]. A larger LS count in BATCH-3 is clearly due to the combined presence of both ^{239}Pu and ^{241}Am . The removal efficiency of radionuclides was followed by monitoring ^{241}Am and ^{239}Pu after treatment with the resin and oxalic acid complexant. In addition to the peaks due to ^{239}Pu and ^{241}Am , the presence of ^{243}Cm (albeit small) was also detected in this organic waste.

The gamma spectra of the samples of BATCH-2 and BATCH-3 after the column treatment using PS-DVB-DGAH resin and oxalic acid respectively are shown in Fig. 8. The near-complete removal of ^{239}Pu and ^{241}Am by both the treatment processes was evident from these spectra. The alpha spectrum of treated organic waste of BATCH-3 (350 mL cumulative) using oxalic acid was recorded that divulges a weak signal of ^{241}Am (Fig. 9). As oxalic acid has a strong coordination with respect to ^{239}Pu over ^{241}Am , the cumulative treated sample does not yield the signature of ^{239}Pu with a weaker signal of ^{241}Am .

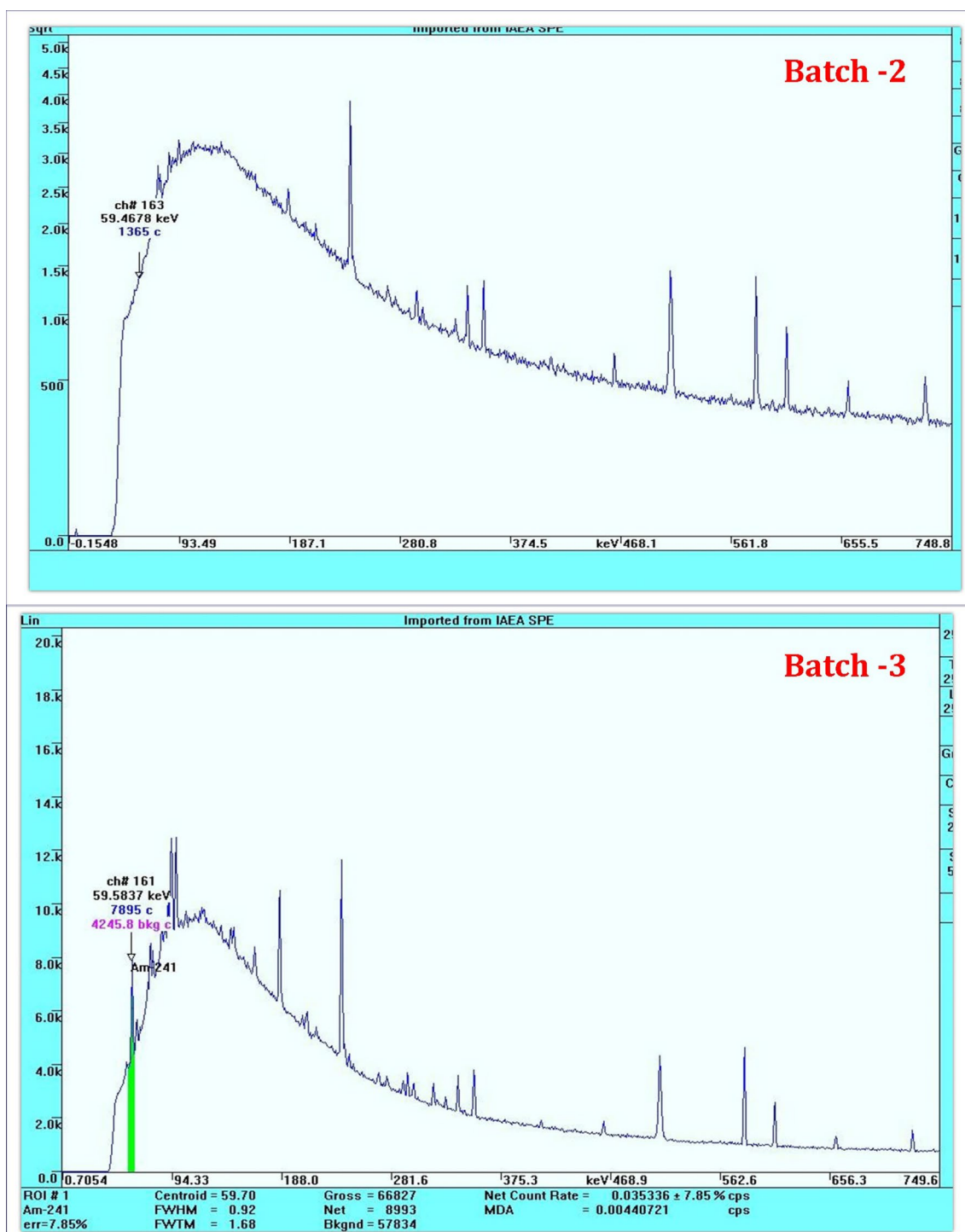


Fig. 8 Gamma spectrum of the organic waste solutions (BATCH-2 and BATCH-3) after passing through PS-DGAH resin and oxalic column respectively

ATR-FTIR results

The samples used for the column studies (BATCH 2 and BATCH 3) were subjected to ATR-FTIR analysis to probe the nature of compounds and metal ion complexes in the

waste solutions. An FTIR set-up that was commissioned inside the Glove Box was used for this purpose. The spectra were recorded before and after passing through the column and the results for BATCH 2 and BATCH 3 samples are compared in Figs. 10 and 11 respectively.

Fig. 9 Alpha spectrum of the organic waste solution (BATCH-3) after passing through oxalic acid column

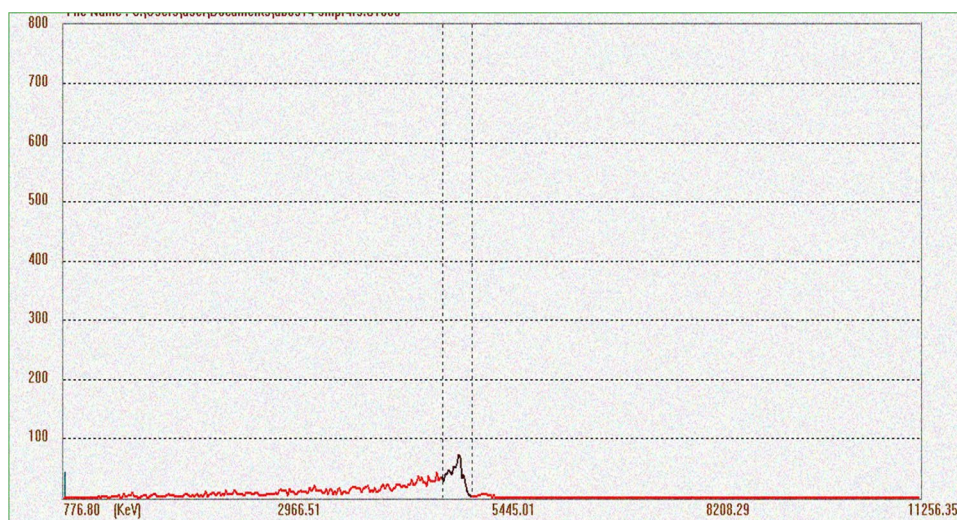
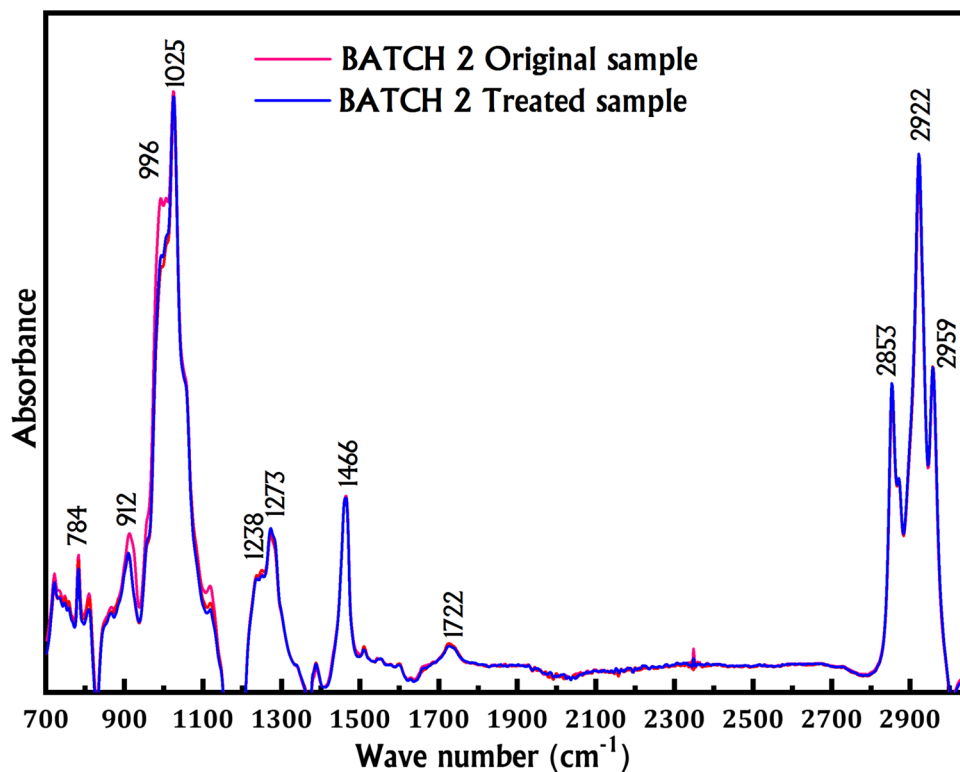


Fig. 10 ATR-FTIR spectra of samples of BATCH 2 organic waste solution before and after passing through PS-DVB-DGAH column

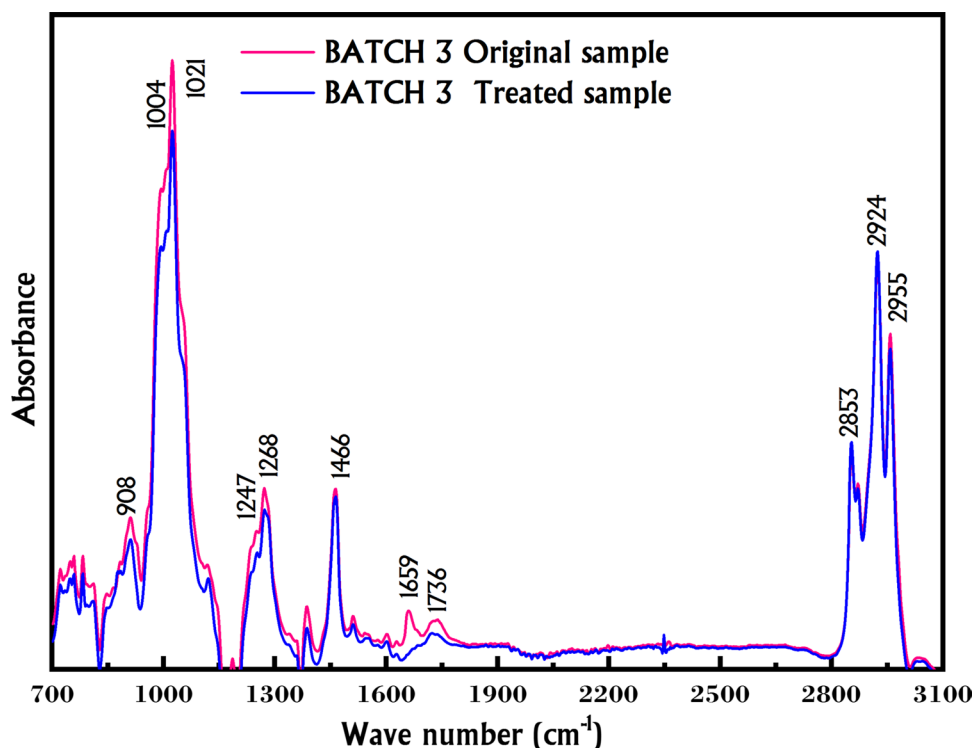


The spectra of both the batches showed identical peaks, indicating similar chemical composition of the bulk in both the samples studied. The major peaks were found to be centered at 2922, 1466, 1273 and 1025 cm^{-1} and the spectra recorded before and after the treatment process showed only minimal variations. The FT-IR peaks at 2922 cm^{-1} and 1466 cm^{-1} are due to the alkyl chains in the diluent as well as extractants and these are generally observed in all the solvent phases containing non-polar diluents and alkyl substituted extractants. The peaks at 1273 cm^{-1} and 1025 cm^{-1} are

usually observed in the spectra of alkyl phosphates such as TBP due to the vibrations of P=O group and P-O-C group respectively. Therefore, it can be inferred that the bulk of the organic waste samples is phosphate based moiety with the contamination from all other different extractants.

As the results of gamma and alpha spectrometry revealed the presence of both ^{239}Pu and ^{241}Am in the samples, both might be complexed with the alkyl phosphate extractants in these samples together with the concentration of all other extractants in smaller concentration. However, a clear

Fig. 11 ATR-FTIR spectra of samples of BATCH 2 organic waste solution before and after passing through PS-DVB-DGAH column



distinction of metal ion complex could not be achieved as the concentration of these ^{239}Pu and ^{241}Am in the samples in comparison to bulk of the extractants is negligibly small.

It is also possible that other extractants which hold these ^{239}Pu and ^{241}Am may be present in these samples, but the presence of these extractants was not indicated in the FT-IR spectra due to the presence of an excess of alkyl phosphates.

Conclusions

Removal of radio toxic pollutants (Am, Pu and Cm) from contaminated radioactive liquid organic waste has been carried out with two different methods: (i) a chelating polystyrene based ion exchange resin (ii) solid phase inorganic complexants (viz. oxalic acid). Near quantitative reduction of the alpha activity of different batches of organic waste solutions was observed during batch laboratory experiments using PS-DVB-DGAH resin and oxalic acid. Laboratory scale demonstration of organic liquid waste treatment was performed by column experiments using PS-DGAH resin and oxalic acid for nearly 500 mL of the waste solutions. Both the PS-DGAH resin and oxalic acid complexant showed excellent decontamination of ^{239}Pu and ^{241}Am alpha nuclides. Gamma and alpha spectrometric techniques were utilized as supporting tools to investigate the complete decontamination of these alpha nuclides. Furthermore the decontamination of ^{239}Pu and ^{241}Am during the column treatment was quantitatively assayed by LSC-analysis. The ATR-FTIR

analysis indicated the presence of bulk alkyl phosphates in the organic liquid waste samples studied.

Overall, the radioactive organic waste treatment is successfully accomplished using the chemically modified diglycolamic acid resin and solid oxalic acid complexant. The complete removal of alpha emitting radionuclides from the organic waste through this solid phase extraction ensures volume reduction as per the radioactive waste management protocol. The treated organic waste, which is free from radioactivity, is amenable for further incineration or pyrolysis.

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Declarations

Conflict of interest The authors wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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